NASA Conference Publication 2088

# The 1978
# Goddard Space Flight Center Battery Workshop

A workshop held at
Goddard Space Flight Center
Greenbelt, Maryland
November 14-16, 1978

NASA

# PREFACE

The papers presented in this document have been derived from transcripts taken at the Eleventh Annual Battery Workshop held at the Goddard Space Flight Center on November 15 to 17, 1978. The transcripts were lightly edited with the speaker's vugraphs assembled at the end of each presentation for uniformity.

The Workshop was attended by manufacturers, users, and government representatives interested in the latest results of testing, analysis, and development of the sealed nickel cadmium cell system. Also included were sessions on metal hydrogen and lithium cell technology and applications. The purpose of the Workshop was to share flight and test experience, stimulate discussion on problem areas, and to review the latest technology improvements.

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# INTRODUCTION

G. Halpert
Goddard Space Flight Center

On behalf of the staff at Goddard Space Flight Center, I want to welcome you to the 1978 Battery Workshop. We are pleased that Goddard management has continued to support this activity through the last ten years. Also, we've had considerable help from NASA Headquarters, which we appreciate.

Each year as we review the accomplishments, it is clear that we continue to improve the technology and continue to gain further experience and have taken steps to better understand and improve the reliability of secondary systems used in space. However, the more we advance, the more we realize that there is still much to be learned. Furthermore, the interest in these systems continues to be high. This year, there are three sessions on the nickel cadmium system alone, including discussions of the new electrodes, structures, materials, cell design improvements, and tests. Also, to indicate the interest and how far we have progressed, there are papers on modeling and prediction.

The subject of nickel hydrogen and silver hydrogen will also be addressed. Presently, two nickel hydrogen battery experiments are in space, and additional hardware is being produced and tested by several contractors around the country. We hope that this kind of work continues in the future.

Finally, you recall in the 1977 workshop we found that there was interest in the lithium primary cells in the NASA community. Not only was the interest there, but NASA centers were already testing cells for various applications. In the session last year, it became clear that not only was there interest in the lithium system, but considerable concern for the safety aspects as well. As a result, several attendees went home somewhat confused as to whether they should buy the system or be concerned about its safety. With this in mind, the lithium session was organized this year to provide information on systems availability, systems usage, and safety considerations.

We are pleased that the Army and the Navy have joined forces with NASA to provide us all with this latest information on applications. Also, the manufacturers have agreed to share their technology and applications with us.

All in all, we anticipate that this will be another informative workshop. We hope that you will participate by asking questions and by offering stimulating comments.

# SESSION I

# NICKEL CADMIUM MATERIALS AND TECHNOLOGY

G. Halpert, Chairman
Goddard Space Flight Center

# FUTURE THRUSTS OF THE NASA SPACE POWER PROGRAM

L. Holcomb
NASA Headquarters

I would like to provide you with a brief overview of the current NASA space power program with particular emphasis, of course, on the electrochemical energy conversion storage portion of the program, and follow it with a discussion of the direction we see this program taking in the near future.

(Figure 1-1)

The requirements for the electrical storage in space based on the analysis of the programmatic trends and opportunities which are now under study by the NASA Program Office identify two specific causes of need. The first is for high-performance systems to support future electric propulsion planetary and geosynchronous missions. The second area of need is for high-power multi-kilowatt systems at low cost to support shuttle-based habitation and use of nearer space.

The current program support is really broken into five general areas. The first is in the area of solar cells and arrays. The second area of research is in the area of batteries and fuel cells. The third is in thermoelectric, thermionic, and Brayton conversion systems. The fourth is in circuits and subsystems for the management and distribution of power. The fifth area involves the interaction of the environment with the power system and the spacecraft.

I will outline the general objectives and plan directions of each of these efforts with particular emphasis on the chemical energy conversion and storage area. In photovoltaic energy conversion, the aim is to improve the conversion's efficiency, reduce the mass and cost, and increase the operating life of photovoltaic conversion and arrays. Emphasis is being placed on very efficient thin solar cells, lightweight blankets, radiation resistance, low-cost advanced cells, and both planar and concentrator array designs.

In thermal-to-electric conversion, efforts aim at utilization of both nuclear and solar heat sources. They focus on achieving acceptable efficiencies for thermoelectric and thermionic converters and on evaluating Brayton conversion systems for both low- and high-power applications. In addition, some work on ancillary equipment such as heat pipes necessary for system feasibility is also being carried out.

In the area of power systems management and distribution, the effort is on basic high-power components, circuits, and subsystems as undertaken. The concepts of automated power systems management and ground and flight systems are being investigated.

Research is being undertaken to ensure that power systems can adequately cope with the space environment. This work includes both ground and flight efforts on spacecraft charging as a joint effort with the Air Force, and on high-voltage—space-plasma interactions.

Finally, in the area of chemical energy conversion and storage, the objective is to achieve improved energy density, life, operational capability, and reduced cost for space battery and fuel cell systems.

(Figure 1-2)

Research must include, first of all, means to increase the life and energy density of nickel cadmium batteries, to validate flight-weight silver hydrogen cells, to promote the safe space use of lithium primary batteries, to complete the silver zinc batteries and the orbital transfer fuel cell technology, to increase the capacity of space batteries, to evaluate new electrochemical concepts for very-high-energy density. In addition, a new effort is being initiated to involve the fuel cell electrolyzer concept for energy storage in both the dedicated and the truly regenerative mode.

Each of these thrusts is amplified somewhat in the following figures. The major NASA centers involved as well as the planned university/industrial contractors are identified, and current status is summarized, as well as the plans for FY 1979 which are outlined.

(Figure 1-3)

The advanced nickel cadmium battery program will be addressed in greater depth throughout this workshop. I won't go through all the status because you will be hearing more about most of these items this week. Our plans in general in 1979 are to complete a cycle life prediction model based on the accelerated test data to initiate contracts to investigate a wide number of cell components as indicated in Figure 1-3. We also intend to evaluate the General Electric cell manufacturing changes that have been introduced during the past ten years. We also plan to initiate tests of electrochemically impregnated cells manufactured in accordance with the Air Force process.

(Figure 1-4)

Our goals in this area are to reduce the weight of the cell, shown in Figure 1-4, and also probably the most important is to increase the life of the cell for a given energy density. We have heard the industry comment and we believe that this is probably the most important goal in this program, to increase the operational life of the space NICAD cell, sending its life up to ten years in geosynchronous orbit.

(Figure 1-5)

Figure 1-5 summarizes our efforts to advance a silver hydrogen cell. In FY 1979, we plan to design and fabricate a flight weight greater than 77 one hour per kilogram silver hydrogen cell. And we plan to initiate life tests of this cell based on the work that has been done during the past several years.

(Figure 1-6)

Figure 1-6 briefly outlines the lithium primary battery area. This past year NASA held an internal workshop to discuss the applications, shuttle safety, and NASA technology activities in the area of lithium batteries. Some of the aspects of this workshop will be the subject of papers on Thursday.

Our modest plans in FY 79 are to extend safety tests up to the 20-50 amp-hour capacity cells, to initiate tests to establish the heat generation rates of a number of candidate lithium primary batteries, to evaluate the storage life of candidate batteries, and finally, to initiate an effort aimed at sending or directed at higher rate capability for these primary cells.

(Figure 1-7)

Our silver zinc secondary and reserve activities programs are given in this slide.

(Figure 1-8)

The new activity aimed at increasing the capacity and reducing the cost of nickel cadmium or metal gas batteries is indicated in Figure 1-8. In FY 79, activities will be aimed at demonstrating technical feasibility of 100- to 500-amp-hour design NICAD cell and ground tests to evaluate nickel hydrogen cells for low earth orbit applications. In addition, a nickel hydrogen flight experiment definition study hopefully will be completed this year.

(Figure 1-9)

Figure 1-9 indicates two advanced concepts currently under study in NASA's program. They are sodium and lithium secondary batteries. These are classified as advanced concepts since the state of present technology activities makes it very difficult for us to predict the time frame for when these concepts will become technology and actually ready for flight application.

In FY 1979, our plans call for initiation of study contracts to evaluate the solid intercalated cathodes for the liquid sodium cell and for evaluation of the room temperature lithium titanium disulfide cell which uses a similar cathode concept.

(Figure 1-10)

The lightweight propellant grade fuel cell activity for orbital transfer vehicle application is indicated in Figure 1-10. Fuel cell operation with propellant grade reactants has been demonstrated, allowing the economies of shared propulsion and power reactants.

(Figure 1-11)

Performance of less than 3 kilograms per kilowatt has recently been demonstrated on a small stack. Our plans in FY 1979 are to extend the life tests of these units at 500 amp-foot for periods of up to 3000 hours.

(Figure 1-12)

A new program in FY 1979 is aimed at a maintainable fuel cell electrolyzer system for orbital energy storage. In FY 79 we plan to initiate a number of activities in both acid and alkaline hydrogen and oxygen electrochemical technology. The performance advantages of the fuel cell electrolyzer concept are shown in Figure 1-13 for a 10-year application at the 100-kilowatt power level in low earth orbit.

(Figure 1-13)

In comparison to an advanced battery, the fuel cell electrolyzer appears to have a weight of roughly one-third of that of the advanced battery systems at this power level.

(Figure 1-14)

This indicates that a complementary task to the dedicated fuel cell electrolyzer program will be initiated. A modest effort will begin examining the feasibility of a regenerative acid cell in FY 1979. The alkaline technology will be examined in FY 80.

It is expected that execution of this research and technology-based program will increase the range of future mission opportunities that can be accommodated at acceptable levels of cost and risk. However, the pressing near-term high-power needs for low earth orbital systems are very great, and the impact of this program at the current funding levels will be limited to a few key technologies.

Our planning includes a specific program enhancement aimed at this class of needs and is outlined in Figure 1-15.

(Figure 1-15)

The justification for this enhancement stems from the projected growth in space energy demand. NASA has installed in orbit, since its inception, roughly 100 kilowatts (cumulative kilowatts) of solar power capability. Potential missions in the mid 1980's may individually exceed this cumulative total.

In addition, historically, the cost of space energy has been in the range of $1000 per kilowatthour. Missions in the mid 1980's are expected to require $10^5$-$10^7$ kilowatthours per year. This will result in a totally unacceptable cost. Both reduction in cost and advancement in high-power technology are required. These objectives are amplified in Figure 1-16.

(Figure 1-16)

The low-cost orbital energy systems technology enhancement is aimed at enabling a 100-kilowatt power system and at reducing the unit cost by a factor of 10 to 100. It treats solar power generation, bulk energy storage, power management and distribution, and thermal management.

(Figures 1-17 and 1-18)

In May of this year, NASA held a two-day symposium to give leaders from government and industry a broad view of current government-supported technology efforts and future program plans in space power. It provided a forum for comment on our current program and on this proposed low-cost orbital energy systems technology enhancement. As indicated in Figure 1-18, over 150 participants from government, industry, and universities attended. To lay the foundation for the discussions, survey papers were presented to review the technology requirements, planning, and status. A number of industry-chaired workshops were held on the second day of this symposium. Some of the examples of recommendations that came out of these workshops are indicated in Figure 1-19.

(Figure 1-19)

Several examples relate directly to the energy storage area. We should build larger space battery cells. That is, in our program to look at higher-capacity cells, we were aiming at roughly 100 amp-hour capacity. The recommendation for the workshop was to look at 500- to 1000-amp-hour capacity. In the nickel cadmium program, life in deep discharge is a more urgent item than improving the energy density.

In the fuel cell electrolyzer program, our program should emphasize the cyclic endurance and maintenance aspects of the dedicated fuel cell electrolyzer system.

Also a very important recommendation that came out of this workshop was to do a more thorough job of comparing batteries with the regenerative fuel cell electrolyzer or the dedicated fuel cell electrolyzer concept. There was a feeling that these studies were not done with the thoroughness that was necessary to make judgment on advancing the technology program.

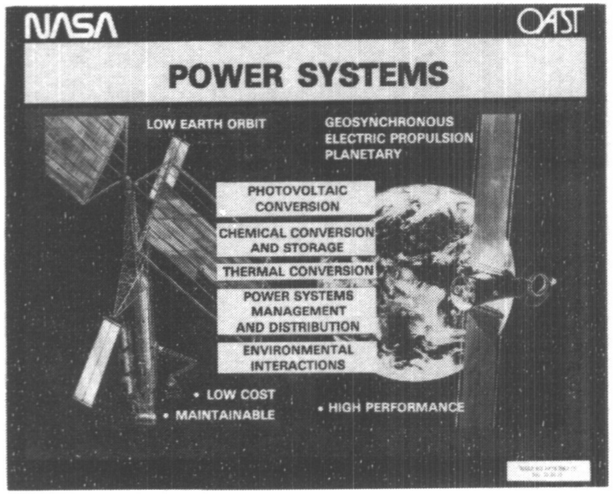
Complete details on the conference presentations and the workshop recommendations can be found in "Future Orbital Power Systems Technology Requirements," NASA Conference Publication 2058.

A second area for which increases in energy demand can be postulated is for future synchronous operations.

(Figure 1-20)

Figure 1-20 indicates that an ad hoc committee under the auspices of the NASA Space Systems & Technology Advisory Committee and chaired by an industry representative has been established to identify the power technology to meet the needs of synchronous space activities through the 1990's and to evaluate the adequacy of our current research and technology efforts in that regard. If warranted, we will seek a specific enhancement in this area in the future.

Finally, it is noted that straightforward extensions of today's technology, which in the main is limited to silicon solar cells, nickel cadmium batteries, and radioisotope thermoelectric generators, may be totally inadequate to cope with the megawatt and kilovolt needs of the more distant future. As we move toward the challenge of the greatly increased power levels in space, we must seek out the technology opportunities that will provide breakthroughs in energy density, efficiency, economy, and life. Accordingly, we foresee an increasing allocation of available resources to the exploration of a more advanced concept of energy generation, storage, and management.



**POWER SYSTEMS**

Figure 1-1

CHEMICAL ENERGY CONVERSION AND STORAGE
MAJOR THRUSTS
(1932/2418)*

| | NEAR TERM 79-85 | FAR TERM 85-95 | ADVANCED CONCEPTS |
|---|---|---|---|
| BATTERIES | • DOUBLE ENERGY DENSITY/ LIFE OF NI-CD BATTERY (26 W-HR/KG;10 YR) (816/878)<br>• AG-$H_2$ AEROSPACE WEIGHT CELLS VALIDATED (>77 W-HR/KG, 10 YR GEO) (163/38)<br>• LITHIUM PRIMARY (> 300 W-HR/KG) (138/110)<br>• AG/ZN SECONDARY AND RESERVE ACTIVATED (238/60) | • HIGH-CAPACITY, LOW-COST NI-CD OR METAL-GAS BATTERY (> 100 A-HR, <$30/W-HR) (87/313) | • NA & LI SECONDARY (> 200 W-HR/KG) (143/136) |
| FUEL CELLS | • LIGHTWEIGHT PROPELLANT GRADE OTV** FUEL CELL (< 3 KG/KW) (347/185) | • MAINTAINABLE FUEL CELL/ ELECTROLYZER SYSTEM (10 YR, < 8 KG/KW) (0/648) | • REGENERATIVE FUEL CELL (0/50) |

* FUNDING (FY 78/FY 79)
** ORBITAL TRANSFER VEHICLE

Figure 1-2

OBJECTIVE: DOUBLE ENERGY DENSITY/LIFE OF NI-CD BATTERY

RESOURCES: 792/795

MAJOR SUPPORT: JPL. LERC, TRW, GE, EP, YARDNEY, SAFT, PROG. COMP., SEVERAL TBD's

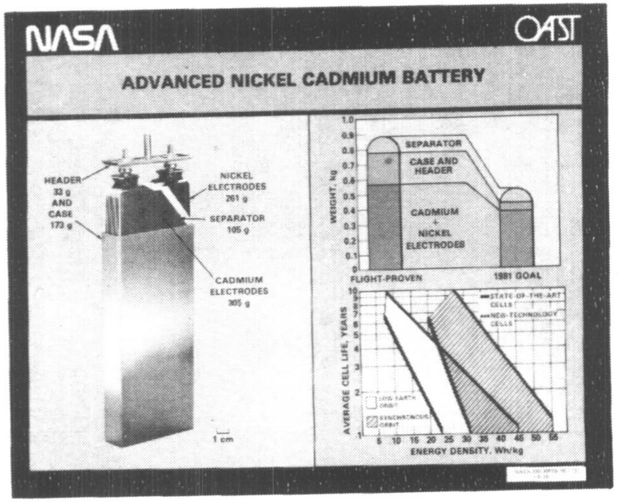
STATUS:

- CONTRACT WITH PROGRAMMED COMPOSITES TO DEVELOP G/E CASE
- COMPLETED ALL BUT 6 PACKS IN ACCELERATED NICD TEST PROGRAM, TEST DATA TO BE PUBLISHED, CYCLE LIFE PREDICTION MODELS UNDER DEVELOPMENT
- I/O SEPARATOR CELLS DELIVERED TO CRANE AND UNDER EVALUATION - INITIAL TESTS INDICATE LOW CAPACITY BELIEVED TO BE DUE TO CELL CONSTRUCTION
- SEALED NON-SINTERED POSITIVE CELLS DELIVERED TO LERC
- SAMPLES OF PLASTIC PLAQUE IMBEDDED GRID HAVE UNDERDONE PRELIMINARY EVALUATION
- INITIATED CONTRACT TO EVALUATE CELL REVERSAL DURING DEEP DISCHARGE RECONDITIONING

FY 79 PLANS:

- COMPLETE ACCELERATED TEST CYCLE LIFE PREDICTION MODEL
- INITIATE ADDITIONAL CONTRACTS TO EVALUATE EI PROCESS FOR BOTH POSITIVE AND NEGATIVE, NEW SINTERED SUBSTRATES, THIN WALL CASES, REDUCED TERMINAL WEIGHTS, REDUCED HEAD SPACE, THINNER GRIDS, PLATE ASPECT RATIO, AS WELL AS EVALUATE PLATE SPACING, TECHNIQUES TO REDUCE $CO_3^=$, DESIGN VARIABLES, ADDITIVES AND OTHERS
- INITIATE EVALUATION OF GE MANUFACTURING CHANGES OVER PAST DECADE
- INITIATE EVALUATION OF AF EP ELECTROCHEMICAL IMPREGNATED CELLS

Figure 1-3



**ADVANCED NICKEL CADMIUM BATTERY**

Figure 1-4

THRUST: VALIDATE ASEROSPACE WEIGHT Ag-$H_2$ CELLS

RESOURCES: 163/38

MAJOR SUPPORT: LERC, ERC

STATUS:
- COMPLETED EVALUATION OF Ag-$H_2$ RESEARCH CELL >900 CYCLES AT 75% DOD (66 W-Hr/Kg DESIGN)
- 77 W-Hr/Kg, 35 A-Hr DESIGN CELLS DELIVERED TO LERC
- CeO-Ag & AuAg ELECTRODES SHOW IMPROVED UTILIZATION (74%)

FY 79 PLANS:

-- DESIGN, FABRICATE AND LIFE TEST > 77 W-Hr/Kg, 50 A-Hr FLIGHTWEIGHT Ag-$H_2$ CELLS

Figure 1-5

THRUST: LITHIUM PRIMARY BATTERIES

RESOURCES: 138/110

MAJOR SUPPORT: JPL, ALTUS, TDP'S

STATUS:
- HELD LITHIUM BATTERY WORKSHOP ON APPLICATIONS, SHUTTLE SAFETY AND NASA TECHNOLOGY PROGRAM
- COMPLETED PRELIMINARY SAFETY TESTS OF ALTUS BUTTON ( 200 mA-Hr) CELLS
- ESTABLISHED LIFE PROJECTIONS FOR RESERVE-TYPE $SOCL_2$ BATTERIES

FY 79 PLANS:
- EXTEND ALTUS CELL SAFETY TESTS TO 20-50 A-Hr SIZE CELLS
- INITIATE CALORIMETRIC STUDIES OF 20-50 A-Hr PRIMARY CELLS OVER A RANGE OF DISCHARGE RATES
- INITIATE LIFE TESTS ON ACTIVE LIGHIUM CELLS
- INITIATE TECHNOLOGY PROGRAM AIMED AT HIGHER RATE CAPABILITY FOR LITHIUM CELLS

Figure 1-6

THRUST: Ag-Zn SECONDARY AND RESERVE ACTIVATED

RESOURCES: 238/60

MAJOR SUPPORT: LERC, JPL, YARDNEY, EP, CRANE

STATUS:
- 12 A-Hr Ag-Zn CELLS ON LIFE TEST
- JOP PROBE Ag-Zn SECONDARY CELLS COMPLETE TESTING
- FINAL REPORT ON PRELIMINARY INVESTIGATION OF REMOTELY ACTIVATED Ag-Zn BATTERY

FY 79 PLANS:
- COMPLETE 12 A-Hr Ag-Zn TESTS
- DEVELOP Ag-Zn PREDICTIVE MODEL

Figure 1-7

THRUST: HIGH-CAPACITY, LOW-COST Ni-Cd OR METAL-GAS BATTERY

RESOURCES: 87/313

MAJOR SUPPORT: LERC, MSFC, SEVERAL TBD'S

STATUS:
- CONTRACTOR SELECTED FOR A > 100 A-Hr TOROIDAL CONSTRUCTION Ni-Cd CELL COMPATIBLE WITH CENTRAL HEAT PIPE OR OTHER MEANS OF ACTIVE COOLING
- OBTAIN STATE-OF-THE -ART 30-35 A-Hr NI-$H_2$ CELLS FOR LOW EARTH ORBIT DUTY EVALUATION IN GROUND FACILITIES
- PRELIMINARY PLANNING OF A LOW EARTH ORBIT (LEO) NI-$H_2$ BATTERY FLIGHT EXPERIMENT

FY 79 PLANS:
- DEMONSTRATE FEASIBILITY OF >100 A-Hr TOROIDAL Ni-Cd
- INITIAL NI-$H_2$ EVALUATION RESULTS AVAILABLE
- COMPLETE NI-$H_2$ FLIGHT EXPERIMENT DEFINITION STUDY

Figure 1-8

THRUST: NA & LI SECONDARY BATTERIES

RESOURCES: 143/136

MAJOR SUPPORT: LERC, JPL, EIC, TBD'S

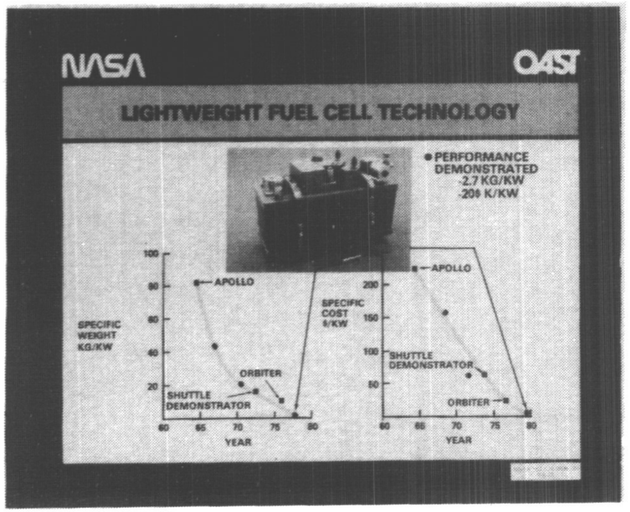
STATUS:

- NA (ℓ)/β-ALUMINA (100-150°C) NEGATIVE PREVIOUSLY DEMONSTRATED
- FURTHER WORK ON SOLUBLE SULFUR ELECTRODE NOT WARRANTED
  - ADEQUATE SOLUBILITY
  - POOR REVERSIBILITY
  - HIGH RESISTANCES
  - POOR LONG TERM STABILITY
- LI/TI $S_2$ CELLS PURCHASED FOR EVALUATION

FY 79 PLANS:

- INITIATE CONTRACT TO STUDY POSITIVE, SODIUM ION SOLID INTERCALATED ELECTRODE
- COMPLETE EVALUATION TESTS OF LI/TI $S_2$ CELLS
- SET UP LITHIUM ELECTRODE TEST STAND TO EVALUATE VARIOUS CATHODE/ELECTROLITE COMBINATIONS

Figure 1-9


NASA OAST

LIGHTWEIGHT FUEL CELL TECHNOLOGY

- PERFORMANCE DEMONSTRATED
  - 2.7 KG/KW
  - 20$ K/KW

Figure 1-11

THRUST: LIGHTWEIGHT PROPELLANT GRADE OTV FUEL CELL

RESOURCES: 347/185

MAJOR SUPPORT: LERC, UTC

STATUS:

- OPERATION ON PROPELLANT GRADE REACTANTS
- STABLE FUEL CELL PERFORMANCE ACHIEVED FOR 16 HR AT 1000 ASF, 265°F WITH PROJECTED HARDWARE WEIGHT -2.7 KG/KW
- PBI MATRIX MATERIAL SUPERIOR TO ASBESTOS AT 250°F QUALITY CONTROL PROBLEM
- B-501/$ZrO_2$ FRAME MATERIAL SUPERIOR TO FIBERGLASS AT 250°F

FY 79 PLANS:

- EXTEND LIFE TEST OF 500 ASF TO 3000 HR AND IMPROVE CATALYST STABILITY

Figure 1-10

THRUST: MAINTAINABLE FUEL CELL/ELECTROLYZER

RECOURCES: 0/648

MAJOR SUPPORT: JSC, LERC, UTC, GE, LIFE SYSTEMS, TBD's

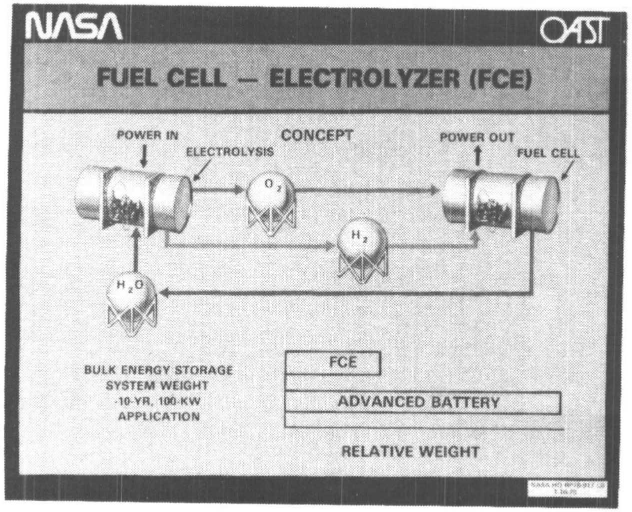
STATUS:

- NEW PROGRAM

**FY 79 PLANS**

- ACID TECHNOLOGY
  - PERFORM STATE-OF-THE ART ASSESSMENT
  - INITIATE FUEL CELL TECH. FOR ENERGY STORAGE APPL.
  - INITIATE RESEARCH TO IMPROVE SPE MEMBRANES
  - INITIATE CIRCULATION SYSTEM TECHNOLOGY
- ALKALINE TECHNOLOGY
  - PERFORM STATE-OF-THE-ART ASSESSMENT
  - INITIATE FUEL CELL TECHNOLOGY FOR ENERGY STORAGE APPL.
  - INITIATE ALKALINE ELECTROLYSIS TECHNOLOGY

Figure 1-12



FUEL CELL — ELECTROLYZER (FCE)

Figure 1-13

<u>THRUST</u>: REGENERATIVE FUEL CELL

<u>RESOURCES</u>: 0/50

<u>MAJOR SUPPORT</u>: JSC, LERC, TBD'S

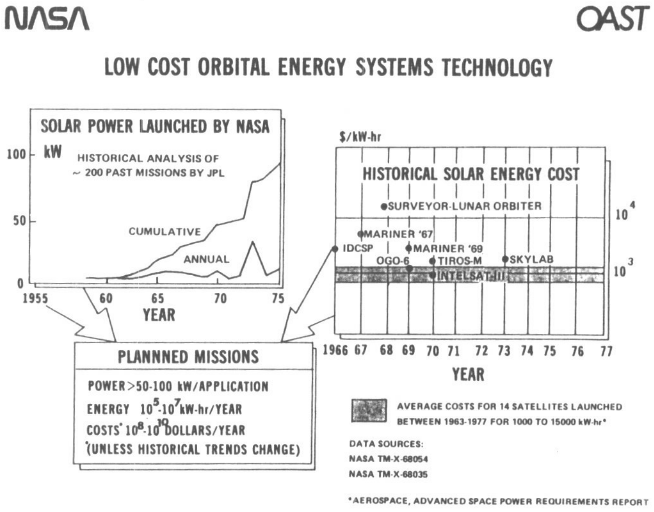
<u>STATUS</u>:

- NEW PROGRAM

<u>FY 79 PLANS</u>:

- INITIATE PROGRAM TO INVESTIGATE REVERSIBLE CATALYST FOR REGENERATIVE ACID FUEL CELL

Figure 1-14



LOW COST ORBITAL ENERGY SYSTEMS TECHNOLOGY

PLANNNED MISSIONS

POWER > 50-100 kW/APPLICATION

ENERGY $10^5$-$10^7$ kW-hr/YEAR

COSTS* $10^8$-$10^{10}$ DOLLARS/YEAR

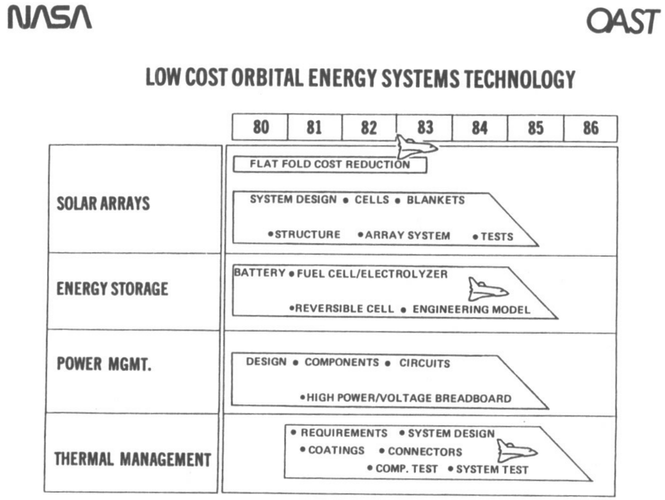
*(UNLESS HISTORICAL TRENDS CHANGE)

▨ AVERAGE COSTS FOR 14 SATELLITES LAUNCHED BETWEEN 1963-1977 FOR 1000 TO 15000 kW-hr*

DATA SOURCES:
NASA TM-X-68054
NASA TM-X-68035

*AEROSPACE, ADVANCED SPACE POWER REQUIREMENTS REPORT

Figure 1-15



LOW COST ORBITAL ENERGY SYSTEMS TECHNOLOGY

SOLAR ARRAYS
- FLAT FOLD COST REDUCTION
- SYSTEM DESIGN • CELLS • BLANKETS • STRUCTURE • ARRAY SYSTEM • TESTS

ENERGY STORAGE
- BATTERY • FUEL CELL/ELECTROLYZER • REVERSIBLE CELL • ENGINEERING MODEL

POWER MGMT.
- DESIGN • COMPONENTS • CIRCUITS • HIGH POWER/VOLTAGE BREADBOARD

THERMAL MANAGEMENT
- • REQUIREMENTS • SYSTEM DESIGN • COATINGS • CONNECTORS • COMP. TEST • SYSTEM TEST

Figure 1-16

## LOW COST ORBITAL ENERGY SYSTEMS TECHNOLOGY

OBJECTIVES:

- PROVIDE A SET OF ENERGY TECHNOLOGIES TO ENABLE >100-kW POWER SYSTEMS FOR AN IOC ≥ 1986
- PROVIDE UTILITY CONCEPTS & TECHNOLOGY BASIS TO REDUCE UNIT SPACE ENERGY COST BY 10 TO 100 TIMES BY 1985

BENEFITS:

- REDUCED COST & RISK OF FUTURE HIGH CAPACITY ENERGY SYSTEMS DEVELOPMENTS THROUGH DEMONSTRATION OF CRITICAL COMPONENTS & SUBSYSTEMS; e.g., HIGH VOLTAGE SWITCHGEAR, LARGE AREA SOLAR CELL BLANKETS, ETC.
- REDUCED UNIT ENERGY COST THROUGH LOWER COST COMPONENTS, LIFE EXTENSION & AUTOMATION; e.g., ARRAY BLANKETS AT 1/10 PRESENT COST, ELECTROLYTE REPLACEMENT, ETC.
- STEPS TOWARD NEW OPERATING CONCEPTS: e.g., ORBITAL PROPELLANT PRODUCTION, EC/LS
- APPLICABLE TO SPS

Figure 1-17

## NASA/INDUSTRY ORBITAL POWER TECHNOLOGY SYMPOSIUM

### 5/31 – 6/1/78

- 150 PARTICIPANTS
  - 32 COMPANIES
  - 2 UNIVERSITIES
  - 6 NASA CENTERS
  - 6 OTHER GOVERNMENT INSTALLATIONS
- 18 FORMAL PAPERS
  - REQUIREMENTS PLANNING
  - TECHNOLOGY PLANNING
  - TECHNOLOGY STATUS
- 10 INDUSTRY CHAIRED WORKSHOPS
  - CRITIQUE OF NEW INITIATIVE
  - RECOMMENDED CHANGES IN CONTENT & EMPHASIS

Figure 1-18

## EXAMPLES OF WORKSHOP RECOMMENDATIONS

- SYSTEM TRADES LACKING & NEEDED
- RADIATION RESISTANCE MORE IMPORTANT THAN EFFICIENCY
- NEED GA AS VERIFICATION BUT LOWER NEAR TERM PRIORITY
- USE 'CLEAN SHEET' APPROACH TO ARRAYS
- SETTLE APPLICABILITY OF CONCENTRATORS
- BUILD LARGER BATTERY CELLS 100-1000 A-H
- LIFE & DEEP DISCHARGE MORE URGENT THEN ENERGY DENSITY
- EMPHASIZE CYCLIC ENDURANCE & MAINTENANCE ON FUEL CELL/ ELECTROLYZER
- ACCELERATE DIRECTED THERMAL MGMT. EFFORT

Figure 1-19

## POWER TECHNOLOGY FOR FUTURE SYNCHRONOUS SATELLITES AND PLATFORMS

OBJECTIVE

- IDENTIFY POWER TECHNOLOGIES TO MEET THE NEEDS OF SYNCHRONOUS SPACE ACTIVITIES THROUGH THE 1990's
- EVALUATE ADEQUACY OF CURRENT OAST & OTHER R&T EFFORTS TO MEET THOSE NEEDS

NUMBER OF MEETINGS

TWO IN FY 79

PROPOSED CHAIRMAN

MR. F. H. ESCH
COMSAT LABORATORIES

Figure 1-20

# LIGHTWEIGHT ELECTRODES

R. Sutula
Naval Surface Weapons Center

About a year ago, I met a young man by the name of Bill Ferrando, a postdoctorate fellow at the American University. Bill decided that he wanted to build an electric car, so he converted a Volkswagen using regular parts and 600 pounds of nickel cadmium batteries.

What he found with the 600 pounds of nickel cadmium batteries was that every time he charged it he got somewhere between 25 and 50 miles. So it wasn't exactly a spectacular success. He asked me, "Is it entirely impossible to conform a material in which the basic structure of the electrode was silica onto which had been vapor-deposited nickel and then using that as a basic building block for going ahead and developing a new nickel hydroxide electrode or even a cadmium electrode?"

His intent was to reduce the plate weight by 50 percent. Now we call that type of material a composite. Composites are not what you call unusual or unknown. We find quite a bit of it in nature. Nature has many very versatile and durable composites and a classic example is bamboo. Bamboo is a long fiber composite that has something like 2000 uses.

(Figure 1-21)

If you remember the movie "The Ten Commandments," you remember our poor slave here mixing mud with straw and forming a brick, which was also another type of composite. In fact, if you look at him you find that you, yourself, are a composite based on bone, muscle, and tendons.

So with that we decided then we should have an objective to develop a lightweight composite nickel hydroxide electrode.

The payoffs of such a system are immediately obvious. First of all, if you keep the power density per unit volume constant, and reduce the weight of both electrodes by 50 percent, then you overall reduce the battery weight by 30 to 40 percent. At the same time, you increase the power density per unit weight.

Use of raw materials such as silver and cadmium can be minimized. If you wanted to fight World War II all over again, even though I don't know why you might, you don't even have enough silver right now in your stock piles to even start that war. The range of near-term electric vehicles is increased.

(Figure 1-22)

Now, how do you go about making a lightweight electrode? First of all, instead of using silica, which was suggested, we started with a graphite mat fiber: Thornel type P. It's VMA grade, Union Carbide. It comes in a mat form so the process is amenable to automation. We coated it with an electroless nickel process and we formed what is called a nickel-coated graphite. This material is placed between two stainless steel plates which have been coated with magnesium oxide as a separating agent, sintered in an atmosphere of hydrogen for 2 hours at 812°. In between we did insert a tab and we formed what I called the composite precursor. It's the sintered nickel-coated graphite. Then we used the method of Dave Pickett for electrochemically impregnating the active species and then we converted that material and formed the electrochemically active electrode.

(Figure 1-23)

Figure 1-23 shows the composite materials that will be used. We have a graphite mat fiber. Four grams are used totally in the electrode. This is the material after it has been nickel coated. We take two pieces of this material weighing about 3 grams apiece, and we sandwich a nickel grid between two of these and then center it. The grid weighs 1.8 grams and it's just nothing more than tiny little strips of nickel and we form a composite precursor.

Here is the composite precursor. It is 6 inches in length, 2 3/4 in width, and has a thickness of about 20 mils, and contains about 65 volume percent graphite.

Commercial electrodes after they have been impregnated normally weigh, at least the ones we were comparing, 34 grams and the composite electrode weighed 17 grams. So there is substantial savings.

(Figure 1-24)

This is a scanning electron micrograph of the fiber itself. It's nine microns in diameter.

(Figure 1-25)

This is the fiber at 100 magnification, coated with the nickel. Notice how smooth the nickel coating is and how it coats the entire fiber very thoroughly.

(Figure 1-26)

This is a cutaway view of the fiber with the nickel coating. Notice that this is the fiber material or the graphite fiber itself. And then outside, you can see the nickel coating.

(Figure 1-27)

This is the fiber at 5000 magnification from the scanning electron micrograph, again with nickel coating. You can see that and you can also see the graphite fiber. What we are interested in is this interface. The interface and the bonding of the nickel to the graphite is excellent. It is metallurgically bonded very well.

(Figure 1-28)

This is the fiber at 15 magnification from the scanning electron micrograph of the compacted sintered material.

(Figure 1-29)

This is a blowup of the fiber at 1000 magnification from the scanning electron micrograph. Of the sintered, you notice that the material has sintered very well along the length of the fiber with the coated nickel.

The orange peel effect is due to the fact that the nickel that is deposited onto the fiber is a very fine nickel and as it is sintered the crystals grow much larger and you get this type of effect.

Now one of the things that you have to ask yourself when you are dealing with composites is once you make a composite you have to know what is its effect on the load to failure and the electrical resistivity. So we did some studies on the load to failure versus compaction pressure and also the thickness of the nickel coating.

(Figure 1-30)

Now, this band is what one would typically find for nickel carbonyl that had been sintered and processed, and then tested for load to failure. We find that with this nickel carbonyl, which is 0.8 of a gram per cc, the apparent density will be between 80 and 100 kilograms per centimeter.

One effect we notice is that as the compaction pressure increases during sintering, we find that the load to failure also increases. But the biggest effect is the effect of having the thickness of the nickel coating. As the thickness of the nickel coating increases, we see that the load to failure increases. And this is quite excellent. We are very happy with these results.

As far as temperature is concerned, we can't say anything about whether or not sintering temperature has an effect on this.

With regard to the electrical resistivity, again, the shaded area in Figure 1-30 is normally what we find in literature. We find again (versus electrical resistivity versus compaction pressure) as compaction pressure increases, we find that the electrical resistivity decreases and also, the trend again, if you look at this temperature — 812 with 0.3 of a micron coating and 812 with 0.6 of a micron coating — as the thickness of the coating of the nickel increases, we find a decrease in the electrical resistivity.

These two seem to parallel each other. These lines, 762 and then 812. They are prepared from the same batches and treated the same way. So maybe this is the reason why they seem to parallel each other. But it is two different samples.

Again, the overall effect is as the electrical resistivity increases, and as the thickness of the nickel coating increases, the electrical resistivity decreases.

(Figure 1-31)

Now, we were not very happy with these data. We would prefer that our data sat with this line.

It was very fortunate for us to put this tab into the nickel grid. Once we did this, the effect on the electrical resistivity appears in Figure 1-33.

(Figure 1-32)

This is what we obtained. This is the composite precursor. We see that we are obtaining values for electrical resistivity between 200 and 300 micron/centimeters, with which we are very happy.

(Figure 1-33)

Now, once we do this, we have to find out whether or not this thing functioned as an electrode. We took the nickel composite electrode, wrapped it with two layers of woven nylon, placed it between two commercially available cadmium electrodes and then charged and discharged it in a very crude fashion. We charged it 4 amperes and it behaved very well with a leveling off digital of about 1.85 volts. The open circuit voltage was 1.35, reasonably good, to a cutoff voltage of 0.9 volts. We discharged it through 0.535 ohms, obtained an average voltage of 1.15 and a utilization of 101 percent. This was in 31 percent potassium hydroxide excess.

(Figure 1-34)

With regard to the nickel composite versus zinc, we took nickel and wrapped it with two layers of cellophane, 1 mil thick, placed it in 31 percent potassium hydroxide, charged it at 2 amperes for 30 minutes just to see what was happening.

I think this was a figment of the artist that transcribed my slide. We had an open circuit voltage of about 1.8, discharged it again through 0.535 ohms, a utilization of 44 percent.

In this case, the zinc electrode, an in-house zinc electode that I made, was a very poor electrode. So the results weren't exactly stellar.

With regard to that nickel electrode that was used in this one, I removed it and put it again in a nickel cadmium system and we've obtained utilizations of over 100 percent. So I know the nickel electrode is functioning very well. It is just that my zinc electrode is very poor.

(Figure 1-35)

These are the performances of the nickel hydroxide electrodes, with regard to the nickel cadmium system and then also with the nickel zinc system. These in the nickel cadmium system were treated all the same way. We had a commercial electrode which had a 75 percent porosity. The volume percent of graphite was none; percent utilization of the active material was 98; and in ampere hours 38 ampere hours per pound of electrode.

Our composites after impregnation had a porosity of between 54 and 67 percent.

This column is the volume percent of graphite in the material. These last figures refer to the volume percent of graphite in the composite precursors before electrochemically impregnating a conversion. It's this one right here.

Once you convert it, the value drops, of course, and it goes between 20 and 39. The important fact of having that graphite in here is the effect it has on the ampere-hours per pound.

These two electrodes were electrodes that we made about 6 months ago in which the quality control and the processing variables weren't as controlled as they are now.

These are the data that we obtain now—between 75 and 84—almost double the value that we obtained for the commercial electrode.

With regard to the nickel zinc system, as I mentioned before, we had trouble making high-quality nickel zinc electrodes. As a result of this, these values aren't anything really to crow about, but they are not very bad.

(Figure 1-36)

In conclusion, we've demonstrated that composite electrodes based on nickel and graphite can be fabricated. These composite electrodes function exceedingly well as far as we can tell in the nickel cadmium cells. We also believe it will function very well in the nickel zinc cells. Composite electrodes can also be extended to other electric chemical systems.

One of the things we are looking at now is whether or not we can use pure lead in the manufacture of lead acid batteries for use in submarines. We would like to go to pure lead for many obvious reasons. But lead has a problem. It suffers from poor fatigue and creep.

What we've done — and I just did this about two weeks ago — I took this graphite material and impregnated it with lead.

I am holding a composite of lead, by the way. It contains 40 volume percent of graphite with pure lead. We believe we can apply this to other systems and we are very happy about this. There seem to be some very nice results.

## DISCUSSION

DUNLOP: In your commercial electrode, I don't know whose it was, but most of the ones we look at are typically about 50 amperes per pound.

SUTULA: 50 amperes.

DUNLOP: That's about pretty standard for everything we look at.

HALPERT: Are you talking about electrochemically impregnated?

DUNLOP: No.

SUTULA: Ours is electrochemically impregnated, right.

DUNLOP: Yes. We reduce the loading and it comes out the same. We do not use as much loading in that.

SUTULA: Thank you. I appreciate that.

ROGERS: Two questions. One, were those data for flooded nickel cadmium?

SUTULA: Yes, there was an excess.

ROGERS: Do you have any idea how it would operate in a starved cell?

SUTULA: No.

ROGERS: And the other question is: Do you use the electroless deposition using about 7 percent phosphorous or so?

SUTULA: 5 percent phosphorous.

ROGERS: Do you expect that would have any effect on the cell?

SUTULA: It doesn't appear to have any effect. We don't see any effect, right now. Let's put it that way. I'm sorry. I should have said that these cells have been cycled to a maximum of 20 cycles so far. So it's relatively new.

ROGERS: Thank you.

LEAR: What depth of discharge of those 40 cycles are you doing?

SUTULA: Depth of discharge? That's hard to say because we're getting utilizations of 101 and 110 percent, so take it from there.

LEAR: Looks like all the way.

SUTULA: Yes, it looks like it's coming out all the way.

THORNEL: Is there any warping of the positive plate at all?

SUTULA: No, I don't see any.

# COMPOSITES

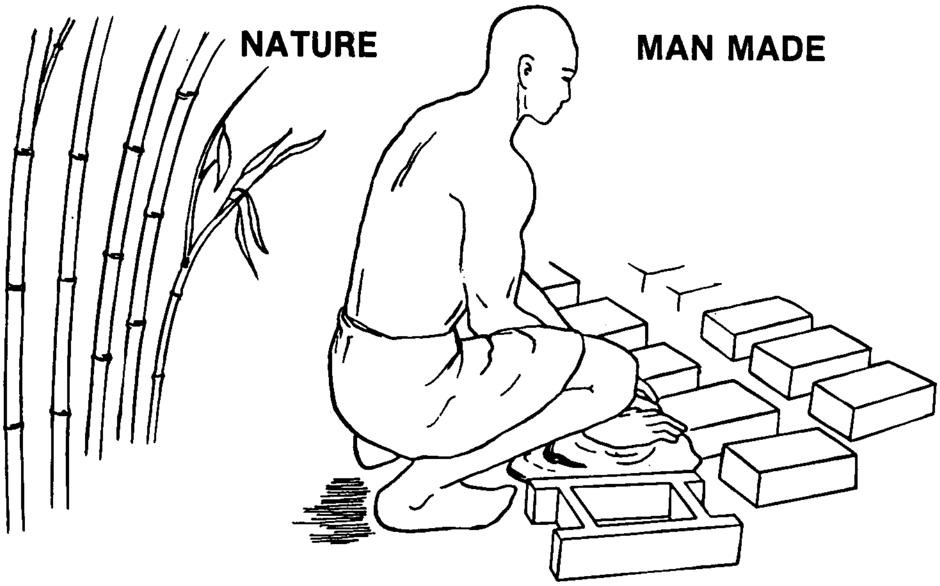
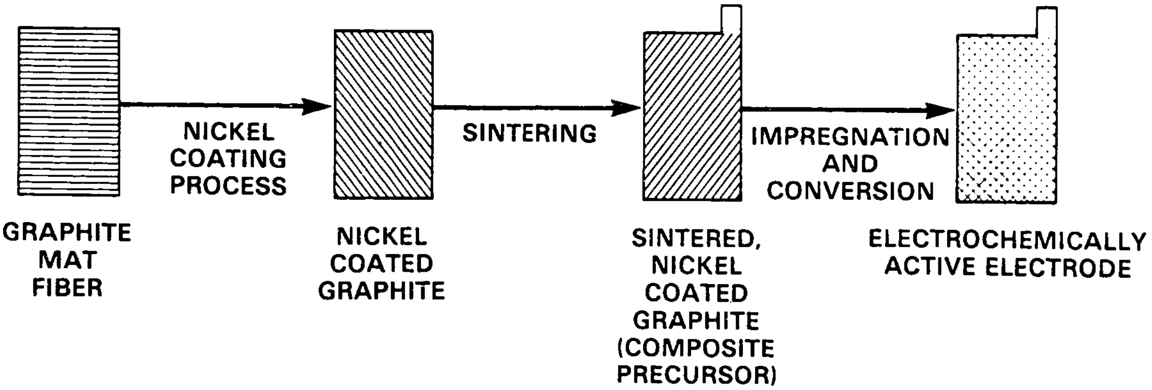


Figure 1-21

# HOW TO MAKE A LIGHTWEIGHT ELECTRODE



GRAPHITE MAT FIBER

NICKEL COATING PROCESS

NICKEL COATED GRAPHITE

SINTERING

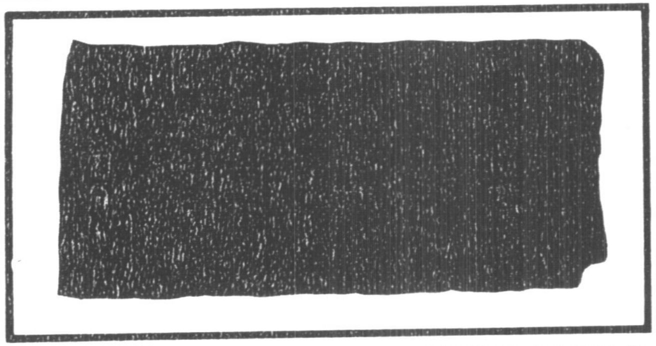
SINTERED, NICKEL COATED GRAPHITE (COMPOSITE PRECURSOR)

IMPREGNATION AND CONVERSION

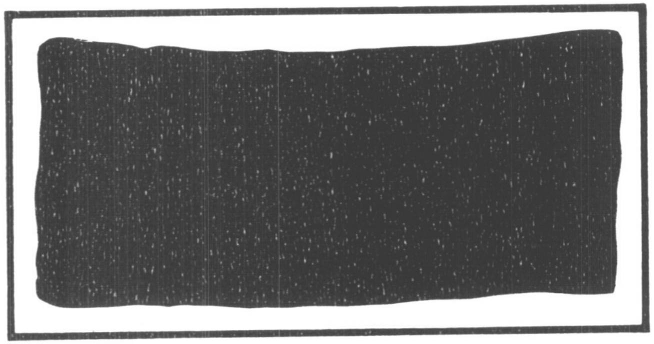
ELECTROCHEMICALLY ACTIVE ELECTRODE

Figure 1-22

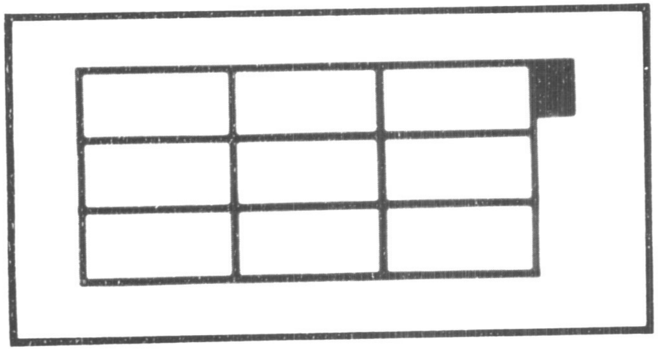
# LIGHTWEIGHT COMPOSITE BATTERY ELECTRODE



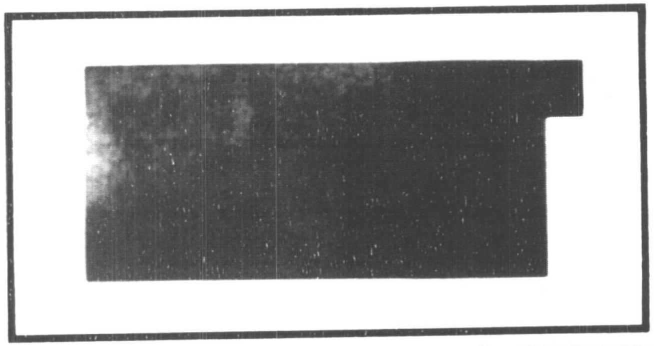
GRAPHITE MAT FIBER; THORNEL TYPE P



NICKEL COATED FIBER



NICKEL GRID



COMPOSITE PRECURSOR 65 v/o GRAPHITE

COMMERCIAL ELECTRODE: 34 gms.
COMPOSITE ELECTRODE: 17 gms.

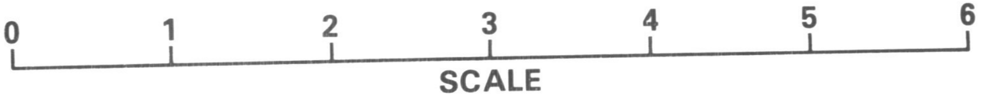


Figure 1-23

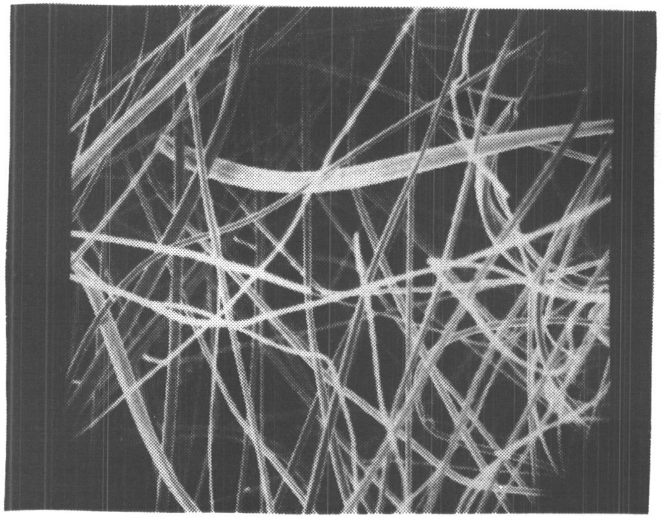


Figure 1-24

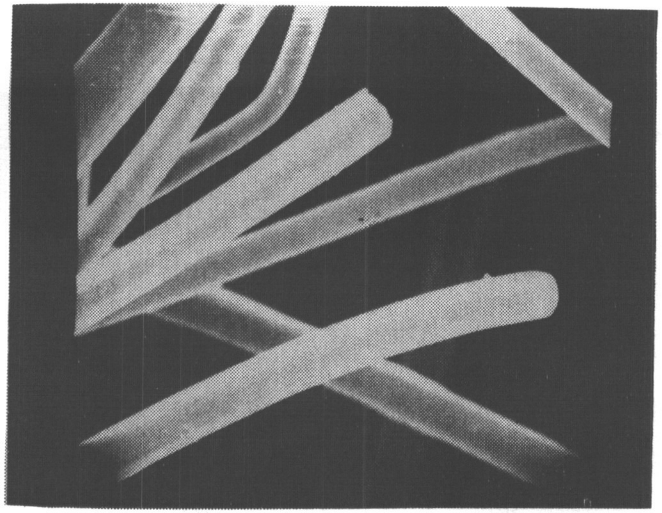


Figure 1-25

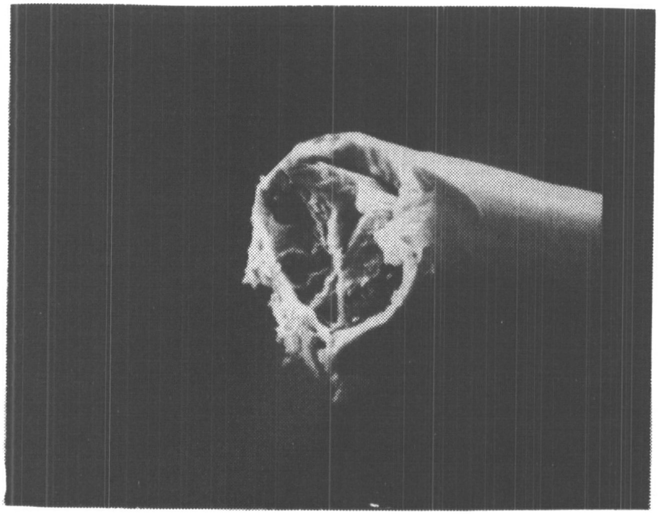


Figure 1-26

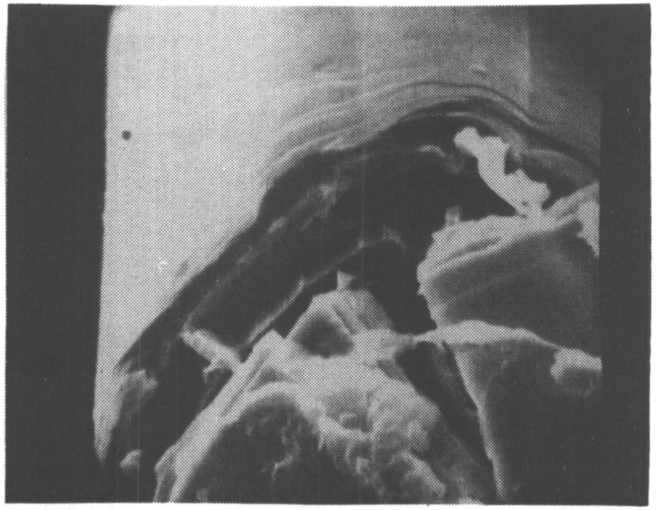


Figure 1-27

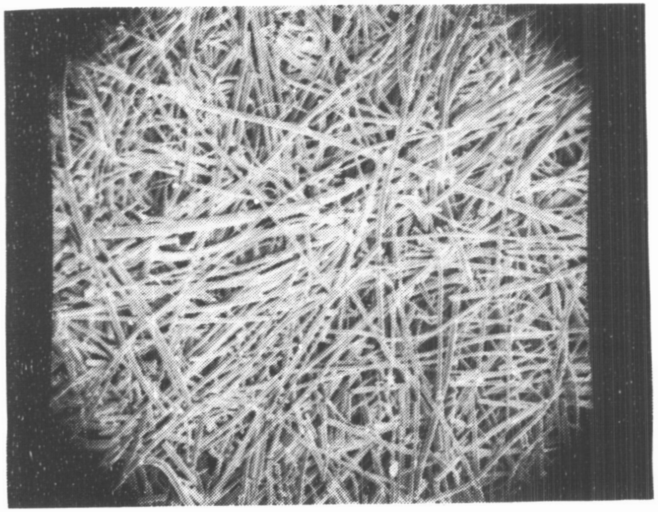


Figure 1-28

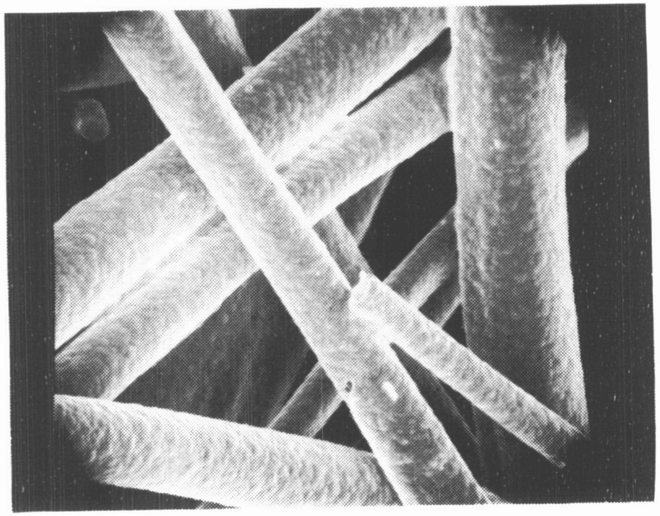


Figure 1-29

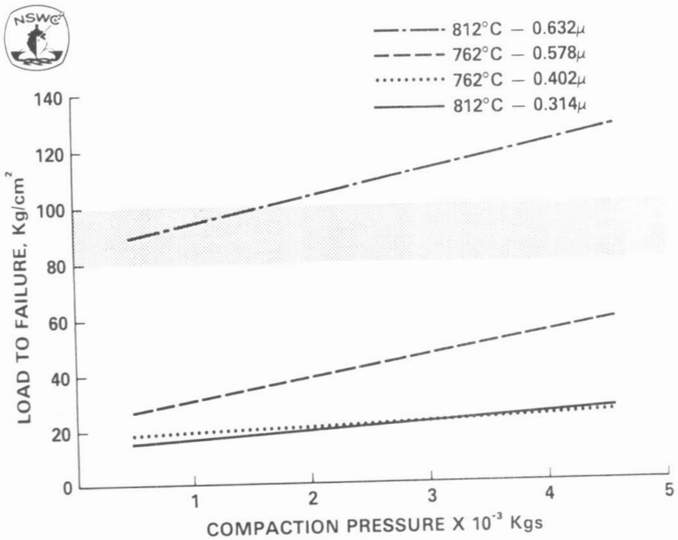


Figure 1-30

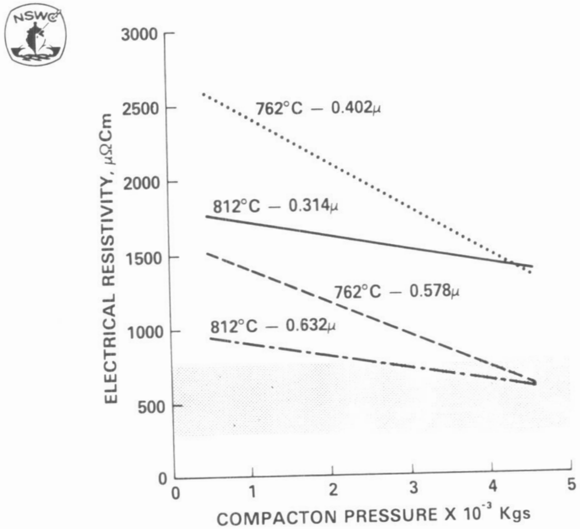


Figure 1-31

## COMPOSITE PRECURSOR

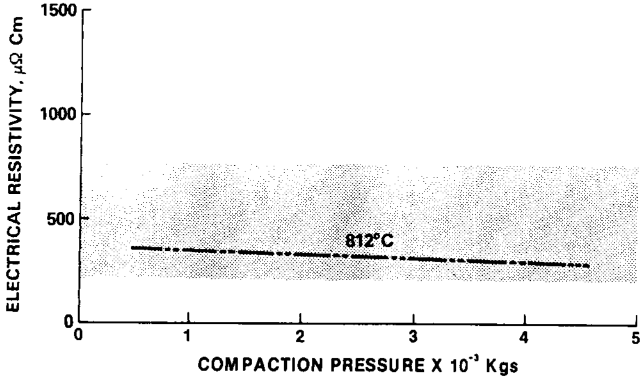


Figure 1-32

## CHARGE-DISCHARGE CURVES

ELECTRODE 23 (NICKEL COMPOSITE) VS CD

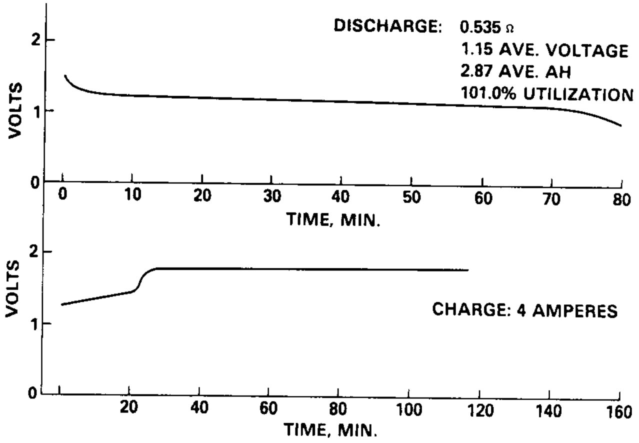


Figure 1-33

## CHARGE-DISCHARGE CURVES

ELECTRODE 24 (NICKEL COMPOSITE) VS Zn

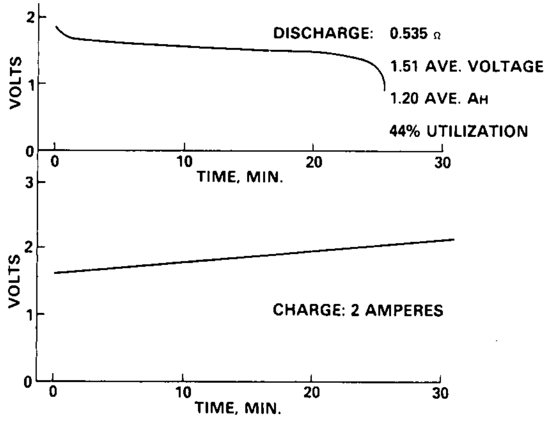


Figure 1-34

## PERFORMANCE OF NICKEL HYDROXIDE ELECTRODES

| Ni - Cd SYSTEM | POROSITY | V% C | % UTIL OF ACTIVE MATERIAL | Ah PER LB |
|---|---|---|---|---|
| COMMERCIAL | 75 % | 0/0 | 98 | 38 |
| COMPOSITE #1 | 54 % | 20/48 | 72 | 48 |
| COMPOSITE #2 | 59 % | 39/67 | 106 | 57 |
| COMPOSITE #3 | 63 % | 27/65 | 101 | 75 |
| COMPOSITE #4 | 67 % | 28/64 | 118 | 84 |
| **Ni - Zn SYSTEM** | | | | |
| COMPOSITE 5 | 63 % | 29/66 | 44 | 32 |
| COMPOSITE 6 | 61 % | 32/57 | 77 | 47 |

Figure 1-35

# CONCLUSIONS

- DEMONSTRATED THAT COMPOSITE ELECTRODES BASED ON NICKEL AND GRAPHITE CAN BE FABRICATED.
- COMPOSITE ELECTRODES FUNCTION EXCEEDINGLY WELL IN NICKEL-CADMIUM CELLS.
- COMPOSITE ELECTRODES CAN BE EXTENDED TO OTHER ELECTROCHEMICAL SYSTEMS.

Figure 1-36

# LIGHTWEIGHT POROUS PLASTIC PLAQUE

M. Reid
NASA

We aren't quite as far along as Dr. Sutula, here. We have had a little different approach and considerably more difficulty in getting the satisfactory plating.

(Figure 1-37)

The project was initiated about 2½ years ago. We sent out RFP's to 14 companies from which we received only four bids and those were all rejected for one reason or another (insufficient experience in plating or lack of a broad view). We decided at that point, before putting out another RFP, to start a small in-house project in order to explore the project a little further for ourselves so we would know a little more of what we were looking for.

And we then investigated all the types of porous substances that could be found. We've looked at plating techniques. We have not put out another RFP because we've felt that at this point we have made better progress in-house than we could have with an RFP.

We have obtained all sorts of porous materials and we've purchased commercial materials and asked several manufacturers to produce some materials for us in the form, thickness, density, and so forth that we were interested in.

I have been working on this. Bob Post worked on this using his background in porous fuel cell electrodes, and recently Doris Britman joined me on this project.

(Figure 1-38)

This is a SEM picture of a commercial nickel plaque. This actually is a fuel cell plaque. The thickness is 25 to 30 mils. The porosity of a commercial nickel plaque is 73 to 78 percent. The density, at least of the samples that we have on hand, is 1 to 1.2 grams per square inch.

(Figure 1-39)

Recently, there has been a battery plaque made by Sony in Japan and used in some small batteries. This is produced by plating electroless nickel followed by an electrolytic plate on top of pellon nylon. The material at 100 magnification is shown on the left. On the right is a 1000-fold magnification of the pellon nylon itself.

(Figure 1-40)

At the time we started this project, the only thing that we knew along these lines, as far as a porous plastic material being plated, was the United Technologies Polysulfone Plaque that was used as a fuel cell reservoir. This material was made from small fine particle polysulfone that was produced by dissolving the polysulfone into a compatible solvent and then spraying this into a solvent in which the polysulfone was not mixed, in which case they obtained very small particles of the polysulfone. They pressed these together, centered, and plated it. They were trying to put solutions through a pump solution through the plaque.

This gave a good plate on the surface but a poor plate on the interior—not good enough for our purposes, at any rate. This material also was not as porous as we would have desired and it was very, very brittle. So we felt that this would not be satisfactory.

(Figure 1-41)

Among the materials that we looked at were carbon felt and carbon cloth. These are 300 magnifications of those.

(Figure 1-42)

We obtained several experimental materials. On the left is the Union Carbide material, a carbon foam which looks like a mass of small soap bubbles with little holes in the walls. And on the right, another type of porous carbon which is called verticulated vitreous carbon, which comes from carbonizing an open cell foam.

(Figure 1-43)

On the left, the flow properties in the porosity would not be comparable to a standard nickel plaque. And on the right, there was insufficient surface areas as far as we felt.

We looked at porous ceramics. On the left is a sample of Corning ceramic that is used as a support for emissions for automobile emissions converter. On the right is a type of commercial battery separator that we treated to increase the porosity of this. This material looked interesting from the standpoint of the structure, but it did not have as high a porosity as we wanted for this. We also felt that the material for this particular item would possibly degrade the oxidizing atmosphere of the nickel electrode.

(Figure 1-44)

Two other materials: Gore Teflon — this has a very nice fine structure, but Teflon would not be well plated. On the right is PVC made from sintered spears of PVC which had a lower porosity than we would have liked. Both of these were flexible and strong, but the porosities and the plateability of both of these were wanting.

(Figure 1-45)

We asked the manufacturers to make samples of the two materials we were interested in. These samples were made in thin sheets, 30-35 microns thick, and were composed of Bendix polypropylene material. This is small particles of polypropylene ground with small particles of salt and the material is pressed and melted so that the polypropylene melts and then the salt is extracted.

On the right is a Monsanto polyurethane, a very interesting material called spheropore. It has a very high surface area and lots of small pores. Both of these we examined in the form of sheets.

We were not able to plate the polyurethane material well. We were able to plate the polypropylene well on the surface, but it does not have as high a porosity as we would have liked and does not have sufficient flow-through characteristics.

(Figure 1-46)

The material that we finally settled on is a proprietary porous plastic that we have modified to further increase the porosity. It comes in sheets from 25-30 mils thick. Some of it is in sheets as thin as 22 mils. It is very lightweight. The edge view is shown on the left. The surface view of one of the modifications is on the right.

This has a porosity, after the treatment that we give it to increase the porosity, of about 85 percent, which leaves room for putting some nickel on the surface of the plastic and still not decreasing the porosity below what you would really like.

The average pore diameter after the treatment is one and a half to ten microns depending upon the type of modification with which you start.

(Figure 1-47)

And here are two more views at 300 and 1000 magnification. If you take that one sheet on the left of yours and put that up then you can compare the standard nickel plaque, so that the pore sizes surface areas of these materials are pretty comparable. They look different, but as far as the porosity, pore sizes, and surface area, this material is comparable to the commercial nickel plaque.

(Figure 1-48)

We were able to plate this by pumping a solution through. We tried several means of plating. Just submersion does not plate the interior well enough. On the surface, yes, but not well enough on the interior. We have tried with the assistance of one of the plating solution manufacturers some ultrasonic work and this has worked out to be just better than submersion in the plating solution, and, of course, much easier than trying to pump plating solution through the plastic. But that has not been worked out well enough, yet. We hope to do some more work with that in the future because there is some promise, in particular, when you go to any sort of large-scale process.

(Figure 1-49)

We've tried in the last several years, having selected this particular material for investigation, various methods of plating. Immersion is not satisfactory. Ultrasonics have been much more successful in producing a uniform plate in the interior of the plastic than immersion. We have concentrated on trying to design a way to get the solution through uniformly so that the material is plated throughout uniformly as well as radially.

The biggest problem we have had so far has been designing a rig. We feel that we have achieved this recently.

The problem is that the material is somewhat flexible and if you pump solution through, particularly the hot nickel plating solutions, then you have to support the material. It's hard to get a porous support that will still allow your uniform flow-through and not plate itself more rapidly than the plastic that we are starting with.

We so far have looked at the published nonproprietary formulations. This is what we started with just to try and see what materials would plate and what would not.

We've looked at some proprietary phosphite baths, we have done a little with a manufacturer on proprietary boride baths. We feel that the proprietary boride baths are the way to go since the boride nickel—electroless nickel—coatings have much lower content of impurities than the phosphite baths. You can get down as low as a half of a percent of one or less. With these you have much better conductivity than with the phosphite baths.

In our material we feel that we are going to have to put a very thin plate of nickel on and we are going to need the highest conductivity obtainable.

(Figure 1-50)

We've looked at variations in the formulation and treatment of the plastic with which we're working. The manufacturer has tried a batch of carbon-loaded plastic to increase the conductivity. We don't feel that it increases the conductivity. We don't feel that it increases the conductivity sufficiently to plate and use without nickel plating on the surface. But we are going to look at that a little further. There seems to be some indication that the addition of a certain amount of carbon makes the production of the material somewhat easier when you put the grid in.

The manufacturer has produced two batches of material with expanded metal grid in between—bonded in the interior of the material. And, of course, when we put the grid in, the first question is, Would there still be conductivity or would the grid itself be completely encased in plastic and not give sufficient conductivity?

We found that the grid was not covered with too much plastic, and we got good conductivity from the plated material and the surface to the grid for the current collection. We can start, then, with the plastic itself with the grid in it and try to plate that. We have the grid already incorporated and don't have to have a second step to add the grid.

So far we have very little in the way of thick plates because we have had problems with uniform plating and in getting the material that we wanted. We've also had problems with the material with the grid in that the manufacturer has to change the processing variables somewhat. The material that we have received so far has not been as porous as the original material without the grid and has not had as good flow-through characteristics. But I think that is something that can be resolved without too much difficulty.

We expect at this point in the near future to do more plating investigations and be able to try to load some samples. And then we hope to try then to charge and discharge curves at electrodes, make cells, and check the long-term degradation of the electrodes.

Just a comment on the conductivities that we've had so far. We don't feel that with this sort of material we will quite be able to obtain the conductivities of the standard nickel plaque. The pieces we have so far have resistances of between two and five times those of the standard nickel plaque. We feel that by using the boride baths we can improve this.

As far as porosities, the material before plating is 85 percent. In the pieces we've plated, we have anywhere from 50 to 75 percent porosity afterwards. We feel that we're going to have to go to relatively thin coatings to keep the porosities at 70 percent or so. We're going to have to go to the boride baths in order to do this.

The weight situation is about the same as with the carbon plaque. You can reduce the weight of the plates by more or less 50 percent which means a difference in the overall weight of the battery by about 25 percent.

The pore sizes of these materials as plated are in the same range as the standard nickel electrodes.

## DISCUSSION

LEAR: Dr. Reid, about the conductivity, did you measure the resistivity of the plates for the phosphorous pad and the boride baths? Was there a variance?

REID: We haven't done that much with the boride baths with material with a grid. Really, we've had an awful lot of trouble in getting uniform flow with what we've done. And most of our work has been concentrated on trying to get uniform flow and getting a rig that we can pump the solution through and get uniform flow. That's been the big headache so far.

We've just recently received the second batch of plastic with grid in it. The first batch did not have regular flow-through characteristics and we had a lot of trouble plating it. We've plated a few small samples, but nothing very large as yet.

We've tried two resistance measurements, one with a rig where you have mercury contacts on both sides and the other is a measurement in solution with some sophisticated electronics which I am not up on. We get in the range of two to five times that of the standard plaque as far as resistance.

MAURER: Two questions. Have you tried to vacuum-impregnate your plating solution? And number two, did you consider vapor deposition?

REID: Well, vapor deposition—I'll take the last first. The vapor deposition we feel would largely coat on the surface. Now, vacumm impregnation of the plating solution? You can vacuum-impregnate and then heat perhaps to decompose what's in there. But that doesn't give you very much and you will have to do a number of cycles. We've talked about this. We haven't tried it yet. I would be happy to talk to you if you can come up with suggestions for depositing an appreciable amount of nickel on there. The nickel plating solutions for electroless nickel are pretty dilute and you have to have quite a few cycles of this. But this is one thing we've talked about. At the moment, we've felt that the most practical thing is to try and design a flow-through system. But that's a possibility.

MAURER: Many cycles of vacuum impregnation to flow through it?

REID: Yes, you would have to do that.

GROSS: One way you can get the good impregnation or the good plating for porous materials is to use salt, a salt tab technique. Of course this is normally done at high temperatures, but if you could use a low temperature salt bath, it might be rather successful.

REID: Well, I think the last question was impregnation of a plating solution rather than the active nickel. Is that what you're talking about, the plating itself?

GROSS: I'm talking about the plating of nickel.

REID: The problem is until you get electroless nickel on there it's not conducted. I think you'll have to put maybe a flash of electroless nickel on.

GROSS: Perhaps.

REID: But that's a possibility, yes.

GROSS: But there are other possibilities.

HALPERT: Did you say how thick your samples were?

REID: 23 microns. I have some samples.

NASA-LEWIS LIGHTWEIGHT NICKEL PLAQUE PROJECT

BACKGROUND OF PROJECT

- INITIATED SPRING 1976
- RFP'S TO 14 COMPANIES
- BIDS FROM 4 COMPANIES REJECTED
- SMALL IN-HOUSE STUDY TO LOOK AT FEASIBILITY OF PROJECT BEFORE PUTTING OUT ANOTHER RFP

PROGRESS OF PROJECT

- INVESTIGATION OF POROUS SUBSTRATES AND PLATING TECHNIQUES HAS BEEN CARRIED OUT ON A SMALL SCALE, POROUS MATERIALS HAVE BEEN OBTAINED AS SAMPLES, PURCHASES OF COMMERCIAL MATERIALS, AND PURCHASES OF EXPERIMENTAL MATERIALS MADE TO OUR SPECIFICATIONS.

Figure 1-37

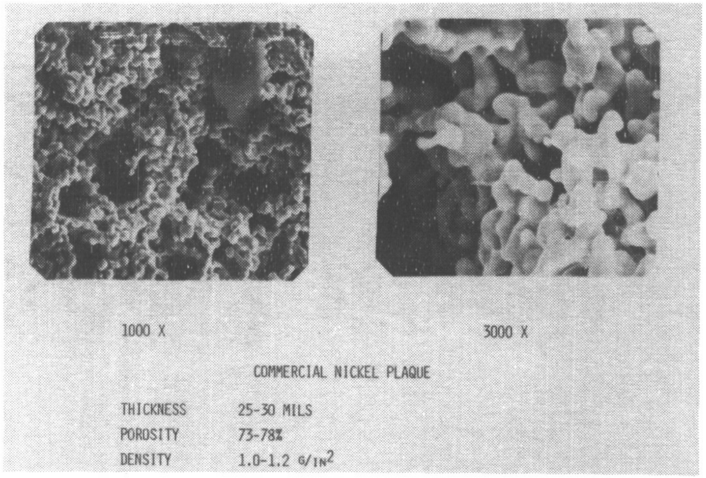
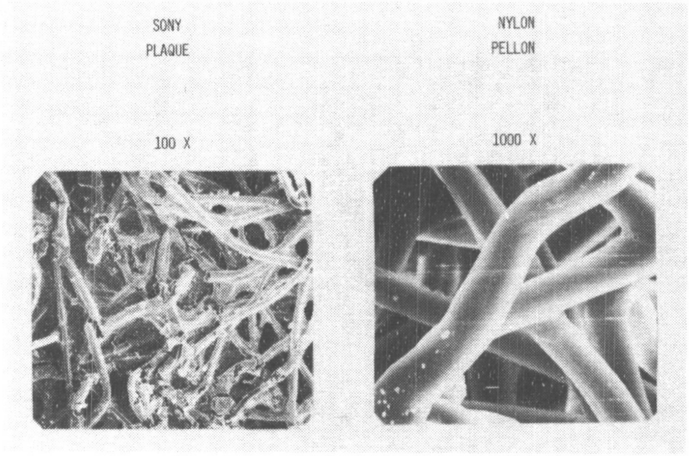


Figure 1-38



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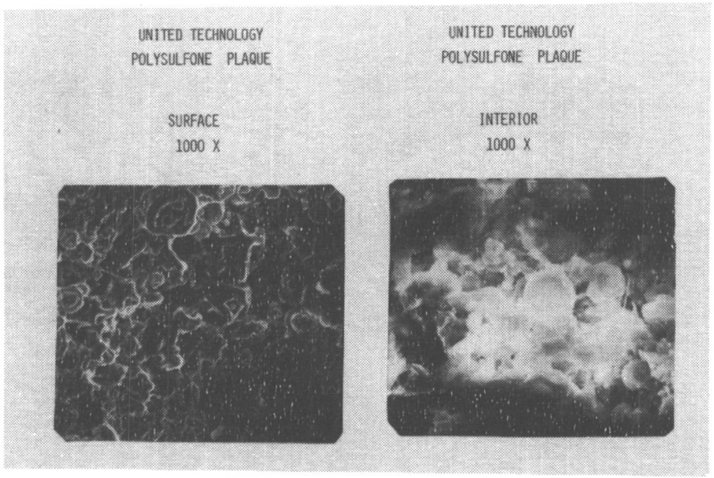

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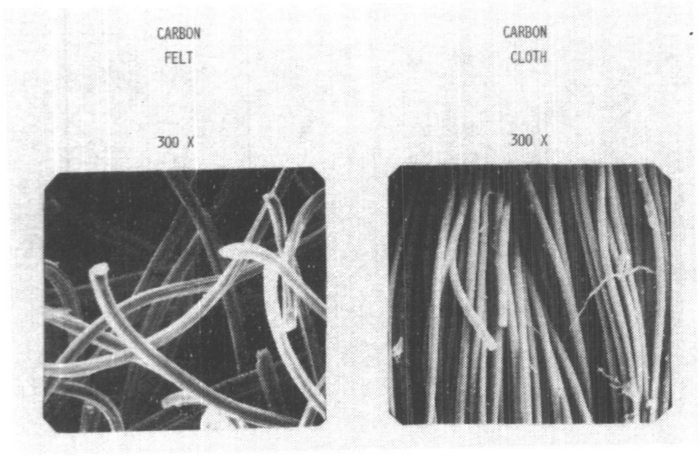

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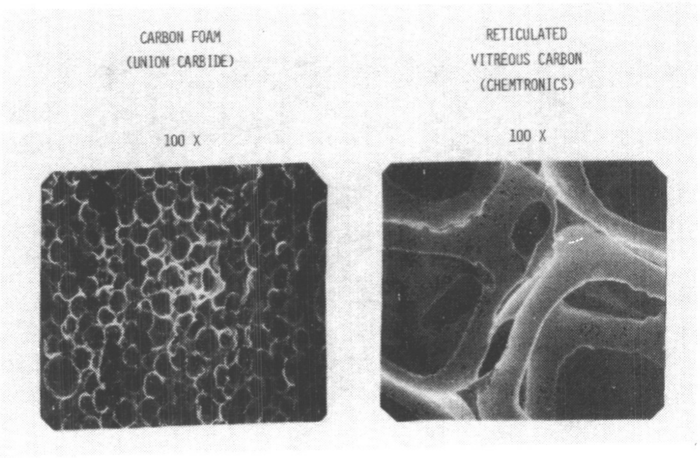


Figure 1-42

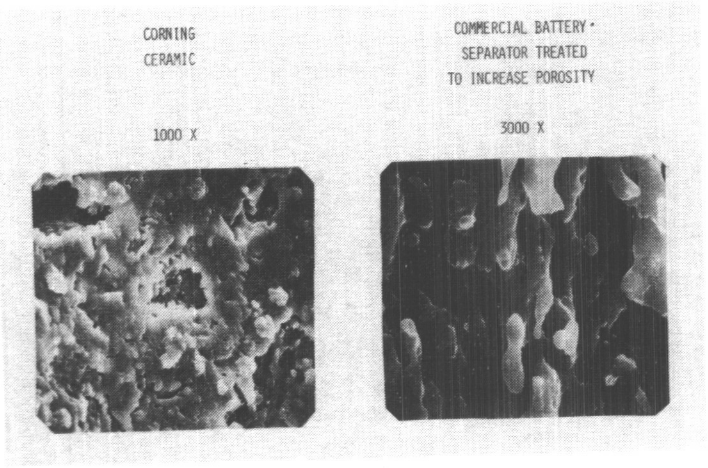


Figure 1-43

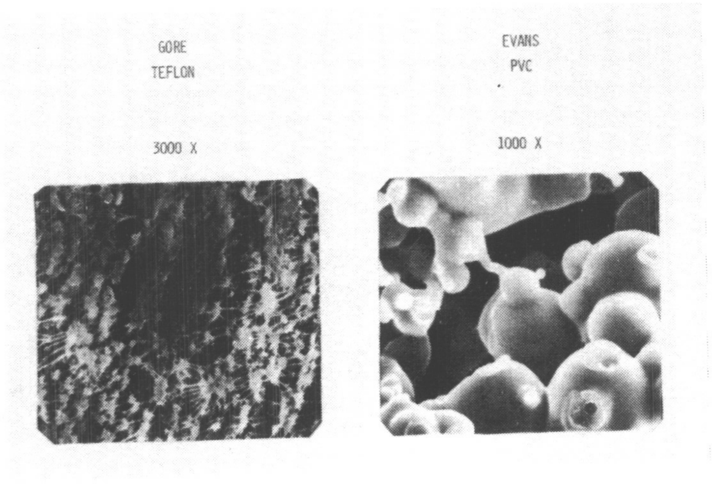


Figure 1-44

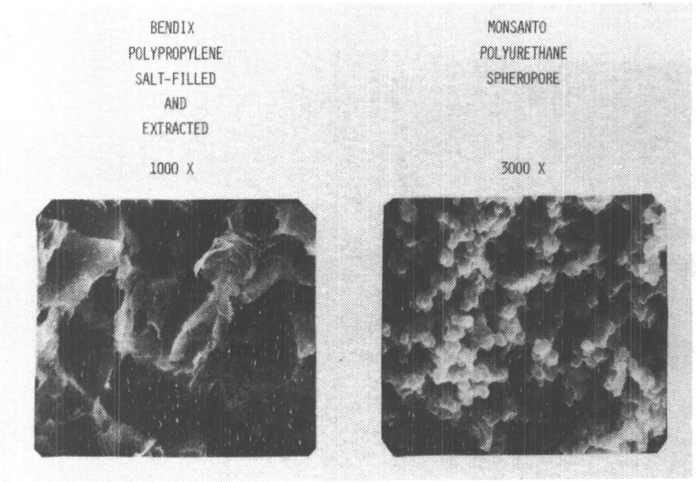


Figure 1-45

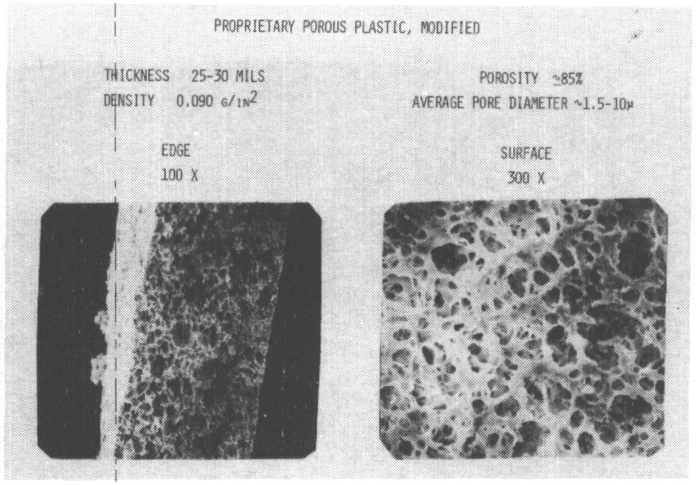


Figure 1-46

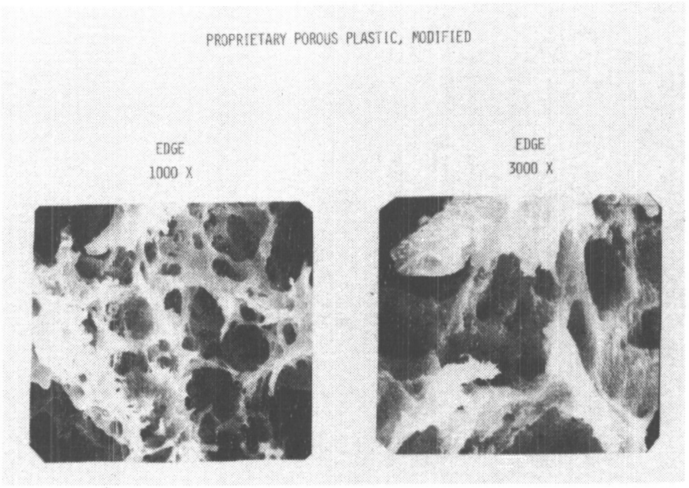


Figure 1-47

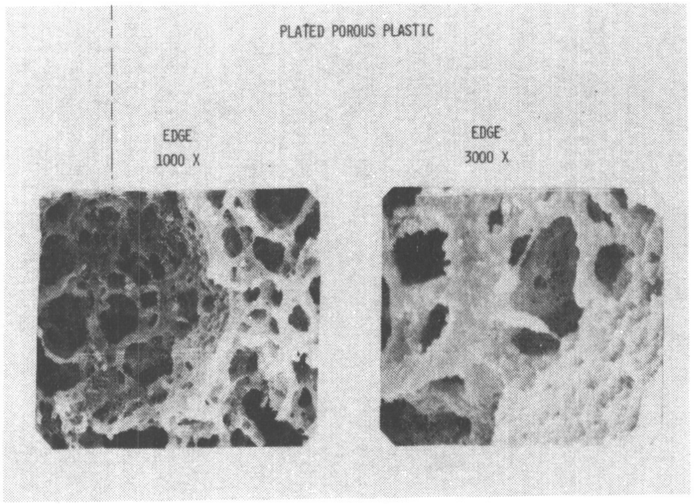


Figure 1-48

## PLATING INVESTIGATION

METHODS OF PLATING

- o IMMERSION
- o ULTRASONICS
- o FLOW-THRU

BATH FORMULATIONS

- o PUBLISHED NON-PROPRIETARY FORMULATIONS
- o PROPRIETARY PHOSPHIDE BATHS
- o PROPRIETARY BORIDE BATHS

**Figure 1-49**

## MATERIAL MODIFICATIONS INVESTIGATED

VARIATIONS IN FORMULATION AND TREATMENT
CARBON LOADED PLASTIC TO INCREASE CONDUCTIVITY
INCORPORATION OF GRID

## PROBLEMS TO BE RESOLVED

CONDUCTIVITIES AND POROSITIES AS FUNCTION OF AMOUNT OF NICKEL PLATED ON THE PLASTIC
LOADING
CHARGE AND DISCHARGE CURVES OF ELECTRODES AT DIFFERENT CURRENT DENSITIES
CELL PERFORMANCE
LONG-TERM DEGRADATION OF ELECTRODES

**Figure 1-50**

# CHEMICAL ANALYSIS OF POSITIVE AND NEGATIVE PLATES - A SURVEY

G. Halpert
Goddard Space Flight Center

At the end of last year's workshop we at GSFC were talking about the work that had been presented. We realized that a lot of chemical analysis data were being presented on the cadmium electrode and the nickel electrode and wondered about the consistency of the analysis results.

We decided to send a letter to some of the people who we know are active in doing chemical analysis and asked them if they would be willing to participate in a survey to evaluate whether the processes were uniform from company to company.

Seven contractors and government organizations responded and agreed to do this. And we sent them some samples in a regular array. These samples happen to be the same group as the NASA standard cell.

(Figure 1-51)

We took six plates, six positives and six negatives, and punched 1-inch diameter discs from them, as you see. They were, of course, chemically impregnated positives and chemically impregnated negatives, six positives and six negatives. We prepared six sets of samples. All No. 1 discs went to one organization. No. 2 went to another, and so on.

Then we waited for the results. Fortunately, we have had four respondees as of this moment, although we do have some promises that the others will respond shortly.

(Figure 1-52)

It is interesting to note what the uniformity was. If you look across disc weight, these are averages now, of the six samples from each of the participants. We, of course, will not identify any of them to you. The idea was to see if there was consistency in analysis.

As you look at this, you can see that it is pretty close in terms of disc weight, pretty close in terms of thickness. Some consistency with regard to the grams of cadmium hydroxide, and of course, some consistency in terms of ampere-hours. And I think you find that as you go down the whole table, there's some degree of consistency across the board.

With regard to the cadmium metal, that is, the charged cadmium in a plate, these were, of course, very small quantities. And there is a little more difference there. But, as you will see there wasn't much significance to those.

In regard to the positive, we have the same kind of result. The disc weights and the thicknesses were all pretty consistent. And so with the rest of the analysis, which kind of gives us some feeling that we seem to have some degree of consistency.

(Figure 1-53)

I scaled this up to show you what would be in a 20-ampere-hour cell. Included in this list now is the manufacturer, so we have his chemical analysis as well as the four others who submitted data.

Although there is a little difference here in No. 5, a little bit higher in terms of the grams of ampere-hours of cadmium hydroxide, you can see that the others were quite consistent, which was interesting.

As far as the charged cadmium was concerned, there is a little bit of difference here, but remember we're dealing with a very small quantity of active material, a 1-inch diameter disc contains only a small quantity of active material. We would expect to have a little bit more error there.

If you look across the total amount of cadmium, in ampere-hours now of the cadmium electrode, there's 68, 68, 69, 71, which is not too far apart. Again, the 86 is a little high because of that top number.

Some of these were done using the procedure that NASA had put into their X document. Others use variations and different wet chemical techniques. Some have used atomic absorption to identify the different species.

On the positive electrode we see some degree of consistency across for the discharged material. There was a little bit of a problem there in No. 8, and it looks like he may have calculated his charge and discharge backward. But if you look at the total active material here, again, they are not too far different. No. 5 which was as high in cadmium was one of the higher ones on the positive electrode as well.

I did make some calculations in terms of the percent of the electrode. It turns out that on the negative, the plaque was about 30 percent, actually 30.5 percent, the substrate about 16.5 percent, and the active material about 53 percent.

In the positive electrode we are talking about as average numbers, 34 percent for the plaque, 20 percent for the substrate, 43.4 percent nickel hydroxide, and then there was 2.5 percent cobalt hydroxide. That was probably one of the surprises, more of a surprise in this than the others. The cobalt is expected to be close to 5 percent.

(Figure 1-54)

Now, what I wanted to do and unfortunately we don't have enough data to show it, was the variation across a single plate. Here we have the way the discs were punched out. Negative plate A and positive plate A are shown. The three numbers indicate the weight, the thickness of the disc, and the active material quantity as measured by the individual participant. You can see that with regard to the negative they were all actually 1.52, 1.59, 1.57, 1.54. The thickness 31, 30, 32, 31 mils is typical of a plaque. And then in the active materials we see 0.78, 0.85, and 0.99 grams. The data is also given for the positive. Here is the low one that we saw in No. 8 before. This is the active material in the discharge condition that we are talking about.

In conclusion, we do hope that the other four vendors will submit their samples to us in a relatively short time and upon receiving their data we hope to include them in the document of the proceedings.

## DISCUSSION

METHLIE: Did you make any effort to separate out the process variants from the analytical variance here? I notice that the same sample doesn't go to the four people that responded. Is that correct?

HALPERT: They get a sample from each one of the six plates, but it's from a different position on each plate.

METHLIE: From your process documentation, can you comment on what variance you might expect to cross the same plate?

HALPERT: No. But it's on the order of what we see here. I would expect there is enough variation between plate to plate that we would see this kind of variation in it.

ROGERS: On the charged cadmium, I am a little surprised you even bothered analyzing it because it will react with the moisture and oxygen in the air and end up uncharged cadmium. I guess I don't see the significance in it. It would be different depending upon where it was shipped, etc.

HALPERT: Yes, it does (as you pointed out) depend on where in the process you take these plates out. And, yes, there can be a significant amount of charged cadmium in a plate if you take it out when the electrode has been charged and not discharged all the way.

One would think that maybe you would react all the cadmium in the air in the presence of moisture. It turns out that we can still measure quite a bit of cadmium in a plate that has been charged and not fully discharged. Though in this particular case, these plates were taken out very early in the process before they had a chance to be charged and discharged.

ROGERS: No, my point was that, by the time you shipped them to someone else, the plates would have changed sufficiently depending on the environment in which they were in afterwards, as well as when you ship them; that the plate could change, and, therefore, the comparison doesn't necessarily depend on the analytical technique but rather on the history of the plate. In other words, the destruction of the cadmium is a time function.

HALPERT: Okay, I would accept that. I would think that probably because of the size of the sample we have the greater error, but there is also that possibility, too.

MAURER: Do these results alarm you since you are seeing plate to plate and variations across plates to the order of 10 to 15 percent? And you would hope to sort plates to 2 percent or so?

HALPERT: Sorting of total plate is in terms of active material now. We sort in terms of weight. I think I will have a better feeling when I have the other three or four samples in. There can be considerable weight differences as there are thickness differences. Of course, we've done a lot of measurements and found that the distribution is such that there is some considerable variation, but in general you can take a center section out of a distribution to have a more normalized sample.

And, of course, when we do the selection in the manufacturer's facilities, we do have a ±3.5 percent weight screening limitation, so that's 7 percent right there.

MAURER: One additional question: Do the nickel hydroxide results have cobalt included in them or does that have the cobalt subtracted out?

HALPERT: In only one case did we actually have a cobalt reading from one of the sources. We have not completed our own cobalt reading analysis. But the 2.5 percent was of concern, although it is not part of the nickel hydroxide numbers that we see.

I was concerned about the 2.5 percent because we normally expect the manufacturer to put in 5 percent. Therefore we are concerned about that. Since I only have the one I don't have enough to go by at the moment, but we are going to check that.

MAURER: How about the cadmium?

HALPERT: It does not include the cadmium and we have not looked for the cadmium yet in the positive.

**CHEMICAL ANALYSIS EVALUATION**
SAMPLE SELECTION

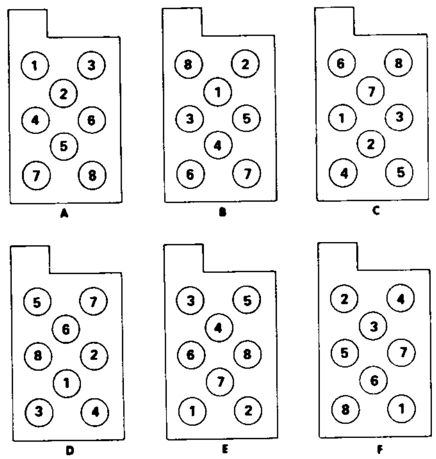


Figure 1-51

CHEMICAL ANALYSIS EVALUATION

(Extrapolated to a 20 amp hour Cell)

| | PARTICIPANT | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Discharged $Cd(OH)_2$ (ah equiv) | | | 68.56 | | 84.67 | 64.15 | 68.97 | 70.12 |
| Charged Cd (ah equiv) | | | .17 | | 1.49 | 3.87 | .73 | .79 |
| Total Negative Electrode | | | 68.73 | | 86.16 | 68.02 | 69.70 | 70.91 |
| Discharged $Ni(OH)_2$ (ah equiv) | | | 33.62 | | 33.38 | 27.61 | 34.01 | 5.77 |
| Charged NiOOH (ah equiv) | | | | | 6.03 | 6.05 | 1.84 | 31.55 |
| Total Positive Electrode | | | | | 39.41 | 33.66 | 35.85 | 37.37 |

Figure 1-53

CHEMICAL ANALYSIS SAMPLE RESULTS - AVERAGES

| | Participants | | | |
|---|---|---|---|---|
| NEGATIVE PLATE | 3 | 5 | 7 | 8 |
| Disc Wt. (g) | 1.593 | 1.576 | 1.595 | 1.605 |
| Thickness (mils) | 31.1 | 30.3 | 31.8 | 31.8 |
| $Cd(OH)_2$ (g) | 0.834 | 1.030 | 0.839 | 0.853 |
| $Cd(OH)_2$ (ah equiv) | 0.30 | 0.38 | 0.31 | 0.31 |
| Cd (g) | .0016 | .014 | .006 | .0096 |
| Cd (ah equiv) | .00074 | .007 | .003 | .003 |
| POSITIVE PLATE | | | | |
| Disc Wt. (g) | 1.320 | 1.319 | 1.304 | 1.311 |
| Thickness (mils) | 27.6 | 26.7 | 27.8 | 28.0 |
| $Ni(OH)_2$ (g) | .565 | .561 | .572 | .097 |
| $Ni(OH)_2$ (ah equiv. ) | .16 | .16 | .17 | .028 |
| NiOOH (g) | - | .064 | .030 | .516 |
| NiOOH (ah equiv) | - | .019 | .009 | .150 |

Figure 1-52

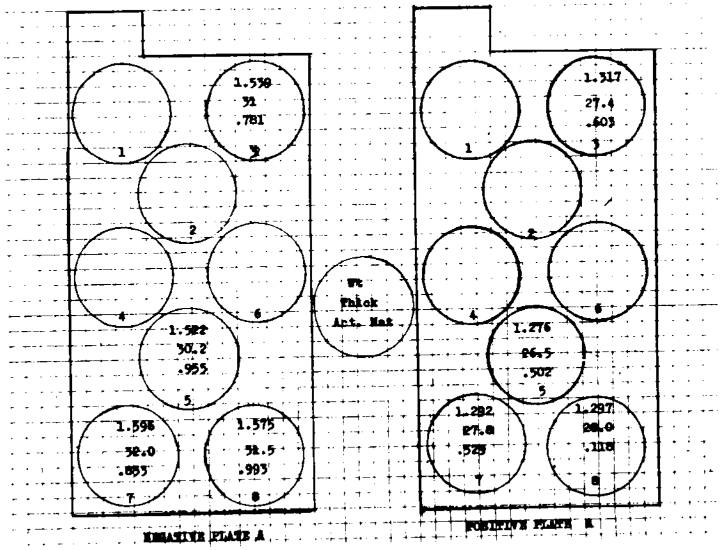


Figure 1-54

# CELL DESIGN AND MANUFACTURING CHANGES DURING THE PAST DECADE

D. Baer
Goddard Space Flight Center

As the title indicates, this talk is really to look at some of the design changes that have taken place over the last decade. The paper will consist of an excerpt from a paper prepared by Floyd Ford and myself. Floyd presented it at the Electrical Chemical Society meeting in Pittsburgh last month, plus some more recent data.

The program was undertaken in conjunction with GE to evaluate eight of what we consider the more important designs that are presently being used and that were used over the last 10 years. Although most of these designs have been tested and evaluated by various users, there hasn't been any systematic approach to compare the relative merits of each design and that's basically the goal of the paper.

(Figure 1-55)

These are GE 12-ampere-hour cells and there are six cells per group. The control cell, Group 1, is the present aerospace design of processes with no extra treatment of the negative. It contains a nonwoven nylon separator with PQ-treated positives, decarbed, and it has IUE loading and 31 percent KOH.

The IUE loading is about 5 percent lighter than the present loading that's been used by General Electric and about 10 percent lighter than what was used in the early 70's. Group 2 is Teflon-treated and it is the same plate as the control group. Group 3 is silver-treated. It is the same plate as the control group. Group 4 is a lighter-loaded plate. And Group 5 is a different spiral than the control and the positives were not PQ-treated. Group 6 is the same as the control except it has a popypropylene separator. Group 7 is the old plate design and old processing. There is no PQ treatment. The negatives were not depleated during the flooded cell tests. And there was no decarb process. Group 8 is the 1968 design plate, but we used present aerospace processes except for the PQ treatment. Group 7 is probably, as best as we can tell, representative of the six-and twelve-ampere hour cells on test at Crane in the synchronous orbit test.

The plate thicknesses are all typical composites of 0.069 centimeters and 0.079 centimeters for the negatives for Groups 1 through 6. Now the older plate had the thicker positives and thinner negatives and the positives weren't sized.

The next column is a figure comparison of the loadings and you can see Group 4's positives are quite a bit lighter load than the others. And the rest of the plates are still loading for the positives and are about the same.

Now, in the negatives, the older plates you can see a thinner plate and you can see the loadings per unit volume. That is gram per DM-3 of sinter and is quite a bit more.

As far as the KOH goes, the goal was to get as much KOH as we could in the cells and still keep pressures in some kind of reasonable range, about 30 to 70 psia was the goal. And you can see, normally in the design of the control you would expect to have something on the order of 35 or 36 cubic centimeters and you can see that they have 40 cubic centimeters of electrolyte.

The precharge adjustment—the Spec called for 40 ± 5 percent of the excess negative. And since for the Groups 1 through 6, we decided to precharge them all the same, and I kept it, I think, somewhere between 38 and 41 percent.

Group 7 wasn't precharged. Since the negatives weren't depleted and there wasn't too much excess negative, really, we didn't put any precharge at all. It's not too unlike what was done in the late 60's.

Group 8 was precharged 1.8 ampere-hours which was about 30 percent of the excess negative.

(Figure 1-56)

This figure shows the positive plate utilization. It's really a percent of theoretical versus the positive loadings and grams per decimeter cube. The top curve is the flooded and there is very little difference in utilization. Group 5 fell out a little bit. And I am not too sure why that happened.

The bottom curve is the final cell. It's an average of 3.2°C capacity test.

Since there's really very little difference in loading between Groups 8, 5, and 1, I think this large drop-off is due to the fact that the Groups 5 and 8 did not have the PQ treatment. And that's what I attribute to the fall-off. And I think that will be more evident perhaps a little later. Those cells do have quite a bit different characteristics.

(Figure 1-57)

This figure is the flooded negative plate utilization. It is a percent of the theoretical. And here you can see a vast drop-off in the percent of utilization with loading. And we have a good spread in the loading numbers there. Although this wasn't the intent of the program when we started, it is some of the data that fell out.

(Figure 1-58)

This figure shows the final cell utilization versus the temperature. Here, again, it is quite obvious that the utilization isn't good for the Groups 5, 7, and 8, which did not have the PQ treatment and it's really terrible at 35°C.

The other things of interest are that the lighter-loaded plate had the best utilization at all temperatures and it had the least amount of change with temperature. Group 2, which is the Teflon group, seemed to have the lowest utilization at zero and twenty of the other standard or control design plates.

(Figure 1-59)

This shows the voltage change with temperature during overcharge. There is also an interesting trend or observation, at this point. It appears that when cells have lower than what we could say normal voltage at a temperature, the utilization also seems to be down. And that's evidenced here with 5, 7, and 8, which is the non-PQ again, which had a very low utilization at 22° and 35°C.

These cells were charged for the most part, for instance in the 0°C for 24 hours. Except for the 0°C test, they were all charged at C temperature for 24 hours. That should be enough to get them fully charged.

The Teflonated (Group 2) which was low utilization at 0, 2, and 22 is also a little lower voltage.

The other item is that since this PQ wasn't done in the late 60's, this also shows why you had some difficulty in using any BT curves that were developed in the 60's and trying to use them with today's cell.

(Figure 1-60)

This shows the pressure range. Incidentally, all this data, so far, was in the GE acceptance test. There's not much you can say about the pressures. They are all over the place, varying from groups, except that all the PQ-treated plates seem to have a decrease in pressure with temperature, except for Group 4, which follows more the non-PQ-treated where it's low at zero and it kind of peaks at 22 and then falls off again at 35.

(Figure 1-61)

Here's a comparison of the capacities that we got at GE and also at Crane. Where it says "Un-A" that date is not yet available. The tests haven't been run; they are in the process of being run now.

The temperature at GE was 22°C and at Crane it was 25°C. The PQ-treated group showed very little change in the capacities. Now, for the non-PQ groups, 5, 7, and 8, there is an increase in capacity between the GE tests and the Crane tests. There was also an increase in voltage where the cell voltages now are almost the same as the cell voltages on the other groups during those tests.

At 0°, there is an increase in capacity for Group 1 and also Group 4. Unfortunately, I don't have the data for the other groups except for Groups 7 and 8, whose capacities also fell off a little bit. However, it looks like those cells are now negative-limited since the voltage exceeded 156 during the test. In fact, the end of charge voltages ranged from 157.5 to 159. So they were cut off a little early and I am not sure whether that had anything to do with the capacities received.

During the 35°C tests, all the capacities are up for Groups 1 and 4, and also for 7 and 8. They are going to continue to test these; which ones will end up to be the best with life remains to be seen.

## DISCUSSION

LEAR: What were the criteria for the acceptance testing shown in one of the previous vu-graphs? What were the charge discharge rates?

BAER: I should probably have gone into a little more detail. All the discharges were done at C/2. And the sequence at GE was C/10 charged for 48 hours at 22°C, then at C/10 for 24 hours at 22°C, and the 35°C tests which were C/10 for 24 hours. The 0°C test was C/20 for 72 hours. Then at GE, it was followed up with a C/10 for 24 hours at 24.

LEAR: There is an absence of the lithium-treated plates up there. Is there some reason for that?

BAER: Well, as usual, there was a little bit of a shortage of funds, plus the fact that at the time I didn't know that this program had really started. I guess it's been a year and a half to two years ago, and I didn't know that lithium was going to get the widespread play that it's getting today. I guess that's the main reason. But we were limited in the number of groups that we could have.

LEAR: Did you notice any silver migration in the silver-treated plates? Have you done any experiment teardowns or anything like that?

BAER: We haven't done any teardowns yet. However, we will be doing some teardowns, since there are six cells per group and we will probably save one. I haven't made up my mind whether to tear it down now or save it until the program is over and maybe tear that one down plus one with some life on it.

ARMANTROUT: When was the utilization calculation made? Was it early, before you had any cycle history, or what's the basis for that?

BAER: The utilization was based on the flooded test. The other utilization was based on the average of the three 22°C tests at GE during the GE acceptance test. There weren't any cycles on it.

ARMANTROUT: Okay, because I was kind of interested in the Teflon being lower in utilization and I felt that with some cycle life that would be up. Did you observe anything?

BAER: There is really not enough test data on it yet to see what's going to come up, although my past experience says that it will come up. I think I presented something on that a couple of years ago.

HALPERT: General Electric has permitted me to tell you what the PQ treatment Dave spoke about in the last paper is. It's a cadmium hydroxide treatment to the positive plate. And if you want further information I refer you to General Electric.

## CELL DESIGN VARIABLES - GE 12 AH CELL

| VARIABLE | GROUP # | TYPICAL POSITIVE THICKNESS cm | TYPICAL NEGATIVE THICKNESS cm | POSITIVE LOADING gm/dm$^3$ OF SINTER | NEGATIVE LOADING gm/dm$^3$ OF SINTER | FINAL KOH QUANTITY cc N/V3rd** | PRECHARGE ADJUST*** Ah |
|---|---|---|---|---|---|---|---|
| CONTROL* | 1 | 0.069 | 0.079 | 2095 | 2180 | 40/40 | 4.6 |
| TEFLON TREATMENT | 2 | 0.069 | 0.079 | 2095 | 2180 | 48/49 | 4.6 |
| SILVER TREATMENT | 3 | 0.069 | 0.079 | 2095 | 2180 | 43/44 | 4.6 |
| LIGHT LOADING | 4 | 0.069 | 0.079 | 1840 | 1833 | 45/46 | 4.6 |
| NO P.Q. TREATMENT | 5 | 0.069 | 0.079 | 2113 | 2180 | 40.3/41.5 | 4.6 |
| POLYPROPYLENE SEPARATOR | 6 | 0.069 | 0.079 | 2095 | 2180 | 39/40 | 4.6 |
| A.K. PLATE-1968 DESIGN, NO PQ OLD ECT PROCESS, NO DECARB PROCESS | 7 | 0.081 (UNSIZED) | 0.066 | 2130 | 2542 | 38/39 | 0 |
| A.K. PLATE-1968 DESIGN, NO PQ PRESENT AEROSPACE CELL PROCESSES | 8 | 0.081 (UNSIZED) | 0.066 | 2130 | 2542 | 39/40 | 1.8 |

*CONTROL CELL REPRESENTS PRESENT AEROSPACE DESIGN AND PROCESSES WITH NO EXTRA TREATMENTS. NONWOVEN NYLON SEPARATOR, P.Q. TREATED POSITIVES, DECARBONATION PROCESS, IUE LOADING LEVELS, 31% KOH

**TWO CELLS IN EACH GROUP CONTAINED SIGNAL ELECTRODES.

***BASED ON 228 cc $O^2$/Ah.

Figure 1-55

## POSITIVE PLATE UTILIZATION

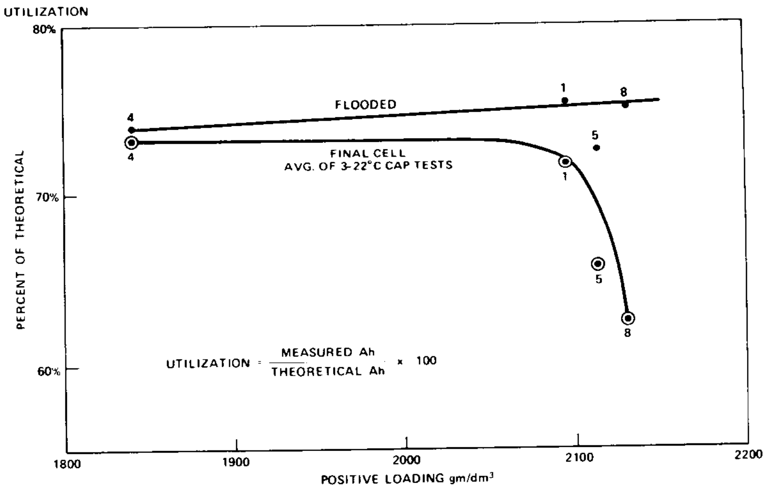


Figure 1-56

## FLOODED NEGATIVE PLATE UTILIZATION

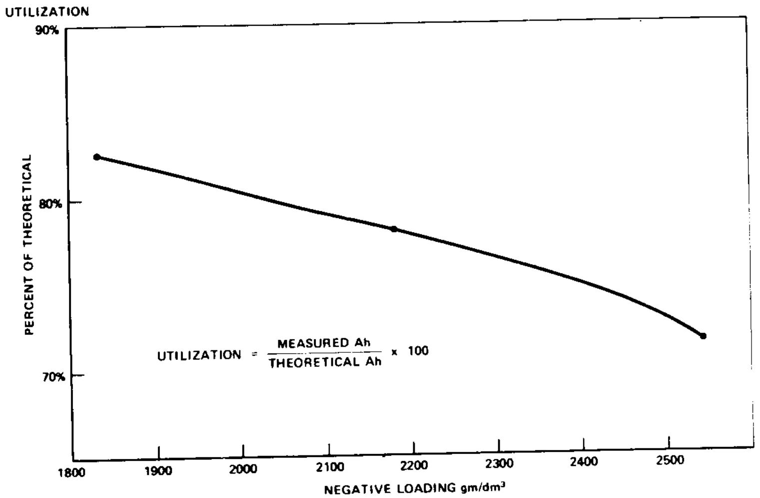


Figure 1-57

### FINAL CELL UTILIZATION

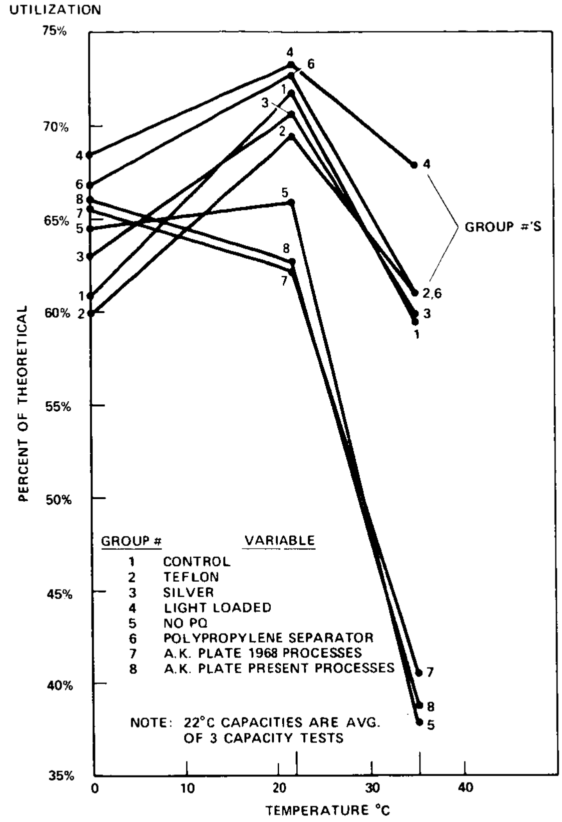


Figure 1-58

### ACCEPTANCE TEST CELL VOLTAGE PERFORMANCE

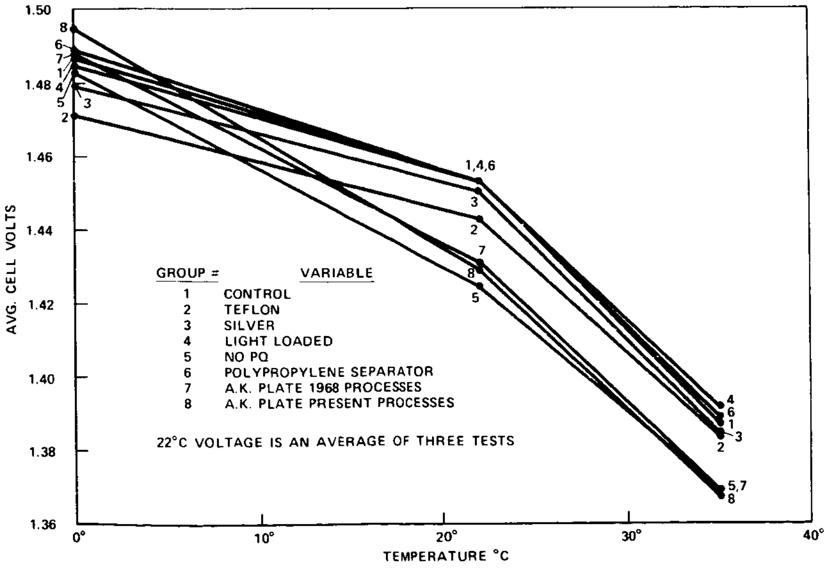
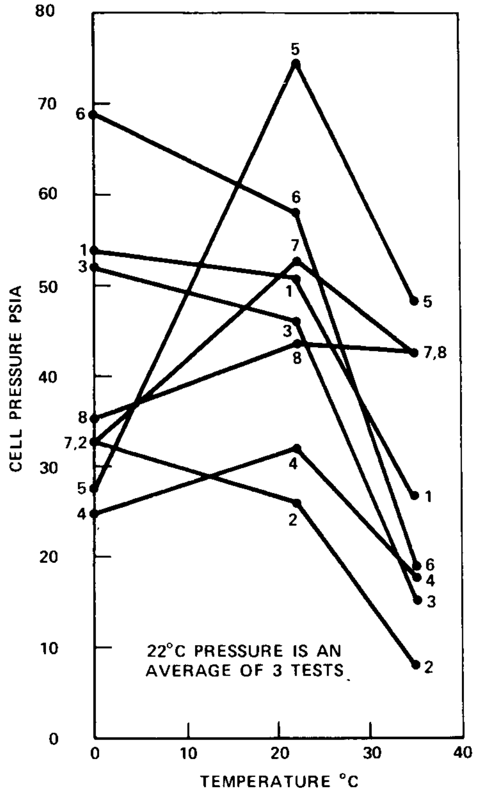


Figure 1-59



ACCEPTANCE TEST CELL PRESSURE PERFORMANCE

Figure 1-60

COMPARISON OF AVERAGE GROUP CAPACITIES BETWEEN GE TESTS AND CRANE TESTS

| | CAPACITY TEST(AH) | | | | | |
|---|---|---|---|---|---|---|
| | 22°C | 25°C | 0°C CAPACITIES(AH) | | 35°C CAPACITIES(AH) | |
| GROUP | GE* | CRANE* | GE | CRANE | GE | CRANE |
| #1 | 15.3 | 15.3 | 13.0 | 14.5 | 12.7 | 15.9 |
| #2 | 14.4 | 14.8 | 12.7 | NA | 13.0 | NA |
| #3 | 14.9 | 15.0 | 13.4 | NA | 12.7 | NA |
| #4 | 13.8 | 13.7 | 12.8 | 13.1 | 12.7 | 14.1 |
| #5 | 14.2 | 16.0 | 14.4 | NA | 8.2 | NA |
| #6 | 15.6 | 15.5 | 14.2 | NA | 13.0 | NA |
| #7 | 15.9 | 18.0 | 17.0 | 16.8 | 10.5 | 14.5 |
| #8 | 16.3 | 18.1 | 17.2 | 16.1 | 10.1 | 14.7 |

*2ND TEST, C/10 CHARGE FOR 24 HOURS

Figure 1-61

# COMPARISON OF CELLS WITH PELLON 2503 AND 2505 SEPARATOR

G. Halpert
Goddard Space Flight Center

This paper describes some tests we ran because of information we received last year. The Pellon Corporation, the manufacturer of our nonwoven nylon separator materials in nickel cadmium cells, has terminated production of 2505 material. If we wanted to buy some, the minimum lot size would be 50,000 yards. I know you realize that with the limited number of aerospace users in the business, it would be quite a long time before we would ever be able to justify that.

They did recommend an alternative to the 2505 nonwoven nylon. They call it 2503 material which is made using a similar fiber except that in the 2505 material, the laying down of the fibers is in a random direction. They actually run it out one way and cross it the other way so they have a random orientation of the fibers. The 2503 material has an orientation of the fiber all in one direction. So we have random versus oriented fiber.

As kind of a historical note, Tom Hennigan back in the 50's started a program with Gould batteries that evaluated separator materials. They evaluated over 100 separator materials and came up with 2505 which was called ML at the time for maximum loft. We have been using it in nickel cadmium sealed cells since that time.

At this time we have "a NASA standard cell" made with a 2505 material and which we may find is obsolete. It's kind of a shock. There is enough 2505 around for the near time. In the meantime we decided that we should be looking at something as an alternative and the 2503 material was the material.

I will give you some of the information we have about it. We still cannot make a decision and tell you that you ought to go out and buy 2503 instead of 2505

The following are some properties of these materials.

(Figure 1-62)

The material is advertised as being 60 grams per square meter and our measurements are compared here (1) with (2) General Electric's, which indicated that the particular sample that we had was a little higher than that.

We also compared the 2503 which is the new oriented material with another material called 2506 which one of the manufacturers has in use. A similar material, 2506 is made with a similar fiber except that it's a lesser density material advertised as 50 grams per square meters.

(Figure 1-63)

We made some measurements along with the 2503 and the 2505 and some of them are kind of interesting. One interesting measurement is when you measure with an Ames gauge or Cady gauge here on 2505, you see you get a significant difference, that difference being the weight on the measuring device and also the measurement. But the 199 would indicate the maximum loft that the 2505 was supposed to have versus the 15.6.

When the manufacturer, General Electric, measured using the Cady gauge, they get something that is fairly similar and, of course, that would indicate that they have a bigger foot and a larger weight on that gauge.

The apparent densities as given here and the porosities are also similar for the three. The air perm is a little bit smaller for the 2503 than for the 2506 and, of course, the air perm for the 2506 is significantly higher. The fiber diameters of the two fibers, as shown in this picture, are 2503 versus 2505 here.

(Figure 1-64)

Here is the sample of the two fibers. You can see the 2505 randomly oriented on the left side and the oriented 2503 on the right side so you can distinguish the difference between the two.

We looked at some of the other physical properties, in particular, the absorption properties. It's kind of interesting to note here the pickup of the KOH absorbed in 1 hour and 24 hours is not an awful lot different, especially for the 2505. For the 2503 it is somewhat different, and the weight pickup for the 2506 is significantly higher, which is kind of interesting.

No matter which direction you take you see here that there is a difference in the oriented fiber, the capillary absorption similar for the material in the randomly oriented. As a matter of fact, Aaron Fisher of our Polymer Lab who did some of these measurements said that he found a quite interesting situation here in which the electrolyte seems to go along the path or the orientation and didn't spread out at all, which, of course, may be indicative of some kind of difficulty we may have.

The absorption time was less and the rest of these kind of fall in the electrolyte retention, which is quite a bit different here. That was from his comment that the 2503 didn't seem to pick up and distribute the electrolyte very readily in both directions, only in the one direction. The reason why 2503 is significant is because of the tensile and the strength. When you're making some kind of a wound cell or need some kind of strength in the one direction so you don't keep tearing it apart, or if you have strength in the machine direction, that would be of considerable help, too. In the prismatic cells that we deal with, that isn't really too significant and the other one may be satisfactory except that it may not be available.

(Figure 1-65)

The cells we work with offer some cell design information. The General Electric designation of 06/7 has to do with cells with and without signal electrodes. Some of the properties of the 0607, the NASA standard, I will talk about later today.

The 14/15 was the same cell made the identical way except with Pellon 2503 separator. The cells use the similar group of plate positives and negatives. The difference was really the two separator materials and, interestingly enough, the electrolyte. When we put lesser electrolyte in these 2503 cells than the 2505, the precharge was the same. Some of the other kinds of data here on the bottom which are really not significant in terms of what we are trying to prove but will give you some idea of the design.

(Figure 1-66)

Here's a GE cell acceptance test, and before we started this is where we got our big shock. In the very first cycle, a form of what is called a conditioning cycle that is run at General Electric, the pressure on the 2503 cells went quite high, above 100 pounds. It had to be shut off. After it sat for a while, it was run through the conditioning again and there in the 2505 and the 2503 have been right on top of each other through all the rest of the tests. So it was that first cycle that seemed to, or that electrolyte just did not get into that separator well enough during that initial period. Once operated, we can see that there is not too significant a difference between the capacities on the two groups of cells.

This group of cells, of course, having 2505 separator and this group having 2503. We are talking about now having five cells in each group.

(Figure 1-67)

The cells went on to the Naval Weapons Support Center for testing and Jim Harkness has been very helpful and his people have been very helpful in working these tests. Now, in terms of the initial evaluation tests performed at Crane, again, the differences really between the two sets of cells as you go down and the charge voltage pressure and capacity are pretty similar for the two different groups and you would have an awful hard time trying to separate the one group from the other. All of these are close to those that we have seen on our standard cell tests. There is a lot of information there, but I think that I made the significant point.

(Figure 1-68)

Now, the cells have been tested for about 1000 cycles in a near earth orbit at 40 percent depth of discharge and 20°C. And we have just one comparative cycle here. We can show this 1165th cycle. We can see here that the 2503 is running a little lower on discharge and the 2503 running a little higher on charge and there's just that slight break right now in that voltage. Whether that's due to that difference in electrolyte or whether it's actually due to the impedance or the difference in the separator materials, we don't really know at this point.

In conclusion, I would say that we are still not able to make a decision whether 2503 is a suitable substitute, having only 1000 cycles. We may be able to make some determination down the line.

## DISCUSSION

HENNIGAN: I was wondering if you measured the swelling of 2503 versus 2505. The reason I asked that question is I felt the cell with a fuel cell electrode and a 2503 just bowed the fuel cell quite a bit, but a 2505 did not. It was built on approximately the same conditions.

HALPERT: We do not have any swelling information at this time.

ELIASON: Did you do any analysis on the separator emission spec? Are they still using the zinc chloride wetting agents?

HALPERT: We don't have data on that yet, but I understand from what the manufacturer tells us it is made in an identical way except for the way in which the fibers overlap. The same material, ingredients, and temperatures are involved. It's only the overlap of the fabric that is different.

HENNIGAN: Don't forget that the 2505 is probably provided by General Electric and it may be washed out. The 2503 probably is not.

HALPERT: We've got two samples. We have gotten some directly from the manufacturer and some from General Electric as part of the contract that was supplied with the cells. Neither one has been run using an emission spec or done through a chemical analysis yet. Therefore, it doesn't make any difference at this point. But we certainly will take a look and see what we have available.

## PHYSICAL PROPERTIES OF PELLON SEPARATOR

| | 2505 | 2503 | 2506 |
|---|---|---|---|
| % KOH ABSORBED 1 hr | 908.0 | 769.0 | 1037.0 |
| 24 hr | 909.0 | 800.0 | 1074.0 |
| CAPILLARY ABSORPTION 0.1 hr (min) | | | |
| MD | 29.0 | 16.0 | 13.0 |
| AMD | 27.0 | 7.0 | 15.0 |
| ABSORPTION TIME FOR 30 $\mu\ell$ DROP (min) | 8.4 | 13.9 | 28.6 |
| WET OUT TIME (min) | 28.6 | 15.5 | |
| ELECTROLYTE RETENTION % | 659.0 | 257.0 | |
| TENSILE kg/in² MD | 2.0 | 7.0 | |
| AMD | 3.1 | 1.2 | |

Figure 1-62

## MECHANICAL PROPERTIES OF PELLON SEPARATOR

| | 2505 | 2503 | 2506 |
|---|---|---|---|
| WT/AREA ($gm/cm^2$) (1) | 0.69 | 0.60 | 0.50 |
| (2) | 0.60 | 0.65 | |
| THICKNESS (mils) (1) AMES | 19.90 | 15.60 | 12.50 |
| (2) CADY | 10.40 | 10.80 | |
| APPARENT DENSITY (g/cc) (1) | 0.136 | 0.152 | 0.157 |
| (2) | 0.225 | 0.237 | |
| POROSITY (%) | 88 | 87 | 86 |
| AIR PERM ($ft^3/min/ft^2$) (1) | 266 | 239 | 350 |
| (2) | 229 | 205 | |
| AVG. SEM FIBER DIAM. (mil) (1) | 0.61 | 0.64 | 0.55 |

(1) GSFC
(2) GE

Figure 1-63

## SEM PHOTO OF PELLON 2505 & 2503 SEPARATORS

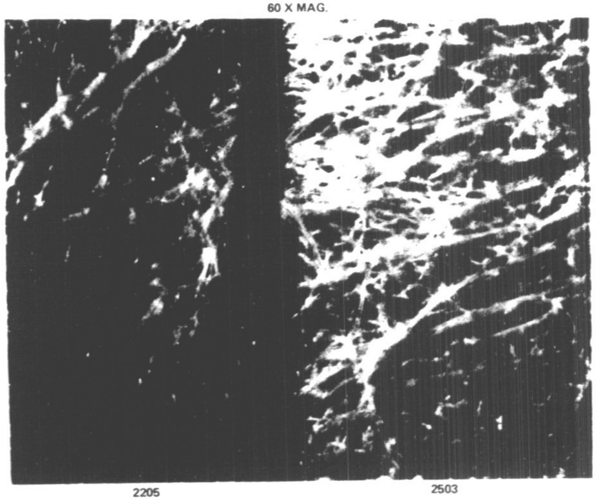


Figure 1-64

## DESIGN OF CELLS
### WITH PELLON 2505 AND 2503 SEPARATOR

| CELL DESIGNATION | 42B024AB06/7 | 42B024AB014/15 |
|---|---|---|
| SIZE | 20 Ah | 20 Ah |
| TYPE | STANDARD | STANDARD |
| SEPARATOR | PELLON 2505 | PELLON 2503 |
| CELL S/N (LOT 03) | 65 - 69 | 70 - 74 |
| ELECTROLYTE 31% KOH (CC) | 85/86 | 83/85 |
| PRECHARGE (Ah) | 7 Ah | 7 Ah |

| TYPE | NO OF PLATES | PLATE AREA ($dm^2$) | AVG. LOADING ($gm/dm^2$) | THEOR. CAP | FLOODED CAP |
|---|---|---|---|---|---|
| - | 12 | 0.95 | 11.39 | 47.52 | 45.28 |
| + | 11 | 0.95 | 10.44 | 31.53 | 25.60 |

Figure 1-65

## GE CELL ACCEPTANCE TEST

| | CELLS 65 - 69 (2505) | | | CELLS 70 - 74 (2503) | | |
|---|---|---|---|---|---|---|
| | EOCV (VOLTS) | EOCP (PSIG) | CAP (Ah) | EOCV (VOLTS) | EOCP (PSIG) | CAP (Ah) |
| 24°C CAP | 1.439 | 31 | 23.25 | 1.436 | 28 | 22.83 |
| 25°C CAP | 1.404 | 1 | 23.11 | 1.405 | 5 | 23.68 |
| 0°C CAP | 1.985 | 27 | 18.80 | 1.485 | 23 | 19.08 |
| CHG EFF | | | 5.67 | | | 5.43 |
| 24°C CAP | 1.445 | 21 | 23.87 | 1.443 | 23 | 23.83 |

Figure 1-66

## NWSC INITIAL EVALUATION TEST

| | CELLS 65 - 69 (2505) | | | CELLS 70 - 74 (2503) | | |
|---|---|---|---|---|---|---|
| | EOCV (volts) | EOCP (psia) | CAP Ah | EOCV (volts) | EOCP (psia) | CAP Ah |
| CONDITIONING | 1.432-5 | 15-77 | 23.4 | 1.431-4 | 15-17 | 23.4 |
| PRE CAP TEST | 1.439-5 | 32-37 | 21-22 | 1.438-46 | 30-36 | 21-24 |
| CAP TEST 20°C | 1.455-6 | 39-40 | 19.8-20.6 | 1.453-6 | 37-46 | 20.2-20.6 |
| OPEN CIRCUIT - 1 WK | 1.320-1 | | 18.8-19.2 | 1.320-1 | | 18.8-19.2 |
| CHG. EFFICIENCY | 1.367 | 8-10 | 6.8-7.2 | 1.367 | 8-9 | 6.8-7.2 |
| CAP TEST 0°C | 1.487-9 | 33-40 | 20.3-0.6 | 1.487-8 | 33-45 | 20.3-0.6 |
| CAP TEST 35°C | 1.393-6 | 17-18 | 22.1-23.1 | 1.394-9 | 17-18 | 22.3-23.1 |

Figure 1-67

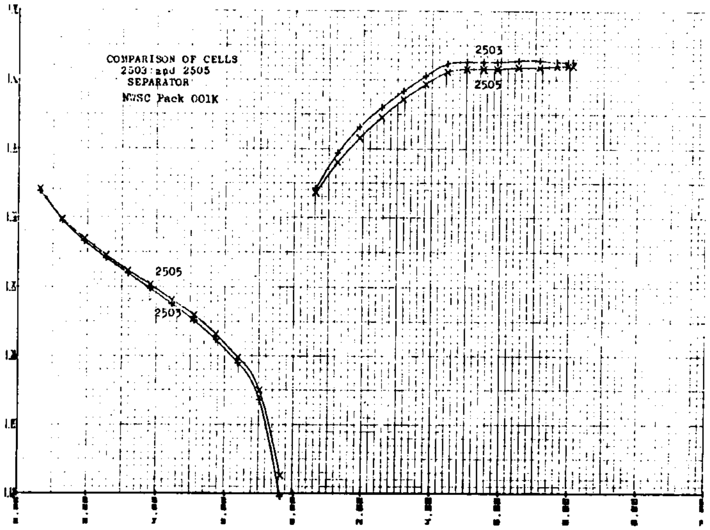


Figure 1-68

# CHARACTERIZATION OF DEGRADED NICKEL CADMIUM CELLS

S. Gross
Boeing Aerospace Company

(Figure 1-69)

The tests that I am going to talk about were tests where we cycled some cells for a long time until they degraded and then we ran some tests to determine the electrochemical characterization of the cells with regard to charge control.

What we wanted to find out was how well cells can be charged after they have degraded and how the charge control characteristic of cells that degraded compare to new cells.

The comparison charts are in preparation and I wasn't able to get those, but I thought you would be interested, at least in the after-data, even though we don't have all the before data.

(Figure 1-70)

This chart shows the cycling data on these cells. These were General Electric $3\frac{1}{2}$-ampere-hour cells with a real capacity of about 4.2 ampere-hours when they are new. The cycle regime was a $3\frac{1}{2}$-hour charge and a 40-minute discharge giving us $3\frac{1}{2}$ cycles per day. And the charge rate was a C/7 charge to a trip voltage and then to a trickle charge at C/30. And the discharge was to 35 percent depth of discharge.

In this particular group of cells, we are plotting the end of charge voltage and the end of discharge voltage and periodically discharged the cells to determine the capacity, and, of course, when that happened this had a reconditioning effect and the voltage went up and then, of course, it degraded. But eventually it was picked up again, and in spite of that there is a long-term degradation which can be seen.

(Figure 1-71)

This is a similar case in which the cells were not tested for discharge except for this one case which was an accidental discharge. When we compare those two charts we see that in one case, there is little difference, whereas in the other case, the reconditioning discharges improved it.

In general, we had considerably more improvements than we had conditions of this kind. So at the battery level, it would be fair to say that the reconditioning discharges were of benefit.

(Figure 1-72)

This group of cells is identical to the others except that the discharge rate, instead of being at a 40-minute rate with 35 percent depth of discharge, was to the same depth of discharge, but it was at a 1.5°C rate.

When we compared these two charts you can see on the bottom chart had no effect. There was some improvement on the top chart. So in general we can conclude that the high-rate discharge was not harmful. It was at least as good as the low-rate discharge. This is the kind of degradation that we experienced as a function of cycle life or plotting, of course, of voltage as a function of time and as a function of cycle life.

Now starting with cells that have been degraded to this point, we then ran some reconditioning cycles. We were able with a reconditioning method to get the capacity all the way up nearly to the original capacity of about 4 ampere-hours.

We did compare some of the different methods of reconditioning and the ones that worked out best were combinations of long shorts, about 4 days, with long overcharges on the order of 2 weeks.

(Figure 1-73)

The method we used for charge control evaluation was a constant voltage charged to a temperature-biased voltage using up to an 8-voltage limit. This curve is somewhat similar to the one in the NASA spec; however, it's a little different. It has a little different slope to it.

Again, we used the same orbit, a 6½-hour orbit per day, charging to 1 ampere to a constant voltage limit and, in this case at 14° C.

(Figure 1-74)

Here we are plotting the end of charge occurrence as a function of different voltage levels, each point being a point of stabilization reflecting 2 or 3 days of continuous cycling to get all the conditions stabilized.

This data on this chart is for 5 percent depth of discharge. You get the expected increase in end of charge current with increase of voltage level.

(Figure 1-75)

The end of discharge voltage for the same condition, 5 percent depth of discharge, shown in this chart, voltage at a six-cell battery group. Can you see that voltages off the side, 1.25, 1.3, 1.35, as a function also of voltage limit? The end of discharge voltage, even at this 5 percent depth, although satisfactory from a battery level, is somewhat lower, reflecting the fact that we don't really have a full state of charge at those lower voltage levels.

(Figure 1-76)

That is shown a little bit better here where we plot for the same condition, the capacity as a function of the different voltage level. And the capacity of the first three or four levels is less than full capacity which can be reached only at the higher levels.

Normally, a full capacity could be reached at the level four. By normal I mean with new cells.

(Figure 1-77)

Here we have the end of discharge for voltage for 20 percent depth of discharge condition as a function of the voltage levels. It turns out that this slope is quite close, nearly identical to the slope that we see for the 5 percent depth of discharge condition.

(Figure 1-78)

The typical current tracing for charging is shown here. This is currently a function of time. You are starting off with 1 ampere and tripping to either of the voltage levels. At level two we are a lower state of charge than we are at level eight. The net results in a difference of slope, the effect of which shows up later with a crossing of curves.

The crossing of those curves shows up as a difference in the end of charge current for that condition, giving you a minimum of end of charge current at the middle charge levels. At the low charge levels, we have insufficient charge to complete the charge. Of course, at the higher charge levels we have a larger driving force causing gassing and a higher voltage.

## DISCUSSION

GASTON: Could you elaborate a little bit more on what you meant by "long periods?" It's a reconditioning technique using long shorts and long overcharges, timewise.

GROSS: Okay, we tried different combinations of shorts and charges, and overcharges. We compared the effects of shorts for from 1 day to about a week. We compared the effect of continuous overcharge for from 1 day to 2 weeks. The combinations of these, especially the longer shorts and the longer continuous overcharges, had the most immediate effect. However, by continuously repeating these we found that in all cases, we were able to bring the capacity back to close to the original capacity. But the combination of the long short and long overcharges had the fastest effect.

REID: When you say "overcharge or a long overcharge," what sort of constant were you using then?

GROSS: I think that was about the C/30 rate. I am quite sure it was.

HAXTON: What reconditioning rates were you experiencing when you went to those shorts—C over what?

GROSS: Well, the procedure for shorting was to discharge at a C/2 rate down as close to zero volts as you can safely do, and then put a 1-ohm resistor across it. Eventually, this can be replaced with a hard short, and the voltage goes goes to zero.

HAXTON: What was the rationale for C/2?

GROSS: The rationale is that a high discharge rate gives you a finer grain structure in the cadmium electrode.

HAXTON: And you noticed no self-shorting problems?

GROSS: No.

HAXTON: No problems.

GROSS: No self-shorting problems. We did not go into reversal.

HAXTON: Oh, so you shorted each cell.

GROSS: We shorted each cell.

BOGNER: Did you do your reconditioning sequential, in other words, let's say at 500 cycles, and do some more cycling, or did you do it on individual cells at a given cycle.

GROSS: Let me clarify that. There were two kinds of events that could be called reconditioning. One was the capacity measurement that occurred during the test where we discharged down to 1 volt, and determined the capacity. That had a reconditioning effect, did not cause any reversal, and was done at battery level.

The other reconditioning I am referring to is that at the end of all the cycle testing, we completely reconditioned the cells by bringing them down to zero volts, combinations of zero volts shorts and continuous overcharge.

BOGNER: Did you try some different experiments on them?

GROSS: We tried different experiments and different groups to find out which kinds of reconditioning methods worked out the best.

LEAR: I have a two-part question for you. How many cycles did you run on the cells?

GROSS: The cells are cycled to close to 3700 cycles.

LEAR: What capacity degradation, percentage wise, did you find initially?

GROSS: The initial capacity was approximately 4.2 ampere-hours and the final capacity was in the range of 1.75 to 2.0 ampere-hours.

OTZINGER: The effectiveness of the shorted versus the overcharge, did you notice any difference in effectiveness?

GROSS: In this case, the overcharge, I think, was very useful. They were both effective, but I think that it was very important the day you get an overcharge.

OTZINGER: I see, so that insofar as the reconditioning lasting after you do the reconditioning, even with the overcharge, it lasted.

GROSS: No, we went to both. We used a combination of shorts and overcharges. The greatest response at the very beginning was that the capacity was gradually building up to its proved steady state level which was due to the two combinations. If you didn't put the continuous overcharge in it, the response was slower.

LEAR: What you are saying is that you lost about 50 percent capacity in 3500 cycles. Okay, was that because of potential charge or because of occurred charge that you are losing all this capacity?

GROSS: The cycling regime for the 3700 cycles was a constant current at one-half an amp to a trip voltage and then to a trip voltage at the C/30 rate. So it's a two-step charge.

FORD: Apparently you operated a few consecutive cycles and maybe a number of consecutive cycles without fully recharging or going into overcharge. Did you notice any apparent effect that these groups of cycles had on cell performance on subsequent cycles where you did go into overcharge?

GROSS: After the 3700 cycles where there was limited overcharge, we did run these conditioning tests, charge control tests, and charge control characterization tests. And we did not then put them into cycling to determine cycling behavior afterwards. But they behaved very well on the characterization tests which would give the impression that they probably would have cycled very well, also.

GARLOCK: Did you measure temperature during the cycling tests, and what did it show if it was performed?

GROSS: Yes. Temperature was controlled closely to 14° C in all the cases we are showing here.

GARLOCK: But were you measuring temperature rise in the cells?

GROSS: Yes, temperature rise was measured and it was negligible. It was less than a degree. The experiment was deliberately controlled so it couldn't rise very far.

GASTON: Since we are dealing with small capacity cells, are we dealing with the cylindrical or prismatic cell?

GROSS: It's prismatic.

LEAR: What type of separators were used in this?

GROSS: These are Nylon separators—2505.

LEAR: 2505?

GROSS: Yes, 2505.

LYONS: My question is directed to Gerry Halpert. On your presentation, earlier, the deniers and the length of fibers on the 2505 and 2503, do you know what they were?

HALPERT: No, I do not.

BETZ: In your characterization, about how many cycles did you run at each condition?

GROSS: Approximately 3 days and in some cases, longer. So that would be a minimum of 3 times 6½ cycles. Where conditions were warranted, and where there was a big change between the previous conditions, we ran a greater number of cycles to make sure we erased previous history.

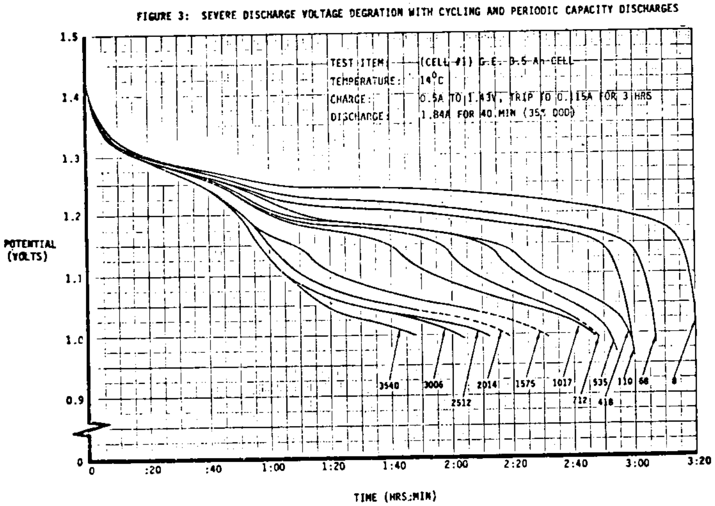


Figure 1-69

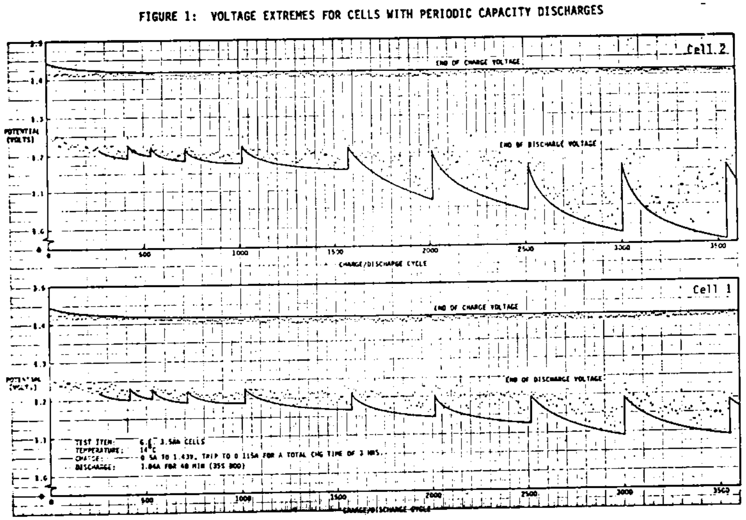
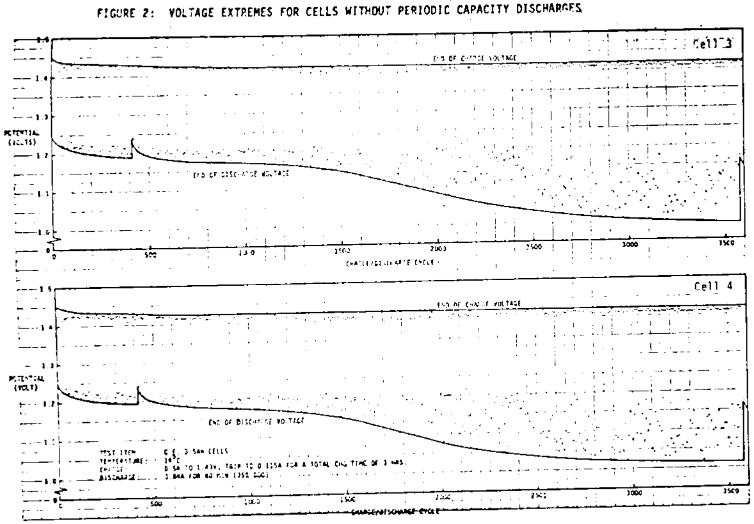


Figure 1-70



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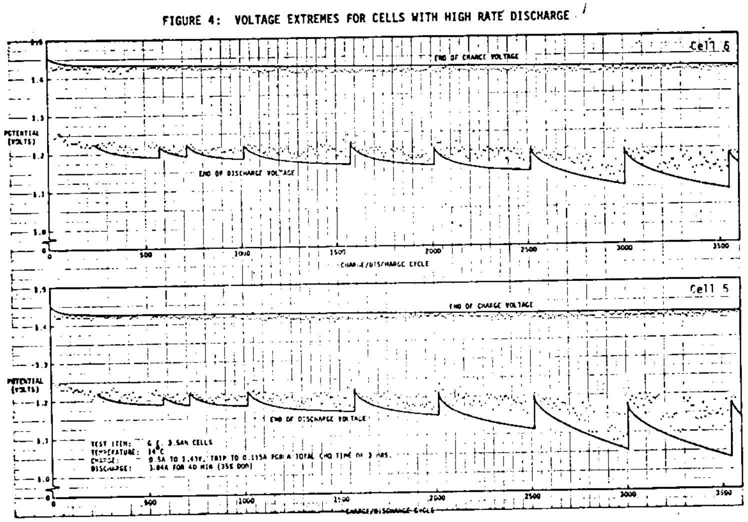

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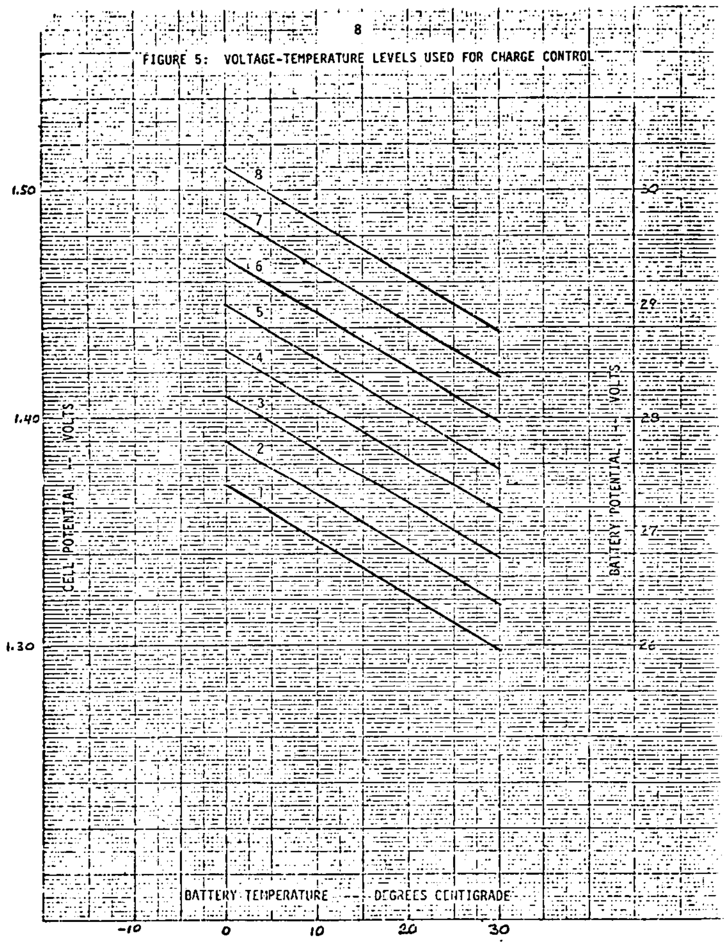

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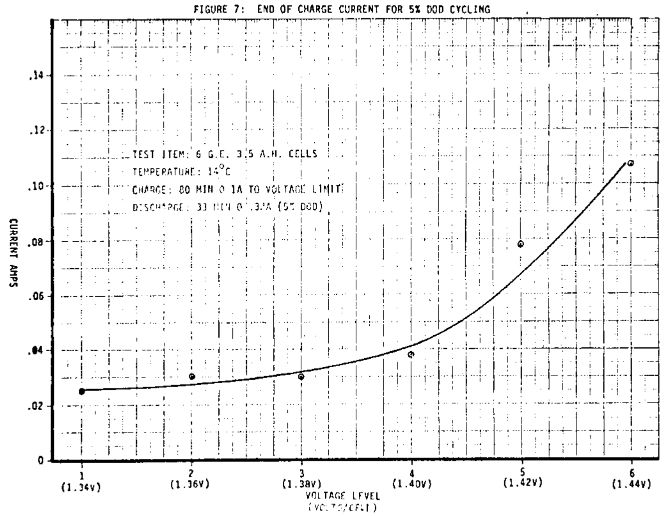

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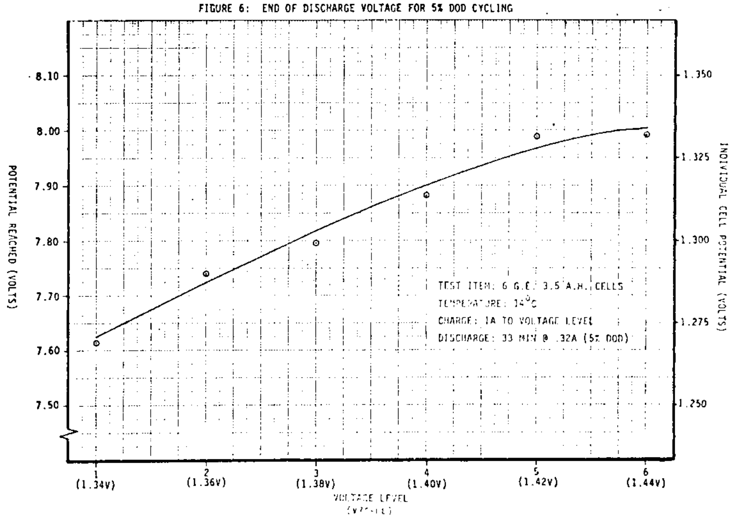

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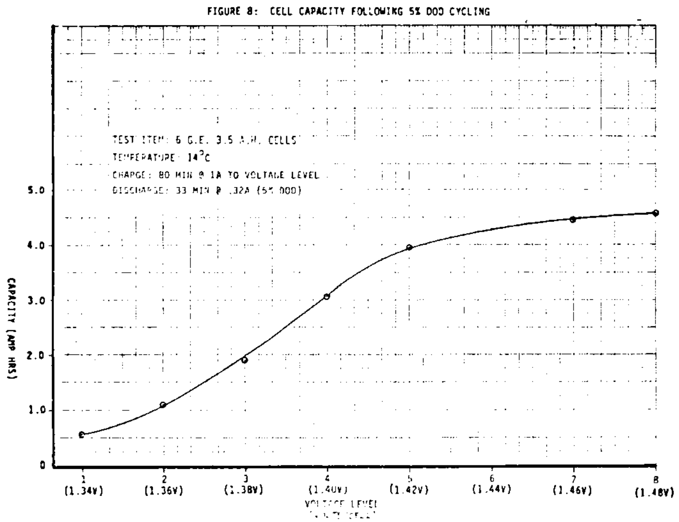

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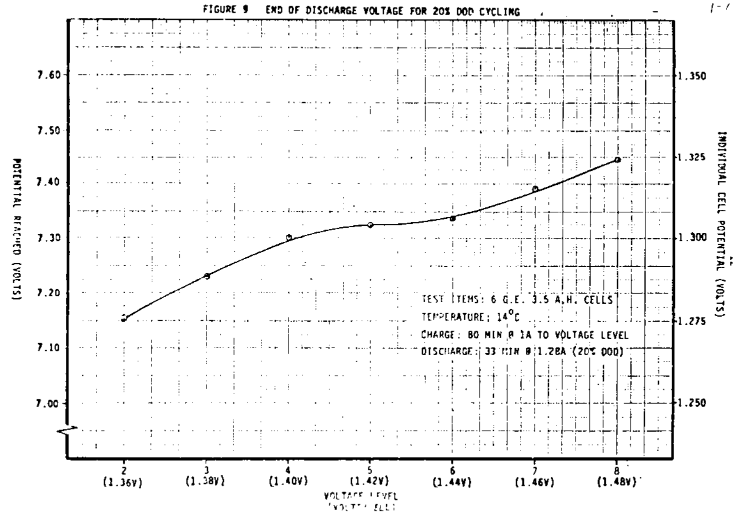


Figure 1-77

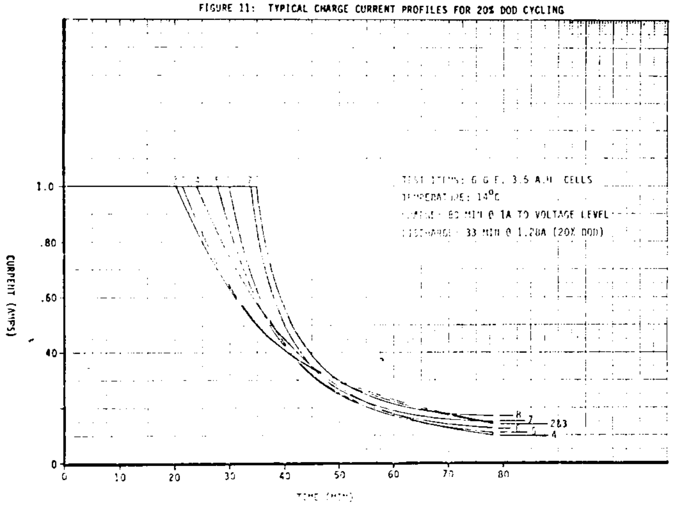


Figure 1-78

# DYNAMICS OF CELL DEGRADATION

P. McDermott
Coppin State College

What I would like to talk about is degradation of cells in the accelerated test program which is being carried on at the Naval Weapons Support Center in Crane, using the data from the teardown analysis.

The structure of the talk is basically this: I would like to give a little background information containing results which I presented in Atlantic City at the Power Sources Conference in the summer and also at the ECS fall meeting in Pittsburgh, and then to present some new data which uses the physical and chemical data in order to try to predict cell failure. I mention these two papers because they will be published in total so I am just going to breeze over them today, and if you are interested you can go back and look at the papers.

(Figure 1-79)

Figure 1-79 shows the cells we are interested in. These are the star point, center point cells which have seven variables in common, and one variable which differs. The bottom line there, pack 81, is called the center point cell. And those seven variables will be common with the center point except for the ones in the boxes which give a different parameter.

(Figure 1-80)

In Atlantic City, I compared essentially failed cells with virgin cells or uncycled cells and got these changes within the star point, center point packs. In terms of chemical capacity, there is an increase in the total positive capacity. These are chemical capacities—and decrease in the total negative. You notice how that total negative is broken down. The discharge negative had a 6-ampere-hour decrease and the charge negative had a 3.59-ampere-hour increase. So there is quite a bit of charge negative in these cells.

In terms of plate thickness, there is an increase in positive thickness and actually a pretty constant negative thickness of very little change. Plate weight showed an increase in positive and a decrease in negative.

(Figure 1-81)

I proposed in Atlantic City to describe with a model the changes in the cells and I have a little outline of that. It was based on the idea that there was considerable amount of corrosion of the nickel center in the positive electrode to form active material. So this is the model for cell degradation. In one, the nickel corrosion, due to the fact that we had this 1.63-ampere-hour increase in the chemical capacity of the positive which could only be explained as creating new active material. There is a corresponding 3.59-ampere-hour shift from the negative discharge material to negative charge material and this would compensate on a Faraday-per-Faraday basis on a change of oxidation number in the nickel of approximately 2.2.

The plate weight had changes consistent with corrosion. That is, if you have an increase in active material in the positive plant, you therefore have an increase in weight.

The overcharge protection is being lost because of that large shift from cadmium hydroxide to cadmium metal and this was seen in a lot of high-pressure failures in these star point center point cells.

The positive plate growth related to corrosion was due to two factors. First, just a weakening of the sintered material, particularly around the wells of the sintered material, due to the fact that it was being corroded away, and second, an increase in the actual positive material which would place stress during the charge and discharge process where it changes density.

The inner electrode space was then determined. You have a squeezing out of the separator as the positive plate expands and this would be seen as the separator drying out which would account for some of the low voltage and also the high-pressure failures.

We had quite a bit of cadmium migration and this is seen in the loss of negative capacity and weight and, finally, related some of the shorting. A few of the star point, center point cells failed because of shorts and this would be related to several other factors there.

(Figure 1-82)

Now we see the changes that go on with cycling and I wanted to find out about the dynamics of change. That is, if we could see whether the positive plate growth is linear, exponential, or logarithmic in nature. In other words, could we see how these changes are occuring with life?

In order to do this, and this is the basis of the Pittsburgh paper, we looked at these scheduled removals which are shown over here in columns 6, 7, and 8. These are cells in the center point, star point, center point packs, where R stands for schedule removal. They were removed prior to failure and these over here are removed, these are actual failures from columns 1 through 5.

So it we were to plot something like positive plate thickness or negative weight versus cycles, the scheduled removals would actually help us to plot a graph from zero time out to whatever failure time you have. We did this. I reported this last year for positive plate thickness and on a pack-by-pack basis you got a linear plot. Negative weight was fairly stable, and so forth. But when I went on to the other variables I really couldn't do much because there was so much scatter in the data, for example, positive capacity or negative capacity, that simply these eight points could not give you any trends. Then I tried to figure out a way that we could combine this data together on one graph so that you would increase this statistical acceptability of the graph and maybe be able to do some trends.

(Figure 1-83)

I plotted all of these on a normalized time base down here. In other words, I take the individual cell failure cycle and divide it by the average pack failure and that gives me a normalized base where one would correspond to the average pack failure cycle. So if this cell failed at exactly when the average pack failure occurred, then that dot would appear at one and you do see that there tends to be more of a cluster around one.

That puts the schedule removals down here, the actual failures up here, and I drew a little dotted line. The schedule removals tend to be less than 0.6, meaning that they all failed at the first 60 percent of life, if you want to call it that.

So I went through and I took packs which fell into these general trends, that is, the positive plate increased in thickness up to about 0.1 centimeters. There are nine or ten packs which fell into this range or into this envelope. Some of the packs were completely off. The low depth of discharge—actually that line was fairly flat so I did not use that in this data base.

This data base assumes, essentially, that all the packs here are failing for the same reasons and that's a high overcharge, high charge rate to condition that they are under and that's why I believe that nickel sintered corrosion is going on. A low discharge pack really wouldn't be failing for that reason. In other words, you would not be getting the real positive plate growth that you are getting with these other packs. So I did not include that in the data base.

The assumption, again, is that if cells are failing for essentially the same reasons, even if they went 5000 cycles one pack, and another pack went 1000 cycles, you could compare them on this normalized scale which supposes that at 50 percent of life both of them are at roughly the same degree of degradation.

So we took the positive thickness which looks linear, increasing a little rise here during the first 20 percent of life, and the negative thickness is pretty flat with a slight rise here during the first 20 percent of life.

I did an equation of fit here that will be in a box for each graph.

(Figure 1-84)

This shows the positive weight and the positive chemical capacity. There is quite a bit of scatter but I think you can see that these points down here would draw the curve down rather rapidly towards the origin here.

You generally have the same shape which is a logarithmic shape and this would fit with the corrosion model because if the positive chemical capacity is increasing, you would expect to see an increase in the weight because you are converting nickel metal to nickel hydroxide.

Notice that the most rapid rise is here in the first 20 percent of life; after that it sort of flattens out, although it is rising slightly out there.

(Figure 1-85)

This shows negative plate weight and negative capacity and here, again, this fits the corrosion model in the sense that as your chemical capacity dies off you convert some of the cadmium hydroxide to cadmium metal also so that you would have a weight drop-off, although you would probably have some of this weight drop-off due to just the cadmium migration to the outside of the separator.

Again, the first 20 percent of life is mostly where the drop-off occurs. This is also an inverse of the previous slide which would be consistent with the corrosion model, since you have to convert some of the cadmium as the nickel is corroding.

(Figure 1-86)

There is a lot of scatter here so I will only show it in a qualitative sense, to show this drop here in the first 20 percent of life. This is separator wet weight versus separator dry weight. When you subtract this from that, you get the electrolyte weight. The reason for all this scatter is due to simply the sampling technique when you try to take the separator off and some of it adheres, and so forth. So I am only suggesting this in a qualitative sense.

Let's look again at Figure 1-85. Now since we saw most of this decline during the first 20 percent of life, I than wanted to find if I could use this as a prediction tool. If we can see or discern certain physical changes going on in the first 20 percent, perhaps, then we can extrapolate and say, "When will the pack average reach 0.1 of normalized life?" So you see you could go back to these equations here and take the scheduled removals and try to use the scheduled removals to actually predict the pack average failure time, simply by plugging in Y which would be the negative plate weight of one of the schedule removals. X would be equal to the cycle at which you removed it over normalized life. So then by simple algebra you could determine what normalized life is.

So I did that using the schedule removal and the results I will show here.

(Figure 1-87)

Here we have the nine packs that were used in the study. We found that the best predictors were the positive thickness, the positive weight, and the negative weight. Remember, the negative thickness was flat, so that can't be a predictor. We went through a rather systematic process of averaging it all together and selecting out throughout one and averaging them and throwing out two and it turned out that these three were the best predictors, and as it turns out, the easiest to determine.

If you pull a pack apart, you can weigh the plates and measure the thickness and you don't have to go through all the chemical analysis in order to get this. So I was happy to see that the easiest things to determine come out as the best predictors.

Utilizing the various parameters, I give the predictions. Now some of them have quite a bit of scatter in them, but the fourth column over here, "the average pack failure—theoretical, "is the average value of those three, positive thickness, positive weight, and negative weight. Then the fifth column out here, "average pack failure—actual," is when the packs actually failed.

All right, now the first two are quite a bit off. I put the ratio of theoretical to actual up there. The first one is about 59 percent off and the second one is 51 percent off. But from there on they are not too bad, 72 N is about eight percent off, 14 percent, 13, 22, 7 percent, 33 and 31.

So it gives hope, at least, that here may be a possible prediction tool using the chemical and physical data rather than, as we will explain this afternoon in some detail, using linear regression models in order to predict failure times.

This is just an alternative method and maybe a backup method; it's a supplement, really, to the regression model.

## DISCUSSION

LIM: Did you find the missing cadmium in the separator or in some other parts of the cell?

MCDERMOTT: I haven't done a stoichiometry of the cell to see if the amount of cadmium that migrated into the separator equalled the amount that came out. You can do a calculation and if so much weight of cadmium hydroxide is converted to cadmium metal, then I can subtract that out and the rest must be due to cadmium migration.

It turns out that the cadmium migration amounts to about half or 60 percent of the loss of that weight. So it is a considerable amount. The problem in experimentally measuring cadmium migration is peeling the separator off and figuring out where the interface really is, but it's a considerable amount of the cadmium loss that's due to cadmium migration.

BARNARD: Were you using the same cells as the previous speaker ? Were they the same type?

MCDERMOTT: These were General Electric 6-ampere-hour cells.

BARNARD: If you had corrosion of the nickel, how would you expect to recondition a cell to make them good again?

MCDERMOTT: I don't think you can recondition it back to the precorrosion state. Reconditioning would probably redistribute the active material differently or expose new active material but it wouldn't reverse the corrosion.

BARNARD: Well, I wouldn't think it would.

MCDERMOTT: Well, these cells, really, are under very corrosive conditions. And the previous cells were not, in the sense that there is very high overcharge, a high charge rate, high temperature. And all these, really, contribute to corrosion. The packs that Sid Gross was talking about would not be under that type of stress.

BARNARD: So that is basically the explanation. I was wondering about the previous speaker. I think he partially answered the question. We can ask him. After you reconditioned the batteries, for how many cycles did they last after that?

GROSS: After the cycling tests were conducted, then they were given a thorough reconditioning in order to prepare them for the charge characterization testing. And there was no cycle testing conducted after that.

BARNARD: I thought that's what you said. How long do you expect it to be under those conditions?

GROSS: I can't guess.

BARNARD: Okay, thanks.

MCDERMOTT: I would like to add one comment on why we have gone into this analysis, trying to discriminate between corroding failure mechanisms versus the noncorrosive failure mechanisms.

If you are running an accelerated test, and you have the cells that you are using to put into your regression analysis which are failing for one reason and your normal packs are your packs cycling at less rigid conditions which are failing for other reasons, you may have this gap in here that you are trying to extrapolate out to. So that's why we have to carefully study how the cells in the accelerated matrix are failing.

LACKNER: I wonder if you can comment on the fact that as the cells degrade, the separator dries out. You said you also had the more charged cadmium which would cause a high-pressure failure. Would the high-pressure failure be reduced by the fact that you have less electrolyte around in the dried-out separator?

MCDERMOTT: Yes. As I showed, I think, on the slide, I would attribute the high-pressure failures to two causes there. I don't know what the percentage of each would be, but the fact that you are losing the overcharge protection and we did have some hydrogen failures, and the drying out of the separator would change the impedance which with the very high charge rate, I think would increase the high-pressure failure also. So I would say there are two main causes there.

LACKNER: That was the function of the higher rate of charge then.

MCDERMOTT: Yes. That would contribute to it plus the high overcharge period. Some of these are 200 percent overcharged.

LACKNER: Were there any cells with polypropylene at all?

MCDERMOTT: No, they are all Nylon.

LACKNER: Just a comment; we've never noticed high-pressure accumulating on degraded cells with polypropylene.

METHLIE: First, you alluded to a hardware failure which occurred somewhat early in your test, there, and I wonder if you will elaborate with that as to what that was. And secondly, what kind of statistical significance and confidence do you have in the prediction you made based on the size of cell test samples that you are in?

MCDERMOTT: The first question: a hardware failure?

HALPERT: I think he's talking about the tab corrosion. Didn't you say something about the tab corrosion?

MCDERMOTT: No, I didn't. Corrosion on the plate. Maybe that was when I was talking about the model to explain the first set of data. It was the corrosion of the nickel plate. I might have said "tab," but I meant "plate."

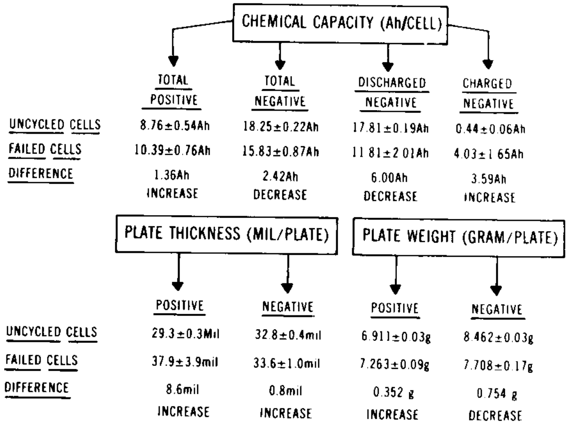
The second question about the statistical—any sort of statistical factor. At this point, no, I haven't gone through this and plotted least-squares fits of the curves and how this would relate to the actual prediction. So the answer to your question is no.

This afternoon you will see when we do the regression analysis, you can get least-squares fit type of data which will give you some more statistical verification or help.

TABLE 1. CYCLING PARAMETERS AND DESIGN VARIATIONS FOR PACKS INCLUDED IN THIS STUDY.

| PACK NO. | TEMP (°C) | DOD (%) | DISCH RATE | DISCH (HRS) | CHARGE (HRS) | CHG RATE | RECHG (% RC) | KOH (%) | KOH (cc) | PRECHG (ah) |
|---|---|---|---|---|---|---|---|---|---|---|
| 65N | 20 | 60 | 2C | 0.3 | 1.02 | C | 140 | 30 | 19.5 | 2.80 |
| 68N | 40 | 100 | 2C | 0.5 | 1.40 | C | 140 | 30 | 19.5 | 2.80 |
| 72N | 40 | 60 | 8C | 0.075 | 0.84 | C | 140 | 30 | 19.5 | 2.80 |
| 74N | 40 | 60 | 2C | 0.3 | 1.20 | C | 200 | 30 | 19.5 | 2.80 |
| 75N | 40 | 60 | 2C | 0.3 | 0.84 | C | 140 | 22 | 19.5 | 2.80 |
| 78N | 40 | 60 | 2C | 0.3 | 0.84 | C | 140 | 30 | 19.5 | 3.30 |
| 79N | 40 | 60 | 2C | 0.3 | 0.84 | C | 140 | 30 | 17.5 | 2.80 |
| 80N | 40 | 60 | 2C | 0.3 | 0.84 | C | 140 | 30 | 21.5 | 2.80 |
| 81N | 40 | 60 | 2C | 0.3 | 0.84 | C | 140 | 30 | 19.5 | 2.80 |

Figure 1-79



| CHEMICAL CAPACITY (Ah/CELL) | TOTAL POSITIVE | TOTAL NEGATIVE | DISCHARGED NEGATIVE | CHARGED NEGATIVE |
|---|---|---|---|---|
| UNCYCLED CELLS | 8.76±0.54Ah | 18.25±0.22Ah | 17.81±0.19Ah | 0.44±0.06Ah |
| FAILED CELLS | 10.39±0.76Ah | 15.83±0.87Ah | 11.81±2.01Ah | 4.03±1.65Ah |
| DIFFERENCE | 1.36Ah<br>INCREASE | 2.42Ah<br>DECREASE | 6.00Ah<br>DECREASE | 3.59Ah<br>INCREASE |

| | PLATE THICKNESS (MIL/PLATE) | | PLATE WEIGHT (GRAM/PLATE) | |
|---|---|---|---|---|
| | POSITIVE | NEGATIVE | POSITIVE | NEGATIVE |
| UNCYCLED CELLS | 29.3±0.3Mil | 32.8±0.4mil | 6.911±0.03g | 8.462±0.03g |
| FAILED CELLS | 37.9±3.9mil | 33.6±1.0mil | 7.263±0.09g | 7.708±0.17g |
| DIFFERENCE | 8.6mil<br>INCREASE | 0.8mil<br>INCREASE | 0.352 g<br>INCREASE | 0.754 g<br>DECREASE |

Figure 1-80

MODEL FOR CELL DEGRADATION AND FAILURE
IN ACCELERATED TEST CELLS

1. NICKEL CORROSION - 1.63 Ah incR. in Pos. Chem. Cap.
3.59 Ah shift from Cd(OH)$_2$ to Cd°
2. PLATE WEIGHT - Changes Consistent with Corrosion.
3. OVERCHARGE PROTECTION - High Pressure Failures.
4. POSITIVE PLATE GROWTH - Related To Corrosion
5. INNER ELECTRODE SPACE - Related To Separator Dry Out
6. SEPARATOR DRY OUT - Low Voltage/High Press. Failure.
7. CADMIUM MIGRATION - Loss in Neg. Cap. and Weight.
8. SHORTING - Related to Plate Growth, Separator Compression and Cadmium Migration

Figure 1-81

TABLE 2. CYCLES AT WHICH INDIVIDUAL CELLS WERE REMOVED FROM THE PACKS. THE LETTER TO THE RIGHT OF EACH CYCLE NUMBER INDICATES THE REASON FOR REMOVAL (R = SCHEDULED REMOVAL; H = HARDWARE FAILURE; L = LOW VOLTAGE ON DISCHARGE; P = PRESSURE FAILURE; A = CELL WITHOUT PRESSURE TRANSDUCER IS REMOVED WHEN HIGH PRESSURE IS SUSPECTED; S = CELL SHORTED).

| PACK NUMBER | CELL NUMBER | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 65N | 3157 H | 5660 L | 3157 H | 4165 L | 4465 L | 2953 R | 1604 R | 771 R |
| 68N | 523 P/L | 471 P/L | 523 P/L | 951 L | 955 H | 300 R | 202 R | 100 R |
| 72N | 1304 P | 1646 P | 1352 H | 1717 A | 1717 A | 149 R | 101 R | 50 R |
| 74N | 1196 P | 1195 P | 1648 P | 1803 S | 1810 S | 375 R | 250 R | 141 R |
| 75N | 2447 P | 1818 P | 1490 P | 2557 L | 2486 L | 2250 R | 1505 R | 750 R |
| 78N | 2245 P | 2359 L | 2347 L | 2354 S | 2368 S | 748 R | 509 R | 251 R |
| 79N | 2158 P | 3310 S | 1480 P | 3679 S | 3732 A | 1463 R | 1112 R | 580 R |
| 80N | 3223 P | 2297 L | 2328 P | 2319 S | 2467 S | 1425 R | 953 R | 511 R |
| 81N | 3014 L | 1579 P | 1039 P | 3055 A | 3055 A | 1510 R | 1001 R | 502 R |

Figure 1-82

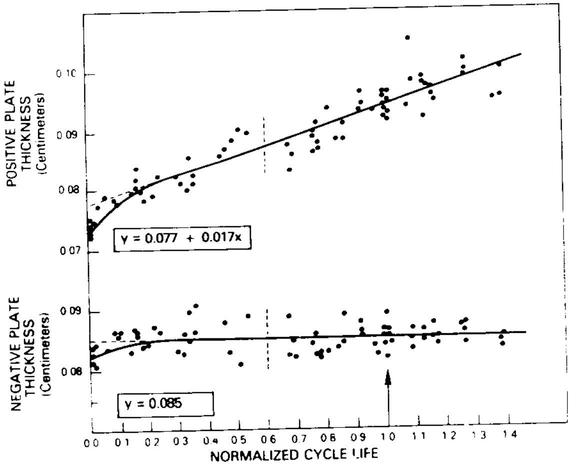


Figure 1. Positive and negative plate thicknesses as a function of the normalized cycle life (cell failure cycle/pack average)

## Figure 1-83

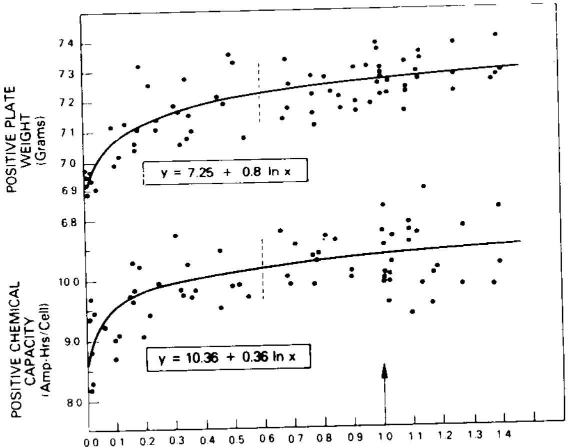


Figure 2. Positive plate weight and capacity as a function of the normalized cycle life (cell failure cycle/pack average).

## Figure 1-84

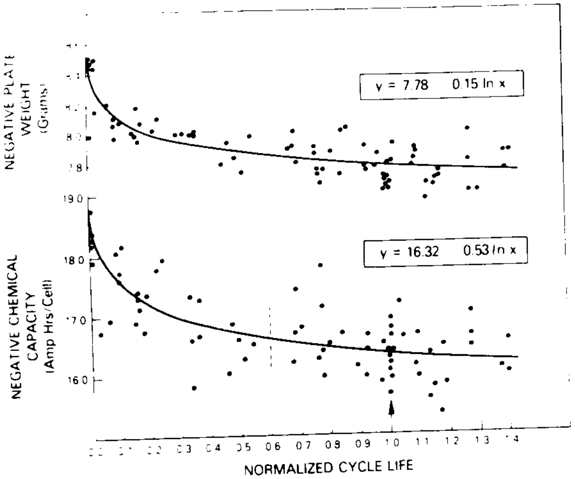


Figure 3 Negative plate weight and capacity as a funtion of the normalized cycle life (cell failure cycle/pack average)

## Figure 1-85

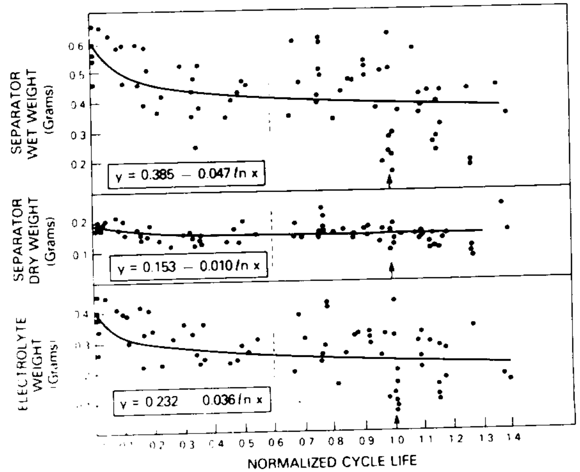


Figure 4 Separator wet weight, dry weight and electrolyte weight as a function of normalized cycle life (cell failure cycle/pack average).

## Figure 1-86

## PREDICTIONS BASED ON TEARDOWN ANALYSIS

| PACK NO. | UTILIZING POS. TH. | UTILIZING POS. WT. | UTILIZING NEG WT. | AVER. PACK FAIL. (THEOR.) | AVER. PACK FAIL. (ACTUAL) | THEOR. / ACTUAL |
|---|---|---|---|---|---|---|
| 65N | 6,223 | 6,597 | 9,089 | 7,303 | 4590 | 1.59 |
| 68N | 600 | 164 | 376 | 380 | 740 | 0.51 |
| 72N | 2,000 | 2,175 | 1,165 | 1,780 | 1,643 | 1.08 |
| 74N | 1,201 | 1,388 | 1,736 | 1,442 | 1,663 | 0.86 |
| 75N | 3,562 | 2,591 | 1,308 | 2,487 | 2,204 | 1.13 |
| 78N | 3,840 | 2,791 | 1,944 | 2,858 | 2,335 | 1.22 |
| 79N | 1,889 | 4,693 | 3,026 | 3,202 | 2,985 | 1.07 |
| 80N | 1,637 | 6,443 | 2,190 | 3,423 | 2,575 | 1.33 |
| 81N | 1,587 | 8,635 | 1,739 | 3,987 | 3,047 | 1.31 |

Figure 1-87

# CERAMIC-METAL SEALS FOR ADVANCED BATTERY SYSTEMS

L. Reed
ILC

We've been working on battery seals for about the past 6 years at ILC and initially all our attempts were in the nickel cadmium and the nickel hydrogen systems. And we reported essentially on our pretty much completed work at the Brighton Parsons Conference 2 years ago. And the results of the seal trials and so forth that we did were quite comprehensively discussed there and they have been published.

And these days, the ILC seals are in several of the NASA battery systems. So I don't feel that I have to discuss those any further. So what I want to do this morning is to talk about some of the more advanced systems that we are working on in the hope that one day the battery manufacturers will catch up on these for space applications. These are the lithium sulfur and the sodium sulfur systems.

Just as a point of departure, I will show you a couple of the seals that we do make for nickel cadmium and nickel hydrogen.

(Figure 1-88)

This is a typical terminal that we make. It is illuminous ceramic to a nickel joint of stainless steel. It uses abrazement of zirconium nickel and we found out that this zirconium nickel braze stands up very well against the KOH. So it's used quite extensively in nickel cadmium systems.

(Figure 1-89)

We then took that seal and we put it into a nickel hydrogen battery. The only difference between that and the nickel cadmium is that because of the high pressure we had to use a backup seal design that would stand the high pressure of 400 to 600 psi that you find in the cell. However, the Zeigler seal seems to have been adopted for the nickel hydrogen and we seem to have lost out on this. But if anybody wants an alternative as a completely brazed system to these compression crimp seals of the Ziegler type then this one is available.

We found that with both of these systems, the di-luminous ceramics were more than adequate because the KOH doesn't attack pure aluminum appreciably and the same is true for the nickel and the seal material itself, which is zirconium. However, when you come to the lithium system, it extensively attacks the aluminum.

So one has to go to beryllia. And we, therefore, hypothesize that a number of seal systems could be employed which would have the right electromotive potential oxidation that could be used with the lithium sulfur, metal sulfide system.

We have been conducting the work under two contracts. One was for load leveling applications, mainly. One is with Eckry and the other is with Argonne National Laboratories. This work has been going on for about 12 months or so, so this is a progress report on work which isn't completed, but it shows the direction in which we are going.

(Figure 1-90)

Very briefly, these are some of the characteristics that are required in the load leveling application. I would just draw your attention to some of the more severe environmental conditions which are obtained in this case versus the NICAD case.

You will see that under environment we have to operate as high as 500°C in moltant salts of lithium chloride and potassium chloride which have a certain amount of free potassium and free lithium around. And the design life is quite long—10 years. And they have to resist a great number of cycles. We haven't been that ambitious in our goals, yet, to go to 7000 cycles. We have just been going to 500 cycles.

The main thing is that the batteries operate at a high temperature and are very, very corrosive. All the materials can danger them. So we have attacked the problem in two ways: one is to just get systems which are compatible by taking a very simple test piece. There is a second phase going on to take some of the successful systems and build them into actual terminals and into half-cells.

(Figure 1-91)

You couldn't have a more simple test piece than this. And we show beryllium oxide on one side and on the other side we put aluminum because we can get a pass between aluminum and beryllium and some of the seal systems that we have tried.

(Figure 1-92)

There are four systems that we have looked at in various degrees so far. Obviously the three systems are the three lower systems, paladium cobalt, the nickel, and the gold. They are all intrinsically electrochemically compatible with lithium sulfide systems. However, there is just the plain corrosion to be taken into consideration as well, and under those circumstances perhaps they will not solve the problem.

We included nickel zirconium as well because we had such good success with the NICAD systems, even though we recognize that zirconium might not be intrinsically electrochemically compatible with the system. But we figured that if it were diluted by being alloyed with the nickel, perhaps we could get by. And, indeed, some early tests which we again reported at the Brighton Parsons Conference 2 years ago, with an aluminous ceramic at that time showed that the nickel zirconium was better than gold, for example.

So I would just like to briefly discuss what these systems really are from our point of view. There are two main ways of joining metals to ceramics. One involves just placing the liquid or the braze alloy between the metal member and the ceramic with no other pretreatment of the ceramic. That's the first case. And in that case we generally have to have an active metal alloy or active metal member such as zirconium or titanium. Something like that will attack the ceramic slightly and enable the abrazened alloy to wet the surface.

In the second case, we have a zirconium hydrite coating. Actually, it's a mistake, it's a titanium hydrite coating that is shown there, and we put the titanium hydrite coating on first because the paladium and the cobalt will not in themselves wet the ceramic. So, again, it becomes an active alloy because the titanium gets taken into solution by the paladium and the cobalt.

In the third system, which is tungsten yttria, this is a variation of the well-known molymanganese process. In most molymanganese processes, you have a reaction between the glassy phase of the ceramic and some additives which might be put into the militinum at a high temperature that is painted on and, say, fired at 1400°C.

In this particular case, one cannot tolerate any silica because the silica will be attacked by the lithium, or if you have a sodium battery, by the sodium.

So one relies on other mechanisms to get a bond other than a bond by a glassy face. It's been found that the tungsten yttrious that's been worked out for aluminum was found to give a yttrious yennell—a solid solution between aluminum and $Y_2O_3$ which would give you a good bond. But no work had been done on beryllia. So for the purpose of carrying out the exercise of the tungsten yttria, it was performed to see if it could perform on beryllia.

In the fourth case, with gold, an intrinsically electrochemically resistant material, we planned to try both the titanium hydroid, not zirconium hydroid, and the tungsten yttrious seal. Very briefly, the results of trying these systems on beryllium is that we found that in cycling tests with nickel zirconium, we could go up to 1000 cycles at 500°C and could even take the seal up to 700°C with beryllia. We believe that we have a good seal system there to proceed onto the next stage.

In the case of titanium, the second system, we found that we did get a good seal to alumina and could, in fact, cycle it many times to 500°C but beryllia is a much weaker ceramic and we found that the system, although it could be made vacuum-tight, after a couple of cycles the system leaked.

In the third case, the nickel phosporous brazened alloy is very corrosive and it attacked the tungsten and so we have to protect it. We first tried it on the aluminum to see whether we could protect the tungsten. So we pretreated the tungsten interface on the aluminum by putting down a very thick layer of nickel. And then we controlled the braze alloy by plating out the braze alloy in the form of a nickel phosphorous plating. Using this system, we found that we could, in fact, get a vacuum-tight seal. We then translated this to beryllia and again tried to produce the tungsten yttria on beryllia.

So far, we can again get a largely vacuum-tight seal but the beryllia seems to be very much weaker than the alumina and the BeO-$Y_2O_3$ that gets formed is not a strong interfacial compound. So we have to do a lot more work on that system.

The last system remains to be tried. So having to move on to the second phase of trying to make some actual feed-throughs, we chose just to go with the top system, the nickel zirconium system. If I could show you some of the feed-throughs we have tried so far, there are two types. There is a type A and a type B. And it depends on the configuration of where the negative electrode and the positive electrode is.

The one thing we are trying to do is to protect the positive electrode. To do that we want to restrict the flow of material from the cell to the positive electrode. So we make the joining very narrow. This is the path that the electrolyte would have to follow. Since corrosion mainly goes to the positive electrode we are trying to restrict the flow to that point. You can see the alumina surrounding it because there is no alumina there because it doesn't see the seal of corrosive materials.

(Figure 1-93)

This just shows you how it's jigged up when we have a concentricity and it allows it to go off the contricity somewhat.

(Figure 1-94)

And this shows the same thing with a little seal refinement. You see the detail here which allows the stress level to be reduced. It is just an additional design feature.

The objective, of course, is to eventually to get these seals down to about \$3.00 or \$4.00 apiece. At the moment they probably cost \$3000 or \$4000 each.

(Figure 1-95)

This shows the second type of feed-through assembly where we have the positive post at the center. Again, you can see how we tried to restrict the flow to the center, between the center post and the surrounding so that we get a positive electrode not corroded, with the least amount of corrosion as possible.

This shows that same geometry which is 911½ cell where we apply the voltage between the two to carry out this test at 500°C. As long as the cell resistor stays infinite, we know we are in good shape. As soon as it stops or the resistance goes down, we know we have a short across the ceramic member between the positive and the negative and that starts the end of life.

We are just in a stage now where we have made the different types of seals, and A and B types of seals, and we are now starting on a program of actually testing in the half-cell for ANL for the actual work. Thomas International is actually going to do the testing in their plant.

This just shows another design which shows a more mechanical design seal, which is close to the Zeigler type seal in some ways, where we boronitroid in and sort of mechanically prevent the electrolyte from getting up into the seal area. In this geometry, one could perhaps get away with much more normal braze materials. So we are reserving this as sort of a backup approach.

This will show you some of the geometries that were being made. This is the A type geometry.

This shows you half-cells that were filled with KCL and the lithium chloride.

This is an example of the boron nitrite cell. We haven't put the boron nitrite in yet; it's ready to be filled.

In conclusion I would say that anything that we can get to work for a lithium cell, we feel we can quite well get to work for a sodium sulfur system because it is less corrosive. I hope that perhaps as people develop space vehicles further within the next 10 to 20 years, they will find a hope for these types of battery systems in them. Meanwhile, if you have any problems with nickel cadmium systems, I would be glad to talk to you about them after this talk.

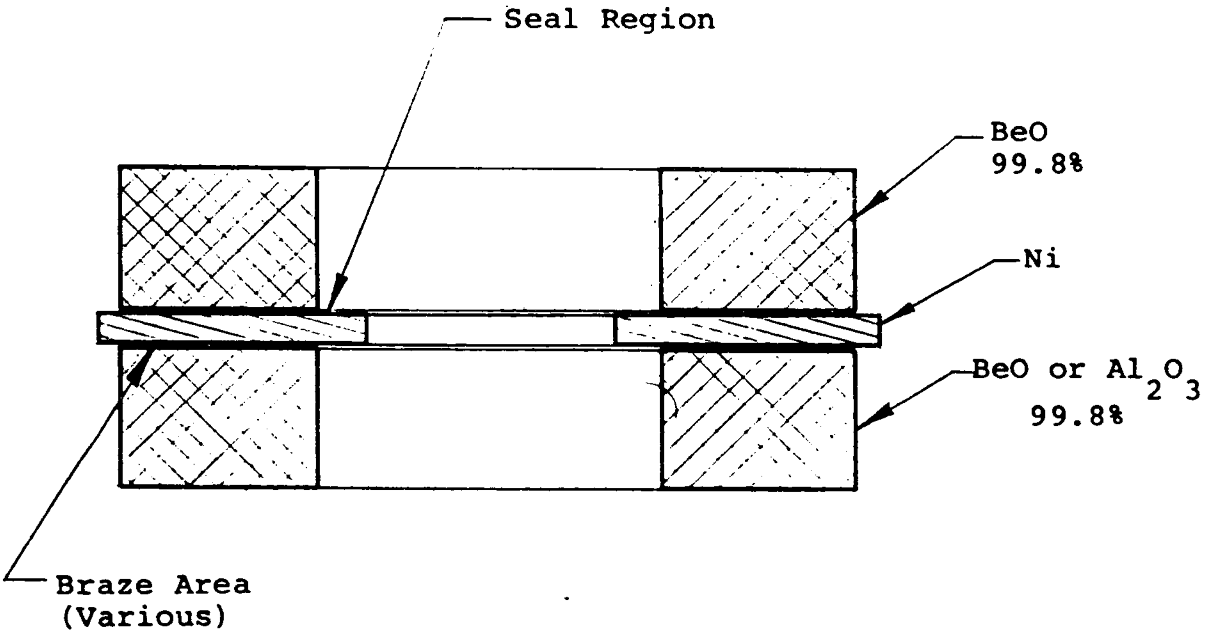


Figure 1-88

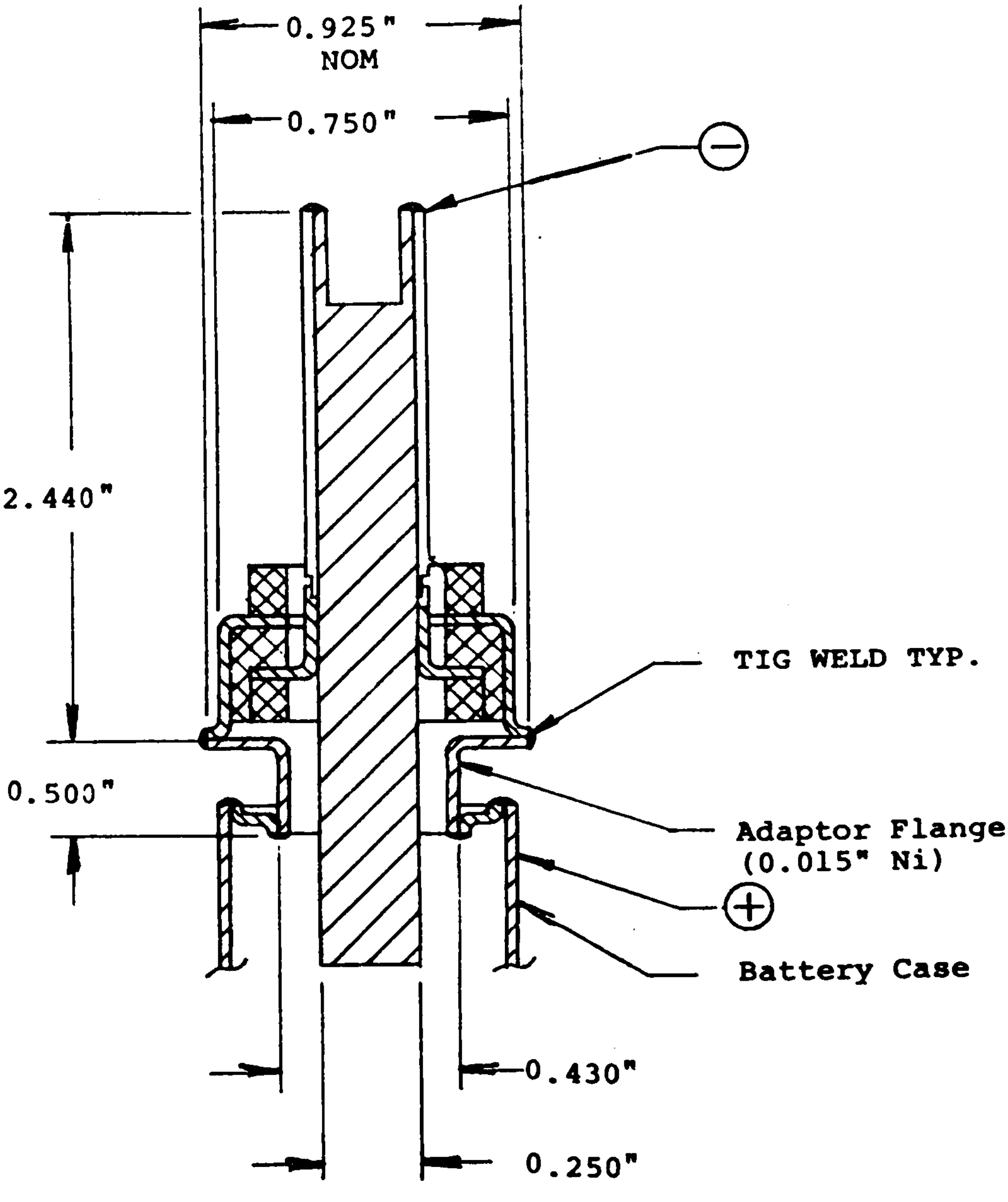

0.925"
NOM
0.750"
2.440"
0.500"
TIG WELD TYP.
Adaptor Flange
(0.015" Ni)
Battery Case
0.430"
0.250"

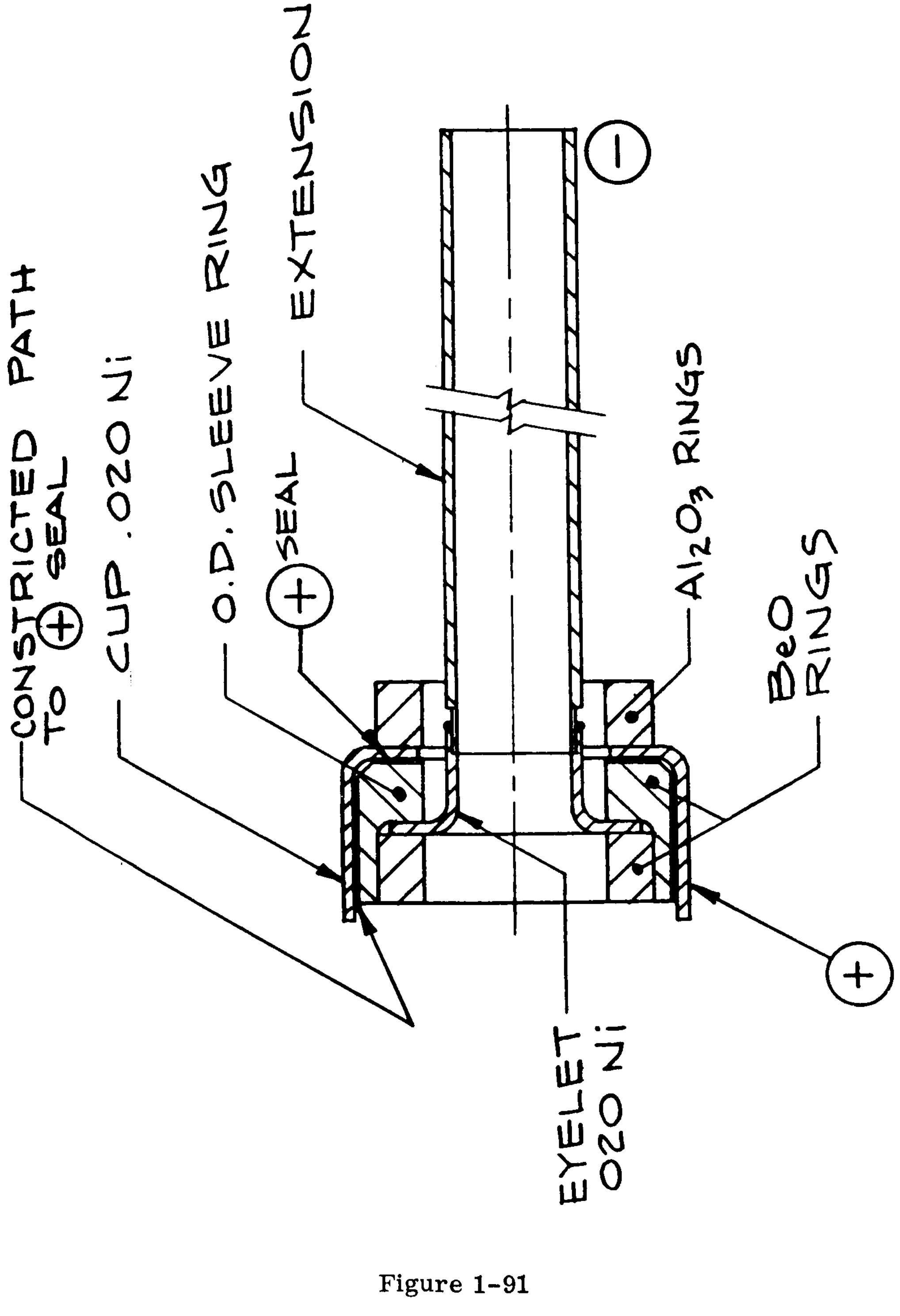
Figure 1-89

# CERAMIC-TO-METAL BRAZING APPROACHES

Ceramic-to-metal sealing systems investigated. Hermetic seals between 99.9 + purity BeO and 200 series nickel were the goal in each case.

| Ceramic Pretreatment | Brazing Alloy |
|---|---|
| None | Ni-Zr |
| $ZrH_2$ coating | Pd-Co |
| $W-Y_2O_3$ | Ni-P |
| $ZrH_2$ coating or $W-Y_2O_3$ | Au |

Figure 1-90



CONSTRICTED PATH TO ⊕ SEAL
CUP .020 Ni
O.D. SLEEVE RING
⊕ SEAL
EXTENSION
⊖
$Al_2O_3$ RINGS
BeO RINGS
⊕
EYELET 020 Ni

Figure 1-91

# ELECTRICAL FEEDHTROUGH DESIGN OBJECTIVES
# (Li/MS LOAD LEVELING BATTERY)*

## SIZE

Minimum electrode diameter: 3/8 in.

Maximum outside diameter: 2 in.

## RATING

### ELECTRICAL

Current: 1000A

Voltage: 2.0 - 2.5, 40,000 hours at potentials above 2.0 volt

## ENVIRONMENT

Outside: Air, 20 - 500°C
(Normal operation temperature 375 - 475°C)

Cell Side: Argon or helium over $Li_2S$ saturated electrolyte
(molten eutectic of LiCl + KCl)

## COMPATIBILITY REQUIREMENTS

Cell Environment: Contact with thin film of hot electrolyte and K vapor

Bus: Nickel, nickel plated copper, copper, iron, molybdenum

Case: 300 Series SS, low carbon steel, Hastelloy B, nickel

## GENERAL

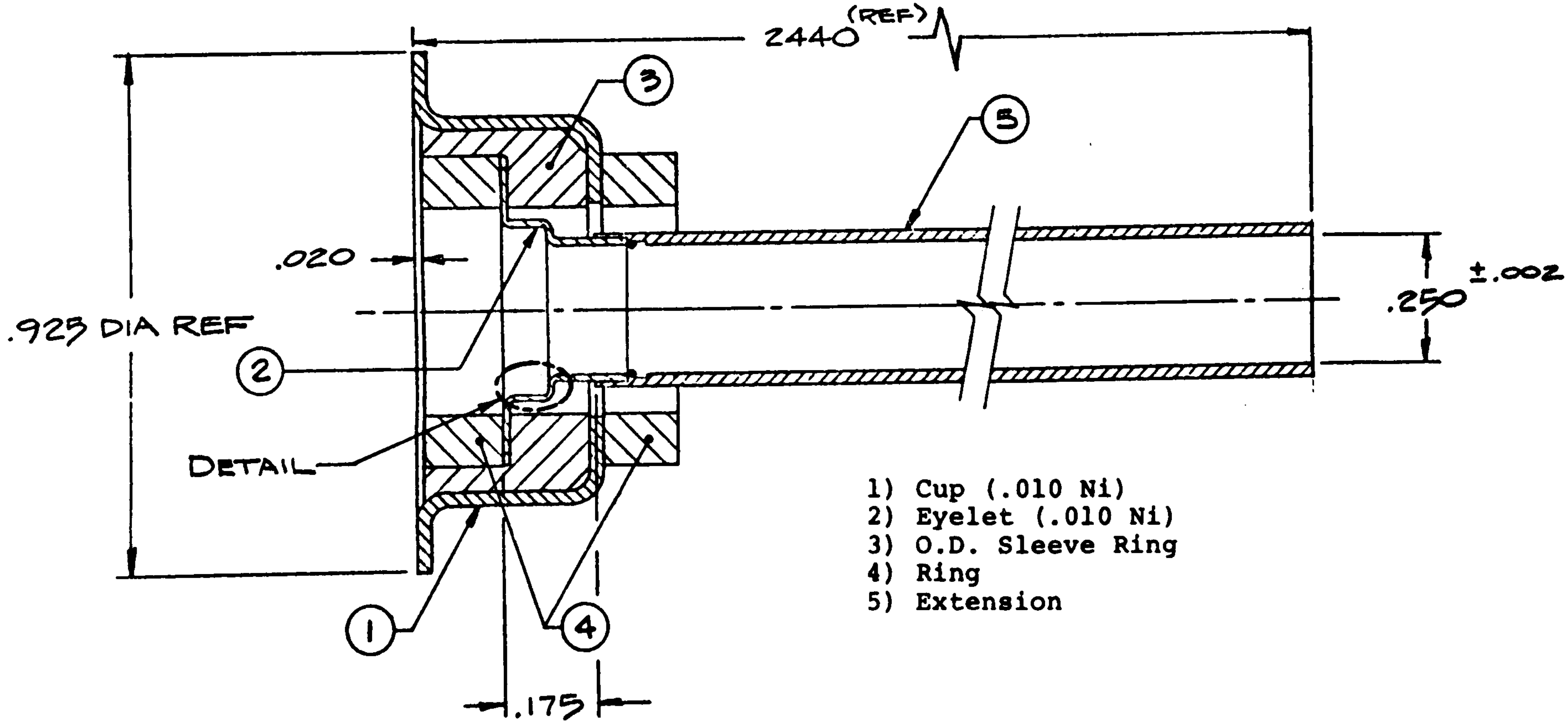
Design Life: 10 years

Thermal Cycles: 120 between 20 - 500°C, each cycle in 10 hours plus 7,000 cycles between 375 - 475°C, each cycle in 5 to 10 hours

Leak Tightness: $10^{-8}$ STD cc/sec helium

Must be designed for rugged commercial handling.

Figure 1-92



1) Cup (.010 Ni)
2) Eyelet (.010 Ni)
3) O.D. Sleeve Ring
4) Ring
5) Extension

Figure 1-93

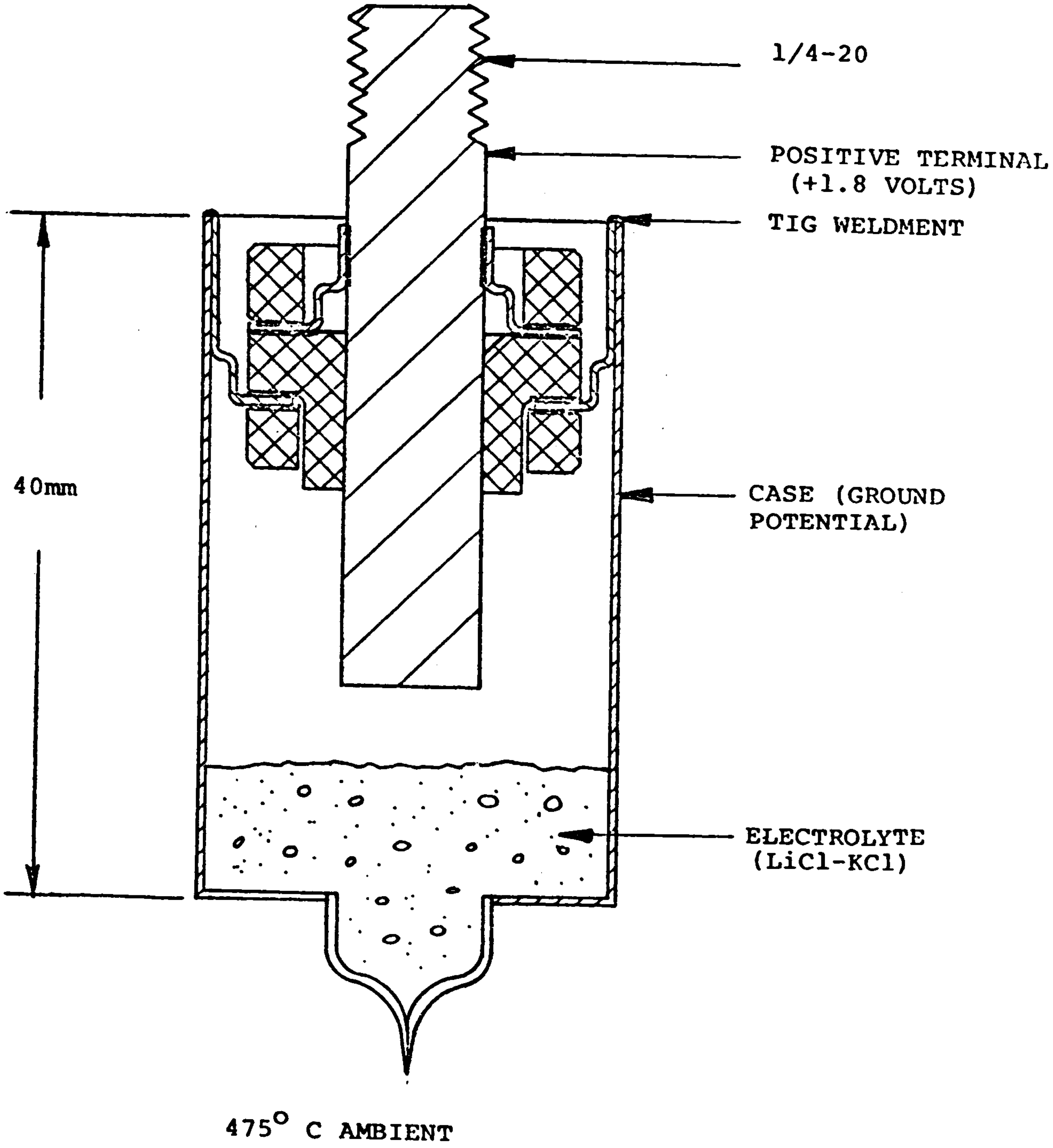

1/4-20
POSITIVE TERMINAL (+1.8 VOLTS)
TIG WELDMENT
40mm
CASE (GROUND POTENTIAL)
ELECTROLYTE (LiCl-KCl)
475° C AMBIENT

Figure 1-94

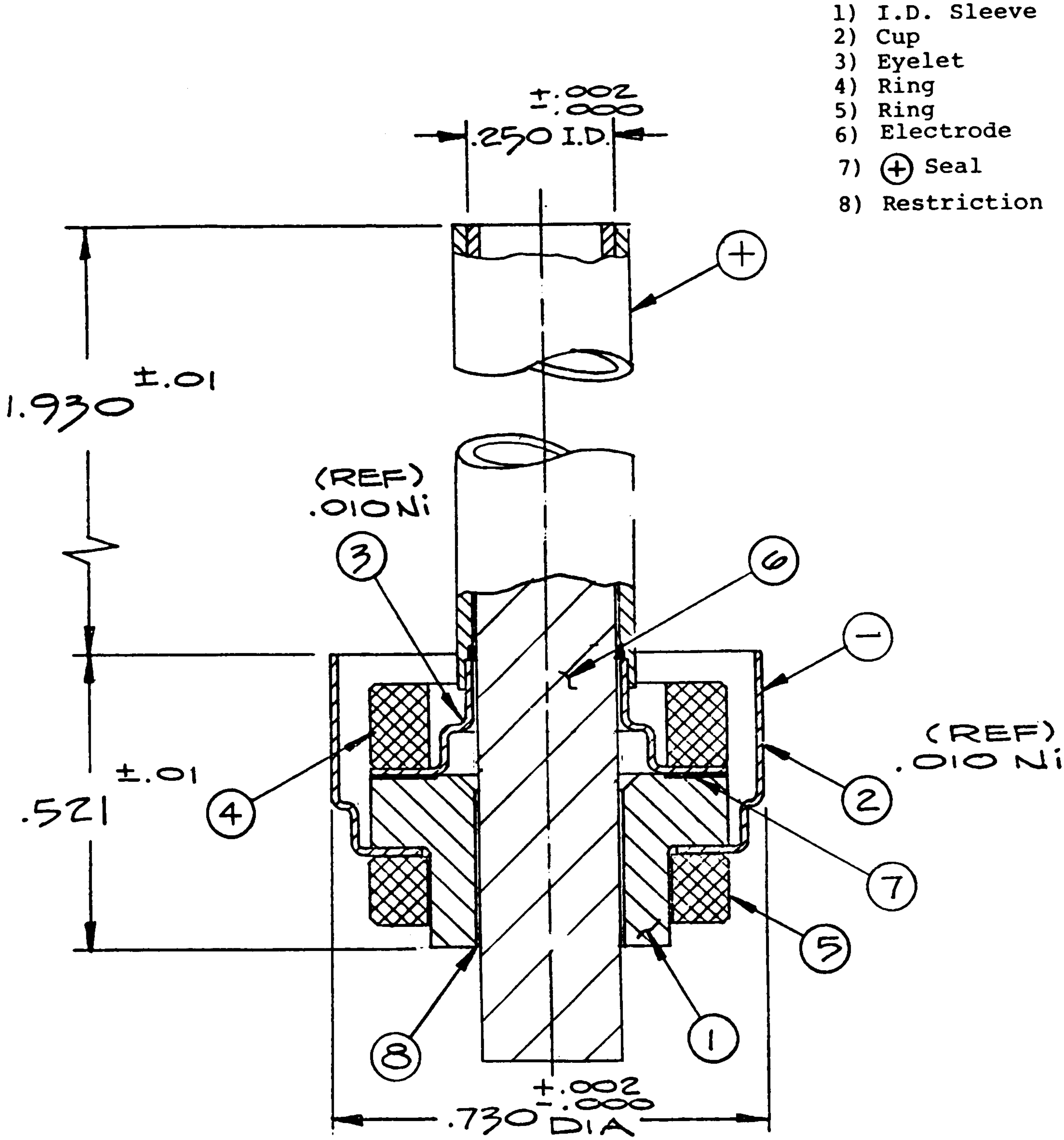

1) I.D. Sleeve
2) Cup
3) Eyelet
4) Ring
5) Ring
6) Electrode
7) ⊕ Seal
8) Restriction
+.002
-.000
.250 I.D.
+
1.930 ±.01
(REF)
.010Ni
3
6
−
(REF)
.010 Ni
2
7
4
.521 ±.01
5
8
1
+.002
-.000
.730 DIA

Figure 1-95

# SESSION II

## ACCELERATED TESTS

F. Ford, Chairman
Goddard Space Flight Center

# ACCELERATED TEST PROGRAM AT CRANE

H. Brown
Crane

For several years Crane has been involved in this accelerated test program and at the last workshop we presented a summary of the statistical work that had been performed at that time and what we planned for the future.

At that point in time several of the packs were slow cycling and today I want to update the program status and tell you about some of the work we have done in the last year. I think, first of all, in order to help the people out who have not been here before and maybe to refresh your memory a little bit and to help the next three presentations out, we will start with just a brief explanation of the matrix.

(Figure 2-1)

This graph shows the test factors we used and the levels of these test factors. We have eight factors from A through H—it should be concentration of KOH, volume of electrolyte, and negative precharge. Then we used them at those five different levels.

Now, the different levels refer to the different types of statistical analysis matrices we are using. We have a composite design in the center point in this design. The center point is item number 3, and in one pack the design takes each of these center points as the test parameters: environmental and physical parameters.

The next items are the star points.

(Figure 2-2)

The star points take the extreme levels of 1 and 5 and combine each extreme level of each quantitative factor. That is, the eight factors we have down the side are in combination with the center level of every quantitative factor. We have a pack that has 20°C temperature and has seven center point levels as its remaining test parameters. It does that for each one of those. So, that makes 16 packs.

These 16 packs come down as this. Shown here inside this band are the two extremes of the star point. Those are the levels 1 and 5, and then below here are the center points.

Now, we also have on test four normal packs which are run at what is considered to be the normal conditions. Once we have a whole matrix and all the test data are in, we will come up with the prediction model. Statistically, that can predict these normal points. We are going to try to see how close we can come.

The third part of the composite design is that I have got more information on today than the rest of this, but this will be used, you know, in a couple of the other three presentations. If you will notice, I will point out one other thing here: these have eight cells in them. Three of those cells are scheduled removals that Mr. McDermott had talked about. They are scheduled to be removed at one-fourth life, one-half life, and three-quarters life. The point at which they were to be removed was predicted prior to the start of the test.

(Figure 2-3)

This figure shows the factorial part of the test. Now, what we have done is we have taken the levels 2 and 4 over here and they make up the factorial levels. In this part, we are trying to determine which main effects and/or interactions have significant effect on battery life.

We used a 2n factorial and since we only needed the main effects and two factor interactions, we chose a one-fourth representation of this which would give it to us. Also, this would limit the number of test cells we had to have. So, if we used all the combinations we could make, we would fill this graph or this chart up here, but since we only wanted a one-fourth representation, we now have 64 packs in that chart and those numbers represent the test point; 11n, for instance, is the pack number.

These packs had only five cells in them. There were no scheduled removals anywhere. You can see here, if you follow the graph, at 30°C, 40 percent DOD, a charge rate of C/2 and a discharge rate of this, then 5n would have a 200 percent recharge, a 34 percent KOH, 20.5 $cm^3$ of KOH and 3 ampere-hours.

The status, then, of the test program at this time is that the electrical cycling is nearly complete. We have only one factorial pack remaining, pack 5n. We have one center point pack that is still on test. We have the four normal packs, of course, still cycling. The factorial pack and the center point pack are expected to fail in the next few months, so pretty soon we will be finished with those and actually have most or all of the electrical data that we need to work with this matrix.

We also perform the chemical and physical analysis, the teardown analysis, and this is the part of the data that Mr. McDermott presented this morning. We have chemically and physically analyzed 160 star point cells and have physically analyzed 70 of the factorial cells.

We have analyzed at least one cell from each factorial pack with the exception of 5n, which is still cycling. So, that moves us on into the analysis. We have also taken all this chemical data, the manufacturer's baseline data, Crane's baseline data, put them into what we call a computerized data correlation file, which makes up 72 variables. We have all this information in a file and we can perform correlations between different parameters, if we want.

At last year's workshop Don Mains gave a detailed presentation of the statistical analysis and at this time we have completed the first phase of this statistical analysis. We have performed the analysis of variants. The purpose of doing this analysis of variants is to determine which of the test factors has a significant effect on the life of a cell, and in doing so we used the fractional points here.

So far, you know, since these cells have just failed recently, and 5n is still cycling, we went ahead and ran this thing. We have put in some information for 5n as to what cycle it is on right now in order to get this analysis of variants. The computerized programs we used to do it can handle the missing points, such as the one missing point there and a couple of others.

(Figure 2-4)

This is the result of the analysis of variants and I am going to have to explain this one a little bit. The T represents temperature, depth of discharge, charge rate, discharge rate, percent recharge, percent KOH, amount of KOH, and precharge. Those are eight main effects.

The rest of these down here are the interactions between those two, between any two of those. The 0.01's you see up there and 0.05's indicate that those are the factors that showed up significant at a confidence level of 0.01 or 0.05. Confidence level of 0.01 means that we would have a 1 percent chance of being wrong if we said temperature affected the life of this cell.

Then, also, up here at the top, there was considerable discussion as to what to use for failure and how to work with this data, so we decided to run it eight ways and we have zero voltage failure, using cycles. We have zero voltage failure using cycle life in hours. We have one voltage failure using cycle on one voltage hours.

The natural logarithm on cycles and hours on each of them was run because statistically it made the results more homogeneous and it was easier to work with the system to work with. As you can see from here, the temperature and DOD show up significant in all the analyses. The charge rate and discharge rate appears in almost all the analyses and then the most common interactions are with temperature and depth of discharge with temperature with charge rate, depth of discharge with charge rate, and charge rate with discharge rate.

It is also interesting to note that the physical variables, the percent of KOH, the amount of KOH, and the precharge show up very little in this analysis, which seems to be saying that in the range we used, they had very little effect on the life. One thing in particular is that the amount of KOH did not show up at all. Now, if you notice over here on the other graph, the amount of KOH we used went from 17.5 to 21.5 cubic centimeters. So, that just doesn't show up in that as a main effort or as any interaction between the two.

(Figure 2-5)

The next step, then, in this analysis is to use these significant variables and run a linear regression to determine an equation, and as of yet that has not been done. It is in the process. In addition to the linear regression, we can also use this information in looking at some of the nonlinear equations. We did some of these equations prior to actually running this analysis of variants.

These four equations were suggested by various members of our working group and they show up here where we used cycle life. These are coefficients that are determined in the computerized run, or regression run, by an iteration process.

The equations defined here, though, only use two or three of the factors that we have in the significant factors. Therefore, they are not giving us as good a prediction as what we could possibly get. I think you will see more of this later on. This is, you know, an area that we are working in and a place where we need to do quite a bit more work.

As I previously mentioned, we are also performing chemical and physical analyses and are incorporating this data into the statistical analysis and of course Mr. McDermott and others are working with some of it.

With the chemical and physical analysis we can see the effect of the five levels of each test factor on the life of the cells. As an example, look at Figure 2-2.

We can take, for instance, 67n, 68n, where we have 20 percent DOD, 100 percent DOD, combine it with the center point, where we have 60 percent DOD, and see the effect that the depth of discharge has on the plate thickness or the chemical capacities of the cell. The electrical cycling tests are nearly complete, but the analysis of the data, I think, has just really begun.

DISCUSSION

REID: What size cells are these?

BROWN: Six ampere-hour.

Factors and Levels

| | 1* | 2** | 3*** | 4** | 5* |
|---|---|---|---|---|---|
| A. Temperature °C (T) | 20 | 30 | 40 | 50 | 60 |
| B. Depth of Discharge (DOD) | 20 | 40 | 60 | 80 | 100 |
| C. Charge Rate (CR) | C/4 | C/2 | C | 2C | 4C |
| D. Discharge Rate (DR) | C/2 | C | 2C | 4C | 8C |
| E. Percent Charged (%C) | 110 | 140 | 140 | 200 | 200 |
| F. Concentration of KOH (% KOH) | 22 | 26 | 30 | 34 | 38 |
| G. Amount of KOH (cc) | 17.5 | 18.5 | 19.5 | 20.5 | 21.5 |
| H. Precharge (AH) | 2.20 | 2.50 | 2.80 | 3.00 | 3.30 |

*Star Point Levels
**Factorial Levels
***Center Point Levels

| | Physical Design Parameters | | | | |
|---|---|---|---|---|---|
| Concentration of KOH electrolyte Percent by weight | 22.0 | 26.0 | 30.0 | 34.0 | 38.0 |
| Volume of electrolyte, cc. | 17.5 | 18.5 | 19.5 | 20.5 | 21.5 |
| Negative precharge, AH | 2.20 | 2.50 | 2.80 | 3.00 | 3.30 |

Figure 2-1

| • Pack No. | Environmental Parameters | | | | | Physical Parameters | | | No. Cells |
|---|---|---|---|---|---|---|---|---|---|
| | Temp (°C) | DOD (%) | Chg Rate | Disch Rate | Rechg (%RC) | KOH (%) | Prechg (ah) | KOH (cc) | |
| **Starpoints** | | | | | | | | | |
| 65N | 20 | 60 | C | 2C | 140 | 30 | 2.80 | 19.5 | 8 |
| 66N | 60 | 60 | C | 2C | 140 | 30 | 2.80 | 19.5 | 8 |
| 67N | 40 | 20 | C | 2C | 140 | 30 | 2.80 | 19.5 | 8 |
| 68N | 40 | 100 | C | 2C | 140 | 30 | 2.80 | 19.5 | 8 |
| 69N | 40 | 60 | C/4 | 2C | 140 | 30 | 2.80 | 19.5 | 8 |
| 70N | 40 | 60 | 4C | 2C | 140 | 30 | 2.80 | 19.5 | 8 |
| 71N | 40 | 60 | C | C/2 | 140 | 30 | 2.80 | 19.5 | 8 |
| 72N | 40 | 60 | C | 8C | 140 | 30 | 2.80 | 19.5 | 8 |
| 73N | 40 | 60 | C | 2C | 110 | 30 | 2.80 | 19.5 | 8 |
| 74N | 40 | 60 | C | 2C | 200 | 30 | 2.80 | 19.5 | 8 |
| 75N | 40 | 60 | C | 2C | 140 | 22 | 2.80 | 19.5 | 8 |
| 76N | 40 | 60 | C | 2C | 140 | 38 | 2.80 | 19.5 | 8 |
| 77N | 40 | 60 | C | 2C | 140 | 30 | 2.20 | 19.5 | 8 |
| 78N | 40 | 60 | C | 2C | 140 | 30 | 3.30 | 19.5 | 8 |
| 79N | 40 | 60 | C | 2C | 140 | 30 | 2.80 | 17.5 | 8 |
| 80N | 40 | 60 | C | 2C | 140 | 30 | 2.80 | 21.5 | 8 |
| **Center Point** | | | | | | | | | |
| 81N<br>82N<br>96N | 40 | 60 | C | 2C | 140 | 30 | 2.80 | 19.5 | 8<br>5<br>4 |
| **Normal Points** | | | | | | | | | |
| 83N | 0 | 40 | C/2.38 | C/1.20 | 105 | 34 | 2.50 | 18.5 | 8 |
| 84N | 20 | 20 | C/4.76 | C/2.40 | 105 | 34 | 2.50 | 18.5 | 8 |
| 85N | 0 | 20 | C/4.76 | C/2.40 | 105 | 34 | 2.50 | 18.5 | 8 |
| 86N | 20 | 40 | C/2.38 | C/1.20 | 105 | 34 | 2.50 | 19.5 | 8 |

Figure 2-2

FRACTIONAL FACTORIAL TEST MATRIX CELL PACK NUMBER

| | | | | TEMPERATURE °C | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 30° | | | | | | | | 50° | | | | | | | |
| | | | | % DOD | | | | | | | | % DOD | | | | | | | |
| | | | | 40 | | | | 80 | | | | 40 | | | | 80 | | | |
| | | | | CHARGE RATE | | | | CHARGE RATE | | | | CHARGE RATE | | | | CHARGE RATE | | | |
| | | | | C/2 | | 2C | | C/2 | | 2C | | C/2 | | 2C | | C/2 | | 2C | |
| | | | | DISCHG RATE | | DISCHG RATE | | DISCHG RATE | | DISCHG RATE | | DISCHG RATE | | DISCHG RATE | | DISCHG RATE | | DISCHG RATE | |
| | | | | C | 4C | C | 4C | C | 4C | C | 4C | C | 4C | C | 4C | C | 4C | C | 4C |
| % RECHARGE | % KOH | CC KOH | PC | CYCLE PERIOD | | | | | | | | | | | | | | | |
| 200 | 34 | 20.5 | | 3 | 5N | | | | | | | 20N | | | | 49N | 40N | | | |
| | | | | 2.5 | | | 56N | | | 33N | | | | 4N | | | | | 21N | |
| | | 18.5 | | 3 | | 64N | | | | | 41N | | | | 12N | | | 29N | | |
| | | | | 2.5 | | | | 13N | 28N | | | | 57N | | | | | | | 48N |
| | 26 | 20.5 | | 3 | | 47N | | | | | 58N | | | | 27N | | | 14N | | |
| | | | | 2.5 | | | | 30N | 11N | | | | 42N | | | | | | | 63N |
| | | 18.5 | | 3 | 22N | | | | | | | 3N | | | | 34N | 55N | | | |
| | | | | 2.5 | | | 39N | | | 50N | | | | 19N | | | | | 6N | |
| | | | | CYCLE PERIOD | | | | | | | | | | | | | | | | |
| 140 | 34 | 20.5 | | 3 | | | 35N | | | 54N | | | | 23N | | | | | 2N | |
| | | | | 2.5 | 18N | | | | | | | 7N | | | | 38N | 51N | | | |
| | | 18.5 | | 3 | | | | 26N | 15N | | | | 46N | | | | | | | 59N |
| | | | | 2.5 | | 43N | | | | | 62N | | | | 31N | | | 10N | | |
| | 26 | 20.5 | | 3 | | | | 9N | 32N | | | | 61N | | | | | | | 44N |
| | | | | 2.5 | | 60N | | | | | 45N | | | | 16N | | | 25N | | |
| | | 18.5 | | 3 | | | 52N | | | 37N | | | | 8N | | | | | 17N | |
| | | | | 2.5 | 1N | | | | | | | 24N | | | | 53N | 36N | | | |

Figure 2-3

| | 0 Volt Cyc | 0 volt Hrs | 0 Volt LN Cyc | 0 Volt LN Hrs | 1 Volt Cyc | 1 Volt Hrs | 1 Volt LN Cyc | 1 Volt LN Hrs |
|---|---|---|---|---|---|---|---|---|
| T | .01 | .01 | .01 | .01 | .01 | .01 | .01 | .01 |
| DOD | .01 | .01 | .01 | .01 | .01 | .01 | .01 | .01 |
| CR | | .01 | .01 | | .01 | .01 | .01 | |
| DR | .05 | .05 | | .01 | .01 | .01 | .01 | .01 |
| CHG | .01 | | .05 | | .01 | | | |
| PKOH | | | | | .05 | | .05 | .05 |
| AKOH | | | | | | | | |
| PC | | | | | | | | |
| T X DOD | .01 | | .01 | .01 | .01 | .01 | .05 | .05 |
| T X CR | | .01 | .01 | .01 | | .01 | .01 | .01 |
| T X DR | | | | | | .05 | .01 | .01 |
| T X CHG | | | | | | | | |
| T X PKOH | | | | | .05 | | | |
| T X AKOH | | | | | | | | |
| T X PC | | | | | | | | |
| DOD X CR | | .05 | .01 | .01 | .01 | | | |
| DOD X DR | | | .05 | .05 | | | .01 | .01 |
| DOD X CHG | .01 | | | | | | | |
| DOD X PKOH | | | | | | | | |
| DOD X AKOH | | | | | | | | |
| DOD X PC | | | | | | | | |
| CR X DR | | | .01 | .05 | .05 | .01 | .01 | .01 |
| CR X CHG | | | | .05 | | | | |
| CR X PKOH | | | | | | | | |
| CR X AKOH | | | | | | | | |
| CR X PC | | | | | | | | |
| DR X CHG | | | | | .01 | .05 | | |
| DR X PKOH | | | | | | | | |
| DR X AKOH | | | | | | | | |
| DR X PC | | | | | .01 | .01 | | |
| CHG X PKOH | | | | | | | | |
| CHG X AKOH | | | | | | | | |
| CHG X PC | | | .01 | .01 | | | | |
| PKOH X AKOH | | | | | | | | |
| PKOH X PC | | | | | | | | |
| AKOH X PC | | | | | | | | |

Figure 2-4

$$\text{Cycle Life} = 1000\left[A - \text{Temp}\; e^{-B(\text{DOD})}\right]$$

PACKS WITH 200% RECHARGE NOT INCLUDED

$$\text{Cycle Life} = \frac{A\left[DR + B\right]\left[1 - e^{C[\text{Temp} - 100]}\right]e^{D(\text{DOD})}}{(CHG)^{E}}$$

$$\text{Cycle Life HRS} = \frac{A\left(1 - e^{B(\text{Temp} - 100)}\right)e^{D(\text{DOD})}}{(CHG)^{E}}$$

$$\text{Cycle Life} = \frac{A\; e^{-B(\text{Temp})}\left[\frac{123 - \text{DOD}}{\text{DOD}}\right)^{C}}{(CHG)^{D}}$$

Figure 2-5

# DATA ANALYSIS FOR THE ACCELERATED TEST

S. Bogner
Jet Propulsion Laboratory

I am going to show one part of the data analysis. It is really a data summary of all the testing that is going on, and I entitled it "The Effects of the Test Variables on the Cycle Life" on this accelerated test program that Mr. Brown just explained to you.

(Figure 2-6)

Here, again, is a table of the test variables and the levels. I wanted to point out the fact that the extreme levels, what they call a star point, on this end and that end, really only amount to one pack for each of those points. The rest of the variables in the pack, if one is cycled at 20°C, has all these variables in it.

The star point, the factorial cells, for each of the variables here, we can add up to 32 cells for each variable, so when you see a plot or a point for that, it carries much more weight because it is an average of 32 cells.

(Figure 2-7)

I wanted to show this chart again to point out one thing and that is, we had 32 different cycle regimes on this test, so that makes things a little bit difficult to analyze. The cycle regimes vary from a low of 0.38 hours to a high of four hours, and in most of the analyses that have been done to date, we have been looking just at cycle life to zero volts. I think we need to bring time into our analysis somehow.

(Figure 2-8)

This is a plot of the cycles, the 1 volt and 0 volts versus temperature. On this slide, it is cycle time in hours for 1 volt and 0 volts. I think we have to look at all of these, becuase if we are going to predict back to normal conditions in a flight battery when the cells reach about 1 volt, we consider that an out or failed battery.

We can see here, in both cases, that temperature has a strong effect on the cycle life and the data is fairly linear versus the cycle number and versus the hours.

(Figure 2-9)

This is a plot of the cycles to 1 volt and 0 volts and also in hours versus the depth of discharge. Here we get an interesting change. We have a typical exponential curve of cycle life versus DOD. I don't know if this was happenstance or not, but here we almost have a linear relationship when we equate it to hours on test. The reason that this particular point coincides at 0 and 1 volts is because those cells shorted shortly after they approached 1 volt.

(Figure 2-10)

We have the cycles versus the discharge rate and this is somewhat surprising and has caused some problems in the analysis to date. That is because when we look at the cycles to 0 volts, we are getting more cycles at the higher discharge rates than we are at the lower discharge rates.

When we equated the time, we come up with fairly linear curves up to the C rate and then it drops off. But I want to caution you, again, that this represents one pack of cells and if you have problems during the test, you could get misled. So, really, one should look at the slope of the lines, on the others too, between these two points, which would be the factorial levels where we have 32 cells averaged in. But I just tried to draw the lines into the best fit I could, so there were no statistics or no weighting given to any one point.

(Figure 2-11)

Here we see the effect of charge rate on cycle life in hours and number of cycles and we should be looking at these two points more strongly than the others. But it says, if you look at it in cycle numbers, the charge rate gives longer cycle life at higher charge rates than at lower.

Over here, up to the C/2 rate, it reverses when you equate it to time. Perhaps the reason the C/4 rate is so low in numbers is the fact you have to remember that this total test amounts to an average of 40°C test conditions.

(Figure 2-12)

Here we see the effect of recharge and I think we can make the same conclusion there. We had one pack at 110 percent recharge and it drops way off, but the reason for that, I think, is because of the high test temperature. So, one could possibly follow this slope on up at some other temperature.

(Figure 2-13)

Here we see the effect of KOH and basically the percent of KOH. Basically I conclude there isn't much difference there, except for this one point in the low percentage. If you look at the two factorial points, the only difference is a slight slope when you go to 0 volts as you go to higher KOH concentrations.

(Figure 2-14)

Here is one that shows the effect of volume of KOH but I decided not to try to draw a line there. I think these kinds of graphs are important. You can see all the stuff coming out of the computer. It gives you the 0.01 level, the 0.05 level, and this, I think, shows why some of those effects are coming out that way.

(Figure 2-15)

Here we have one on precharge and it demonstrates the same relationship as the last one. Really, you can't see any.

(Figure 2-16)

So, just looking at these plots of the data, these were some of the conclusions I came up with. The depth of discharge and temperature are the best accelerating factors and probably the best predicting factors. The relationship between cycle number and the cycle time needs to be more clearly defined. The charge and discharge rates appear to stress the cells, but their effects are not clearly defined.

Percent recharge I did not think was a good factor. It appears to be a fair factor going to 0 volts on cycle life, but when you go to 1 volt or to cycle life in hours, it doesn't look too good. The effects of electrolyte volume and concentration and precharge are not conclusive. I think a good accelerated test should be developed using only temperature and DOD as accelerating factors.

(Figure 2-17)

## DISCUSSION

ROGERS: In the business of using temperature to accelerate your degradation, how do you overcome the effects of the fact that charge efficiency tends to head for the basement, so that you are no longer testing cells under the same condition. In other words, whether you want to keep temperature as a constant, you are not doing it. I don't see how this gives you the interpretation. Maybe it does and I am missing it.

BOGNER: I didn't understand the point you were driving at.

ROGERS: Well, when you test a cell and you accelerate the temperature, your charge efficiency drops. I guess I don't understand how this analysis gets around that problem that you are testing the cell under. You are changing conditions other than just temperature, or am I missing something?

BOGNER: Well, we have got tests run at different temperatures and Diane will show a plot, I think, later on that shows that we do get a break in temperature just past 40°C where we feel that there is probably a different reaction going on, different mechanism. But it is linear between 40 and 0 degrees. Does that answer your question?

ROGERS: Sort of.

MCDERMOTT: I have a comment on that last question. Remember that we are talking about degradation and not necessarily charge efficiency. In other words, what is the effect of temperature and charge rate on the degradation of the cell. In almost all cases, the charge rate was sufficient at the higher temperature to fully charge the cell. In one case it wasn't, and the cell failed before the end of 50 cycles. In other words, you could tell from other parameters that it was not fully charging, but I would say the charge rate was sufficient in almost all cases to fully charge the cell. Is that what your question was aimed at?

ROGERS: Yes.

BOGNER: I might add to that, of course if we ran this test at a lower temperature, I don't think the cells are going to take 200 percent overcharge at 8C rates. It is amazing that these cells, you know, took the stresses they did take.

KILLIAN: Could you describe the charge cutback or cutoff scheme?

BOGNER: There was not cutback. It was a constant current charge for the given test condition. If it was an 8C rate for 200 percent recharge, it was constant current for that period of time. I might add, in the data summary that I showed, I did not include pressure failures. They were all shorts or low voltage failures.

KOEHLER: I am not sure I understand why the curves look so different for the cycle time as compared to the number of cycles. It seems to me that the cycle time is equal to the number of cycles times the time per cycle.

BOGNER: That is right. As I said, there were 32 different cycle periods ranging from 0.38 hours to four hours, one cycle. You can't compare this cycle with this cycle necessarily. There are 32 different cycle periods.

FORD: One other way to look at that is if you put the cells in a 40°C environment for the same equivalent number of hours without cycling at all, how much would they degrade. That is why we looked at the time in the environment along with cycle life.

MOORE: Have you done any testing where you vary for any single group of cells the discharge rates or where you correlate erratic discharge rates with lifetime of the cells? You have been talking about constant discharge rates. I am asking if you have done anything with nonconstant.

BOGNER: You mean from one cycle to the next cycle, change the rate?

MOORE: Yes or even change the length.

BOGNER: Or change the rate during the cycle?

MOORE: Yes.

BOGNER: No, I haven't and this test didn't involve that.

## TEST VARIABLES

| | | | | | |
|---|---|---|---|---|---|
| 1. TEMPERATURE, °C | 20 | 30 | 40 | 50 | 60 |
| 2. DEPTH OF DISCHARGE, % | 20 | 40 | 60 | 80 | 100 |
| 3. DISCHARGE RATE | C/2 | C | 2C | 4C | 8C |
| 4. CHARGE RATE | C/4 | C/2 | C | 2C | 4C |
| 5. RECHARGE, % | 110 | 140 | 140 | 200 | 200 |
| 6. KOH CONCENTRATION, % | 22 | 26 | 30 | 34 | 38 |
| 7. KOH VOLUME, CC | 17.5 | 18.5 | 19.5 | 20.5 | 21.5 |
| 8. NEGATIVE PRECHARGE, Ah | 2.2 | 2.5 | 2.8 | 3.0 | 3.3 |
| PACKS PER LEVEL | 1 | 32 | 1 | 32 | 1 |

Figure 2-6

FRACTIONAL FACTORIAL TEST MATRIX CELL PACK NUMBER Ⓝ AND AVE CYCLE NUMBER AND CYCLE LIFE TIME

| | | | TEMPERATURE °C | 30° | | | | | | | | 50° | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | % DOD | 40 | | | | 80 | | | | 40 | | | | 80 | | | |
| | | | CHARGE RATE | C/2 | | 2C | | C/2 | | 2C | | C/2 | | 2C | | C/2 | | 2C | |
| | | | DISCHG RATE | C | 4C | C | 4C | C | 4C | C | 4C | C | 4C | C | 4C | C | 4C | C | 4C |
| | | | CYCLE PERIOD, HRS | 2.0 | 1.7 | 0.8 | 0.50 | 4.0 | 3.4 | 1.6 | 1.0 | 2.0 | 1.7 | 0.8 | 0.5 | 4.0 | 3.4 | 1.6 | 1.0 |
| % RECHARGE 200 | % KOH 34 | CC KOH 20.5 | 3 | 5 | | | | | | | | | | | 49 | 40 | | | |
| | | | 2.5 | | | 56 | | | 33 | | | | 4 | | | | | 21 | |
| | | 18.5 | 3 | | 64 | | | | | 41 | | | | 12 | | | 29 | | |
| | | | 2.5 | | | | 13 | 28 | | | | 57 | | | | | | | 48 |
| | 26 | 20.5 | 3 | | 47 | | | | | 58 | | | | 27 | | | 14 | | |
| | | | 2.5 | | | | 30 | 11 | | | | 42 | | | | | | | 63 |
| | | 18.5 | 3 | 12 | | | | | | | 3 | | | | 34 | 55 | | | |
| | | | 2.5 | | | 39 | | | 50 | | | | 19 | | | | | 6 | |
| | | | CYCLE PERIOD | 1.52 | 1.22 | 0.68 | 0.38 | 3.04 | 2.44 | 1.36 | 0.76 | 1.52 | 1.22 | 0.68 | 0.38 | 3.04 | 2.44 | 1.36 | 0.76 |
| 140 | 34 | 20.5 | 3 | | | 35 | 20 | | 54 | | | | 23 | | | | | 2 | |
| | | | 2.5 | 18 | | | | | | | 7 | | | | 38 | 51 | | | |
| | | 18.5 | 3 | | | | 26 | 15 | | | | 46 | | | | | | | 59 |
| | | | 2.5 | | 43 | | | | | 62 | | | | 31 | | | 10 | | |
| | 26 | 20.5 | 3 | | | | 9 | 32 | | | | 61 | | | | | | | 44 |
| | | | 2.5 | | 60 | | | | | 45 | | | | 16 | | | 25 | | |
| | | 18.5 | 3 | | | 52 | | | 37 | | | | 8 | | | | | 17 | |
| | | | 2.5 | 1 | | | | 36 | | | | | | | 53 | | | | 24 |

Figure 2-7

## EFFECT OF AMBIENT TEMPERATURE ON LIFE

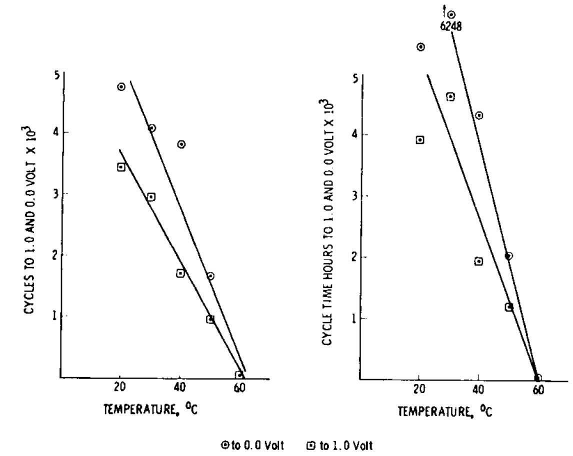


Figure 2-8

## EFFECT OF DEPTH OF DISCHARGE ON LIFE

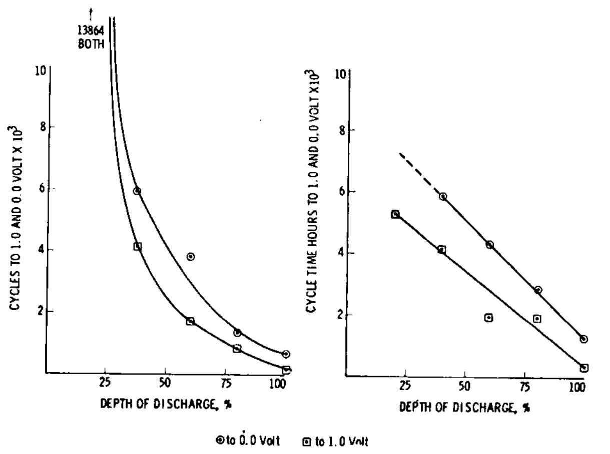


Figure 2-9

## EFFECT OF DISCHARGE RATE ON LIFE

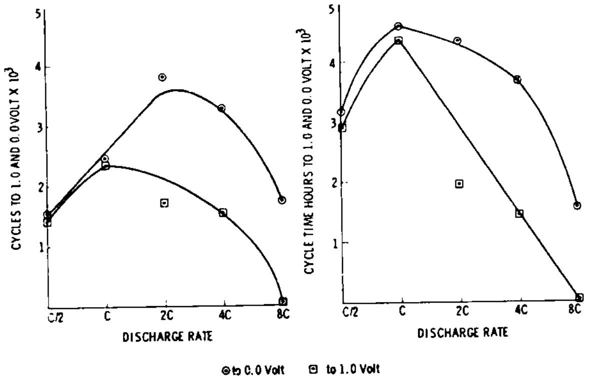


Figure 2-10

## EFFECT OF CHARGE RATE ON LIFE

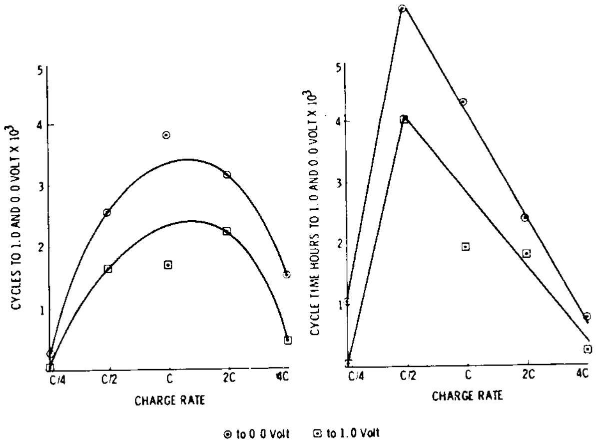


Figure 2-11

## EFFECT OF PERCENT RECHARGE ON LIFE

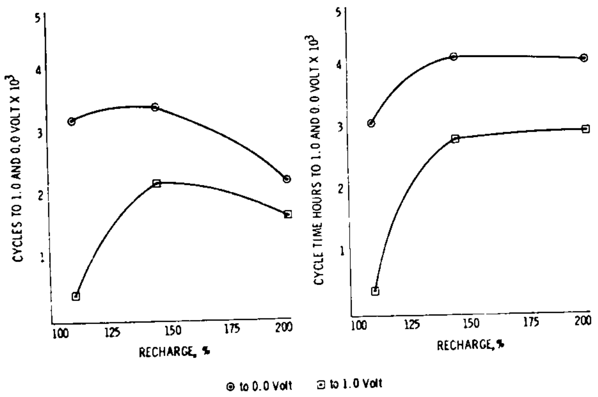


Figure 2-12

## EFFECT OF ELECTROLYTE CONCENTRATION ON LIFE

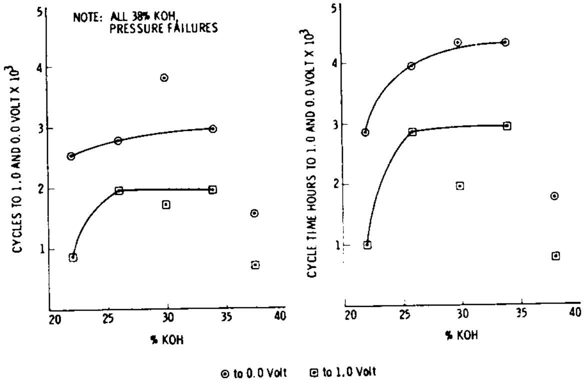


Figure 2-13

## EFFECT OF ELECTROLYTE VOLUME ON LIFE

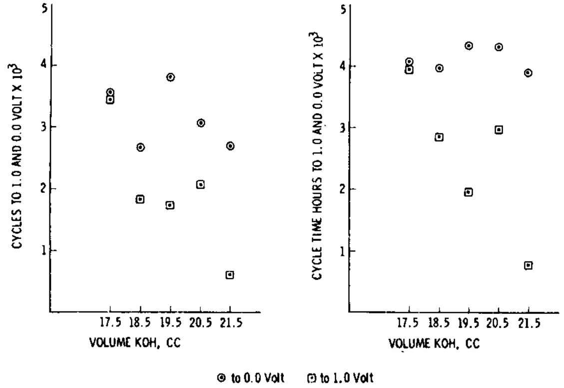


Figure 2-14

## EFFECT OF NEGATIVE PRECHARGE ON LIFE

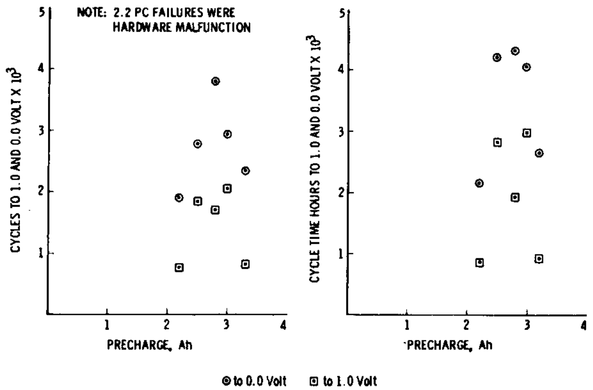


Figure 2-15

## EFFECTS OF TEST VARIABLES ON CYCLE LIFE CONCLUSIONS

- DEPTH OF DISCHARGE AND TEMPERATURE ARE THE BEST ACCELERATING FACTORS
- THE RELATIONSHIP BETWEEN CYCLE NUMBER AND CYCLE TIME NEEDS TO BE MORE CLEARLY DEFINED
- CHARGE AND DISCHARGE RATES APPEAR TO STRESS THE CELLS, BUT THEIR EFFECTS ARE NOT CLEARLY DEFINED
- PERCENT RECHARGE IS NOT A GOOD FACTOR
- EFFECTS OF ELECTROLYTE VOLUME AND CONCENTRATION AND PRECHARGE NOT VERY CONCLUSIVE
- A GOOD ACCELERATED TEST SHOULD BE DEVELOPED, USING ONLY TEMPERATURE AND DOD AS ACCELERATING FACTORS

Figure 2-16

## ACCELERATED TEST - POSITIVE PLATE SWELLING

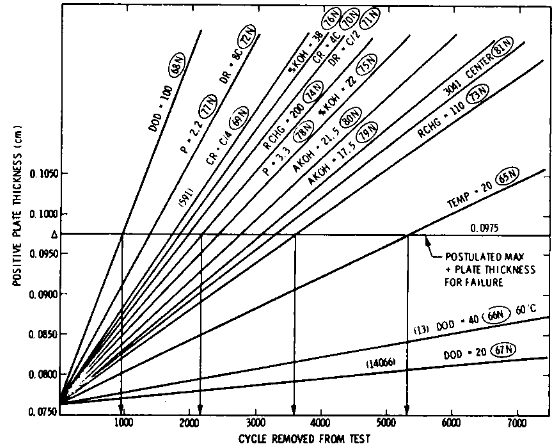


Figure 2-17

# ACCELERATED TEST MODELING

D. Schwartz
Jet Propulsion Laboratories

We have looked at many models of accelerated test modeling. I am talking about one fairly simple one, a broad brush stroke type model. Pat McDermott is going to talk about another one. Crane and myself, and probably Pat, also, have done lots of linear regressions type models, also.

(Figure 2-18)

I thought I would just give this an overview of our objectives and methods for accelerated test modeling. All right, one reason to try and describe cycle life as a function of the various test parameters, meaning cycle life as a function of the depth of discharge, temperature, charge rate, discharge rate is to just get a handle on what our data actually are.

We have 82 packs of five cells each and lots of data points. It is hard to make good graphs so you must try to get a regression model which takes all the data and comes up with some functional form. Sometimes that is useful. I think of the first point as a cycle life regression model; it is a description model of our data in one equation.

The second type of modeling is what we might call a cycle life prediction model and this is a model that I may want to use to predict the cycle life of cells cycling at conditions which are nonaccelerated, or possibly to predict the cycle life of other types of NICAD cells cycling at the accelerated test conditions. You will have to specify which kinds of predictions you want to do.

The two methods, the two models, are sometimes in conflict. A regression model which describes the accelerated test data and a prediction model which does well in predicting at less stressful conditions, may not be one and the same model and that is what we will see today. That would have been my way of going about it.

The other objectives of the modeling, and there are probably lots of others, are acceleration factors. The question, Does increasing the discharge rate decrease cycle life and, if so, by how much? might be answered with modeling.

(Figure 2-19)

Here is a brief runthrough of the method being used in the accelerated test program. Almost everyone doing modeling picks out a mathematical model. The model might be polynomial with some unknown coefficients. You then have to determine the model coefficients using the accelerated test data. You then have a nice equation but you might want to determine how good an equation it is. That is a very hard question to answer, so I picked two choices of testing the question.

Test how well your model actually fits the accelerated test data and test how well it predicts normal packs. The normal packs are those packs on accelerated tests that are being tested at nonaccelerated conditions and haven't failed. We can't tell how well they predict, but the group usually has a feeling of how long they should go and so if our models predict very low, we will get immediate evidence.

(Figure 2-20)

Here is what I call my broad brush stroke model. This is almost as simple as we can possibly get. I take the natural logarithm of cycle life and I would like to express it as a linear combination of the depth of discharge at which it was cycling, the temperature and the percent overcharge, percent recharge.

I do not know the constants A, B, C, and D. Those are the constants that have to be fit with the accelerated test data. The rest of this short talk is going to be with this equation.

What are the conditions under which this equation might be a reasonable model? The first thing, just from the mathematics of it, says that the logarithm of cycle life must be a linear function of depth of discharge, a linear function of temperature, and a linear function of recharge.

Now, linear functions have slopes. This model has built into it the fact that if you take log cycle life versus depth of discharge, you get a slope. That slope should be independent of temperature and the percent recharge. That is what this model is saying. Now, we are going to look at some of the actual data from the accelerated test program to see how well those assumptions hold, so you need linearity and you need slope independence, independence from the rest of the variables.

(Figure 2-21)

Three nice parallel lines, linear, and you might say what a setup. Those little dots on the line actually represent data from the accelerated tests. Certain of the points indicate that it is a logarithm, cycle life versus depth of discharge. I have three lines indicating the three different temperature levels.

The 30 and 50°C levels are very strong data points. They have a lot of packs cycling there. I guess there would be 16 packs cycling at 30°C and 40 percent depth of discharge. The 30 and 50°C lines are strong lines in the sense that we have confidence in those lines, at least in those four points.

Then that 40°C line is put in there using the star points and center points which were discussed by the other two speakers, and a slope seems to be pretty much similar, but I have to point out that those points each represent only one pack. We had only one pack cycling at 20°C and 100 percent depth of discharge, so those points you might not have so much confidence in.

This one is an average of about 10 packs in the star points. For those who are really interested, I can tell you what they are. Now I have the idea that I have a linear relationship between log cycle life and depth of discharge. The slopes are parallel lines and are pretty much independent of the temperature and if you did it for percent recharge, they are pretty much independent. That is the slope, roughly -0.038. That will be one of the coefficients, the coefficient of discharge in my equation.

(Figure 2-22)

Now, remember, there are three variables I am using, DOD, temperature, and recharge, and this is the recharge one. I will do the easiest ones, first. Recharge, again, these are all the dots, data from the accelerated test program. You have the most confidence in the 40 percent and 80 percent lines because we have 16 packs cycling here: 16 here, 16 there, and 16 there. It is a fairly strong statistics there.

We have less data in the 60 percent DOD. It is all from star point and center point. Again, extremes have only one pack apiece. They represent one pack's worth of data and this represents the eight or 10 star points. I get a linear, since I have only two lines here, two points here. It is always going to be a line if I graph it. If I connect them, I am going to get a straight line. That is why I have to bring in this middle line. At least I have three points and they are falling along pretty much a line, give or take the fact that the thickness of the dots helps a little. However, they are roughly in the same slope, They are not exactly the same slope, but pretty close, and for our purposes we will call that slope -0.007.

(Figure 2-23)

Now, we got into trouble when we started doing the temperature because temperature is a very complicated effect, at least in my opinion. We have log cycle life versus temperature and I wanted to break it out according to the various depths of discharge levels. Before I draw any lines I want to give you the rough graph, so I don't bias your thinking.

Here we have these triangles representing 16 packs each and they are strong points. These circles also represent 16 packs each; again, a strong trend here. Notice if you connected a line from here to here, from there to there, you have roughly the same slope. Now, these X's are star and center points and what happens is we have a slightly different slope here, a definite falloff,, and that is this high temperature condition. I have other graphs later which I could show. Right around the 40 or 50°C mark, we have a break and we tend to have great falloffs no matter how we look at this data.

(Figure 2-24)

We obviously need more data and it is hard to use nonaccelerated test data to find out what is operating down there. These are guesses. These are not straight lines by any stretch of the imagination, but if I come up here maybe the effect of temperature versus log cycle life is fairly linear in this region, meaning if you keep the temperature low enough, below, 30-35°C maybe I will have a linear type effect. Given that thought, I drew the lines that way and I computed the slopes.

The slopes, again, are fairly similar. They are not all equal exactly; this is an average. So, we will give that a slope of -0.019 with the and this model now becomes valid only for temperatures lower than 30.

(Figure 2-25)

Well, now, with that kind of information we can fill in the blanks. You could have done this with some sort of computer program, but you could get roughly the same numbers by hand. The slope of log cycle life versus DOD curve is .038. The slope for the log cycle life versus temperature curve is 0.019, and remember that is valid at lower temperatures. A slope value of 0.007 is we got on the recharge curve.

Now we have determined three of the coefficients and have only the last one to do. Now, this is the crux of the matter. This, in my mind, determines the level of the model, the level of the prediction that you are going to get. These other three are just relationships with the environmental variables. If you were plotting it, this tends to tell you what, kind of level you are sitting at. There are lots of ways to get A. No one method is particularly right or particularly wrong, but I picked one way.

To obtain the constant A, I substituted the average cycle life at the 30°C, 40 percent depth of discharge condition. We have 16 packs there. If this model is right for the lower type temperatures, then I should be able to substitute in for cycle life the average cycle life at those conditions, 30° and 40 percent, for A, because I will know the DOD, temperature, and recharge, and that is what we have done in this last equation.

The value of 8125 is the average cycle life of all of our cells cycling at the 30°C, 40 percent depth of discharge condition. Where does that 170 come from? That is kind of an average, because of those 16 packs, half of them are cycling at 140 percent recharge and half at 200 percent. A is 12.29.

There is another way to do this. I will come back to this method later.

(Figure 2-26)

Here is our model. All the coefficients are plugged in and the conditions where we suspect it might hold. This is the prediction model and I care about predicting for the normal packs. This doesn't worry me that the DOD is only good for smaller than 40 percent. Which is why I used that to get A.

It turns out if you use different ones, the model is pretty robust, but the temperature is very important. You must have lower degree temperatures. This is the logarithm model, and if you write it in terms of exponentials, it looks like that.

(Figure 2-27)

We have a mathematical model, the coefficients and we have two things to do, one of which I did here and the other I don't have a slide on. We have to see how well it does against the accelerated test data and also how it predicts the normal packs. Now, I gave up on having to do well on accelerated test data by the choice of getting the temperature at a low of coefficient -0.019. I opted for looking at the low temperature levels, so half of our accelerated test data are high temperature levels. This equation might not be thought to fit very well, however it turned out it did fit pretty well.

Anyway, let's do the normal pack predictions. We have four packs and they have the various temperature and DOD conditions, you can see there. They are all at 105 percent recharge and these are the predictions. To get those, I just plugged into the formula for the model formula. I plugged in these three variables and then you come out with this number. These are a little low, but we know we are low from other people in our accelerated test group. We feel that these could go a little longer than that, but also, we are cycling the normal cells right there, and in cycling the normal cells, we have already exceeded 86n. It is obvious that our model is not taking everything into consideration.

We haven't got discharge rate or charge rate in there. They are very hard to put in, because the fact of the matter is, the discharge rate on cycles to 0 volts increases cycle life, which is sort of counterintuitive, or at least I had thought it was. It is going to be hard to put accelerated test data in right, or when we put that in, it won't necessarily increase these. It will probably decrease them making a big problem.

I can get different predictions if I use A differently. Remember when I was getting that coefficient A, my method was to use the average cycle lives of the pack cycling at 30°C and 40 percent DOD, that was at 8215. If instead of putting 8215, I put in this number, this model gives me my relationships to DOD, temperature and recharge, and this A gives me the level. To pick the level of my logarithm cycle life, I would like to pick a pack that is cycling as close as possible to the normal test conditions.

You could go into the accelerated model and find it, but that doesn't change this very much, unfortunately. I used this one because I thought that it would be the first one to fail. Let's put in the 18,700 for the 8215 and you get a new A, and hence you get new predictions.

Your new predictions would be 27,000 for this one, 40,000 here, 58,000 and then this is 18,700. It will bang on this last one. So, you can raise the prediction levels if you choose your A from data that are as close as possible to normal test condition. That takes everything else into consideration that we didn't take into consideration already for good or bad.

Just to make a comment on how useful these models are for other NICAD cells and other NICAD testing situations. If you go back and look at the old data, it is not hard to find, but it is harder to do things with because it is all over the place.

(Figure 2-28)

Peter Fono, I believe from Hughes, looked at some Crane data for roughly these years. He took lots of averages and got lots of numbers and these dots represent the type of numbers he got, and so what I have done here is plot log cycle life versus temperature using his data. These are NICAD cells, and I have been told by the manufacturers that they are a little different, these newer ones from the older ones.

Nevertheless, you can see the kinds of slopes you are getting. Now, all I can say is the slopes are different. Here is one that is almost the same. We have -0.019. Here the slopes vary with DOD, something we didn't see on the accelerated test data. Does that really present a problem? It is really hard to tell, because this data comes from many, many different tests done at different times with different sized cells, 20 ampere hours mixed up with 6 ampere hours, and so forth.

These are kinds of old type results you get.

(Figure 2-29)

Also, again, the same data base. If you plot log cycle life versus depth of discharge for various temperatures, you get the linear relationship, which is what we wanted, however we have different slopes. Remember, I had -0.038 there is one right there. We got this, -0.069 to figure out what happened here, and, also, the slopes vary with temperature, something we didn't see on the accelerated test data.

So, I bring up these last two slides just to show you that the accelerated model has some problems in extrapolating to other types of test conditions. All right, thank you.

## DISCUSSION

FORD: Are there any questions for Diane?

HENDEE: Have you considered changing your return to the amount of actual overcharge as opposed to the amount returned?

SCHWARTZ: You mean changing from 140 to 40 percent?

HENDEE: No. Actually, when you are saying 140 percent, that is assuming 100 percent efficiency, you are returning 140 of what you took out.

SCHWARTZ: Right.

HENDEE: You are probably starting to reach an overcharge at one temperature, maybe at 115, or at another temperature of 140 percent.

SCHWARTZ: No, we haven't played around with that and that probably would be of some interest.

HENDEE: I would think that would be—

SCHWARTZ: Crucial?

HENDEE: Well, again, sort of intuitively, I would think that that would be the thing that you should be more concerned with, the amount of actual overcharge you are putting in. You show actually at 100 percent, it doesn't even get charged up at 100 percent.

SCHWARTZ: When we say 140 percent, it is basically just trying to get back out what you took in. You take a certain amount out when you discharge it, apparently, and you are going to fill it back up 1.4 times the amount you took out.

HENDEE: Not really.

SCHWARTZ: Well, no, but that is how the formula—

HENDEE: At 100 percent you are saying it was best. Actually, at 100 percent, you are going to fail very shortly.

SCHWARTZ: Okay, not actual, but in time.

HENDEE: Okay, thank you.

LACKNER: Your figures went to 0 volts.

SCHWARTZ: Yes, I should have made that really clear.

LACKNER: Now, in spacecraft use this doesn't really help us too much. One volt, or 1.1 volt would be a little bit handier. Some of Sam Bogner's data did go to 1 volt. Do you have any more information?

SCHWARTZ: This is a beginning. We will do the same kind of analysis on all four different definitions we are using. The cycles to 1 volt, this is from memory, has almost identical type of relationship of log cycle life to DOD with a slope of -0.038 holds for cycles to 1 volt pretty much. One of those graphs would look similar if you went cycles to 1 volt. I do not know about the temperature one at this point.

LACKNER: I think in some of the information we have seen over the years there is quite a shift to a lower voltage potential with life due to various factors. It seems to cut off about 108 volts and then it drags out to 1 volt and below, so it is quite significant at that point.

SCHWARTZ: Well, I don't know if this would be an answer or of any interest, but it is true in all of our packs we have collected the voltage, the end of discharge voltage, for every cycle and when you have the low discharge rates relative to our test, the difference between cycles to 1 and cycles to 0 volts is very little. You get practically the same, but when you have the high discharge rates, it is quite different, which is explainable. But that is why we were always doing cycles to 0 volts until we did a few averages and studies and noticed the effects were different, particularly our discharge rate. Discharge rate increases cycle life when you go to 0 volts, but decreases cycle life when you go to 1 volt, and those are the kinds of things we haven't come to complete terms with yet. That is one reason why they are not in these equations.

GROSS: Diane, you just started to touch on the question I was going to ask, how did you get around the fact that some of the cycles were at very short times and others for very long times?

SCHWARTZ: At this point, it is not—

GROSS: It is all averaged out, then?

SCHWARTZ: It is all averaged out because to get any of the data, you would look at the 30°C, 40 percent depth of discharge packs and you would just average those cycle lives as you found them, and because of the overcharge being different, they will have somewhat different times. Those are problems. You are picking out all of the difficulties, all the problems. That is good.

MCDERMOTT: I just wanted to comment on Joe Lackner's question, because it is very important whether you describe the cell failure at 1 volt or at 0 volts. Now most cells reached 0 volts, I think, not too long after they would reach 1 volt consistently.

SCHWARTZ: The low discharge ones, basically.

MCDERMOTT: Yes. Now, the problem is, when you get to the high discharge rate cells, you can go below 1 volt just because of the high discharge rate, it sort of drives them there, the cells are still, I would consider them okay. They are still functioning, but you are driving them so hard at 8C discharge, that it is really driving you under that 1 volt. So that to compare that cell with another cell that is being cut off at 1 volt is not, I don't think, a good way of comparison. Both cells may be in fairly good condition, but you are driving it so hard, discharge voltage-wise, that you are putting it under 1 volt and calling it a failure when you really shouldn't.

LACKNER: I can see what the problem is, but it is just from a spacecraft level we have to use it and 0 volts doesn't help you very much. If you are going to use this as a prediction model, you should try to predict it to a higher level.

FORD: I would like to pick up on that and come back to it later.

KILLIAN: All of your prediction and modeling was done on averages, rather than the 99 percentile, which is what spacecraft designers usually use.

SCHWARTZ: Our problem doing that, really, is that we have very few cells at any one particular condition. If you have one pack cycling at, say, 30°C 40 percent DOD, and certain recharges, you have terrible clustering problems with the five cells. They usually fall very close to each other and to get a nice distribution is going to be some doing.

BETZ: Just a comment regarding the slopes. Were slopes that you saw and those in Peter Fono's data, which came from the NAD-Crane at that time, all run at a constant time period? If so, the increase in the depth of discharge would also be at a higher discharge rate, so that would account for the differences in slope there.

You also have a percent recharge factor coming in at higher temperatures, so that might be complexing the numbers and, in fact, causing them to agree with your numbers. You also see that dipoff up towards 40°C. So, it looks like your numbers might be able to correlate when you consider all that.

SCHWARTZ: Explainable when you put the rest of the things in, maybe.

BOGNER: We just really got this data base in and together in the last month or so. Diane was just showing one attempt at a model and we will be looking at 0 volts, 1 volt, and also time, using each one of those to come up with a model.

LIM: Could you tell me what is the average distribution of cycle life cell in the same pack?

SCHWARTZ: You mean statistical distribution?

LIM: Yes.

SCHWARTZ: As I was trying to point out before, I think that is almost impossible to get with the kind of data we have, because we have averages right now; given certain environmental conditions, we can predict an average. If you want a distribution like normally distributed and so forth, I have for each condition no more than five cells to work with and sometimes we have had to throw out one or two of those because they have had pressure failures or hardware failures. We have a lot of censoring of this data, and so I think to call it a Wibel density or a normal distribution is not at all justified on this data base.

LIM: Just for example, by a factor of two would only be 50 percent or something like that?

SCHWARTZ: You mean what the range is?

LIM: Right.

SCHWARTZ: I understand. You don't want a statistical distribution. This is just my feeling. You know, I don't have the numbers sitting here with me, but if something goes, 30,000 cycles, there are five cells in the pack. Most of them will be plus or minus a few hundred cycles and often enough they will all fail about the same time because you have really not three failures; but one failure and two hardware problems. Something went wrong and they were censored. So a lot of these are very close, in fact closer than we would have liked them to be. Plus or minus a few hundred cycles is what I would say, in general. There are exceptions to that.

NICKLAS: In the examples that you used, it appeared as though the most sensitive parameter was the value of A, yet that is the one for which you solved and it would appear as though your most important parameters are the ones that you arbitrarily changed. How could you?

SCHWARTZ: Because it is our level.

NICKLAS: Not necessarily because it is level, but you could change all your other parameters by a factor of two and make only a very small difference in your cycle prediction, whereas if you changed A by a factor of two, you get almost a factor of two change.

SCHWARTZ: That is true.

NICKLAS: So, it looks like most of your important parameters are in A, yet that is the one you have solved for after you had all your data in.

SCHWARTZ: That is a fair comment. What we have in this model, as far as I am concerned, are relationships which we might say tell us something about increasing the depth of discharge and the effect that has on our cycle life. It becomes less significant, but I think the predictions it is giving us now are not much different from the normal cells. So, I guess what it comes down to is I I am not sure that we can, and I hate to make this statement categorically, but it looks very difficult to do a prediction of the normal packs based on the accelerated test data, without a couple of cells fairly close to those normal test conditions.

SLIFER: Would you put up Figure 2-25; the model so far? This is the one where the question on A comes up. I have a suggestion. As I understand it, your 170 comes from the average between two groups, which are fairly large samples.

SCHWARTZ: Yes.

SLIFER: I think if you would separate those and take a look at what happens to A between the two groups.

SCHWARTZ: It is not sensitive, I mean it is fairly robust. If you use 30 C 40 percent and 140 percent recharge, all right, fix that, A turns out to be something like 12.23. So, I mean, you are changing the A a little bit when you do that, and if I put in the 200 percent, I get a slightly different.A. That will change things, but it is nothing like putting in cells that are cycling very close to the normal test conditions.

SLIFER: Well, I think by doing that you have shown that A is fairly robust.

SCHWARTZ: Robust on accelerated test data, if you use that data itself.

ACCELERATED TEST MODELLING - OBJECTIVES

- CYCLE LIFE REGRESSION MODEL
- CYCLE LIFE PREDICTION MODEL
- ACCELERATION FACTORS

Figure 2-18

ACCELERATED TEST MODELLING - METHOD

- SELECT A MATHEMATICAL MODEL
- DETERMINE MODEL COEFFICIENTS USING ACCELERATED TEST DATA
- TEST MODEL FIT OF THE ACCELERATED TEST DATA
- PREDICT NORMAL PACKS

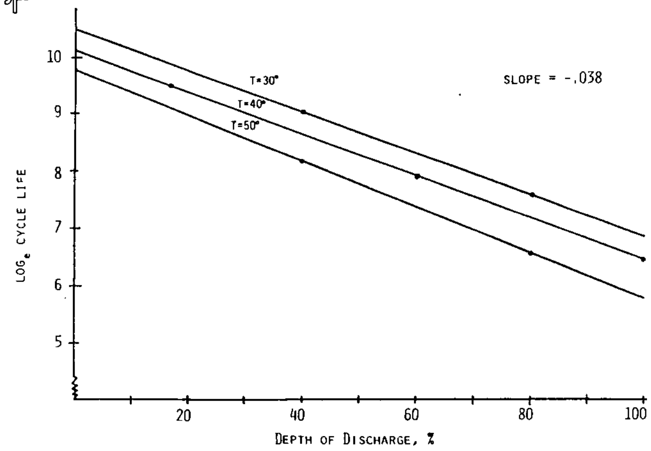
Figure 2-19

A CYCLE LIFE PREDICTION MODEL

$$\mathrm{LOG}_e\ \mathrm{CYCLE\ LIFE} = \mathrm{A} + \mathrm{b}\,\mathrm{DOD} + \mathrm{c}\,\mathrm{TEMP} + \mathrm{d}\,\mathrm{RECHG}$$

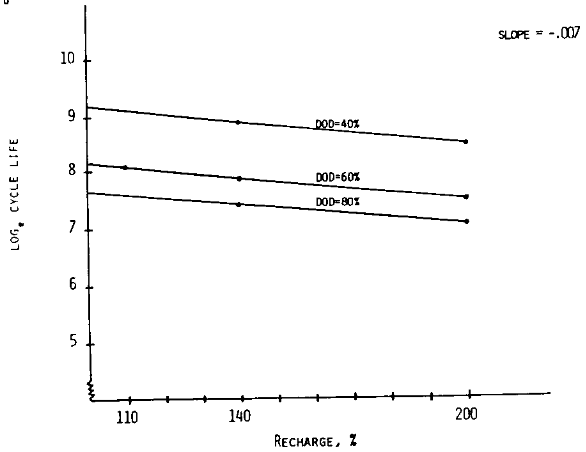
DOD = % DEPTH OF DISCHARGE
TEMP = TEMPERATURE (°C)
RECHG = % RECHARGE

Figure 2-20



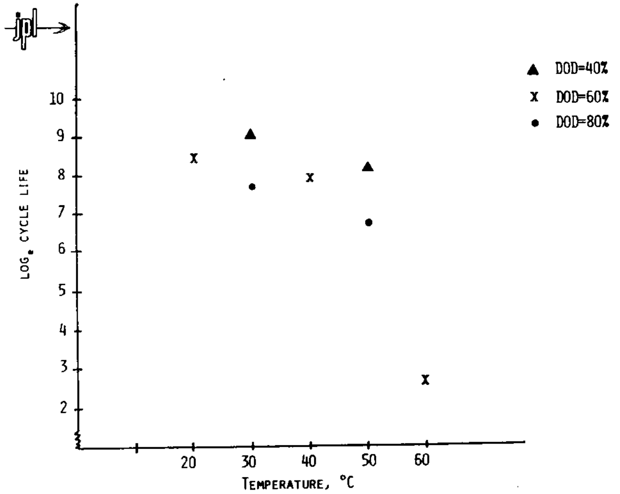
NASA ACCELERATED TEST DATA - CYCLES TO 0.0 VOLTS

Figure 2-21



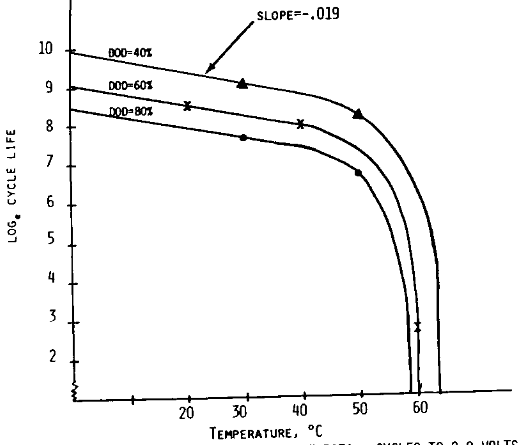
NASA ACCELERATED TEST DATA - CYCLES TO 0.0 VOLTS

Figure 2-22



NASA ACCELERATED TEST DATA - CYCLES TO 0.0 VOLTS

Figure 2-23



NASA ACCELERATED TEST DATA - CYCLES TO 0.0 VOLTS

Figure 2-24

PREDICTION MODEL SO FAR:

$$\text{LOG}_e \text{ CYCLE LIFE} = A - .038\text{DOD} - .019\text{TEMP} - .007\text{RECHG}$$

TO OBTAIN THE CONSTANT A, SUBSTITUTE THE AVERAGE CYCLE LIFE AT TEMP=30°C, DOD=40%.

$$\text{LOG}_e\ (8215) = A - .038(40) - .019(30) - .007(170)$$

$$A = 12.29$$

Figure 2-25

CYCLE LIFE PREDICTION MODEL

$$\log_e \text{CYCLE LIFE} = 12.29 - .038\text{DOD} - .019\text{TEMP} - .007\text{RECHG}$$

WHERE

$$0\% \le \text{DOD} \le 40\%$$

$$100\% \le \text{RECHG} \le 200\%$$

$$0^\circ \le \text{TEMP} \le 30^\circ$$

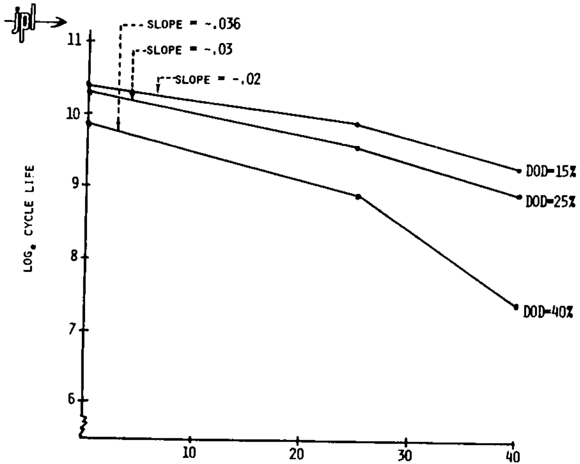
$$\text{CYCLE LIFE} = \text{EXP}\left\{12.29 - .038\text{DOD} - .019\text{TEMP} - .007\text{RECHG}\right\}$$

Figure 2-26

NORMAL PACK PREDICTIONS (CYCLES TO 0.0 VOLTS)

| PACK | TEMP | DOD | RECHG | PREDICTION | CYCLES TO DATE (11/78) |
|---|---|---|---|---|---|
| 83N | 0 | 40 | 105 | 22811 | 19300 |
| 84N | 20 | 20 | 105 | 33356 | 18500 |
| 85N | 0 | 20 | 105 | 48776 | 19600 |
| 86N | 20 | 40 | 105 | 15600 | 18700 |

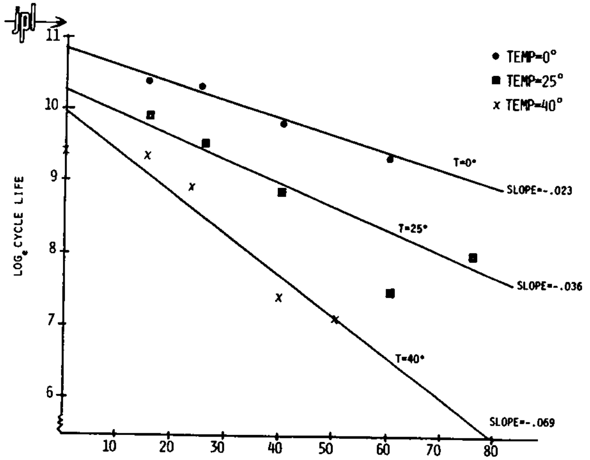
Figure 2-27



NAD-CRANE CYCLE LIFE TEST DATA - (1963-1971)

[Ref. Fono, P., "Spacecraft Nickel-Cadmium Battery Cycle Life Assessment" Hughes Aircraft Co.]

Figure 2-28



NAD-CRANE CYCLE LIFE TEST DATA - (1963-1971)

[Ref. Fono, P., "Spacecraft Nickel-Cadmium Battery Cycle Life Assessment", Hughes Aircraft Co.]

Figure 2-29

# NONLINEAR PREDICTION MODELING FOR ACCELERATED TESTING

Dr. P. McDermott
Coppin State College

I would like to show this as a historical development. I feel that we are further down the line, I guess, than the two previous speakers. We have really had these equations with us now for about a year and have been modifying them and working on them. I am much more optimistic that we are further down the road, I guess, and let me put up two figures simultaneously.

(Figures 2-30 and 2-31)

These were given at the ECS meeting last fall in Atlanta and also at the Goddard Space Center. Now, these are curves which are similar to the ones that Sam put up. I took these from star point, center point cells only. They are a little different than Sam's, because I used a data base which was not as complete, but also I chose the packs that failed slightly differently; in other words, I took some cells that were hardware failures and threw them out, and so forth.

But you see the general trends are roughly the same; that is, the temperature is going up now, I think that the temperature is linear down to around 50, Diane was saying 40, I think it is probably a little lower than that, I think it goes up to 50. Here is the depth of discharge, which is definitely an exponential type of growth function.

Here is rate of recharge or percent recharge, which in my equation is going to be linear. It is a little nonlinear here, but I think a linear approximation is good enough.

The others, variation in KOH, was flat enough that I disregard it. That doesn't mean that percent KOH does not have an effect on cell life, but in terms of the prediction model, it is flat enough that we can try to eliminate it from the equation. At this point I am trying to get just what the basic features are, rather than adding in as many effects as you can.

Here is variation in precharge and percent KOH. Factorial cells would come in about here and here, sort of between the three points you would find the factorial cells. We have had trouble all along with this variation in charge rate and variation in discharge rate. The problem is that if you lower the discharge rate, you are stressing the cell less and therefore you are going to get more cycles on it, where we seem to find the opposite here, and the same for charge rate.

If you decrease the charge rate, you are going to stress the cell less, and therefore have more cycles, but there are particular problems with that point, which Diane and Sam pointed out. There is only one pack there and I think the charge rate was just too low. It was not charging well enough at that temperature and therefore it is showing a low.

So, we are trying to handle charge rate and discharge rate very carefully, because they are not as good predictors as the three which I am going to concentrate on, which are depth of discharge, which seems to be a good exponential function, variation in temperature, which is quasi-linear, and variation in recharge, percent recharge, which is linear up to a point here, and these are the ones which are monotonically increasing or decreasing.

The others are either hyperbolic or changing in directions that we would not intuitively feel is right, so that is why I am going to depend on the temperature and depth of discharge as the primary factors for acceleration and for prediction. Last year I put up this graph, in which I took cycles to failure versus temperature at various depths of discharge.

(Figure 2-32)

This is really a variation, or Diane's data is really a variation on this, in the sense that we are taking the log function. Or we are going to find that there is a log function here in the slopes of these lines and that exponential function is going to come out with 0.038 as the coefficient.

Now, the closed circles are where I put star point pack data, the open circles are extrapolation from the star point, center point data, and the boxes are actually averaging over many factorial cells, so there is a lot of weight, again, to these closed boxes here.

(Figure 2-33)

Using that graph, I then derived this equation here, which is an empirical equation as opposed to one that is derived by regression analysis. In other words, I am sitting down with a pad and a pencil and graphs and coming up with this equation versus putting all the data into a regression analysis and coming back out. I will do that later, but this, remember, was a year-and-a-half ago and we didn't have the nonlinear program then, so what I was trying to do was to get an approximation equation so we could see which are the main effects.

I found if I tried to do this at the 200 percent recharge I couldn't get it, but I could get it at 140 percent recharge, so that is why this equation as is, stands only for the 140 percent recharge, 1C charge and 2C discharge. You see there are roughly three terms here, just a multiplying factor. This is a temperature term, which is essentially linear, 70 minus temperature, and here is the exponential term, which in Diane's case would be on the other side of the equation as a log cycles to failure.

All right, and there is the 0.038 that she got when she plugged her equation into the computer. Did you do that as a hand calculation ?

SCHWARTZ: Yes.

MCDERMOTT: She did that as a hand calculation.

SCHWARTZ: We will talk about the computer later.

(Figure 2-34)

MCDERMOTT: All right. Now, here is the prediction of the normal packs using this equation. Here is the test conditions. Now, really, this data has merged all the physical parameters, that is, percent KOH, volume of KOH, precharge and so forth.

We come out with 10,000, 13, 22 and 31. Now, at the time I felt these were low, so I took a fudge factor. I add 30 percent or 50 percent. Now, it is not toally a fudge factor, but it is due to the fact that if you remember the graph on percent recharge, it was sort of linear going up towards 100 percent recharge. So I did basically take in that linearization.

I said 30 percent would probably be low and 50 percent would probably be high under these mild conditions of 105 percent recharge, lower charge, and discharge rates. Now, about six months ago the nonlinear regression program was developed out at Crane, so they put my equation in. Mine was the first one that Harry had up there, where he had A, I don't know if you recall it, but he had A times B minus temperature times E to the C depth of discharge, where A, B, C were constants, which corresponds roughly to that equation.

I made a more generalized equation and we started putting this into the nonlinear regression computer program out at Crane. So case 1 really corresponds to this equation over here, where B1 equals 1000, B2 is left out, so that drops that term out, B3 is 70, corresponding there, and B4 would correspond to that minus 0.038. So, here is case 1, the old equation and I put down the predictions plus 50 percent, my upper fudge factor.

Now, case 2 and case 3 are actual nonlinear regression programs run on the computer, where B1 is 2000, B2 is 6.6, and this is 66. The computer generated 0.037 instead of 0.038, so that told me we were on the right track. For case 2 we didn't have a discharge rate term, nor did we have a charge rate term. In case 2, I left those out.

As you will see down here in the normal predictions, adding the recharge term came fairly close to my old equation plus fudge factor of 50 percent. Now, that is not too surprising because the 50 percent was based on that extrapolation of the recharge term back to the 105 percent. Then we added a discharge term here. This whole thing here is a linear which has interactions, recharge, temperature and depth of discharge, which means you not only have those terms, but you have the interactions of them. The two main ones, I think, are going to be depth of discharge and temperature interaction as the main effect.

Then we add these two and we get the case 3, where you have the different B1 through 6 here. Now notice we still come up, instead of 0.037 we got 0.045. This term changes a little and that one changes, so adding the discharge rate and the charge rate does change these B's here, which are the coefficients, the fitting coefficients, for the nonlinear regression.

But when we get down here to predict, you notice these same numbers coming out. These are the numbers that Diane came out with: 15,000, 22, 33. So we are all hitting around the same ones with our various equations, which I don't feel are too bad, even though we have gotten to 18,000 on this.

I would rather be predicting low if I was a manager having to make a decision about how long the battery is going to last. I would rather predict that I could at least get that and have it go longer. Now, what might be happening here is we may be actually predicting the minimal cell life or battery life with whatever equation we come up with here. I might mention that when you make these normal predictions, you have to go back and you plug in 105 percent here, 20 or 0°C here, 40 or 20 depth of discharge here. You then get down to charge rate here, or discharge rate, notice it is C/1.5 and C/2.4.

Now C is 6, so that means that these terms are like 4 to 3, somewhere in that ball park. Multiply it by these, so that these two terms are really only adding about one or two hundred cycles down here on the prediction of normal packs, which means, I think, that the charge rate and the discharge rate at the high temperatures and high depths of discharge really do have an effect.

But when you get down to the predicting normal packs, that is, with the low charge rate and low discharge rate, it is not having that great an effect. That is why we had to handle this charge and discharge rate delicately, because I think it does have an effect in the accelerating part of the matrix, but it is not having very much effect down at the normal predictions.

So, I would say in closing that I feel we are pretty far down the road on the prediction equation. We are going to take some interactions of charge rate with depth of discharge and so forth and try to modify it some more, but we may not actually come up with predictions which are much different from this. I feel that we are further along in the program than maybe some of the other people in the team.

## DISCUSSION

NAPOLI: On the screen on the side you had that empirical equation, which did not show the charge and discharge portions of that equation. Did you calculate those cycles on the bottom without those two parameters in there?

MCDERMOTT: I basically had merged all of that charge and discharge rate data in, which means—

NAPOLI: In the first two parameters that you had in the equation?

MCDERMOTT: Yes, I disregarded the fact that they were charged and discharged at different rates. In other words, I just added it together. That is essentially what the computer program would do if you told it to ignore variation in charge or discharge, if you didn't have a term in there, just add all that data in.

MAURER: I have a problem with the charge rate and discharge rate terms. You have entered them as linear terms, yet the data shows a parabola effect. By entering them as linear terms, you are almost negating their effect because you are forcing them to be essentially a constant value, and so naturally they don't have a very big coefficient.

MCDERMOTT: Okay, we did put in a charge rate against that exponential term, E to the something DOD, so that would interact, charge rate with temperature, the discharge rate we interacted with depth of discharge, and we didn't get that much difference in the normal predictions

We did get a jumbling around of the other coefficients, but we didn't get too much change in the actual prediction of the normal packs. I agree with you, I think there are these parabolic effects in there which we can get by entering charge rate and its square, and we are going to do that.

I mean, we are going to tamper some more with the equation by entering charge rate, discharge rate, and their squares, which would give a parabolic effect, but I am saying I don't feel that is going to change it that much. It may adjust it this way or that, but I think what is happening is if you feed the program a confusing sort of thing as charge rate and discharge rate that are really not clearly discernible in terms of more or less life, than the program is going to weight that less.

It is going to say this depth of discharge is really a good predictor, so I am going to weight that a lot. This temperature seems to give us good consistent results when it varies, so I am going to weight that a lot. The regression program sort of says that, and recharge rate also seems to be fairly consistent, so we will weight that heavily.

It says the charge rate and discharge rate do have effects, but it is confusing and, therefore, we can't really use it as a good predictor.

KILLIAN: Pat, would you care to comment on the possible utility of these data and the modeling techniques for synchronous orbit, 24-hour orbit applications?

MCDERMOTT: Okay, this is another whole area. I think what my equation lacks and what is going to get built into it in the future is something that Diane was talking about, also. We have got to build in the length of time that the battery is actually on test. All right, that is not built in here yet, but it can be.

We actually built that into the linear regression model and it did not show up as a big factor, but I think if we do put it into the nonlinear regression model, it may have an effect. What you could do then is when you go into synchronous orbit, then you take the eclipse seasons versus the time in the light and you will then have a term which can cover the long periods of time where the battery is just sitting in overcharge.

So, I would say this model right now would not be a good application to synchronous orbit as it would be too near earth orbit, but we can adjust it, I think, with this time factor to make a better fit.

FELDER: I had the same question that Harry just had. It has been shown here that the life is directly related to the depth of discharge, very strongly related to depth of discharge, and of course in synchronous orbit I have not seen data that shows that. Is there any plan to relate this and synchronous orbit? Because we haven't seen data that shows that the depth of discharge really is an important factor in the life.

MCDERMOTT: It is or isn't?

FELDER: Is not.

MCDERMOTT: Is not in synchronous orbit. Because you don't have that many cycles on it and the high correlation here with depth of discharge is versus cycles and you are running up into several thousand cycles, which you may never put on a battery in synchronous orbit.

FELDER: On this accelerated test program, is there any plan to do any synchronous orbit work?

MCDERMOTT: It is hard to do, because on accelerated tests you can't leave it sitting there for six months on overcharge, so that is not an accelerated test.

DUNLOP First question, on that depth of discharge, is that rated or actual?

MCDERMOTT: It is based on the rated.

DUNLOP: Okay, I think that is one point that we find a little confusing, because the D rating that the manufacturers use can be a variable and it seems to be becoming more and more a variable, depending on which guy writes the spec, but that is just a comment.

MCDERMOTT: Let me comment directly to that, because it may be germane. If you based it on the actual rather than the rated, wouldn't that just change the coefficient out in front of depth of discharge? It really wouldn't change the form of the equation. It would simply change that coefficient out in front.

DUNLOP: I agree. The other comment is, we have spent a lot of time in the last year or two, trying to look at regression equations and see how they relate to synchronous orbit. The real problem you run into is, if you really look at the synchronous orbit data that we have, for example, in four, which I presented at this last meeting and presented a paper on this summer, we do have seven years in orbit and eight years of real time in tests on that data. We have been working with Ed Henley about five to six years, so we have a lot of real-time data.

What it seems to indicate is that there is very little correlation between the number of cycles you get and the lifetime. In other words, if you look at the

50 percent depth of discharge based on actual capacity, or an 80 percent depth, even 80 percent with the model that, I just looked at the model that she put up. That would come out to 8000 cycles, roughly.

That is equivalent to 80 years in synchronous orbit. What you really find if you try and run in synchronous orbit that depth of discharge, is that you are lucky to get five years before you start. We are actually operating in the ENOSET Four spacecraft at 43 percent depth of discharge actual, or 60 percent depth of discharge based on the rated, and after five to five-and-a-half years in orbit, we have had to cut back on every spacecraft to manage to maintain the voltage about 1 volt.

I don't know whether this audience is interested in synchronous other than the few of us that work in that field, but the point is that it is a very, very difficult thing to try and go from these regression equations or accelerated test data to prediction of your lifetime for synchronous orbit.

I actually was just talking to Sam about that point. I would like to provide the kind of data that we are now accumulating to make it available to some of the people who are doing these regression studies, if they would like it, to see if they can see what it would mean in terms of synchronous. Dean Maurer and I have been spending a lot of time lately trying to come up with some kind of a reasonable model to predict what the battery lifetime is going to be for synchronous orbit.

FORD: Dean, you mentioned earlier you had a couple of vu-graphs. Would you like to come on up while we are taking another question from the floor? Does somebody have a microphone in their hand?

NAPOLI: Yes, I would like to comment on just that one point. I think in synchronous orbit you have possibly essentially different failure mechanisms going on at the near earth orbit; therefore, if we derive an equation for near earth orbit, I would not trust it to go into a synchronous orbit situation.

That doesn't mean that you couldn't develop an equation for synchronous orbit, but I don't think you ought to develop it from test results which are essentially near earth.

HALPERT: Your definition of failure, the cycle life failure, is the failure of the fifth cell? What is your definition of failure, when the fifth cell fails or when the first cell fails?

MCDERMOTT: Oh, no. Each cell is pulled when it fails so when you are averaging all those cells together it gives you a pack average.

HALPERT: So it's a pack average failure.

MCDERMOTT: Yes. Now, somebody asked, "What is the variation of individual cells within that average?" It's more than a couple of hundred cycles. It's very broad, in fact. If you remember the graph that I put up there on the normalized cycle life, you saw one which is the pack average and you saw them go all the way out to 1.4 and all the way back to roughly 0.6. So you can see the tremendous spread in the cells that are failing within packs. It's not a sharp narrow band.

HALPERT: I would like to go back to something that Harry Killian mentioned a while back. You are obviously interested in when the first cell is going to fail as much as the pack average.

MCDERMOTT: Right.

HALPERT: I am wondering if you started to feed that into the equation whether that would be more practical?

FORD: Yes, I would like to address that fact because it seems to be something is coming up particularly oriented for the user. When this program was set up, there was a lot of dialogue and deliberation on what constituted cell failure. So it was decided that a cell failed, when it would no longer sustain a voltage. Now bear in mind that you have data between all the points, from brand new to fails, so you can backtrack and you can get cycles to failure to specific voltages, if you have an interest. Right now they are concentrating on areas near the end, which is zero volts by definition. There has been some work and in the course of these meetings that are held quarterly, they have gone back and looked at the effects of the redefining cell failure. But the point is that data base is there based on the definition of cell failure to zero volts. It will not sustain any further energy release at that point.

But there is data and there is a whole wealth of things that you can do to it once you have it down to zero volts.

NAPOLI: I would like to reenforce Jim Dunlop's comments on the need for a similar equation that can work for a synchronous altitude. While you presented that I just did some back of the envelope calculations here for our particular synchronous satellite and I get a 400-year life cycle using that equation.

MCDERMOTT: I don't think anybody meant for this to be a synchronous orbit equation, to tell you the truth. What this might tell you is only that this cell is manufactured in a certain way and here is another set of cells manufactured in a certain way. You run this accelerated test matrix and Set A outperforms Set B. If you took both those sets and put them in a synchronous orbit regime, I would bet that A is going to last longer. Do you see what I mean? In other words, it is not going to predict how long it is going to last, but it may tell you which is the better batch of cells.

KRAUSE: Jim Dunlop, over there, says that all this data and the equations being developed are not applicable to synchronous orbit. I think they are probably not applicable to a lot of elliptical orbits that we see. I agree with what Jim said. Pat McDermott says that there are probably different reactions going on and I probably agree with that, too. Can we get a restatement of the objectives of this accelerated testing at Crane and how it relates to a major portion of the applications that we have for our satellites and for which we have some very long term applications and are trying to find ways of predicting battery lifetime by short term testing? I kind of thought that part of the objective of this testing was to do that but that doesn't seem to be happening. Perhaps it is premature to assume that it is happening. Does anyone want to comment?

MCDERMOTT: I would like to comment. I think that if you were taking cells manufactured in 1978, I would not use these equations. I would set up your own accelerated matrix which is much smaller than the matrix that we use. I think what the accelerated test program has said is that depth of discharge, and I am talking about for the time being the near earth orbit, depth of discharge and temperature are going to be the best factors for predicting cell performance. Okay, disregard the others. Charge them until you have a charge rate that is going to be comparable with getting them fully charged. Don't overcharge them too much, but really accelerate temperature and DOD, then set up a small matrix. It might be a nine by nine matrix making 20 or 25 cells. You can run those on a matrix which will last maybe three to four months, six months at the most, and then you've got a pretty good prediction of what those cells will do under a normal condition.

I disagree with other people on the team. I do not think this would be a good equation to use with new cells that you are buying off the shelf in 1978. But I think what the program has said is that there is a matrix which you can build is an abbreviated form for this. It is not 100 packs, but possibly 9 packs. You set it up so that the main interaction is temperature and depth of discharge but you vary temperature and depth of discharge so that you get all of the packs to fail in five months or whatever your requirement is. Then you get a fairly good predicting.

So if you have to decide as a manager between a lot of cells or manufacturer of cells A, B, C, you set up a matrix and you test them to find out which cells are going to last the longest. Those are the ones that I would use. So I am saying that the accelerator test program has proved a methodology not necessarily giving you an equation which is fool proof.

FORD: I would like to let Dean go ahead and present his couple of vugraphs and then we will get back. If you will just hold your questions, we will get back to them in a minute.

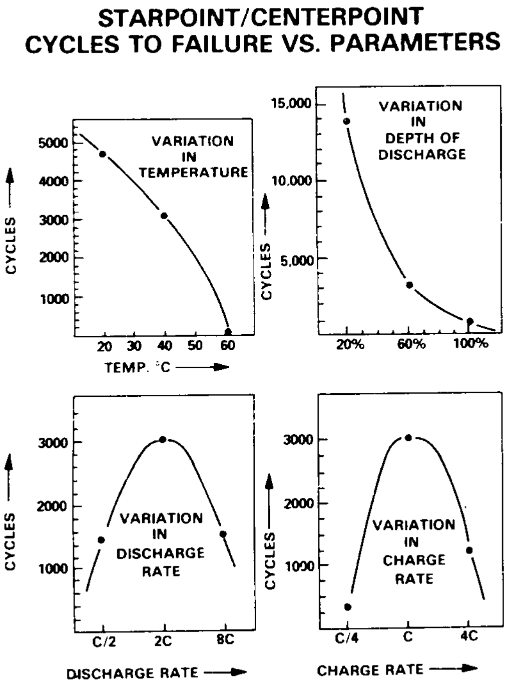

STARPOINT/CENTERPOINT CYCLES TO FAILURE VS. PARAMETERS

Figure 2-30

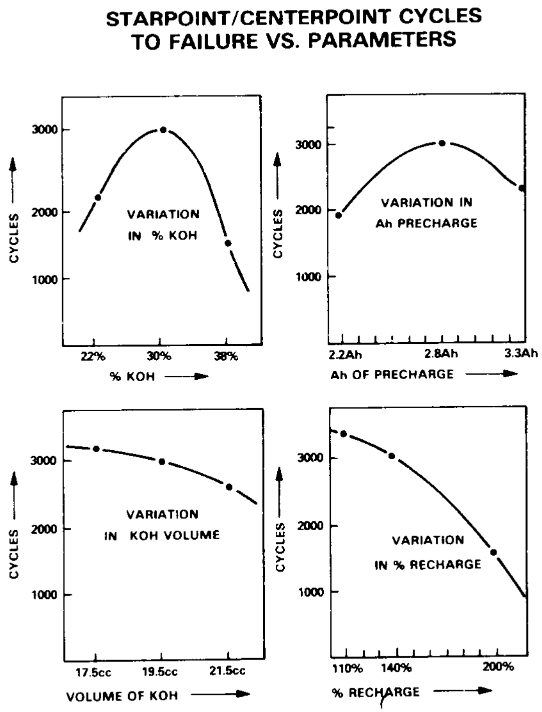

STARPOINT/CENTERPOINT CYCLES TO FAILURE VS. PARAMETERS

Figure 2-31

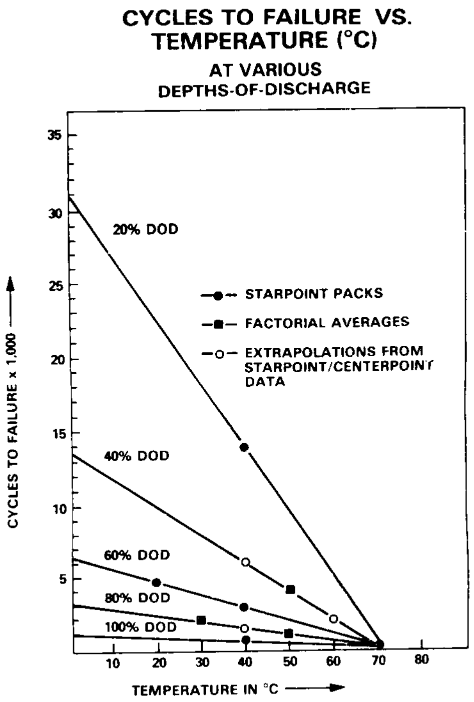

CYCLES TO FAILURE VS. TEMPERATURE (°C)
AT VARIOUS DEPTHS-OF-DISCHARGE

Figure 2-32

## PREDICTIONS BASED ON NON-LINEAR REGRESSION

REGRESSION EQUATION

$$\text{Cycles To Failure} = (b_1 + b_2 RC) \times (b_3 - T) \times e^{b_4 DOD} + b_5 DCR + b_6 CR$$

RC = RECHARGE RATE

CR = CHARGE RATE

DCR = DISCHARGE RATE

DOD = DEPTH-OF-DISCHARGE

T = TEMPERATURE

| | CASE 1 | CASE 2 | CASE 3 |
|---|---|---|---|
| $b_1 =$ | 1000 | 2,100 | 3,083 |
| $b_2 =$ | — | 6.6 | 10.3 |
| $b_3 =$ | 70.0 | 66.0 | 62.0 |
| $b_4 =$ | -0.038 | -0.037 | -0.045 |
| $b_5 =$ | — | — | 38.6 |
| $b_6 =$ | — | — | 34.6 |

PREDICTION OF NORMAL PACKS' CYCLES TO FAILURE USING →

| PACK | TEMP | DOD | RC | DCR | CR | OLD EQN + 50% | ADD RC TERM | ADD DCR & CR TERMS |
|---|---|---|---|---|---|---|---|---|
| 86N | 20 °C | 40 % | 105 % | C/1.2 | C/4.8 | 15,000 | 14,700 | 14,350 |
| 83N | 0 °C | 40 % | 105 % | C/1.2 | C/4.8 | 20,400 | 21,800 | 21,120 |
| 84N | 20 °C | 20 % | 105 % | C/2.4 | C/2.4 | 33,750 | 33,900 | 34,600 |
| 85N | 0 °C | 20 % | 105 % | C/2.4 | C/2.4 | 46,500 | 44,700 | 51,030 |

Figure 2-33

## I. EMPIRICAL EQUATION DERIVED FROM CYCLES-TO-FAILURE VS. TEMPERATURE GRAPH

FOR CELLS CYCLED AT 1C CHARGE, 2C DISCHARGE, 140% RECHARGE

$$\text{CYCLES TO FAILURE} = 1000 \times \left\{ 70 - \underset{(^\circ C)}{\text{TEMP.}} \right\} \times e^{-\left\{ 0.038 \times \text{D.O.D.} \right\}}$$

## II. PREDICTION OF NORMAL PACKS CYCLES-TO-FAILURE

| TEST CONDITIONS | | AT 140% RC 1C CHARGE 2C DISCHARGE | FOR 105% RC AND LOWER CHARGE AND DISCHARGE RATES | |
|---|---|---|---|---|
| TEMP. | DOD | | ADD 30% | ADD 50% |
| 20°C | 40% | 10,000 CYCLES | 13,000 CYCLES | 15,000 CYCLES |
| 0°C | 40% | 13,600 CYCLES | 17,700 CYCLES | 20,400 CYCLES |
| 20°C | 20% | 22,500 CYCLES | 29,250 CYCLES | 33,750 CYCLES |
| 0°C | 20% | 31,000 CYCLES | 40,300 CYCLES | 46,500 CYCLES |

Figure 2-34

# SYNCHRONOUS ORBIT MODELS

D. Maurer
Bell Laboratories

For those of us interested in synchronous orbits, I did a little model playing with some existing curves, namely, the NASA design guidelines for synchronous orbit.

(Figure 2-35)

This has been corrected by Jim Dunlop for depth of discharge in terms of absolute capacity rather than rate of capacity and plotted in terms of the log of the lifetime in years. You will notice that there is a drop off here at the lower depth of discharge. Then to orient you with the curves that you have seen in the past couple of papers, if you turn this upside down and backwards—So you have depth of discharge running across the bottom and log of the lifetime vertically. You get the straight line that you saw before, but it's bending over at the top. It's this bending over that we think is due to a time temperature effect. I chose to divide this life model into two parts, one which I call a temporal part. It has noting to do with cycling, only with the temperature and other things. Another part has to do with cycling.

(Figure 2-36)

I then assign a value for the temporal aging mode choosing twelve years. I will show you why in a minute. This line has some function of temperature and probably other things. Now, if I subtract this part from the guideline curve, I get a nice straight line, which I call cyclic mode. The cyclic mode is perhaps a function of temperature, but this data being only at 15°C doesn't tell you anything about that.

(Figure 2-37)

Now the sensitivity of where you put the temporal line is shown here. For example, if I move this line out to 15 years, then the other curve or other line begins to curve. It drops down again, indicating that we haven't taken enough temporal effect out of the model. Twelve years is a reasonably sensitive selection of where the temporal line should be. The slope of this line turns out to be 0.138 rather than 0.0038 which Diane found to be the higher rates. These are lower rates and 24-hour cycles. That is also corrected for the fact that this isn't a log to the base E but a log to the base 10.

(Figure 2-38)

Now we have the two factors, temporal and cyclic. One can now correct the guideline curve for different temperatures just to see what that does to you. I used an activation energy on the temporal line of 15 kilocalories which is what we found for long term high temperatures stress aging studies. Basically, it's a degradation of nylon and whether you use 14 and a half or 15 isn't a great effect. But this is what it does to the expected lifetime of the synchronous orbit battery.

It has an effect at the lower depth of discharge where you might expect it to, because now you are getting far enough out in time for the temporal effects to take over. Whereas, at the higher depths of discharge, the lifetime is so short that the temporal effects are minimal. I am just throwing this out as an interesting observation that might be worked into some of the equations that we have been hearing a little bit of this afternoon.

(Figure 2-39)

Now, one other crosspoint check on this. If you take this line now, since it's a cyclic effect, it should be independent of time so one should convert the lifetime of this scale to a cycle lifetime. Just assuming that there are 80 cycles in geosynchronous orbit per year, one can redraw that line to give up the dotted line shown here on this curve where the lifetime is a function of cycles. Also part of the NASA design guidelines is a line for near earth orbit battery design life. If you recalculate that line in terms of number of cycles, you get this line. So that they agree somewhat in lifetime to the failure in terms of depth of discharge.

The other thing I wanted to talk about here for a minute is going from these guidelines to try to predict the lifetime of a real acting satellite. One finds when you look at the satellite data that the depth of discharge isn't constant afterall. They change it from one value to the next, from season to season and even during a given season to do whatever things the system people want to be doing with the satellites. How do you handle that by taking the design guideline curve?

(Figure 2-40)

We came up with a simple battery life model here which just says that the fraction of life expended in any one season is the sum of the fractions of all the seasons. And the fraction within a given season is just the season lifetime, namely a half of year divided by the lifetime it would have had if it had spent its entire life at that depth of discharge.

(Figure 2-41)

You can go through the actual satellite data now and add all these things up and see what you come out with. So courtesy of Jim Dunlop, I did that on one of the Intelsat IV batteries and got this kind of result. These are the currents that the battery saw during each season, translated to depth of discharge in actual capacity, the lifetime it would have had if it had spent all of its lifetime at that depth, and then the cumulative fraction of life expended. What you find is after 14 seasons it's about all used up. This model and the guideline curve are somewhat compatible with what we have seen happening in a real life situation.

## DISCUSSION

GROSS: A somewhat related approach that I found to be successful for doing a similar task where you had varying temperatures, varying depth of discharge, and even varying light and dark periods is to instead of using lifetime as a parameter, to use its reciprocal which is a failure rate. Then you take the failure rate or lifetime data and you can then break it down into the failure due to time or the degradation rate due to time and the degradation rates due to discharges at any depth of discharge.

Then you can integrate all this information for any particular mission of varying depth of discharge, time, and temperature. It is a very flexible approach to solving that kind of a problem. It all depends on having good data in the first place.

MOORE: I am getting the feeling that we are sort of losing track of the purposes of coming up with a model and doing prediction and I want to comment on it.

We apparently don't know how to design our satellites, whether it's elliptical orbit or geosynchronous orbits, so that our batteries will last for the desired lifetime. We are trying to develop mathematical models which will take into account all of the variables and help show us how to design our systems, probably not how to redesign our batteries, but how to design our systems so it maximizes a life.

I think it is a mistake to get hung up on only temperature and depth of discharge. I keep averaging, which is good for first cuts, but we are trying to find out and I know in my mind I am very disturbed by the tremendous variations in rates of discharge depending on what load we have on the bird at the moment. I think that that is going to have an influence on the lifetime of the battery. Different rates of discharge heats it up at different rates and that effects the life.

We have people who think that the ultimate failure mechanism in our batteries is dry out of the separators. And then there are other people who say that the ultimate failure mechanism is swelling of the positive plates which eventually short through the separators. What we need is a model that correlates all of these parameters and tells us which ones we have to control.

HENDEE: I sort of see the opposite. I look back and I see there are cell designs. We have seen some minor shortcomings. We have overcome it. We have seen shortcomings in our management. We have overcome it. We have changed it. The positve plate swelling, hopefully, we are overcoming the electrochemically impregnated positives. I really believe that the math modeling that we do today is not going to be much good four or five years from now. I think we ought to be looking at the designs, how we can handle them, how we build it, at least for the geosynchronous satellites.

FORD: We have one over here on the left, Charlie.

DUNLOP: One of the comments that I would like to make addressing this whole idea of accelerated testing for synchronous orbit work for battery design. My opinion is that you don't need it. The reason I say that is this: the best way to find out what your battery manufacturer is doing for you is to take the cell, cut it open and find out what he put inside it. If he hadn't put inside that cell that you wanted in there, you are not going to get any lifetime out of it. If you have to base a seven-to-ten-year mission on an accelerated test, you are not going to get the kind of data that you need from the accelerated test to really tell you whether or not you have a good cell.

If you want to know whether or not you have a good cell, you have a lot of background data that you have accumulated over the years to tell you what has happened in technology. Right now, the best way to decide whether the manufacturer is making you a good cell or not is to cut the thing open and do a good analysis and find out if he is making the cell the way that you want it made.

ROGERS: It would seem to me that what you are doing is not taking into account, and it was alluded to a moment ago, the mechanism that is causing the cells to fail. You are not sure what that is. I don't understand how you can do accelerated testing of something when you don't even know what the mechanism is. I mean this is sort of basic chemicokinetics which is what you are dealing with. You really have to understand the reaction before you can even theorize what is happening much less actually count on it.

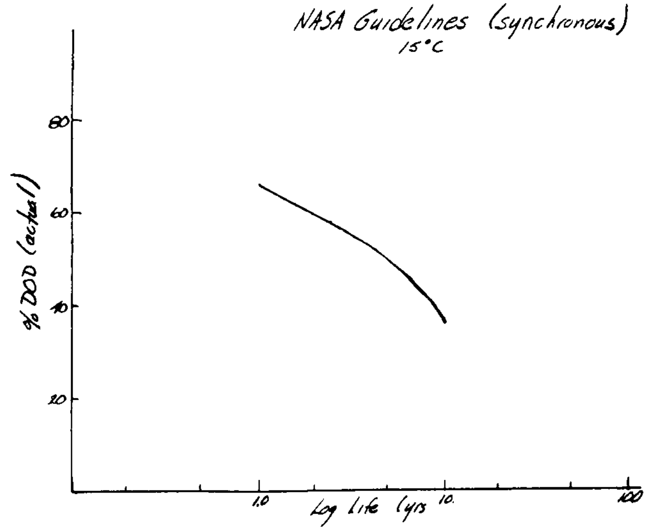


Figure 2-35

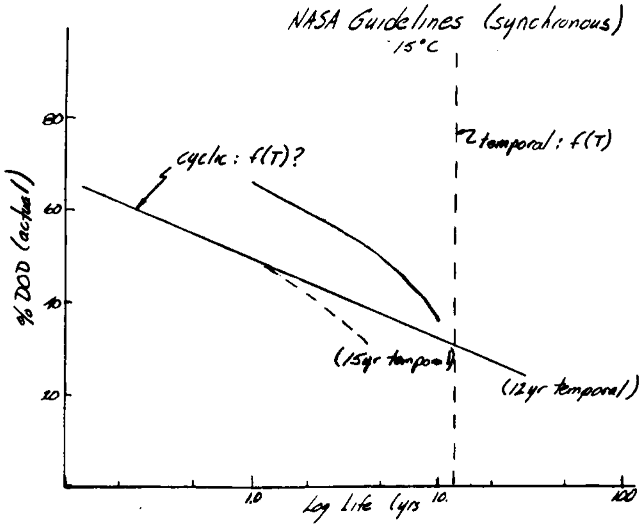


Figure 2-36

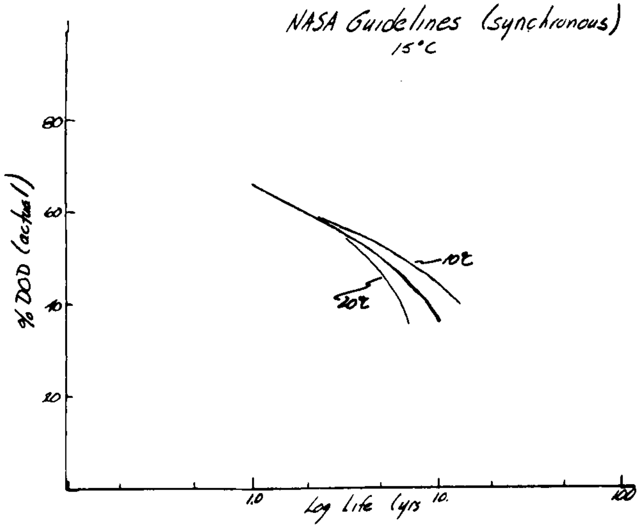


Figure 2-37

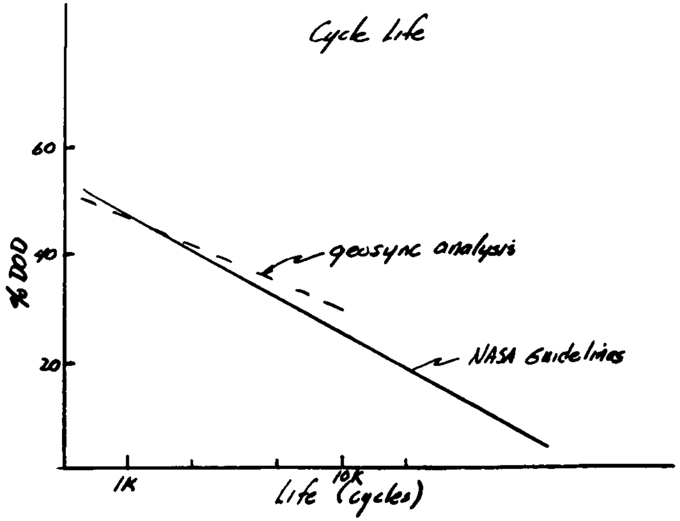


Figure 2-38

# BATTERY LIFE MODEL

FRACTION OF LIFE EXPENDED, $F = \sum_{I} F_I$

WHERE I IS THE ECLIPSE SEASON

$F_I$ IS THE FRACTION OF LIFE EXPENDED DURING THE SEASON

$$F_I = \frac{0.5 \text{ YRS}}{L_I}$$

WHERE $L_I$ IS THE PREDICTED LIFE OF A BATTERY AT THE GIVEN DOD FOR THE SEASON, I.

Figure 2-39

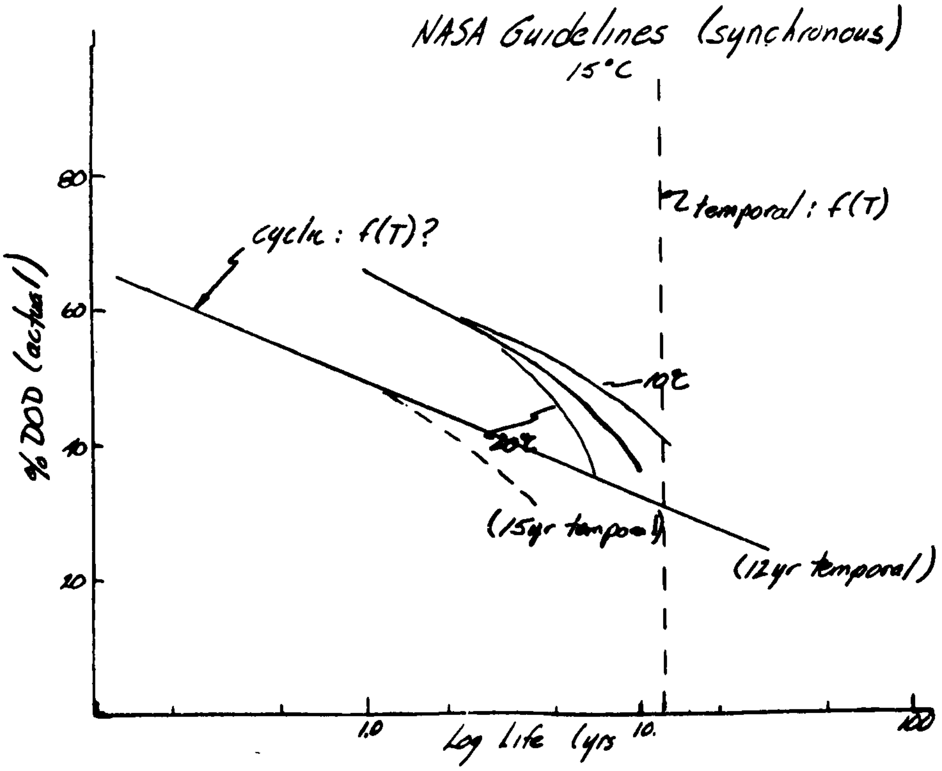


Figure 2-40

# HUGHES/GE IMPROVED NiCd CELL DESIGN

S. Krause
Hughes Aircraft Company

This is not about accelerated cell testing, although I still have a few things to say about it. However, I will forego the temptation. In spite of what some of the accelerated test data seems to show, we at Hughes, based on running long term synchronous orbit and some elliptical orbit life tests, feel that when it came time to make some improvements in cell designs for some of our current spacecraft applications, that we needed things like increased electrolyte volume. We wanted to increase the surface area in our cells to reduce the current density on charge and discharge; however, we would keep the charge rates consistent with reasonable efficiencies at our operating temperature.

We also felt that we wanted to get a slight increase into electrode space since we are still using chemically impregnated electrodes and probably will for another year or two in our flight cells. We want a little more space to allow the electrodes to grow. We also could achieve a little increase in electrolyte volume if we did increase the inter-electrode space.

We had been running a fairly extensive program over a period of about three years evaluating teflonated negatives and felt that they were of some advantage. The results of that program show that after four or five years in the cell, TFE is fairly wettable; however, it does initially provide you with the advantage that you can again get more electrolyte into the cell which was one of our primary objectives.

Low carbonate level has been important. We continue each year to try to drive down the carbonate level in the cell to get better voltage performance. Cadmium migration is also reduced womewhat with lower carbonates; however, our battery temperatures nowadays are low enough that cadmium migration is not a significant problem.

We also wanted to reduce plate mass for some improvement in vibration characteristics to reduce the stresses on plate connections. We had been designing for shuttle launches now which had some fairly severe vibration environments with the type of busses that we are going on compared with some of our prior designs.

We also felt that an improved cell should have a reasonably square plate geometry to help equalize voltage across the plates and to try to keep current densities fairly distributed across the plate. Everybody has been doing the remainder of the things, basically, and I won't elaborate any further on those.

(Figure 2-42)

So in reviewing the results of our life testing over the last five or six years and reviewing all the data, we came up with this list of improvements. We have tried to implement these improvements in a cell that we call a Hughes/GE cell design. The reason for that name is the basic concept or approach to achieving a significant electrolyte volume increase was conceived at Hughes and the engineering details were worked out by Guy Rampel at GE. Of course, we called it "improved cell" because thats what it is supposed to be.

(Figure 2-43)

For comparison purposes, that thing called a conventional cell over there is a cell that we have been using in flying for about four years now. It is a pretty standard 24-ampere hour cell. Those are actual capacities, not rated. It is somewhat small in size as you can see by the weight than a so-called 20-ampere hour rated cell.

This improved cell for which we have actual capacities is going through the acceptance tests at GE now. It's very comparable in capacity, around 24 ampere hours or thereabouts. It weighs about 815 grams. It is about 15 grams less than the so-called conventional cell. It has 27 plates in it as opposed to the normal 23 plates that most of us have been using with General Electric cells in the past. The 27 plates result from changing the plate thickness to 0.61 millimeters on the positive and 0.69 millimeters on the negative compared with the standard thicknesses that you see here for typical GE plates. What comes out of that, of course, then is that we achieve a fairly sizable increase in the plate area for a cell of this size which was one of our goals. As you can see here, the plate volume is substantially similar as you would expect from the similar capacities.

One of the things we achieve with the higher plate area is a reduction in current density of about 20 percent down to well under 5.2 down to under 5 milliamps per square centimeter. Most of our synchronous orbit satellite operation to date has been somewhere between five and six milliamps per square centimeter on discharge. Again, notwithstanding some of the results of the starpoint packs and the accelerator tests, we think that for synchronous orbit application, reduction in current density will improve plate life.

The negative/positive ratio we have kept about the same. The only exception is that as we will see after the negatives are TFE coated we will probably have a negative cause ratio slightly less than a conventional cell that does not have teflonation.

(Figure 2-44)

The interelectrode space on a conventional cell is about 7000ths of an inch. We have increased it on this improved cell to around 8000ths. It should nominally be somewhere around 8000ths.

The significant difference in the cell here can be seen in terms of the separator volume. It was obvious to us that if we increased the number of plates and made them thinner that we could get a significant increase in the separator volume just by virtue of using more pieces of separator in the cell of the same capacity.

As you can see here in looking at the ratio of the plate volume to the separator volume, we have substantially reduced the amount of cubic centimeters of plate for every cubic centimeter of separator volume. In effect, what we are really creating in the cell is a substantial reservoir using the separator at conventional saturation levels. So if the rate of takeup of electrolyte is basically similar to a conventional cell by virtue of the fact that it has approximately the same volume and the same porosity of plate, you have significantly more electrolyte available to those plates to take up electrolyte.

We have also reduced the positive loading. This is in grams per square decimeter equivalent back to 0.69 millimeter positive and 0.89 millimeter negative just for the sake of matching these up against each other. We have reduced the positive loading substantially and have taken only a small reduction in the negative loading at this time.

As you can see what we have achieved is a 50 percent increase in the electrolyte quantity in these cells. The conventional cell is right around 2½ cc's of electrolyte per actual ampere hour. Typical GE cells that most of us have been flying have varied between 2½ and 3 cc's per actual ampere hour.

This cell, based on an 86 cc electrolyte fill is running at better than 3.6 cc's per ampere hour. That is based on a 24-ampere hour actual capacity which is the high end of the capacity distribution for a substantial number of the cells that are at GE right now. We used 31 percent of electrolyte.

So in approaching that list of improvements that we wanted, we did get the significant increase in the electrolyte volume that we feel that the long life synchronous orbit has to have. We have reduced current density. We have a fairly square plate geometry that is almost dead square. We have a high electrode space. We are using standard separators, standard electrochemistry. So we feel fairly confident that the cell will run fairly well and it should represent a significant improvement on the lifetime capability as opposed to the conventional cells whicn we have been using. That's all I have right now.

DISCUSSION

KRAUSE: Are there any questions?

THORNELL: What reduction do you get in carbonate?

KRAUSE: We are specing the cell now at a five percent carbonate level. That is five percent in the electrolyte extracted after initial cycling. I think we are achieving around four to four and a half percent.

I also wanted to point out that these are real cells. They are not prototypes. They are going into a qualification program for a satellite system that we are working on now and we are using this concept on the GOES spacecraft for NASA in the near term. We are basically committed to this design concept pretty much across the board.

ELIASON: Stan, what is the schedule on the cells? Do you have them built already? Are you acceptance testing? What is the schedule on that?

KRAUSE: The first lot are completing acceptance testing at GE. They will go into qualification next month.

HENNIGAN: What kind of limits are they holding on that interelectrode spacing at 8000ths.

KRAUSE: It is about plus or minus a half thousandth.

HENNIGAN: Do you depend on the separator to do that?

KRAUSE: No. It is the stackup of plates and the idea of the cam. Each plate pack is measured and it has to fall within certain tolerances. We haven't changed the way the GE measures the plate pack and the way that they are tolerancing interelectrode space, but it has been biased to increase it over the conventional spacing by 1000ths of an inch, but the tolerances are essentially the same.

HENNIGAN: Thank you.

OTZINGER: Stan, what is your estimate on the life? Is this a ten-year life cell or what are you projecting on it?

KRAUSE: We will get a model here pretty soon. It is better than old cells, than conventional cells. How much better it is difficult to say. We will know a little more when we get a little more experience with it.

HALPERT: You had, I think, 850 grams per cell. What kind of cell thicknesses?

KRAUSE: The new cell is 815 grams. It is a 15 mil case.

MAURER: In your objective vu-graph you said you improved the negative/positive ratio and in your final vu-graph you showed that the negative/positive actually went down a little. Can you comment on that?

KRAUSE: Well, I don't think that the vu-graph said that it improved it. I think it just said "to keep a high negative/positive ratio.". And in ECT tne plates are the same ratio as they are before. We are not reducing the 1.6 to 1 ratio prior to TFE coating. But what was shown there was that we expect to see about a 1.5 to 1.6 ratio after the TFE coating. There may be a slight reduction in the negative capacity after the TFE treat. That may also be related to the difficulty in measuring it. So we are spacing it a little lower or closer to what we are able to measure.

GROSS: What was all the rationale behind increasing the plate area?

KRAUSE: We have some limited data which we feel shows an increase in discharge current density accelerates that plate growth or positive plate swelling that we are worried about. We felt that if we could reduce that discharge current density and take some reductions in charge current density as well, that we might see some reduction in the rate of plate swelling. That coupled with the lighter loading was the objective.

SHULMAN: Are these cells going to receive any particular or special treatment within the vehicle to extend their life?

KRAUSE: If you consider that running them at a temperature right around 0-5°C especially, yes. These will be running through most of the charge period in synchronous orbit between 0 and 10°C. Fortuitously, the way the vehicle is being designed, we are doing our eclipse discharge between 10 and 20 so we are getting a fairly high capacity output and then we cool down right after eclipse and run pretty cold all through the charge and the remainder of the 24-hour day.

SHULMAN: Are you contemplating any reconditioning of any sort?

KRAUSE: Yes.

SHULMAN: Deep or otherwise?

KRAUSE: We won't have the capability to recondition individual cells but we expect to recondition these down to probably something under a half a volt at least on the first cell on the battery. We have the capability to monitor individual cell voltages. It will probably be done at around a C/60 rate, typically.

NAPOLI: Is this the mission that is going to be flying a spare battery on board as well?

KRAUSE: What mission is that, Joe?

NAPOLI: Well, I know the mission that I believe you people may be working on that had requested at one time that they fly a spare battery in a shorted state that would reactivate at the end of life and extend the omission.

KRAUSE: This particular cell is going to be flown. This extact cell will be on the SBS program.

NAPOLI: I am not making reference to that.

KRAUSE: No, in that program there are two batteries on board and they are both doing their thing right from launch. We have the capability on another program where we have three batteries on a sychronous orbit satellite to turn off the heaters on any two of the batteries that we want between eclipses and take those batteries down to a very low state of charge and then short them with resistors and then cool them. So they will be in cold storage between eclipses. The vehicle operator will have that option.

NAPOLI: Thank you.

KRAUSE: They are not spare batteries, though. They do have to operate during the eclipses.

SHULMAN: If you had to occuse any single reason for the extension of life of this particular system, would you think it was the cell design itself or your special treatment of the battery?

KRAUSE: My ego would like to tell me that it is the cell design, because it is my design. But I would suspect that the biggest factor in extending the life in any NiCd is to get them cool. I think that the preponderance of data shows that you can do that. I think, secondarily, and not very much less important, is the cell design itself.

HUGHES/GE IMPROVED NICKEL-CADMIUM CELL DESIGN

SUMMARY OF DESIGN APPROACH

**HUGHES**

- INCREASED ELECTROLYTE VOLUME
- INCREASED PLATE AREA
- PLATE INTERELECTRODE SPACE INCREASED TO 0.008 TO 0.009 IN.
- LOW CURRENT DENSITY ON DISCHARGE
- TFE NEGATIVES
- LOW CARBONATE LEVEL TO REDUCE CADMIUM MIGRATION AND IMPROVE VOLTAGE PERFORMANCE
- REDUCE PLATE MASS FOR IMPROVED VIBRATION CHARACTERISTIC
- SQUARE GEOMETRY PLATE DESIGN
- GE BUTT GEOMETRY TERMINAL SEAL WITH Ni-Au BRAZE
- LOW TEMPERATURE OPERATION FOR REDUCED SEPARATOR DEGRADATION AND REDUCED OVERCHARGE PROTECTION LOSS
- OPTIMIZED PRECHARGE LEVEL FOR LOW TEMPERATURE OPERATION
- INCREASED OVERCHARGE PROTECTION
- HIGH NEGATIVE/POSITIVE CAPACITY RATIO

Figure 2-41

HUGHES/GE IMPROVED NICKEL-CADMIUM CELL DESIGN

**HUGHES**

| | IMPROVED CELL | CONVENTIONAL CELL |
|---|---|---|
| • ACTUAL CAPACITY @ 25°C | 24.0 AH | 24.0 AH |
| • WEIGHT (MAXIMUM) | 815 GMS | 830 GMS |
| • PLATE QUANTITY | 27 | 23 |
| • PLATE THICKNESS | 0.61/0.69 MM | 0.69/0.80 MM |
| • PLATE AREA | 2231 $CM^2$ | 1890 $CM^2$ |
| • PLATE VOLUME | 151 $CM^3$ | 148 $CM^3$ |
| • DISCHARGE CURRENT DENSITY (BOL) | 4.2 $MA/CM^2$ | 5.2 $MA/CM^2$ |
| • NEGATIVE/POSITIVE CAPACITY RATIO | 1.5:1 (W/TFE) | 1.6:1 (W/O TFE) |

Figure 2-42

HUGHES/GE IMPROVED NICKEL-CADMIUM CELL DESIGN

**HUGHES**

| | IMPROVED CELL | CONVENTIONAL CELL |
|---|---|---|
| • INTER-ELECTRODE SPACE (NOMINAL) | 0.22 MM (0.008") | 0.18 MM (0.007") |
| • SEPARATOR VOLUME | 53.9 $CM^3$ | 35.5 $CM^3$ |
| • PLATE/SEPARATOR VOLUME RATIO | 2.8 $\frac{CM^3\ PLATE}{CM^3\ SEPARATOR}$ | 4.2 $\frac{CM^3\ PLATE}{CM^3\ SEPARATOR}$ |
| • PLATE LOADING (EQUIV. $GMS/DM^2$ HYDRATE) | | |
| o POSITIVE | 11.4 $GMS/DM^2$ | 13.0 $GMS/DM^2$ |
| o NEGATIVE | 15.9 $GMS/DM^2$ | 16.0 $GMS/DM^2$ |
| • ELECTROLYTE VOLUME INITIAL FILL | 86 $CM^3$ | 61 $CM^3$ |
| • ELECTROLYTE VOLUME/CAPACITY RATIO | 3.6 $CM^3/AH$ | 2.5 $CM^3/AH$ |
| • ELECTROLYTE CONCENTRATION | 31 % | 31 % |

Figure 2-43

# STANDARD CELL DATA

G. Halpert
Goddard Space Flight Center

About two or three years ago NASA made a decision to produce "a standard cell." There has been a lot of discussion about what a standard cell is and the NASA definition of a standard cell is one that had been flown before or one in which we had some experience, that we could talk about with regard to that cell and also that we could reproduce again. It did not mean in our context that every manufacturer that we would deal with would build the same cell in the same way.

So we put together a series of mechanical designs and tried to build an envelope around what we would consider a design that would be consistent within the framework of those people manufacturing NiCd cells. I did want to mention a couple of critical areas that were significant in that there were some guidelines in the manufacture of the cells so that we would first of all increase our electrolyte and at the same time reduce our loading. We did not tell the manufacturer what loading to use, but we did tell him that we wanted a minimum of 22 ampere hours and a maximum of 26 ampere hours because in the past we were getting a "nominal 20 ampere hour cell" with 27, 28, and 29 ampere hour capacity in it. We tried to get him to compromise in that area and bring his loading down and at the same time we hoped that we would maximize the amount of electrolyte as you will see in the vu-graphs coming up that we did that.

Four manufacturers responded and four manufacturers have now delivered cells, samples of which have been submitted to the Naval Weapons Support Center at Crane. They have been put on test and I will show you some of those results today.

All four manufacturers experienced some difficulty in building the first series of cells and actually resorted to a second lot or some kind of a rebuild. General Electric had a problem with the original positive plates that were cracking or chipping and they replaced those. SAFT America had a problem with a high pressure at the end of the final series of room temperature tests and they replaced those, rebuilt those and tested again. Eagle Picher had a problem with high voltage at 0°C and high pressure and they rebuilt. Yardney Electric had a problem with well and ceiling. There were enough extra cells that we accepted the good ones from that lot.

It was not a simple matter of being able to build a cell right off from the design pages. We asked each of the four manufacturers to provide us with a manufacturing control document, a document that detailed every step of the process and it was found that writing down this every step of the process and trying to reproduce it was not a simple task.

(Figure 2-45)

What I am going to show you today are some of the variables in the test program. What each of the manufacturers produced and some of the results. From the basic numbers here we can see that the number of plates vary between the four manufacturers. The plate areas are slightly different. Incidentally, this is not a square type design of the type that Stan Krause was just talking about. It is a prismatic cell but it is long and narrow rather than square.

The plate thicknesses varied, of course, to be consistent with being able to get in a similar type of case envelope. The plates weight were of the type shown on there.

As you see the increasing electrolyte was significant and we show that the cc's of electrolyte could be increased with a lighter loading design. Here you see that we are already up to 84 and 85 in the conventional cell of 72 in the case of SAFT and in the case of Yardney Electric the electro-chemically impregnated positive we were up to 98.

The precharge, as you see, varied and here is where we had a problem. It was supposed to be 40 perceht of the excess negative and the first lot of Eagle Picher cells failed with 40 percent of the excess negative because they continued to increase in their precharge. They convinced us and convinced themselves that they could build it without precharge and have five ampere hours of precharge in there and that they were able to do. So since it was their cell and their design to qualify, we accepted it.

In the other cases, you see that there was a change. These precharges measured were measured on the very first cycle after the precharge was put in.

(Figure 2-46)

Some other design variables here. The manufacturer loading and the loading under the GE is pretty close to what Stan is proposing to do now. These are cells that have already been manufactured and are being tested now. The other ones are also consistent with the lighter loading concept to come out with somewhere between 22 and 26 ampere hours. As you see, going down the list there, the theoretical capacities and some of the flooded plate tests that are consistent with that requirement.

We have a flooded cell test which we tried to get the manufacturers to implement, but it has been like pulling teeth. We have asked that they run just five plates in a batch over a certain type of cycle regime and show us that the plate positives will need a certain criteria and the negatives will need a certain criteria. It would save them from running through the complete manufacturing program with a set of plates and not knowing until they do their cell tests or at least up through their flooded formation tests that a plate stack would meet their capacity requirements.

In any event, we did get them all to do it and the numbers are somewhat consistent with what we would expect, at least in the positive and close on the negative. It would certainly help in terms of knowing the capacity that we have met the goals.

Below that, we have the sealed cell capacity as met or as tested by the manufacturers and you see that there are some interesting results. All of the 20°C tests were within 22 and 26 except the electrochemical ones. Their loading was so low that we felt as though we had met the requirements in trying to keep the loading down and it just happened that because they had such high efficiency that the capacity was high that we agreed to go ahead and accept that.

The 35°C capacity is as shown. We have run that 35°C capacity in the case of at least two manufacturers and have felt that when that capacity test is met that we know and we are confident that there is an adequate amount of electrolyte in the cell. There is some reluctance to run that test by some and it continues to prove to us that we know that we are confident of what that 35°C test is.

At 0°C, as we expected, would lose a little capacity and except in the case of SAFT America we got an unusual result which we still can't explain.

We sent the cells to Crane for their initial evaluation tests and these are now completed.

(Figures 2-46 and 2-47)

Thirty cells are in the same series circuit. We find that there are some unusual occurrences as indicated by the numbers in parentheses.

In the 0°C test, we ran again into the high voltage situation with Eagle Picher during the charge. Also on the 35°C test we exceeded 100 psi in pressure.

Of the others, GE, as you see, passed with flying colors. Their cells continue to be cycling for a year and a half in four different modes, which I will explain later. We have not yet had a failure.

With the SAFT cells, we had some problems exceeding pressure limits and with Yardney at 0°C there were a couple of high voltage cells.

We built cells to a certain design as based on a manufacturer's control documents and these are the kinds of results that we got from that kind of situation.

I have some interesting voltage comparisons of some of these tests at 20, 0, and 35. You can get an idea of how they are actually operating.

(Figure 2-48)

This is a charge at 20°C. For some reason we aren't able to get the GE charge data. J. Harkness of NWSC/Crane has been providing data on a regular basis on all of these tests and we appreciate his assistance.

(Figure 2-49)

Here is the discharge data. E.D. means Eagle Picher and Y.D. is Yardney Electric. You can see somewhat lower voltage on discharge and charge for Yardney and we don't have any comparison on the charge but SAFT is lower on the discharge at 20°C.

The line up the center there with the cross bar indicates the same position on both charts. So you can compare them.

(Figures 2-50 and 2-51)

This is a charge at 35 and the discharge at 35. Again, you see the same kind of situation with the Eagle Picher and the GE cells running at the higher level on discharge. SAFT and GE are pretty close at the top level and Eagle Picher at the higher level on the charge below.

(Figures 2-52 and 2-53)

The charge at 0°C is given and you can see where some of the problems are. The Eagle Picher cells were running into high voltage on charge at 0°C.

So at this point in time, these initial performance tests on all four manufacturer's cells are completed. They have all been started in a qualification test program. Each manufacturer will have four packs running in a near earth orbit, one at 10°C and 40 percent depth of discharge; one at 20°C and 25 percent depth of discharge: 20°C and 40 percent depth of discharge; and 30°C and 40 percent depth of discharge.

To date, we have gotten over 7000 cycles on the GE cells and none of those have failed in that cycling regime. The others have just been put on within a matter of weeks and we don't have very much data to go by. Each manufacturer also has five cells in a synchronous orbit test. And they are at 20°C, 65 percent depth of discharge.

They will continue to test as expected to go for two years or until the cells reach their failure limit of high pressure or high voltage or capacity.

## DISCUSSION

ELIASON: Do you have any comparisons on the weights of the cells ?

HALPERT: Yes, I do. The GE cell was around 900. Incidentally none of these were made with what we call a thin case. These are all made as they have been in the past. The GE cells were running about 900 grams. The SAFT cells were running about 800 grams. The Yardney cells are also about 800 and the Eagle Picher is 850.

HENDEE: I might have missed it. Did you shut the pore volume of the plaque, cc's of void volume per decimeter squared so when you are talking of loading, I can convert to something that I am familiar with ?

HALPERT: You would be able to do that at some later date. I am trying it all into another subject, plaque volume and other physical properties of the materials.

HENDEE: Thank you.

HALPERT: I don't have the data at the moment.

NASA STANDARD 20 AMPERE HOUR CELL DESIGN CHARACTERISTICS

| Cell Disignation | Eagle Picher<br>RSN -20/2/38 | | General Electric<br>42B024AB06/07 | | SAFT America<br>805120/38 | | Yardney Electric<br>YNC 20.1/.2 | |
|---|---|---|---|---|---|---|---|---|
| | + | - | + | - | + | - | + | - |
| Number of Plates | 11 | 12 | 11 | 12 | 9 | 10 | 8 | 9 |
| Plate Area(dm$^2$) | 1.01 | 1.01 | 0.96 | 0.98 | 0.91 | 0.91 | 0.98 | 0.98 |
| Plate Thickness (mils) | 28.0 | 30.2 | 28.1 | 30.2 | 25.8 | 33.7 | 30.4 | 42.3 |
| Plate Weight (g) | 21.77 | 26.96 | 23.18 | 29.88 | 27.34 | 29.31 | 31.14 | 33.22 |
| Electrolyte Volume (cc) | 84 | | 85 | | 72 | | 96 | |
| Precharge Added (ah) | 0 | | 10.0 | | 6.2 | | 5.2 | |
| Precharge Measured (ah) | 5.0 | | 5.8 | | 2.5 | | 2.7 | |

Figure 2-44

STANDARD 20 AMPERE HOUR CELL CAPACITY CHARACTERISTICS

| | E.P. | | G.E. | | S.A. | | Y.E. | |
|---|---|---|---|---|---|---|---|---|
| | + | - | + | - | + | - | + | - |
| Manu. Loading (G/dm$^2$) | 9.14 | 13.05 | 11.77 | 15.75 | 12.59 | 16.69 | 12.80 | 16.00 |
| Theo. Capacity (ah/cell) | 29.37 | 57.95 | 37.42 | 69.17 | 29.80 | 55.59 | 29.00 | 51.65 |
| Flooded Plate Test (ah) | 25.76 | 41.93 | 24.62 | 51.80 | 27.31 | 43.20 | 22.10 | - |
| Flooded Cell Test (ah) | 26.10 | 48.40 | 25.60 | 48.90 | 28.48 | 43.89 | 29.60 | 40.20 |
| Sealed Capacity 20°C (ah) | 24.30 | | 22.73 | | 23.57 | | 26.28 | |
| Sealed Capacity 35°C (ah) | 23.16 | | 23.30 | | 21.18 | | 23.86 | |
| Sealed Capacity 0°C (ah) | 21.15 | | 20.04 | | 26.62 | | 25.23 | |
| Manufact Chem. Analysis (ah) | - | 41.89 | 33.66 | 68.02 | 29.25 | 55.64 | - | - |

Figure 2-45

## STANDARD CELL QUALIFICATION
### INITIAL PERFORMANCE TEST – NWSC CRANE

| TEST | SAFT | | | YARDNEY (YSI 20.1/20.2) | | |
|---|---|---|---|---|---|---|
| | EOCV (volts) | EOCP (psia) | CAP (Ah) | EOCV (volts) | EOCP (psia) | CAP (Ah) |
| CONDITIONING | 1.438 | 2 | 24.1 | 1.439 | 3 | 26.7 |
| PRE CAP TEST | 1.446 | 29 | 23.2 | 1.447 | 21 | 24.4 |
| CAP TEST 20°C | 1.457 | 82 | 22.8 | 1.458 | 29 | 24.1 |
| PRE OCV CHARGE | 1.467[1] | 90[1] | – | 1.463 | 27 | – |
| OPEN CIRCUIT-1 WK. | 1.291 | – | 20.8 | 1.286 | – | 21.6 |
| CHARGE EFFICIENCY | 1.365 | 0 | 7.2 | 1.357 | 3 | 6.1 |
| CAP TEST 0°C | 1.505[2] | 59 | 23.5 | 1.522[3] | 10 | 26.6 |
| CAP TEST 35°C | 1.397 | 60 | 20.4 | 1.405 | 20 | 23.1 |

(1) 3 CELLS EXCEEDED 100 psia, 2 CELLS EXCEEDED 1.48 V

(2) 4 CELLS EXCEEDED 1.52 V

(3) ALL BUT 3 CELLS EXCEEDED 1.52 V

Figure 2-46

## STANDARD CELL QUALIFICATION
### INITIAL PERFORMANCE TEST – NWSC CRANE

| TEST | EP (RSN-20/20S) | | | GE (42B024AB06/07) | | |
|---|---|---|---|---|---|---|
| | EOCV (volts) | EOCP (psia) | CAP (Ah) | EOCV (volts) | EOCP (psia) | CAP (Ah) |
| CONDITIONING | 1.440 | 28 | 25.9 | 1.442 | 3 | 24.6 |
| PRE CAP TEST | 1.447 | 45 | 25.1 | 1.452 | 16 | 23.4 |
| CAP TEST 20°C | 1.459 | 44 | 24.6 | 1.454 | 18 | 27.8 |
| PRE OCV CHARGE | 1.452 | 40 | – | 1.458 | 20 | – |
| OPEN CIRCUIT-1 WK. | 1.301 | – | 22.0 | 1.320 | – | 20.6 |
| CHARGE EFFICIENCY | 1.375 | 6 | 6.1 | 1.368 | 0 | 6.9 |
| CAP TEST 0°C | 1.492[1] | 43 | 23.3 | 1.488 | 12 | 23.5 |
| CAP TEST 35°C | 1.400 | 71[2] | 20.9 | 1.398 | 0 | 24.5 |

(1) ALL CELLS EXCEEDED 1.52 V DURING CHARGE

(2) 3 CELLS EXCEEDED 100 psia

Figure 2-47

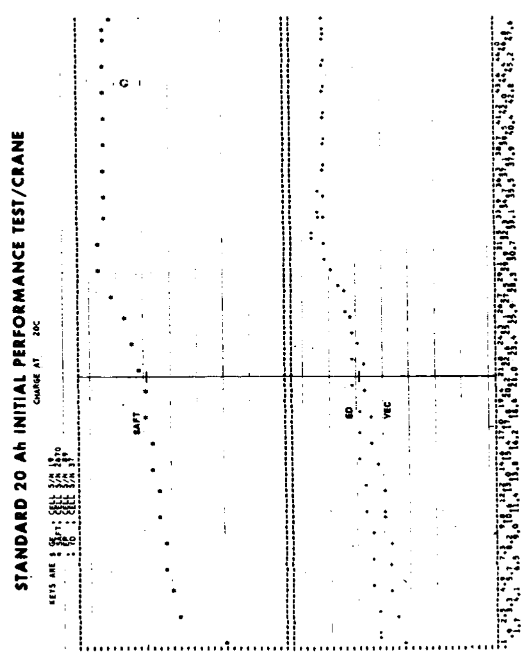


Figure 2-48

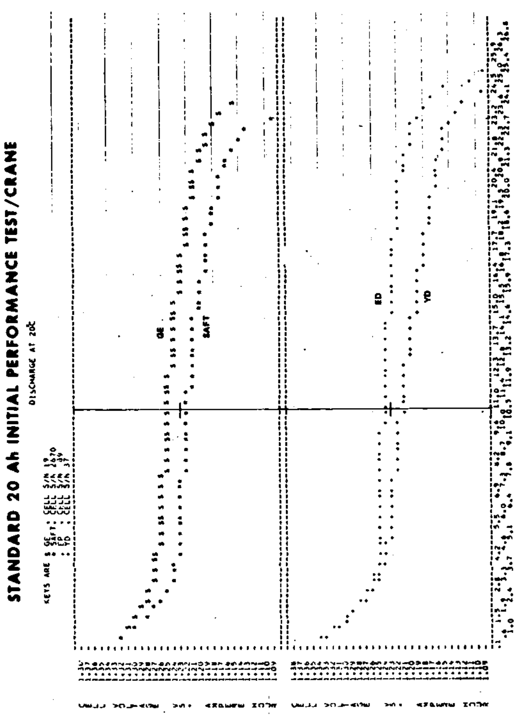


Figure 2-49

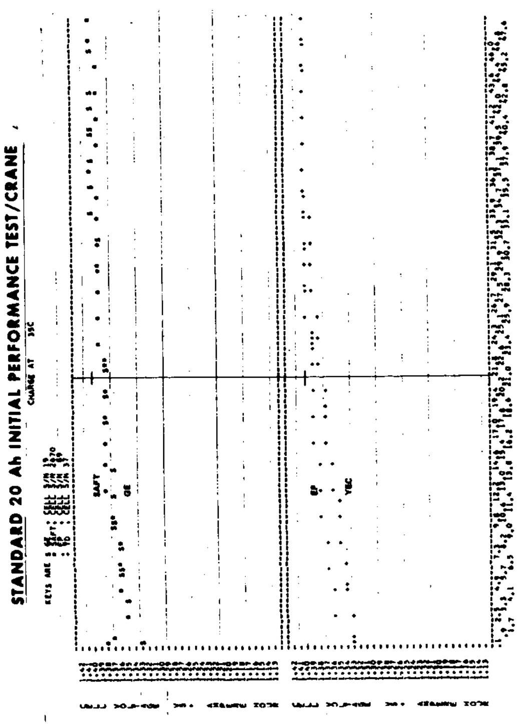


Figure 2-50

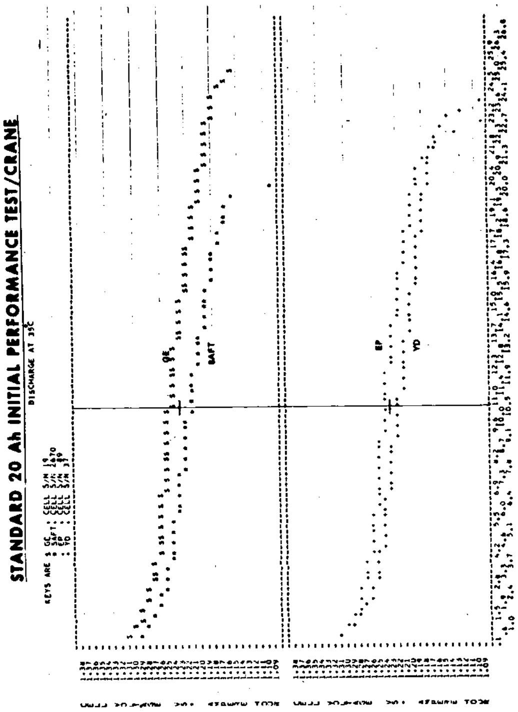


Figure 2-51

STANDARD 20 Ah INITIAL PERFORMANCE TEST/CRANE

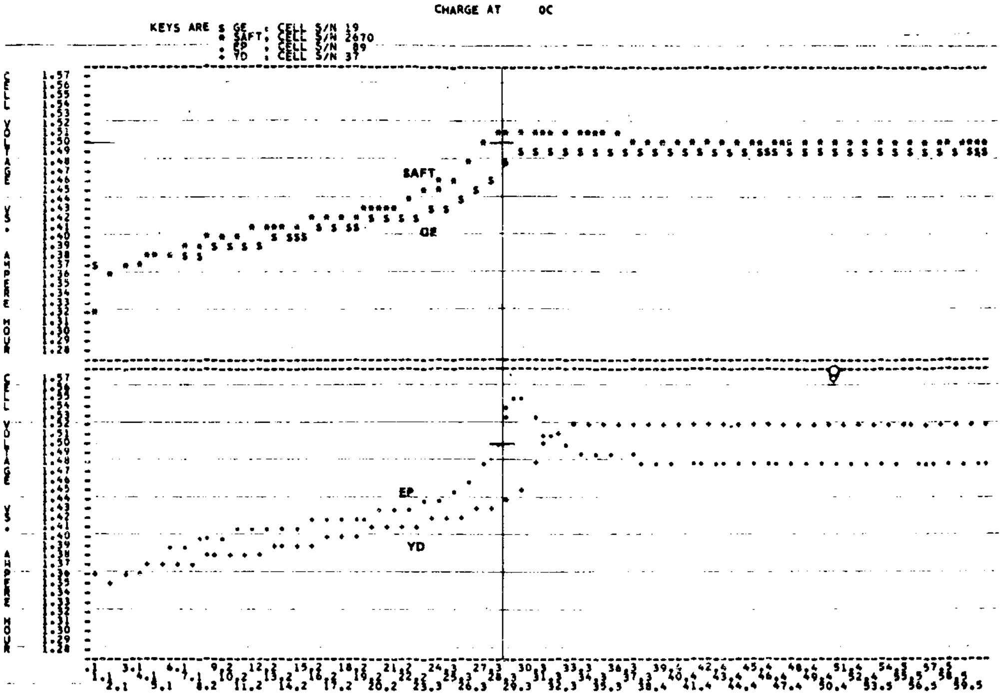


Figure 2-52

STANDARD 20 Ah INITIAL PERFORMANCE TEST/CRANE

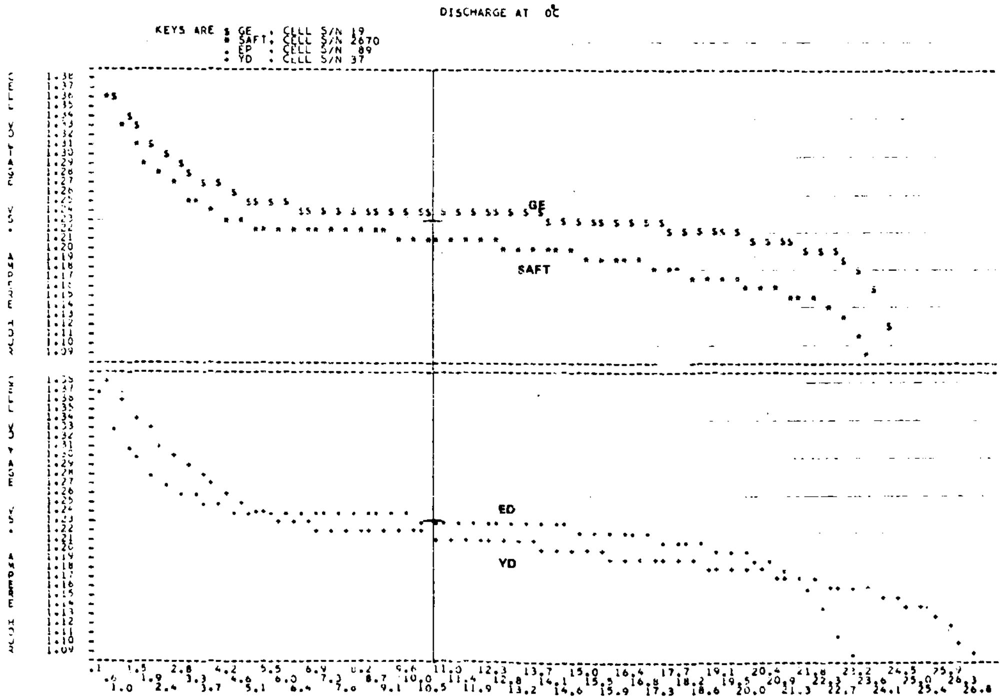


Figure 2-53

# SINGLE CELL RECONDITIONING TEST

V. Mueller
McDonnell Douglas Astronautics Company

Phase one is to report the results of a test we have been doing on one cell and we have been reconditioning it using the Marshall technique developed by Lanier Pascal. The second is to report to you a phenomenon that is at least new in my experience and possibly get some inputs from you as to what is happening.

(Figure 2-54)

It so happens that we were running a test on a 36 ampere-hour cell similar to the ones that we had flown on the Airlok program and supplied by Eagle Picher. It's their part number RSN-36, 36 ampere hour rated. And at the time that we decided to do the reconditioning we had completed some 29800 test charge cycles at 80°F. We then did the reconditioning procedure and again I say this is similar to the one that was developed by Marshall Space Flight Center.

Our reconditioning was a discharge at 18 amps, first of all to 0.9 to one volt per cell. Then we reduced the discharge current to 3 amperes. We took it down to a 0.3 of a volt clamp. We left it there for three days until the discharge current was reduced to five milliamperes, whichever took longer.

In actual fact, since we did these in our lab for their convenience, it was usually done over the weekend and the discharge current typically ended up somewhere around one to three milliamperes.

Then when we recharged to one and a half volts, cutoff, and our recharge was first one hour at two amps, and then we went to a ten amp charge. We maintained that charge until we reached the voltage cutoff, then we went back into cycling.

(Figure 2-55)

Periodically, then, we checked the capacity by discharge at 18 amps to one volt. We did the capacity check immediately after the reconditioning and then we did capacity checks at 200, 400, 800, 1600, 3200 cycles, 3200 cycles being intervals between which we did reconditionings.

We have done some seven reconditionings since we started this test and a total of 13,800 cycles completed refers to 13,800 cycles after we completed the initial test at 29,900.

We have done the most recent reconditioning at 13,210 cycles and the test is continuing at this point.

(Figure 2-56)

This is a profile of a reconditioning discharge. You can see the initial discharge at 18 amperes until we get to 0.9 of one volt and then we back off to three amps. We take it on down to the clamp voltage at three amps and you can see at this point as we clamp it the current starts to taper off.

In this particular case which was following 13,210 cycles, the final discharge current was one milliampere.

I won't bore you with all tnese discharge curves. This is just for the most recent sequence, 13,210 cycles. They show the typical shape. By the way, I did two reconditionings here back to back. I was hoping to possibly get some additional capacity recovery but it didn't work out at the same capacity since they both timed. And you can see the development of the second plateau with the recession from the first plateau moving back as we get more and more cycles.

(Figures 2-57 and 2-58)

This is the last cycle then before the reconditioning.

(Figure 2-59)

These are plots of all the reconditioning cycles we have done so far starting at zero cycles. Here is where we started out. We were about 22.4 ampere-hours at the end of the 29,800 cycles at ten percent DOD. And I might mention that during those 29,800 cycles we did not do any capacity discharge deliberately. We did a couple of them, I think, because we had laboratory problems.

Then we did the initial reconditioning and immediately after reconditioning, we got some 26 ampere hours. That was the first cycle after the reconditioning procedure. Then, as we put 200 cycles on for our first check on capacity and we always saw an increase in capacity. The point there at 400 cycles, I happened to be talking with Lanier at Marshall and I mentioned our results and comparing them with the results that he had seen on their batteries. And they had gotten a recovery of capacity very nearly what hhe initial capacity was.

We hadn't been quite that lucky. The initial capacity on these batteries on this particular cell was about 41 ampere hours. So I decided to do another reconditioning at 400 cycles. And that gave me a little improvement, but not a whole lot. And then you can see the decay, and of course, as we go on, it appears that we are losing capacity with increased cycling although we see a recovery each time we go through the reconditioning procedure.

(Figure 2-60)

This is just another plot of that same data. Here I plotted it as a function of Delta cycle since the last reconditioning, so that you can see how the capacity is decayed. Now these were fit to a curve of the form Y equals AX to the B. That is all I have to say about reconditioning per se.

The next subject is something that we have seen during running these tests. I apologize for a very busy chart.

(Figure 2-61)

But I wanted to show you what is happening here over a very long period of time. I have plotted on here end of charge voltage which are the circles; end of discharge voltage are triangles; and the ampere hour return factor which are squares. Down at the bottom I have indicated when we did capacity checks and when we did reconditioning, it explains somewhat the improvement at the end of discharge voltage.

Now, there are a number of cases that we noticed that our cell did not get back to the 1.5 volt cutoff. We had a tolerance band 15 millivolts wide on that. It occurred first. It was here when I first noticed it. Later on, I noticed that actually it happened on the first cycle. But it occurred here. Then we had a recovery. It occurred again and repeated for some time. And as you can see, it occurs again randomly throughout this history.

We don't seem to see any particular correlation within the end of discharge voltage or battery capacity to deliver during the capacity check related to this particular phenomenon.

When I first noticed it back in this area, around cycle 900, it appeared very much like a high impedance short. Just to check on that somewhat, we charged it up on cycle 930, and then we just let it sit for a day to see what happened. As you would expect, the battery capacity or the voltage decayed. However, after about 24 hours, it was fairly stable. It was decaying at this point at one half a millivolt per hour. So we put it back on cycling.

And the cycles immediately prior to this time and the cycles after that, in fact, for a period of about 1000 cycles failed to reach the voltage limit. Voltage got as low as about 1.37 volts during charge. This is a typical cycle. We discharged 35 minutes at 6 amperes and then we charged for 25 minutes at 10 amperes or until we reached the voltage cutoff.

(Figure 2-62)

Now these are essentially normal cycles and you can see that each of them reach a voltage cutoff. The cycle at 13,256 has a much higher end of discharge voltage because it immediately after the reconditioning at cycle 13,210.

Now, compare that with some more cycles.

(Figure 2-63)

Here we have one cycle where it failed to reach voltage cutoff. And it is right between two cycles that did. The dash line, cycle 13,379, it did not reach voltage cutoff; however, it did at the cycle immediately prior to that that we have data for 13,329, and the one after it, 13,539.

(Figure 2-64)

These are the capacity cycles that we have done since the most recent reconditioning at 13,210 cycles and then they are repeating the same kind of characteristics. However, on the recharge, immediately prior to cycle 13,400 after we did a capacity check, they were charging along and everything was looking great and all of a sudden, the battery voltage started to decay, or the cell voltage rather started to decay. We have a criteria that we charge until we reach the voltage limit or until we have returned 120 percent of the ampere hours removed during the previous discharge.

At this point the voltage started to decay and here the laboratory shut the cell down because we had returned 120 percent. We at that point were down to 1.367 volts per cell.

Well, since that time, it wandered around for roughly two weeks and we did have another return to the voltage limit. And now, I understand again, that it is failing to reach the voltage limit. It is something that I really can't understand, but the cell continues to perform.

## DISCUSSION

ARMANTROUT: I don't know if Lee Miller is here to defend himself, or not, but probably what is happening is if you can do a failure analysis of your plates, they are probably expanding and shorting and your loss of capacity is probably related to the electrolyte being tied up in the plates or squeezed out of the separator or something like that.

MUELLER: You mean the gradual decay in the capacity?

ARMANTROUT: Yes, and if you do a failure analysis and compare the thickness of the plates to what they were in the beginning, I think that you will find that that is what your problem is.

MUELLER: Well, frankly, I hate to interrupt the test now. It is very interesting.

HENDEE: Don't interrupt it. I got a couple of cells in my lab going on and doing the same thing. One of them, I just very simply put it down to shorting on charge. It gets up to a certain charge and I have seen the one cell that is a real time simulation of a synchronous orbit, but one cell has been on open circuit storage for the duration of test which is now past six years. It goes up and it kind of quite nicely just clamps. And it won't go. It is sitting now, I think on zero over ten charge return at, it is around room temperature at that point. It is clamping out at about 1.39, I believe is the last value. This clamp value is going down very, very slowly. Obviously, the capacity is going to go out because you are not putting it all in. You are just limiting. They are getting to the point where your cell voltage is matching the internal resistance within the cell which is just matching so you are putting in as much as you are dumping.

I've got another cell which has been on slow charge. It was sort of a contingency test that what happens type of test. It is showing about once or twice a day. It is on as I say a slow charge storage mode. It shouldn't be on show charge. It should be on trickle charge, but the particular space craft that we have this test dedicated to has no trickle charge. So it goes along twice a day about average depending upon the recovery. You can see about an hour a very significant depression of the voltage, a very very sharp and then a drop down and it steadies back out. This will happen a couple or three times a day.

But let it run. Actually, we have not seen that much of a degradation in the capacity.

MUELLER: It is decaying gracefully, but I don't see any sharp decreases in capacity and it seems to be perfectly random if you make a plot of end of charge voltage, why, it may drift down for a few days and then come back up and then finally it will hit the voltage limit again and it will work that way for maybe 1000 cycles, before it repeats it.

HENDEE: That is precisely what we see as far as the on charge voltage goes. It is totally random up, down, all over for the one cell. And for the other one you will see it coming in twice a day or so.

NAPOLI: I am going to be showing some data tomorrow which shows the capacity that we measure after reconditioning after six eclipses. Actually, we have done six reconditionings down to 0.01 volts per cell. And we have measured that against the capacity checks that we took at the beginning. When I say capacity checks I am talking about capacity down to 0.01. And there is an immeasurable difference in the six reconditioning periods.

MUELLER: And how many cycles are we talking about?

NAPOLI: It's a synchronous satellite, so you figure 140 cycles a year.

MUELLER: I see.

LACKNER: I would like to ask what your charge rate is.

MUELLER: It is ten amperes.

LACKNER: With C/3?

MUELLER: Roughly, yes. The cell is rated at 36 ampere hours. Actually, it measures at about 41.

LACKNER: Do you have any way of increasing the charge rate?

MUELLER: Oh, yes, very simply if we wanted to. We haven't changed them.

LACKNER: To increase the charge rate you should be able to drive the voltage back up to your 1.50 if you wanted it there. If you lower the charge rate, it would drop below that.

MUELLER: Yes, well normally, it will cut off between 1 and 3 minutes before the end of the cycle. What we do is if it does reach voltage cutoff we just open circuit the cell where the balance is simulated during the daylight period.

So when the cell is hitting voltage limit with a room temperature condition of 0.75 plus or minus 5 degrees out, we see a return factor that ranges anywhere from about 1.05 to 1.10. Of course, as soon as the thing fails to reach voltage limit, then we charge for the entire daylight period and the return factor goes up to 1.2. Now, it can go along like that for some time and then it will recover for no apparent reason.

LACKNER: Well, I think as the cells age they get a cell discharge characteristic in them which requires a longer time to recharge because you are not only putting the capacity back that you took out, plus you have to put back in the capacity the cell discharge took out. That is why you may be up to 120 percent. But I think if you charge at a little higher rate you might get a little more efficient charge and it would get you up to your 1.50.

NAPOLI: I would like to make a correction to that last statement I made regarding the number of cycles. It is 88 cycles a year.

MUELLER: Which amounts to 2 years in synchronous orbit?

NAPOLI: Well, it is about two and a half. Yes, two and a half years, now.

HENDEE: Effectively, you have a 1.15-ohm short in your cell. It is nothing other than that and it is bouncing around at its variable. Sometimes it is above it and you are able to reach your 1.5. I would suggest that if you took a look at your charge curve, sometimes you will see it peaking out later than you think it should be. And it is just apparently wandering around the 1.15-ohm level in its variable.

## SINGLE CELL RECONDITIONING TEST

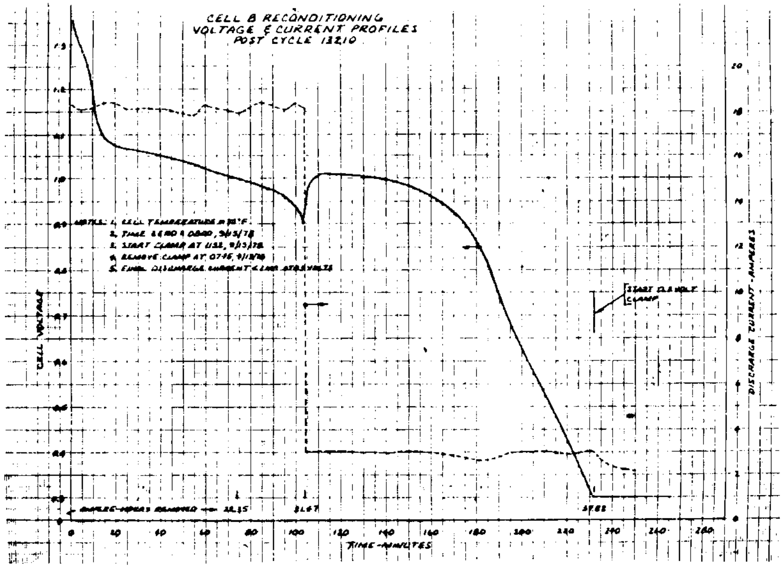
TEST SPECIMEN: EAGLE-PICHER RSN-35 NICKEL-CADMIUM CELL

PRIOR HISTORY: 29837 CHARGE/DISCHARGE CYCLES AT 10% DOD AND 75°F

TEST PROCEDURE:
- o RECONDITION BY DISCHARGE TO 0.300 ±0.050 VOLTS. CLAMP TERMINAL VOLTAGE FOR 3 DAYS MINIMUM OR UNTIL DISCHARGE CURRENT IS LESS THAN 5 MILLIAMPS
- o RECHARGE TO 1.500 $^{+0}_{-0.15}$ VOLT CUTOFF
- o CYCLE AT 10% DOD AND 75°F
- o PERIODICALLY CHECK CAPACITY BY DISCHARGE AT 18 AMPS TO 1.0 VOLTS

TEST STATUS:
- o TOTAL OF 13800 CYCLES COMPLETED
- o MOST RECENT RECONDITIONING AT 13210 CYCLES
- o TEST IS CONTINUING

Figure 2-54



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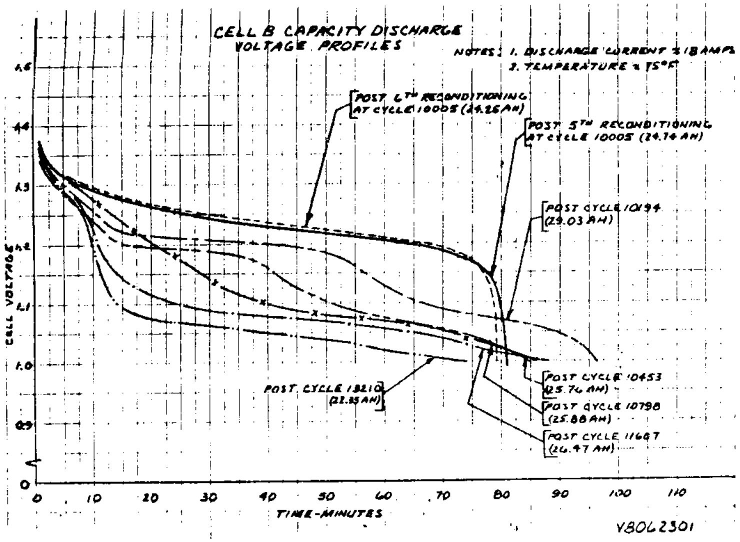

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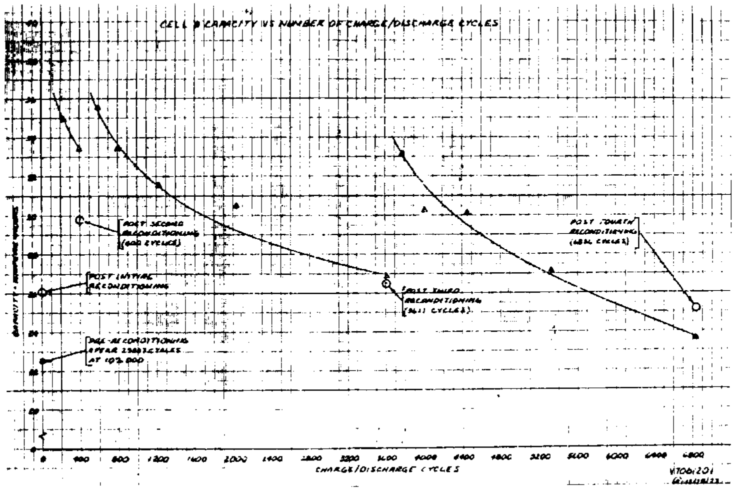

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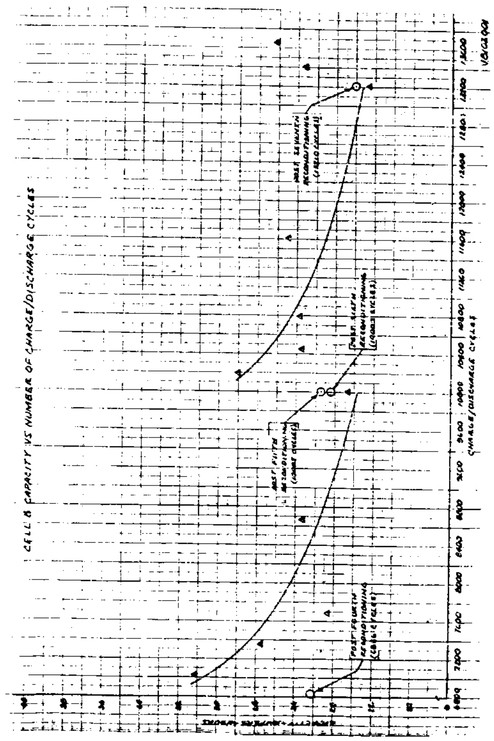

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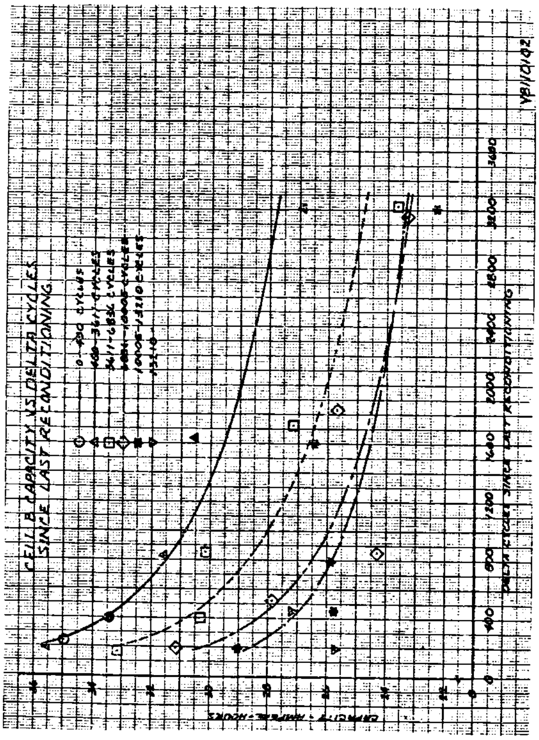

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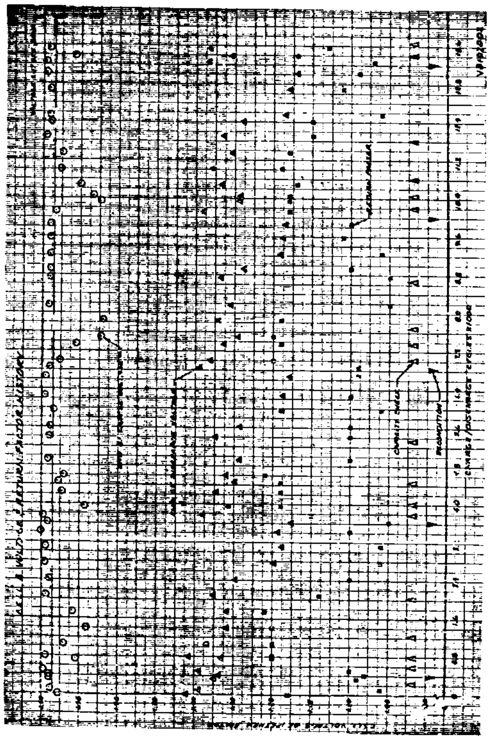

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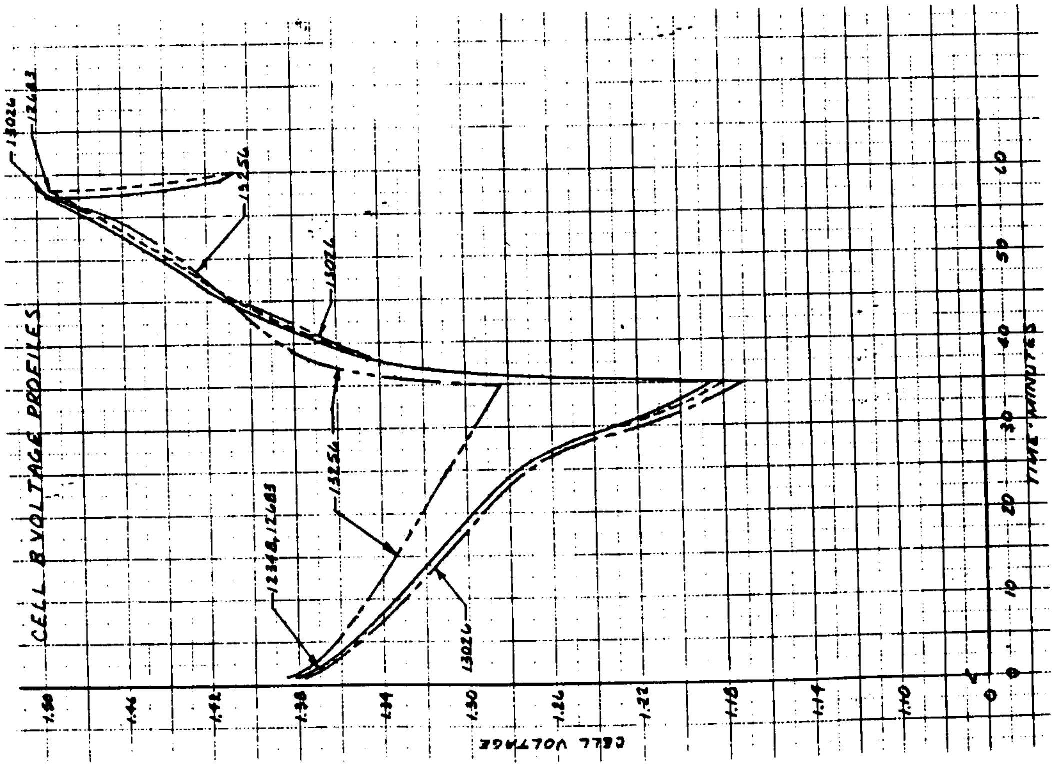

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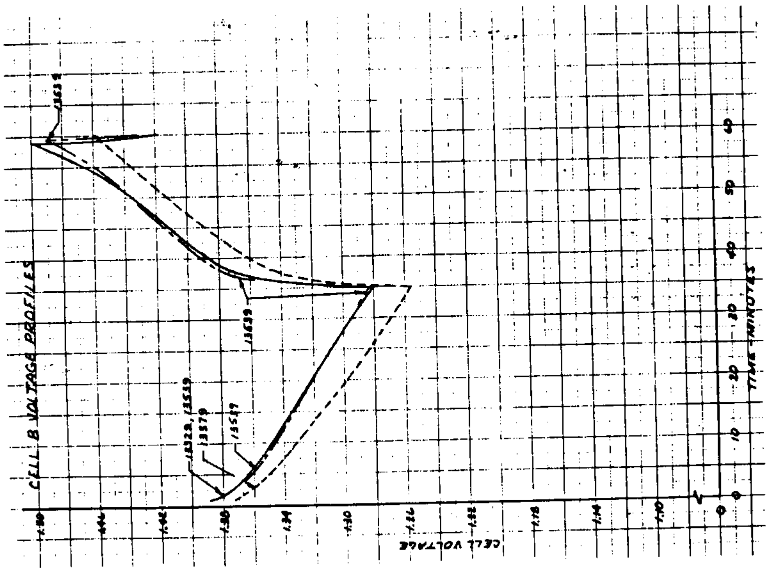

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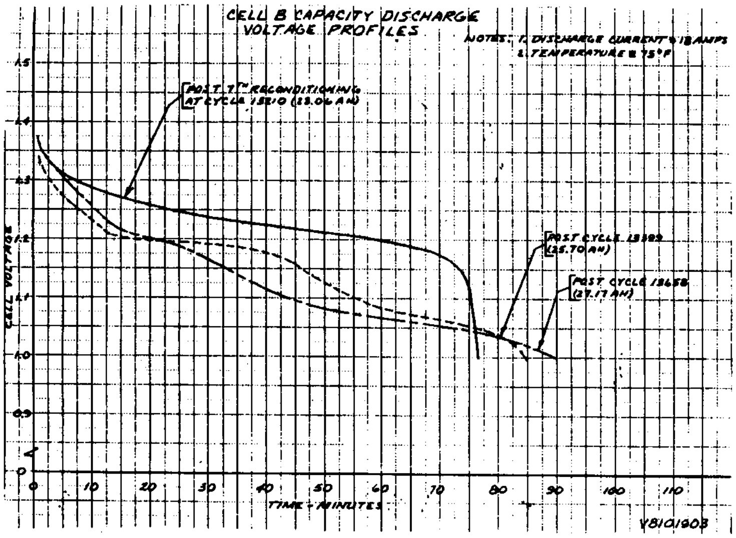


Figure 2-63

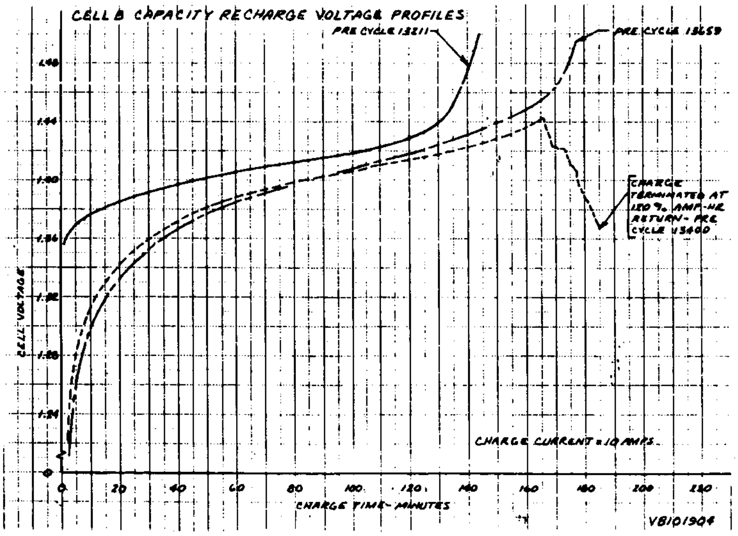


Figure 2-64

# HIGH RATE OF REVERSAL OF NiCd CELLS

H. Killian
Aerospace Corporation

I am going to tell you about some testing we did on three cells at Aerospace. A lot of people in the audience have heard this at least once, but for the benefit of the few of you that haven't I will present it here.

We did this testing as a result of a problem that the Air Force was having on a satellite. This satellite had been in space for about a year in a 12-hour orbit and suddenly battery number 3 underwent a temperature excursion and when the dust settled, it was about one cell low in voltage both on charge and discharge. Not too long after that the other two batteries started evidencing sick cells as illustrated in this curve here.

(Figure 2-65)

You can see that it was that the cells were dropping out as the batteries discharged. It became evident that some of the high-resistance shorting that you are talking about was occurring in the number 1 and 2 batteries there in some of the cells and that these cells were experiencing rather rapid stand loss, so as you discharge them, instead of getting the full capacity out through the load, you are getting a lot of this stand loss and a very small amount out through the load.

So the question becomes, what happens in your eclipse orbit when you discharge past the capacities of these weak cells and you will drive them into reversal and negative voltage and you will get hydrogen generation and perhaps rupture of the cells. This is just illustrating the standard equation.

(Figure 2-66)

When you run out of capacity on your positive plate and the positive limit of cells, the charge transfer has to occur by the generation of hydrogen and the release of the OH radical. And, of course, by Faraday's law and so forth you predict pressure rise versus time as shown here.

(Figure 2-67)

However, some people said that perhaps the pressure will not ramp up like this, that they had seen in older cells that the pressure plateaued out and that although these cells weren't very old, because they looked like old cells with this internal shorting, that perhaps the pressure had plateaued out.

So then we initiated this test program to determine what the pressure response characteristic would be of cells as a function of their age. And these were 10 ampere-hour cells. They had polypropylene separators. We got one that was two and a half years old with polypropylene identical to the flight cells—one 5 years old with polypropylene, again identical. We had none older than that which had polypropylene. However, there was an 8-year old cell which was identical in every respect except for the separator. And it had slightly more electrolyte, I guess. Just a little more electrolyte. It was basically very similar.

The temperatures in the satellite were running around room temperature, so that was the way we did the tests. The discharge rates, the lows, were being controlled to 1 to 2 amps, so we carried that parameter there.

A couple of points about the procedure which we did, an initial and final characterization. And then you see that later it was important that we did charge these cells after every reversal test. Of course, in orbit after every eclipse discharge, there is charging of the battery and any cell that did get reversed would get subsequently recharged, and we duplicated that in our tests.

(Figure 2-68)

This is a simple schematic of the test setup. We could discharge at the cell through a resistor to short circuit it or could force-discharge it.

(Figure 2-69)

Here is a typical cell in its test configuration. The pressure gauge was installed at the factory. The cell was compressed between a couple of aluminum blocks to prevent bulging of the sides and to help stabilize temperatures. Right in there, we had a temperature monitor that is kind of a conductive glop that was at the end of the thermocouple. The thermocouple is not shown in this picture, obviously.

What were the results ?

(Figure 2-70)

This shows pressure in the cell in the two and a half year old cell which is timed under various reverse current levels. First, we did the one and a half amp reverse current and the pressure kind of ramped right on up. It would always stop at 100 psi in every case. We didn't go higher than that. I'm sorry, we did the one amp case first and allowed the pressure to decay back down to starting point practically and then did the one and a half amp.

I have shown the theoretical based on that prior equation I showed just for comparison purposes, and we find that the slope here is very close to the slope there with about a slight delay due to any number of possible reasons.

(Figure 2-71)

Here is the data on the five year old cell, pressurized versus time. We did the one amp test first and what do you know, we got the plateau that people thought we might. We allowed the pressure to decay and did the one and a half amp level and I think you would expect that it might be a higher plateau and we got this. So it wasn't very consistent.

Much later on, we did the two amp test, and that kind of fell back into how you might think the things would go.

(Figure 2-72)

Okay, here are data on the eight year old cell. Again there is pressure versus time. We did the one amp test first and there was a nice low plateau with hardly any pressure rise at all. Okay, remember this is a C/10 rate. Allowing the pressure to decay, we then did the two amp reverse and got a much higher pressure plateau. And we decided at this point that there was an obvious question: in a twelve orbit, you don't have much time for the pressure to decay, and will the pressure keep ramping on up or, the next time you reverse it, will the pressure stabilize at this plateau level? So right here we investigated that question without allowing the pressure to decay below this point. We again hit with two amps and it went on up higher. We did it again, and it started out higher. So whatever is going on in the cells, it is not very pressure sensitive.

I am illustrating the same thing in this chart here.

(Figure 2-73)

Which shows pressure in that same eight year old cell versus time, how the one amp reverse allowed it to decay. We hit it with two amps and so forth and so on. You can see the pressures in succeeding orbits will just keep on going and perhaps up to rupture levels.

(Figure 2-74)

I am going to show this same data now plotted a little differently, pressure rise versus time. And here we see the correlation between age at the one amp reverse level. And there is a pretty nice correlation that would appear. The older it got the lower the pressure rise was.

(Figure 2-75)

Similarly for the two amp reverse current levels—in this case, the eight year old cell—this was just the initial pressure rise and plateau. The questions came up: well, what about reconditioning? If we reconditioned these batteries as we might like to do to help some of the healthier cells, are we going to hurt these weak cells ?

(Figure 2-76)

And so we tried the reconditioning. It is reversing at reconditioning levels of 150 milliamps onto the cells and in the youngest cell it looked like it was not going to get very high and, of course, in the medium age cell, it was negligible. And we didn't do the eight year old cell. So it doesn't look like there was going to be too much problem with reconditioning—that is, reversing at reconditioning current levels.

(Figure 2-77)

We kept of all the pressure decayed data and they are all shown here. The interesting thing about it is that they were clearly separated by whether or not it was Nylon or polypropylene. All the data from all the pressure decays are shown in here. I guess the main message of this chart is that the pressure decay rates, as you undoubtedly realize, are slow and that you could not hope for any significant pressure decay in a period of 12 hours or even longer than that—that is, even 24 hours.

(Figure 2-78)

This shows the initial and final characterization discharges on the two and a half year old cell and this is probably the worst in terms of similarity. And you can see that we got out 14 ampere-hours after all of this reversing compared to the initial 13.4 ampere-hours before the reversing.

You can see that it is kind of a lousy cell, anyway, based on those voltages. And it was still a lousy cell when we finished.

It was a highly degraded cell, I guess is how you would put it. Okay, what was going on to cause all this plateauing? I called up Guy Rampel down at GE in Gainesville and talked it over with him and what I have shown here is basically what he suggested as the mechanism that was taking place during this plateauing process.

(Figure 2-79)

It is fairly accepted, I guess, that in an older NiCd cell there is a lot of cadmium migration into the separator in the form of cadmium hydroxide, which is nonconductive. So the mechanism is then that when we run out of positive plate capacity and start generating hydrogen, we simultaneously somehow have electronic contact with that cadmium hydroxide and start converting it to cadmium. As this conversion process takes, in this direction, shorting paths are eventually established between the plates, and those shorting paths are the current that is the charge transfer paths. And this reaction no longer takes place, the pressure plateaus, etc.

When you recharge as I did in every case, that whole shorting path is destroyed again as the cadmium hydroxide basically is reestablished as you are discharging the short path. And now I would like to say that this mechanism describes everything that we saw. And whether it is true or not, it is hard to imagine what could be going on in there if there were not some direct short path. And in two amps of reversal and no pressure rise from hydrogen, there has to be something like this going on. I think this is probably what it was and what it is.

I know that at TRW Paul Ritterman has postulated recombination reactions for the hydrogen, but I don't think that the rates involved there could possibly explain what we are seeing here. Plus the fact that the reactions that he described I would imagine would still be active after you stopped the reversal and, of course, we see that the decay (pressure decay) is very slow after the reversal and this stops. So I don't think that could explain what we saw.

Okay, then, what are the conclusions that we arrived at? We saw that pressure rise during high rate of reversal was rate-dependent, age-dependent, and not very consistent.

(Figure 2-80)

We concluded that these repeated cyclings (charge, discharge reversal) can cause excessive pressure buildup, that we have a shorting mechanism which may explain the plateauing, but we found, whether that is significant or not, that the reversal did not show any impact that we could see on this cell performance.

As far as the program office was concerned we recommended that we void any cell reversal, but if they wanted to go ahead and recondition the batteries, we didn't think that it would hurt the cells, the weak cells.

## DISCUSSION

BAER: I have one question. These older cells: were these on cycling or were they in storage? What is the background on the older cells?

KILLIAN: On the two and a half and five year old cells, I haven't data at all on what happened to them during their storage or during those periods of time. All I can say is that they were at room temperature at all times, by policy, since they were never going to be flight cells and they were not stored cold. Other than that, I just don't know what was happening to them during that time.

In the case of the eight year old cell, I do have a history on that. It did undergo several cycling tests, but nothing extensive in terms of cycling. I just told you all I know and that isn't very much about the history on these cells.

BAER: So in other words these cells weren't all that old.

KILLIAN: Chronologically, yes, but cycle, no, as far as I know.

ELIASON: I have seen the same thing that you have been talking about, especially on the older cells. My proposed mechanism on that was that you were getting oxygen evolution of the cad-electrode even in reversal, even though you do have some cadmium left. This would give you an oxygen-hydrogen combination producing water, which would account for your low gas pressure on your older cell.

KILLIAN: That sounds possible. I am not sure whether it would need some kind of a catalytic service and all that?

ELIASON: Yes, well, your nickel or your cadmium, either one, would readily combine your --

KILLIAN: Support that reaction?

ELIASON: Yes.

KILLIAN: Very well.

GROSS: Your last conclusion was that a reconditioning is acceptable. That would be valid only if, only based on pressure curves, theoretical pressure curves as a function of time rather than the experimental because of the possibility of shorts. But you cannot always depend on that short and so you have to assume that the short is not there to get a worse case.

KILLIAN: At the reconditioning the discharge rates involved it is not clear whether shorting was occurring or not, whether those short paths were being built up. Ritterman did take these data, compare them to similar data on his part, and compare them to his theoretical hydrogen recombination mechanism and so forth and there was a good comparison. So I don't know if he thinks that perhaps the recombination mechanism is operative up to certain levels beyond which this gets established.

I think the only intent of my conclusion was that the pressure rise might be limited, and you might even be hurting the cell in some way, but the pressure would not be sufficient to rupture it, and I am not sure whether that is based upon any shorting mechanism in there, necessarily.

ROGERS: If you did have a hydrogen-oxygen recombination, you would find that it would be pressure-dependent, and apparently you didn't see that so I think you could rule that out.

LACKNER: I found the paper quite interesting because the tests we did showed that for an older cycled cell you wouldn't get the pressure buildup. Now, I don't think that it is a question of age. It is a question of the type of deterioration that you would have in the battery which comes from cycling. And it is a question of the cycling degrading the battery and tending to form a soft short. And if it is sufficiently degraded, the likelihood of building up pressure was slight, and I think last year what I showed was that there were two cells made of the identical same lot. One has been cycling for over two years and one had been stored at zero, shorted, and then reactivated. The pressure buildups on the reactivated cell that was 28 months old certainly did follow the pressure rise. So age didn't affect it. It was a viable cell. In fact, it had more than its rate of capacity.

The aged, the cycled cells which were the same chronological age, but had been cycled, and exhibited signs of soft short, did not build up an appreciable pressure. I think it was about 25 psi. So I think it is not the chronological age. It is the condition that they are in.

KILLIAN: Yes, your --

LACKNER: Did you characterize the cells at all?

KILLIAN: Yes, well, you are absolutely right. I think that the mechanism implies that because the more cadmium hydroxide or cadmium migration you have into the separator the sooner you would expect the short to develop during reversal, so that however you get cadmium migration, whether that is through age or cycling or whatever, temperature or what, that would cause this to happen rather than just strict chronology.

LACKNER: I think that you pointed out by your capacity that you got out of the cell that you certainly have a reasonable cell.

KILLIAN: Well, it had reasonable capacity, but boy, the voltages—you know, I couldn't charge it higher than about a C/10 rate and the voltages were very low during discharge, so I guess maybe it could have been reconditioned into good shape, but it was a pretty high impedance cell, I guess you would say.

## BACKGROUND

### In-Flight Experience

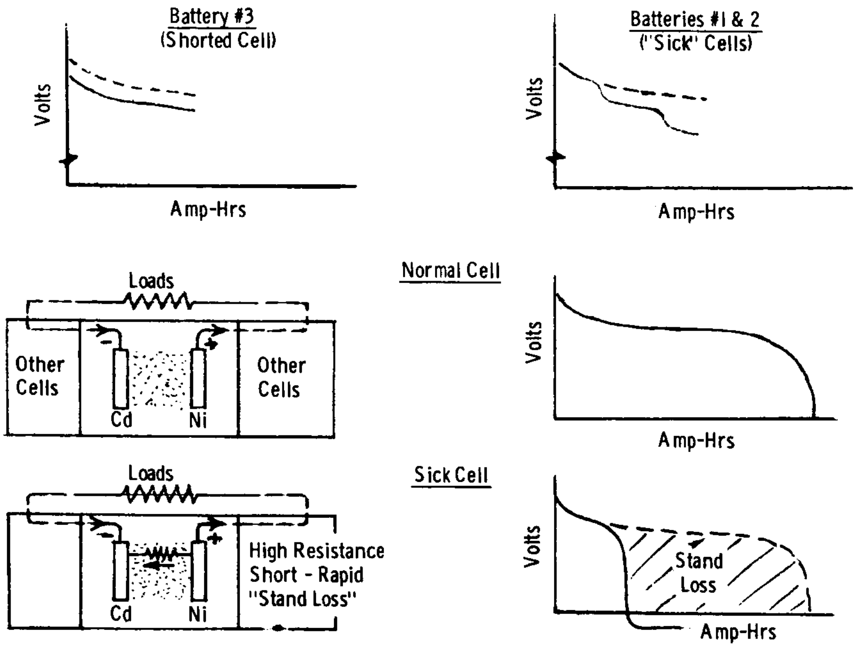


Figure 2-65

## HYDROGEN GENERATION DURING REVERSAL

At Nickel Electrode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH$

At Cadmium Electrode
With Cadmium (Precharge) Remaining: $Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$

With Negligible Recombination:

$$\text{Pressure Rise (psi)} = \frac{0.81 \times \text{Current (Amps)} \times \text{Time (min.)}}{\text{Gas Volume/Cell Volume}}$$

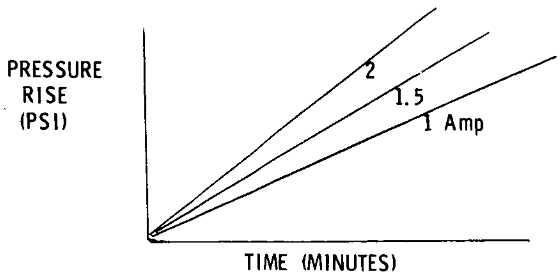


Figure 2-66

## NiCd CELL REVERSAL/PRESSURE TEST

| | |
|---|---|
| OBJECTIVE: | DETERMINE PRESSURE RISE IN NiCd CELLS OF DIFFERENT AGE UNDER VARIOUS CONDITIONS OF CELL REVERSAL. |
| CELLS: | TEN AMP-HOURS<br>(1) 2 1/2 YEARS OLD, POLYPROPYLENE<br>(2) 5 YEARS OLD, POLYPROPYLENE<br>(3) 8 YEARS OLD, NYLON |
| REVERSAL CONDITIONS: | ROOM TEMPERATURE,<br>1 AMP, 1.5 AMPS, 2 AMPS |
| WHEN: | 10 FEB 78 - 20 APRIL 78 |
| PROCEDURE: | INITIAL AND FINAL CHARACTERIZATION DISCHARGES<br>CHARGING AFTER EACH REVERSAL |

Figure 2-67

### TEST SETUP

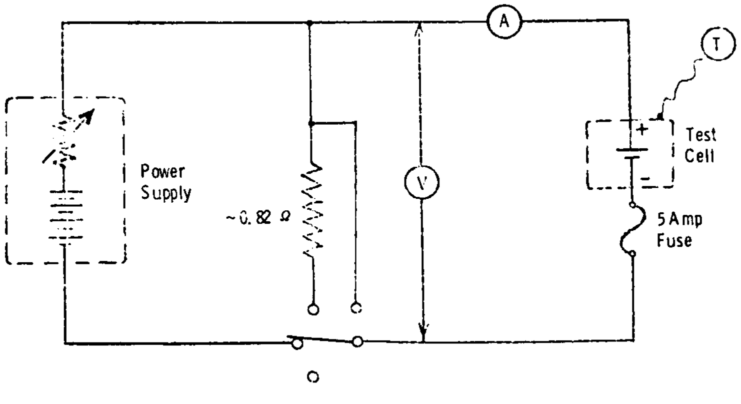
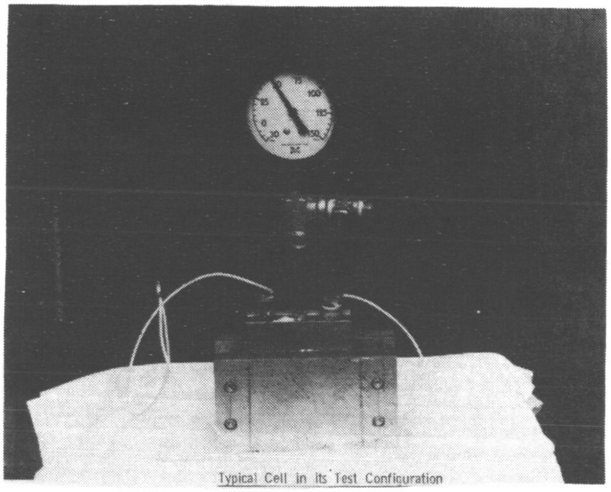
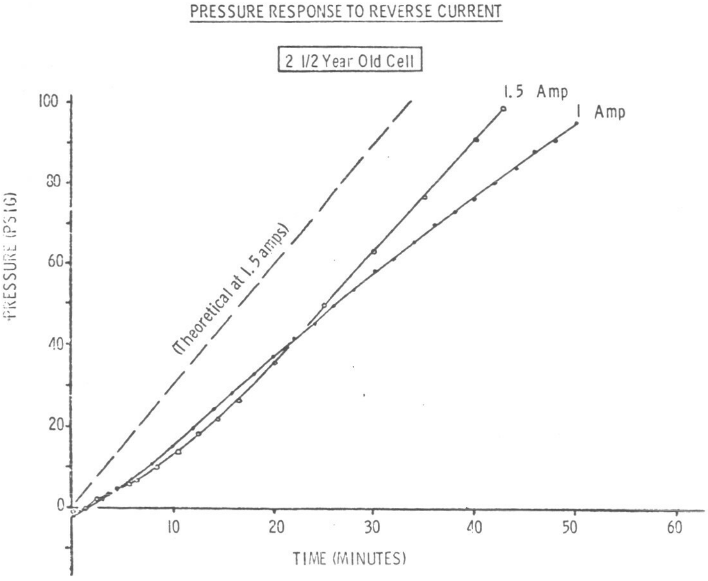


Figure 2-68



Typical Cell in its Test Configuration

Figure 2-69



PRESSURE RESPONSE TO REVERSE CURRENT

2 1/2 Year Old Cell

Figure 2-70

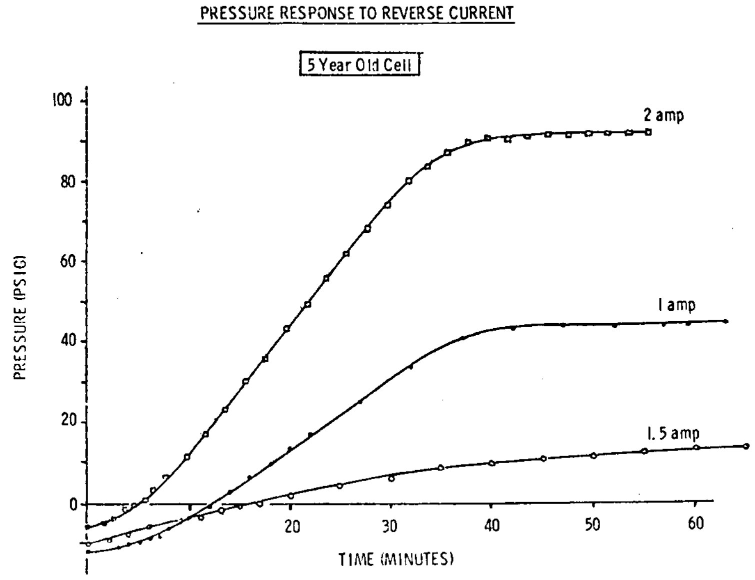


Figure 2-71

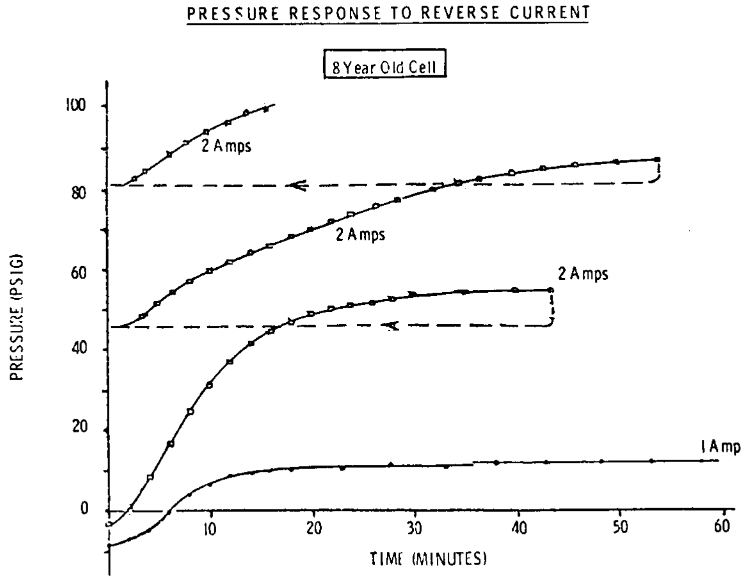


Figure 2-72

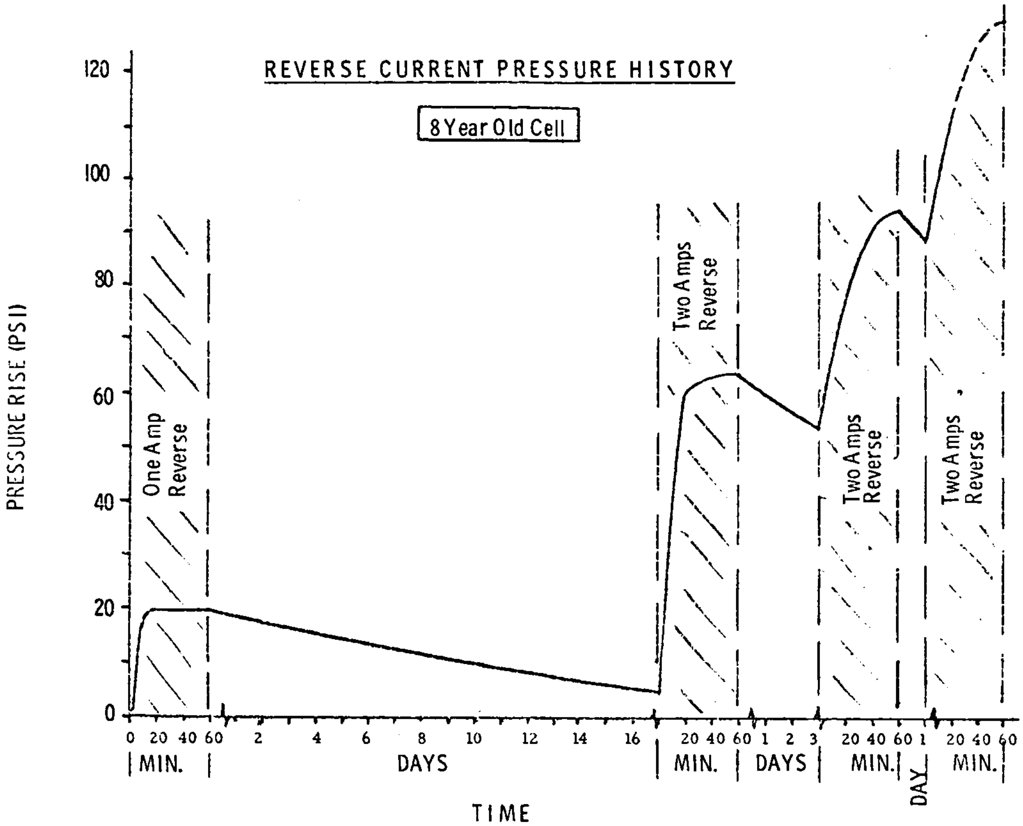


Figure 2-73

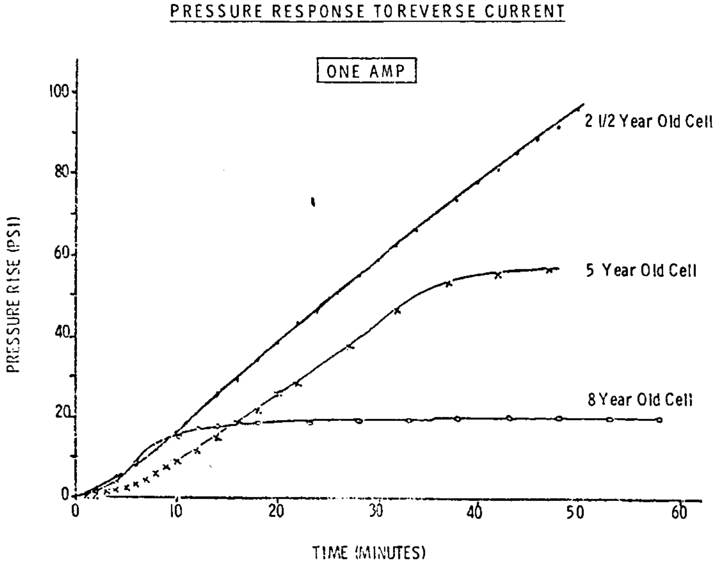


Figure 2-74

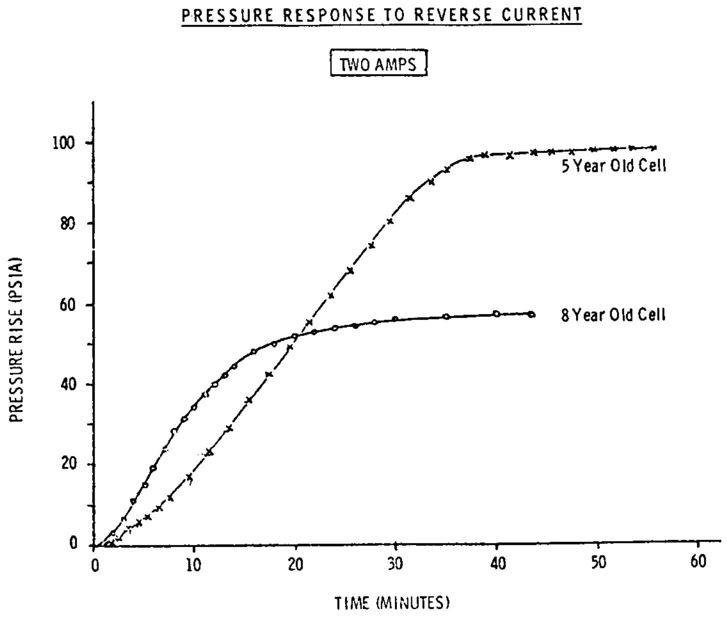


Figure 2-75

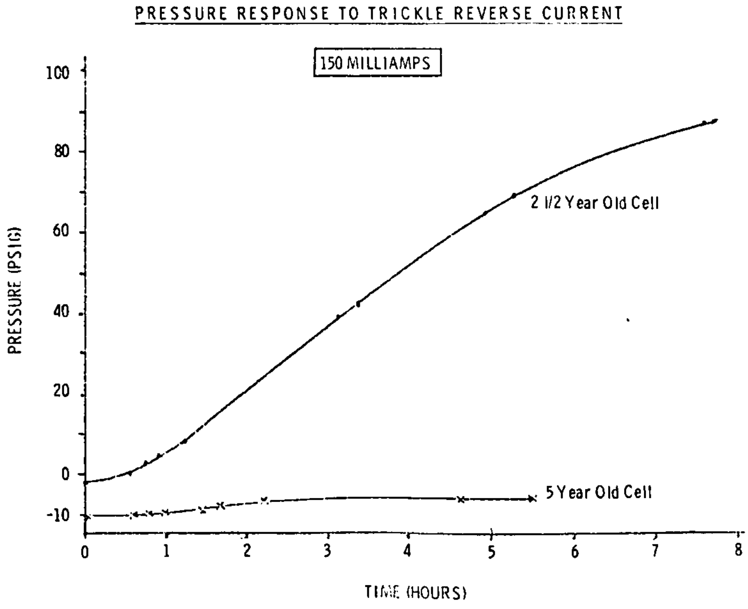


Figure 2-76

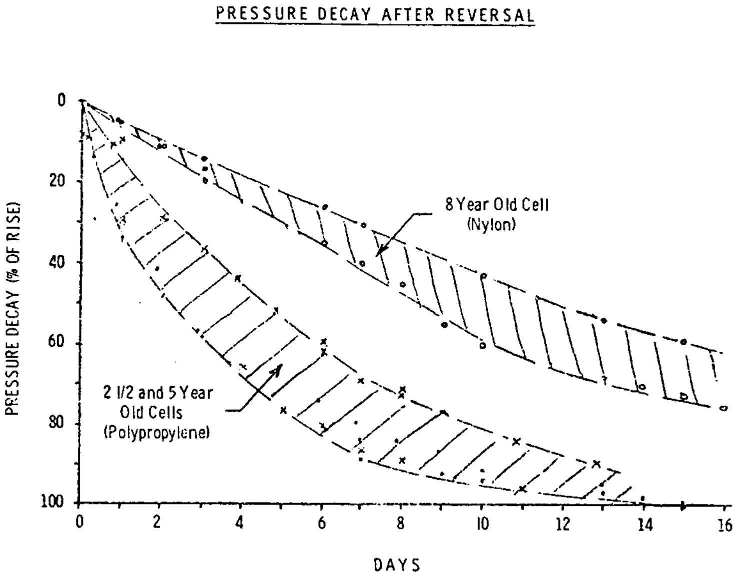


Figure 2-77

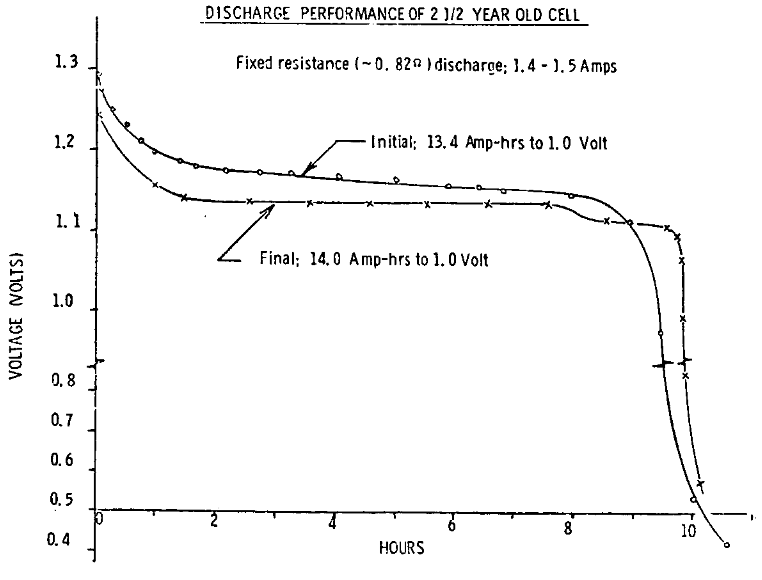


Figure 2-78

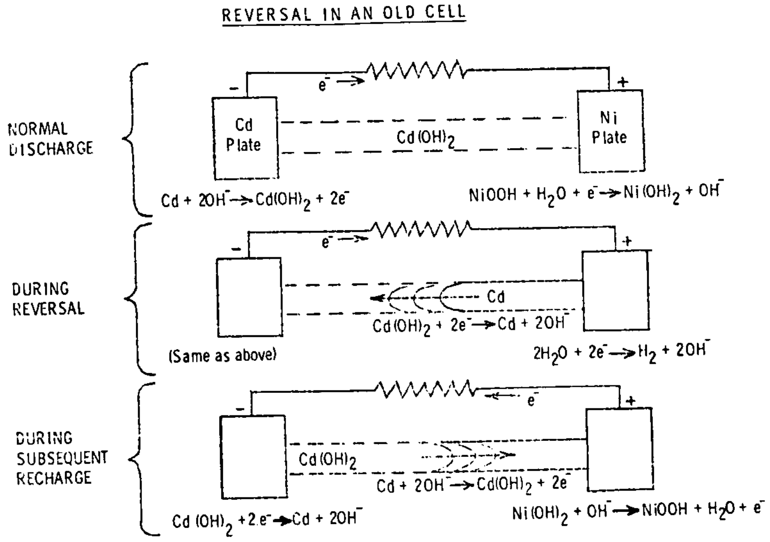


Figure 2-79

## CONCLUSIONS

### TECHNOLOGY

- Cell Pressure Rise During Reversal Was
  - Rate Dependent
  - Age Dependent
  - Inconsistent
- Repeated Charge/Discharge/Reversal Cycles Can Cause Excessive Pressure Buildup
- Internal Shorting Mechanism May Explain Pressure Plateauing During Reversal
- Reversal Did Not Have A Major Impact on Cell Performance

### PROGRAM

- Avoid Repeated Cell Reversal
- Cell Reversal At Reconditioning Rates Should Not Cause Cell Rupture

Figure 2-80

# SESSION III

# NICKEL CADMIUM BATTERY EXPERIENCE

D. Baer, Chairman
Goddard Space Flight Center

# PARALLEL BATTERY TEST RESULTS

C. Palandati
Goddard Space Flight Center

During the next several minutes I will be discussing the effects of disabling and enabling the charger on one of two batteries that are operating in a parallel mode. The test results are a follow-up of some of the data that I presented last year at the Battery Workshop.

(Figure 3-1)

Basically the tests were an engineering evaluation of the Multimission Modular Spacecraft power system. Battery charging is accomplished by one charger with eight commandable voltage versus temperature levels. The battery capacity can range from the standard 20 ampere hour to 50 ampere hour designs. Each battery has 22 cells. The number of batteries that can be handled in parallel could be up to three. The orbital regime is a 100-minute orbital regime, 36-minute shadow, 64-minute sunlight. The nominal depth of discharge is a 25 percent depth of discharge based on rated capacity for each battery.

The particular tests that we were performing used two 12 ampere hour batteries and the tests are actually an isothermal test; there is no requirement as far as the tests are concerned, as far as trying to duplicate the thermal vac situation that takes place in outer space.

(Figure 3-2)

This is a simplified block diagram of how we run the tests. Each battery has a shunt and series with it where we are capable of monitoring the current going in and out of the battery; and therefore, we can actually calculate the ampere hours in and out of the battery.

Each battery has a series diode and in the normal operational requirements, the diodes are shorted. Should you remove a short across either diode, at that point you are actually simulating disabling the charger to that particular battery. Current can only flow out of the battery during the shadow portion. Current cannot flow into the battery during the recharge portion.

We discharged the battery with a power supply, which is a constant current discharge. The current rate for each battery totals ten amps, and the batteries are basically five amps per battery.

(Figure 3-3)

One looks at the overall resistance of the power cables; one is looking at the power cable that comes from the negative terminal post to where we have a junction where the batteries come into parallel. From there and from the positive terminal post to this point, the total resistance is a 77 milliohms for one battery and 76 milliohms for the other battery.

One looks at the actual resistance of the power cable going from the parallel junction back to the power supply. We have a total at that point of 20 milliohms.

Now, last year when I presented data, I gave numbers that came out to be roughly 94 to 95 milliohms per battery. That included the measurements for both batteries. At that point, the measurements always included the same power cable that went to the power supply.

One looks at the internal impedance of the batteries. For these particular cells, we ran a cell acceptance test several years ago, and the data we obtained said that each cell had approximately three milliohms per cell internal impedance. So as far as the 75 are concerned, 66 of that are the internal impedance of the cells; the remaining impedance has to do with the leads that come out from the battery terminal post to the connector.

(Figure 3-4)

What I am showing here is a table that shows where we disabled and then enabled the charger from the "B" battery with the aid of either shorting or unshorting the diode that was in series with that particular battery.

For this particular test, we ran approximately three orbits with the charger disabled from the "B" battery and during minute 38 plus 50 seconds, at that point, we enabled the charger to the battery. Prior to enabling the charger, the total capacity that had been removed from the "B" battery during the shadow periods was a negative 5.34 ampere hours. The "A" battery was similar at that point.

When we enabled the charger, the current went from zero amps (and we are now in a charged mode) to 23 amps. In the next condition, we had the battery again disabled (the charger disabled from the battery), and at the end of the charge mode, at minute 97 plus 50 seconds, we had a condition where the accumulative discharge capacity of the "B" battery was again 5.34 ampere hours; the "A" battery was completely recharged at this point. So basically if one is looking at the state of charge of the two batteries, there is approximately a 5 ampere hour differential between the two batteries.

When we enabled the charger at that point, we saw a 32-amp spike. We also simulated this condition again where we were now in a discharge mode and at this point, one looks at the accumulative discharge capacity of the "B" battery, we were down by again 5 ampere hours. We had approximately 1.9 ampere hours discharge on the "A" battery, so we did have again a differential between the two battery capacities.

When we enabled the charger at this point, the current went from about one-tenth of an amp on the "B" battery to a 1.6 amp spike. Again we performed this test where we are now at the end of the discharge or the end of the shadow period. At that point, if one is looking at the capacity balance between the two batteries, they are fairly similar. At this point, the "B" battery was delivering a negative 2.7 amps prior to enabling the charge. As soon as we enabled the charger, the battery current went to 6.5 amps.

(Figure 3-5)

One of the questions that was brought up was the fact that while we saw a certain impedance that was roughly 76 milliohms to the power cables, plus another 20 to the cycle, the question came about as to actually in the satellite mode, the impedance would probably be a lot less since we are running a test where each battery is sitting in its own temperature chamber where we have quite a bit of space between the two batteries, where in a satellite you don't have this condition.

The question was: what would happen if you lowered the battery cable impedance? So at this point, we did make an attempt to change as best we could to lower the resistance of each battery cable. In this particular case, we changed from roughly 75 milliohms to 10 milliohms, the resistance of the power cables from each battery. We were able to decrease the resistance of the power cables to the charger from roughly 20 milliohms down to 8 milliohms. Then we also at this point performed the same test again to see what type currents we were producing.

(Figure 3-6)

These are the actual sequences that the tests were run at. The first condition we simulated was at the end of the charge. That is 97 minutes and 50 seconds. Prior to enabling the charger, one looks at the ampere hour output of both batteries. We are talking here of 4.1 ampere hours, which is a cumulative ampere hour output for the one battery that does not have the power supply and series with it.

There is a difference between the two capacities. The instant we enabled the charger, we saw a 49-amp spike. When we simulated this condition at approximately 10 minutes into the orbital mode where both batteries at this point are supplying power, the current of the "B" battery was still zero. The "A" battery was supplying all 10 amps. The ampere hours between the two batteries again were different. The instant we enabled the charger, the current for the "B" battery went up to a negative 6 amps. The "A" battery dropped from 10 to 4 amps.

At that point, we simulated a condition where we are basically at the start of a recharge or the sunlight period and at this point, as you can see, we have a differential again between the two batteries' ampere hours. The "B" battery is receiving no current because of the series diode. The moment we enable the charger, 25 amps go into the "B" battery. Since the pouch supply is capable of delivering only 12 amps, it can be assumed that at this point the remaining current is coming from the "A" battery.

We also duplicated the situation again at the end of 34 minutes and 50 seconds, which is towards the end of the charge. If one is looking at the capacity again, we have a capacity of balance between the two batteries. I am sorry, we are in a discharge mode right here. The "B" battery is supplying one and a half amps. The moment we enable the charger (in this case, it is a discharge power supply), the current goes from a -1.5 to 9 amps.

What we did in this last step, we created a condition where we had a severe capacity imbalance between the two batteries. We discharged the "B" battery to a point where we took out the nominal rated capacity of the battery. The "A" battery was completely recharged.

At approximately 20 minutes into the orbital regime, we enabled the charger and at that point we saw the current go from zero amps to 57½ amps.

(Figure 3-7)

This is an actual photograph of the last test condition where we saw the maximum current output of roughly 57½ amps. The zero reference is this particular line here. The divisions are 10 amps per division on the left. The total trace covers 1 milliamp per division. So, as you can see, the actual current spike is taking place in milliseconds and not seconds or several seconds.

(Figure 3-8)

This is an actual comparison plot of what took place in the last condition that we tested to. What you have here is the voltage of the "B" batteries, which is actually an open circuit voltage at this point. The "A" battery is fully recharged and the battery voltage is 31.61 volts, which is a test condition for voltage level five on the actual spacecraft charger.

The current of the "B" battery at this point, since it has a series diode in it, is zero amps. The "A" battery starts off where it starts to take a current, and then the current drops down. Prior to enabling the charger on the "B" battery, the current into the "A" battery was roughly a half amp.

The instant we enabled the battery, as I mentioned, we saw a 57-amps spike into the "B" battery. The data I am showing here takes place with a data system that requires roughly 37 seconds to monitor all data points.

One of the first data points that we looked at is the current into the "A" battery. At this particular point, and this is now 12 seconds after we enable the charger, the current on the "A" battery was 15 amps coming out of the "A" battery.

Since we know that 12 amps also came out of the power supply, one looks at the current for the "B" battery at this particular point; it was 27 amps. When we look at the current going into the "B" battery, this is now 32 seconds later, and what we see here now is only 22 amps, which is due to the time lag between the two data points.

When looking at the battery voltages, it was a very small difference between the two battery voltages that were in parallel. But obviously, if one is looking at current there is a significant difference between the two currents. This is the current for the "B" battery, which had been discharged to 100 percent depth. At the end of 64 minutes, the current going into that battery was 8.54 amps. The current going into the "A" battery, which had been fully charged prior to running this test condition, is roughly seven-tenths of an amp.

(Figure 3-9)

Last year at the battery workshop, I presented a voltage profile of the battery and basically we were at 5000 orbits. This is a plot that takes us out to 7500 orbits. Battery voltages are on the left; the corresponding average cell voltages are on the right. The orbital regime or number of orbits are based on a logarithm output, and we start from ten, 100, 1000, and 5000.

At last year's battery workshop, I mentioned that roughly at 5000 orbits, we were seeing a change in the battery voltage profile; while we had hoped to run a capacity test we felt that we would rather leave the test run in the particular condition it was in. We did run to 7500 orbits, and these are the end of discharge voltages based on a 25 percent depth. This is the battery voltage degrading as time goes along.

(Figure 3-10)

Approximately 100 orbits later, we decided to run a capacity test on both batteries to see what kind of capacity the batteries had in them. Again, as you see, under a normal 36-minute discharge regime, the profile we see is like this, from here to here. With 100 percent depth of discharge, of course, what you are seeing here is now again a significant change in the voltage profile down to 100 percent depth of discharge.

When looking at the ampere hours out of both batteries, we are now seeing approximately 12 ampere hours. Last year when I discussed the results we had obtained up to 5000 ampere hours, we had been seeing roughly 14 to 14½ ampere hours out of each battery. So we have seen a loss in capacity.

Also, if one is looking at how the batteries share their load, at this particular point we don't really know why, but we suddenly saw a slight difference between the two battery voltages here. We are only talking of roughly a tenth of a volt between the two batteries.

One looks at the actual current coming out of the batteries. At this point, there was a significant difference the way the both batteries supply power.

If one looks at the 100 percent depth of discharge, at the end of the discharge, the average cell voltage and the lowest cell in either battery was similar. They were approximately one volt per cell at this point.

(Figure 3-11)

After the discharge (and this was the first time we had ever done this), we reconditioned all cells. By reconditioning, what we did at the end of the discharge was to run a test whereby we placed the 1 ohm resistor across each cell for 16 hours. At that point, we let the batteries sit in an open circuit condition for 4 hours. Then we recharged both batteries in a parallel mode and then ran a discharge to see what the voltage profile would be.

As you can see, it is a voltage profile that is similar to what you expect to see on new cells. Once we reconditioned, we no longer had the various plateau voltages.

The current sharing capability of both batteries was very even during the entire discharge. The recharge prior to this discharge was a recharge where both batteries were being charged at the maximum output of 12 amps from the power supply, 6 amps for battery; and the charge was terminated when 16 ampere hours were put into each battery.

As you can see, the ampere hour output is still down compared to what we had seen fairly early in the test program.

## DISCUSSION

GROSS: Can you tell me approximately how long the switching trends lasted?

PALANDATI: Yes, less than 1 millisecond. Every time we enabled the power supply or charger, in all cases, whether it was in the shadow period or whether it was in the sunlight mode, the current transfers were always less than a second.

GROSS: That scope photo that you showed, however, showed that it did peak up and then dropped down, but it had dropped down to roughly (it seemed to me) around 80 percent of its peak value.

PALANDATI: This is true. Again, when I showed the actual battery profile, which was 20 to 30 seconds later, the battery current, such as going into the "B" battery, is still 20 amps, even though with the initial pulse it was 50 amps at the incident where you enabled the charger.

WERTHEIM: A couple of things: what battery cell was this?

PALANDATI: This was a GE 12-ampere hour cell.

WERTHEIM: Do the cable resistances you show in your diagram include the connections and the shunts?

PALANDATI: Yes, definitely.

WERTHEIM: Finally, I noticed on the very last chart that during the capacity discharge after reconditioning your low cell voltage on battery "A", I believe it was, had a negative value. Is that correct?

PALANDATI: That is correct. In fact, I am sorry, I meant to highlight that. Yes, on the initial discharge after 7500 orbits, all cells were similar, and that is 22 cells in each battery. When we recharged the batteries, at this point we suddenly found when I looked at the discharge, that yes, one cell was negative.

Now let me explain that. When we discharge batteries, we have safety limits. One of the safety limits are a software program where should any cell of the 22 in either battery drop below a half a volt, the test will be terminated. We also have a safety limit that looks at each 11 cells or each half battery output, and should any group of 11 cells (the lower 11 or the upper 11 in either battery) drop below one volt per cell or less than 11 volts, at that point the test will automatically terminate.

The first condition which you saw there was the half battery voltage which terminated the test. The second condition that you saw was where an individual cell voltage definitely dropped below a half a volt and we were scanning the data now every minute. One minute prior to that negative half a volt, that particular cell had approximately a 1 volt output. One minute later, it was down to a negative voltage. That is what terminated the test.

ENGINEERING EVALUATION

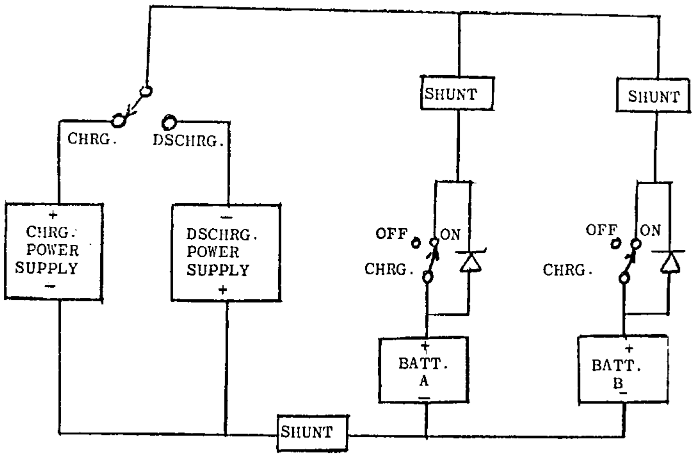
OF

MMS POWER SYSTEM

- o BATTERY CHARGING — ONE CHARGER WITH 8 COMMANDABLE VOLTAGE Vs. TEMPERATURE LEVELS
- o BATTERY CAPACITY — STANDARD 20 Ah or 50 Ah DESIGN
- o NUMBER OF BATTERIES IN PARALLEL — UP TO THREE
- o ORBIT REGIME — 100 MINUTES ( 36 SHADOW, 64 SUNLIGHT)
- o NOMINAL DOD — 25% of RATED CAPACITY

- o TEST USED TWO — 12 Ah BATTERIES FOR SIMULATION (ISOTHERMAL TEST)

Figure 3-1



SIMPLIFIED BLOCK DIAGRAM— POWER SYSTEM EXERCISER

Figure 3-2

BLOCK DIAGRAM OF POWER CABLE RESISTANCE

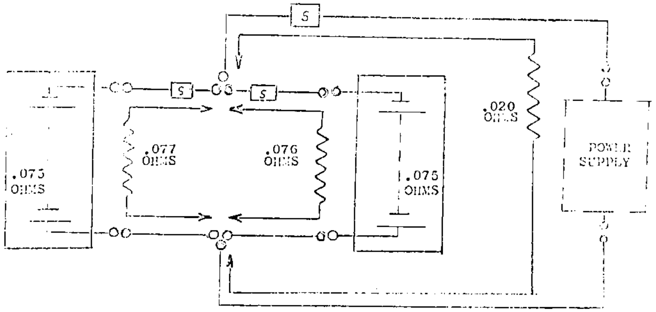


Figure 3-3

EFFECT OF DISABLED/ENABLED CHARGER BUS TO "B" BATTERY (LEVEL 5 + 10°C)

| STATUS OF CHARGER TO BATTERY "B" | BATTERY "B" I (AMPS) | BATTERY "B" A HR (CUMULATIVE) | BATTERY "A" I (AMPS) | BATTERY "A" A HR |
|---|---|---|---|---|
| DISABLED | 0.00 | -5.34 | 12.00 | -5.37 |
| ENABLED (MINUTE 33+50 SECONDS) | 23.00 | | -11.00 * | |
| DISABLED | 0.00 | -5.34 | 0.75 | -0.00 |
| ENABLED (MINUTE 97+50 SECONDS) | 32.00 | | -20.00 * | |
| DISABLED | -0.10 | -5.35 | -9.90 | -0.90 |
| ENABLED (MINUTE 6+50 SECONDS) | -1.60 | | -8.40 * | |
| DISABLED | -2.70 | -5.41 | -7.30 | -5.11 |
| ENABLED (MINUTE 33+50 SECONDS) | -6.50 | | -3.50 * | |

* CALCULATED VALUE I (BATT A)= I (BATT B) − I (CHARGER)

** EACH BATTERIES POWER CABLE = 76 MILLIOHMS

*** POWER CABLE TO CYCLER = 20 MILLIOHMS

Figure 3-4

BLOCK DIAGRAM OF POWER CABLE RESISTANCE

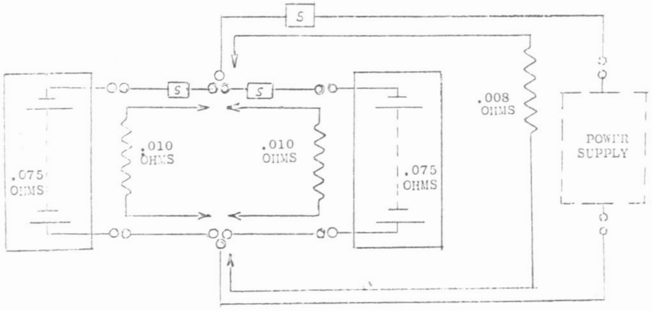


Figure 3-5

EFFECT OF DISABLED/ENABLED CHARGER BUS TO "B" BATTERY (LEVEL 5 @ 10°C)

| STATUS OF CHARGER TO BATTERY "B" | BATTERY "B" |  | BATTERY "A" |  |
|---|---|---|---|---|
|  | I (AMPS) | A HR (CUMMULATIVE) | I (AMPS) | A HR |
| DISABLED | 0.00 | -4.10 | 0.32 | -0.00 |
| ENABLED (MINUTE 97+50 SECONDS) | 49.00 |  | -37.00 * |  |
| DISABLED | 0.00 | -3.50 | -10.00 | -0.50 |
| ENABLED (MINUTE 9+50 SECONDS) | -6.00 |  | - 1.00 * |  |
| DISABLED | 0.00 | -3.70 | 12.00 | -4.70 |
| ENABLED (MINUTE 40+50 SECONDS) | 25.00 |  | -13.00 * |  |
| DISABLED | - 1.50 | -4.40 | - 5.50 | -5.70 |
| ENABLED (MINUTE 34+50 SECONDS) | - 9.00 |  | - 1.00 * |  |
| DISABLED | 0.00 | -12.00 | - 0.57 | -0.00 |
| ENABLED (20+50 SECONDS) | -57.50 |  | -15.50 * |  |

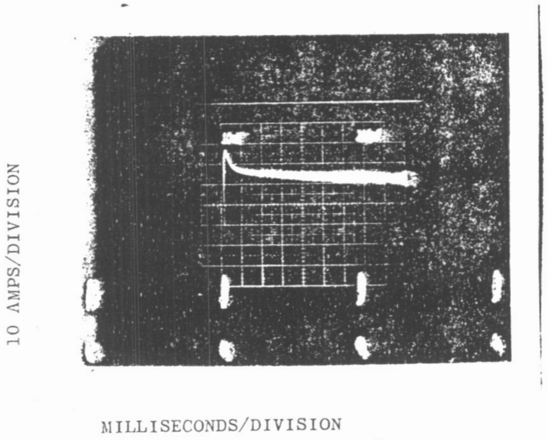
* CALCULATED VALUE I (BATT A) = I (BATT B)- I (CHARGER)

** EACH BATTERIES POWER CABLE = 10 MILLIOHMS

*** POWER CABLE TO CYCLER = 3 MILLIOHMS

Figure 3-6

CHARGER ENABLED TO BATTERY B DURING CHARGE



TIME IN ORBIT- 20 MINUTES + 50 SECONDS

* 0 REFERENCE IS 1 CM FROM THE BOTTOM GRID LINE.

** EACH BATTERY'S POWER CABLE RESISTANCE = 10 MILLIOHMS

*** POWER CABLE TO CYCLER = 8 MILLIOHMS

Figure 3-7

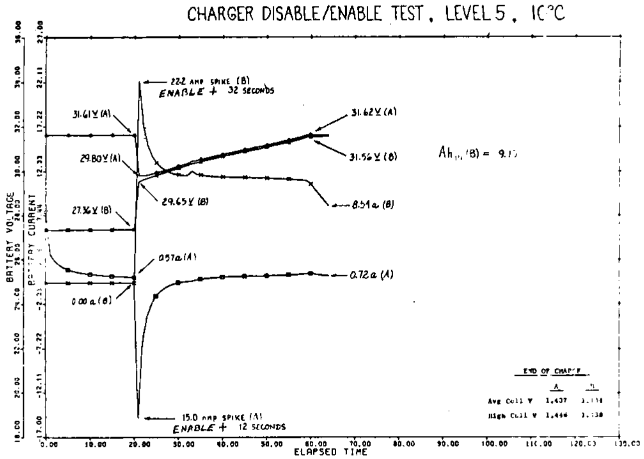


**Figure 3-8**

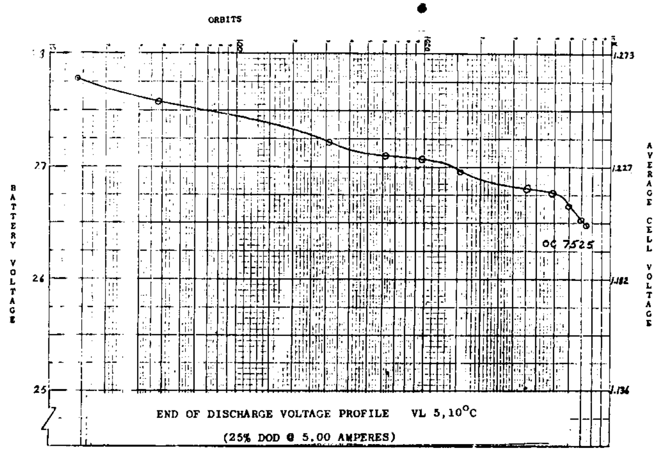


**Figure 3-9**

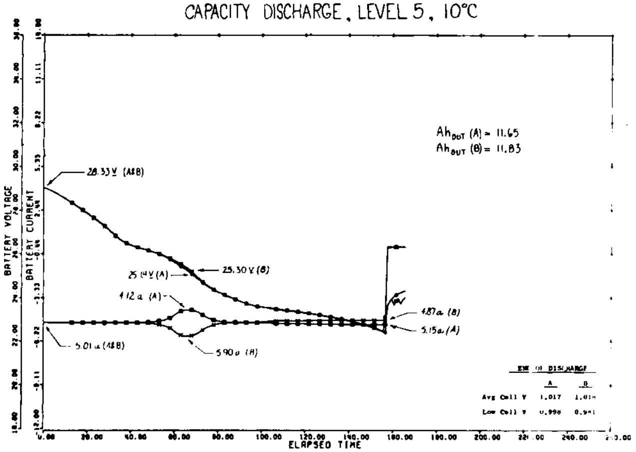


**Figure 3-10**

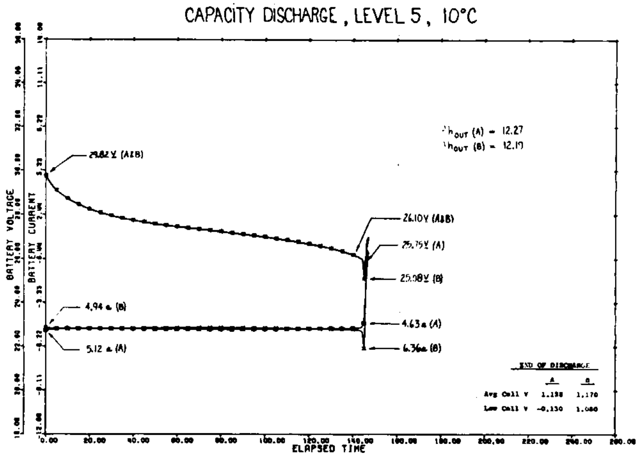


**Figure 3-11**

# VOLTAGE/TEMPERATURE CHARGE CHARACTERISTICS

F. Betz
NRL

Actually, I guess I renamed this thing along the way and called it a charge voltage limit study, and in the true sense of the word, maybe it wasn't even a good study. It was kind of oriented towards evolving a voltage temperature limit for a specific application. It is not as comprehensive as it might have been if one were trying to look at all aspects of voltage and temperature.

The application, much like (I guess) some of the Hughes problems, the orbit values from full sun to a full eclipse, a 36-minute eclipse, one-third of the orbit; temperature varies on the satellite quite a bit; at least it was predicted to, and it did.

Charge power is highly variable because of the orbit, and the loads vary. So you have to come up with a charger to meet all kinds of requirements. Also, there are two batteries, and theoretically either one of them should be able to support all loads.

(Figure 3-12)

So we decided to look at a number of factors. A lot has been said about percent recharge, the final charge/discharge ratio, which has been used for the NASA curves quite a bit. But in addition, we decided to look at capacity versus voltage limit, the charge/discharge ratio, and the final charge current in the orbit.

We were looking at that to find out essentially how far back the current would taper in a given orbit to get some feel for ultimately what the thermal characteristics in a full sun period might turn out to be. The test turned out to be in two parts. Part One started a little earlier. The second part, starting a few years later, we added a varying depth of discharge to.

(Figure 3-13)

To give you some idea of this, these were the test conditions that we used. A cycle period of 108 minutes corresponding approximately to the orbit period. The maximum discharge period of 35 (about 36 minutes), 35.7, a charge period of 72.3. Maximum charge rate of two and a half amps did not come from anything associated with the satellite. Really, that was the maximum current that the past transistor could handle in the charger.

All the Part One tests were 18 percent depth of discharge; most of the Part Two tests were at 18 percent depth of discharge. We took some spots at 5 percent and 30 percent to get some "what if's;" the depth of discharge changes, and how does that affect these other parameters?

Each test condition consisted of about 43 cycles or 40 cycles at a given voltage/temperature combination, depth of discharge combination. For Part One, there were 14 tests (14 test conditions); Part Two, about 24.

(Figure 3-14)

The test cells were immersed in a laboratory bath at the temperature plus or minus 1°C. I put the NASA/BVLS or battery voltage levels on there. Level 7, 6, 5, 4, and 3. All of our tests fell between Levels 7 and 3. That is why that is all I put up there.

You will notice that the general trend of the test points that I used were somewhere between Levels 7 and 3, and it kind of sloped down. They tended toward the low side with the higher temperature.

As we proceed, I will give you additional reference points. You might want to look at temperature, I guess.

(Figure 3-15)

The test samples are always of interest. This figure shows Part One test, six Ah, General Electric part number, as you can see. All the cells here have a polypropylene separator. Please don't let that disturb you. The characteristics will not be the same with your cells even if you have polypropylene separators.

They vary from cell to cell. I think Dave Baer mentioned this yesterday. They are cells from different years. They are going to change; they are going to change from manufacturer to manufacturer; they are going to change from one manufacturing lot to another.

We used the polypropylene separator. The first lot came in 1974, and Part One tests began then. The second lot was delivered in the fall of 1975 and also into the spring of 1976, and testing was concluded in the spring.

I put some acceptance test data up here on the cells so you can see how these cells, essentially built to identical specs, varied in one important parameter anyway, and that is the capacity during a burn-in and a three-cycle capacity test.

There is about 1 ampere hour difference between the Part One and Part Two cells in the third cycle capacity. I think it was six-tenths of an ampere hour difference after 160 cycles of burn-in at 18 percent depth of discharge. Fortunately, the voltages were rather close, both 25°C and 0°C, and you will see the results of these differences as we go through the tests.

(Figure 3-16)

This is a typical in-cycle characteristic, and I wanted to point this out because some of the numbers that I am referring to are included here. There is the final current down here, the final charge current. The percent recharge is a function of the current ampere minute discharge and the integration of the charge curve of the ampere minutes returned. You all know what a capacity is. After the charge cycling, this was the 41st discharge cycle and the 42nd charge cycle. The following discharge would be for capacity at the C/2 rate.

(Figure 3-17)

Let's look at some data. This first one is charge/discharge ratio, that important parameter for both Lot 1 or Part One and Part Two cells, at 0°C.

The interesting thing here is that for all voltage limits, the entire range from 144 at a Level 4 all the way up almost to level 7, the charge/discharge ratio of percent return was not significantly different from 100 percent: a little more than 100 percent, to less than 120 percent. Relatively insensitive.

Note the 5 percent data point up there. A lot more recharge, percentwise, gets back into the battery when you have a little depth of discharge. I think this is obvious, but it hasn't really come out in some of the other points. You can't use percent recharge as a sole criterion.

(Figure 3-18)

Okay, we will take a look at capacity at 0°C. This also shows a relative insensitivity to the voltage limits. With the exception of the two different lots in there, you can see the capacity difference. But the voltage limit at 0°C, it doesn't make any difference; pick any voltage limit you want. You have got enough capacity.

(Figure 3-19)

The final current at 0°C, this is how far back it is tapered. Here you see the 18 percent, Part One and Part Two tests show a very good correlation. At five percent, it tapers back more.

Essentially, this is how far back it ultimately would taper, given a full sun period, approximately. It is a little more than 100 milliamps C/60; 100 milliamps is probably about C/40.

The 30 percent depth of discharge gives you a much higher taper-back, but again, a relative insensitivity to the voltage.

(Figure 3-20)

We only did Part One tests at 15°C so I have combined them all on one curve. Incidentally, when I say "we," it is Wilbur Barns and I who worked at the lab on these life cycle tests.

Capacity, the top curve, is insensitive within the temperatures tested or within the voltage limits tested at 15°C. Again, in this range, you see a relative insensitivity to the percent recharge and final charge current, ranging between 110 and 120 percent. This is all 18 percent depth of discharge for on-testing.

(Figure 3-21)

This is Part Two now. Here we see some sensitivity. This is 25°C and here you can see the percent recharge, charge/discharge ratio changing quite a bit within a fairly small band of temperatures.

You can see the Lot One cells running fairly well into the Part Two cells, at 18 percent depth of discharge. The percent recharge, however, is actually less than 100 percent at 1.37 volts down here.

It is over here. 1.37 volts and 30 percent depth of discharge; they are kind of marginal down at 18 percent depth of discharge. Percent recharge reached up to 165 percent at 1.41 volts and 5 percent depth of discharge.

(Figure 3-22)

The capacities would give you some concern, using the lower voltage limits. Would you believe 4 ampere hours at 1.37 volts?

Down in here, 30 percent depth of discharge, $2\frac{1}{2}$ ampere hours. You get up here around 1.39 volts, and you are getting up to numbers close to 6.

But remember, for the Part One cells, 6 ampere hours is three-quarters of the actual capacity and 6 ampere hours is probably about 80 percent of the actual capacity on the Part Two cells. So there is a restriction in capacity here as you pull the voltage limit down below 1.4. There is some uncertainty in these two data points at 30 percent depth. I ran the test twice and one came high; one came low. I should have run it three times, I guess.

(Figure 3-23)

Capacity didn't look so good there. The same—becoming more sensitive to voltage limit. Here, in the final taper current, you can see how far back it tapers and much more clearly here, you can see the effect of depth of discharge and how far back it will taper in any orbit.

Again, the taper-back in 1.39 to 1.4 is less than C/30 number; the battery ultimately will taper back that far.

For those people who don't know, you can use polypropylene at higher temperatures. Here are some test results at 35°C.

(Figure 3-24)

Here is the percent recharge, more sensitive than ever before. I think that is probably enough—204 percent recharge. Maybe it doesn't mean that much because the current, the final current, is actually tapered back to a very low value and the overcharge rate is quite low. But again, the percent recharge is just barely 100 percent at 30 percent depth of discharge.

(Figure 3-25)

There is a little confusion here between Parts One and Two and 5 percent. The Part One cells again show their superior capacity. Part Two has a general curve shape. For the absolute value at 35°C, almost 50 percent of actual somewhere in here. So it is a fairly low capacity at 35°C.

(Figure 3-26)

Here is the last curve, the final current as a function of the voltage limit, of 35°C. Again, the 30 percent is high; the 18 percent is in the middle; the five percent is just slight low, but maintaining in the region of 200 milliamps for a final taper-back.

(Figure 3-27)

I think the conclusions of what it all leads to are here. Some of these, of course, are obvious, but battery voltage limit charge method works best at below 25°C. At least, they are less sensitive there.

Also, you can use almost any voltage limit. You don't have to be all that careful below 25°C. Decreasing the voltage limit may restrict capacity. You really have to run the test to find out where you are and what voltage limit you are using. Decreasing the voltage limit decreases the charge/discharge ratio, obviously.

But it needs to be said because you can't just use charge/discharge ratio by itself. You have to understand the context here. Decreasing the depth of discharge increases the percent recharge. I think that is an important factor also.

As you go to 5 percent depth of discharge, your percent recharge is going to grow, but it may not mean all that much because you are tapering back to very low current.

Some correlary conclusions: again, some obvious ones—increasing the initial charge current would increase charge/discharge ratio because you have more time to charge as it tapers back.

The opposite is also true. If you decrease the initial charge current (we use two and a half amps), you can make your charge/discharge ratio look better for any given condition.

If the charge period changes, like if we go into a full sun period, we have an intimate charge/discharge ratio.

So, in conclusion, the selection of a proper temperature compensated voltage limit should really consider a lot more than percent recharge. You must consider your satellite operating characteristics and the cell operating characteristics. And you can run these tests in the matter of probably 3 or 4 months, to get some good data, on your individual cells if you intend to use this type of charge voltage limit.

You must know, of course, or at least have some predictions of your battery operating temperature range, the depth of discharge. Finding the final current means something if you go into full sun periods because this becomes your thermal dissipation for the battery at that point.

DISCUSSION

KILLIAN: I have often thought if you used V-T curves that when you hit them on the voltage, you switch down to a trickle charge, it might take a lot of pressure off a selection of those curves. Do you have any comments on that?

BETZ: Well, I tried that once a couple of years ago and you have to go to a much higher voltage to get the capacity in. If you use a fairly low trickle charge—in other words, you switch back to a low voltage—you are not going to do any effective charging of the trickle charge rates, so you really have to use a higher voltage.

I think there is a lot more pressure on the cells as they get older by pushing the voltage higher. I prefer, personally, to see the average voltage of the battery and the cells pulled down a little bit, and let them taper back naturally. That is, of course, opinion.

HALPERT: How many cc's of electrolyte were in those cells?

BETZ: Sixteen and a half—no, wait a minute—let me see. Eighteen and a half—sixteen and a half plus two. That is about the same as the typical nylon separator cell, so they run on the wet side. We had a fairly high pressure allowance. We were not concerned with the initial pressure on the cells when we were building them. We figure that as they get older, this electrolyte does get into the plates and the ultimate pressures are going to get down anyway.

FORD: I would like to comment on Harry Killian's question and say that we found that the contrary to that is true, particularly in the low earth orbit.

In trying to collect the voltage which is indicative of 100 percent recharge, your threshold at overcharge is much more sensitive. So you end up trying to recharge the batteries almost fully. Pick a point and then do something with that point.

We found from the voltage taper method that Fred has described and which the eight levels that we use now frequently, we found that offers a distinctive advantage. I think the one thing that is kind of hidden in this is that when you go into overcharge, when you get to C or D, whether it be 105 or 110, you are doing it at a very moderate rate. So the rate of thermal dissipation is already being cut back as you reach the 100 percent.

Now Fred's data is quite interesting because in looking at characterization of cells for OEO and also for OSO which Webster presented here, I think 3 or 4 years ago, if you have got missions that have a wide interaction, charge rate because of solar angle, solar output, and that certainly changes with life, depth of discharge is a function of the orbit or function of the load profile, temperature is a function of the orbit load profile. There is no way I can see that with NICAD batteries, you can take a single V versus T, be it a switch-down type concept, or this early taper type where you taper around 50, 60, or 70 percent recharge. There is no way you can take a single one and make it apply to such a wide variation because, in fact, there is a tremendous interaction of all these variables that Fred is talking about.

This is the reason that we have resorted to the multiple V versus T level. In the in-orbit flexibility, you have to compensate for bad designs on the ground; it is very forgiving, in that sense.

BETZ: My approach was to try to come up with a good design on the ground. But we really couldn't practically use the multiple curve because in some cases, we would be switching that level-by-level literally every couple of days, because the temperatures are changing that much.

I didn't put up the selected curve that we use, but you will notice that it has a steeper slope than the V-T curve in the NASA presentation. We would have really been bound to a difficult problem, I think, as our temperatures changed, in changing V-T limits all the time—also as we got into full sun periods.

GASTON: Just one comment. Your characteristics are very useful for very early life characteristics. Of course, you like to have the flexibility in changing characteristics and, again, multiple level comes in very hands (as in cells 'h"), and they continue upwards.

BETZ: Sid Gross ran some tests on older cells with voltage limits, but I just want to make one comment. Pack I, the first six-cell pack, continued on with the selected voltage limit until it failed. The failure mode began as partial shorting in one of the cells or two of the cells in the pack. The result was that we began to draw more and more current through the cell.

So one would say obviosly, oh, I will switch, if I had the option, to a lower voltage. But the partial short is a parasite. So in so doing, I only had $2\frac{1}{2}$ ampere hours as it turned out in the cell with the partial short anyway—all I could get into it, the normal voltage. If I had switched to a lower voltage limit, I would have had even less, and that cell literally would have had nothing. I had no alternative: I couldn't go to a higher voltage limit; I could not have gone to a lower voltage. I was in a box.

GASTON: How many cycles did you get on those cells?

BETZ: I remember the total number, which included this charge study and the first 160 burners. It was about 7800 cycles, close to 8000.

GASTON: Did you have any wetting agents? Did you take precautions to remove any wetting agents?

BETZ: I believe the separator was clean.

IMAMURA: I agree with Floyd in a need to have a controlled flexibility over several V-T curves. Now, if you have to start all over again, using one single V-T curve, what would be your driving or the most important factors to use to select those voltage limits of the single V-T curve?

BETZ: Well, again, my point was you can't really use one driving factor. You must be able to store sufficient capacity. I am not even saying that I have to store a nameplate capacity out of an 8 ampere hour cell that has a nameplate of 6. I must know that I have a reasonably adequate capacity; I want to be assured that the cell will taper back or the current will taper back to a reasonably low value, and I certainly want to have a reasonable charge/discharge ratio of percent recharge. But I don't hold that as the most important criterion.

When you have varying orbits' sunlit periods and varying loads, you have varying depths of discharge; there is no one.

PALANDATI: You mentioned that the C to D ratios are not the only criteria to look at and I happen to agree with you. Just recently, in the parallel battery tests, we ran a test condition where we virtually starved both batteries. We worked the batteries at a voltage level one whereby if you looked at the C to D ratios in regards to ampere hours (in versus ampere hours out), we never reach a C to D ratio of one; it was always roughly 0.97.

We ran this condition for approximately 100 to 150 orbits. We calculated the ampere hours in versus ampere hours out at this point and both batteries should have lost approximately 9 ampere hours. At that point, we ran a capacity test and we were able to get out almost 11 ampere hours out of each battery. I know darn well that these batteries were not capable of delivering 18 to 19 ampere hours.

The interesting thing is when we looked at the data, there was one area that we have not been really looking at, and that is the watt hours in versus watt hours out. In all conditions during all the orbits, the watt hours in was always one or greater than one and the ampere hours were always on a minus condition. This may be a significant point to look at.

LACKNER: On the point that you made about the fact that if you lower the voltage too far, you may lose capacity, we found that if you don't have at least 1.40 volts per cell, you are not getting an adequate recharge into the battery, particularly at the higher temperature.

BETZ: Do you mean above 25°C or 35°C ? In that area ?

LACKNER: That's right. You should have at least 1.40, so if you are around 1.38 and your curves seem to point out, that is, 1.38 and below, you are having to increase the C to D ratio considerably and getting less capacity out of it. There are various ways of putting additives in to enhance that voltage.

The other point is that there is a natural variation in cell voltage with temperature. If you just changed the temperature and did nothing else, the voltage would fall as the temperature went up and rise as the temperature went down. So that has to be taken into consideration.

The other thing is that the charge efficiency decreases as you go up in temperature, so you should really increase your volts as well as your charge rates to compensate for that.

But the tendency would be to not have a high rate charge at high temperatures because you are going to have thermal problems. And actually, if you did a thermal balance, which Webster and I did a few years ago, you find at the higher charge rates that you do get an endothermic effect at high temperatures, but at low charge rates—even at 25°C, low charge rates being C/20—you do not get any endothermic effect; you get more heating.

BETZ: Yes, I would agree. Our initial charge rate was 2½ amps, which is close to C/2, so we were initially hitting it fairly high to try and get the benefit of the higher charge efficiency at the higher temperature. We did not go that high in voltage above 25°C.

BAER: Thank you. Our next speaker is Sid Tiller of Goddard, and he is going to talk on IUE flight experience, but before he does, I think I ought to refresh everybody's memory as to the sole design of the IUE.

(Figures 3-28 and 3-29)

These slides were originally presented at the '76 workshop and are just to refresh everybody's memory. Just ignore any reference to 12-ampere hour cells. Although we did build the 12's, the IUE used a 6-ampere hour cell. In the General Electric cell with a dual nickel brace, surrounded with metal seals, 2505 separator, and the negatives were teflonated to 101. They were decarbonated and the positive plates had a PQ treatment; and they were also lighter loaded, 10 percent below the nominal air time. They had the higher quantity of KOH; the goal was to get 4 cc's per rated ampere hour.

Here is a little bit of the early manufacturing data. There was 12.7 grams per decimeter squared of positive hydrate and the negative loading was 16.2 grams per decimeter squared. It worked out to the theoretical capacity of 10.1 ampere hours and on the negative, of 18.2.

During the flooded cell tests, the positives yielded 7.8 ampere hours and the negatives, 14.5. It worked out to a ratio of 1.85 to 1.

With the metal electrolyte, we managed to get 4.17 cc's of electrolyte per rated ampere hour. There are not normal plates in these, 10 positives and 11 negatives. The positives were about 27 mils and the negatives were 31 mils.

If you recall, they did not quite get to all the wetting agent and get it washed out of the separator, and the wet-out time was 39 seconds, which is more typically what the wet-out time is going to run in an orbit of 500 seconds.

CHARGE VOLTAGE
LIMIT STUDY

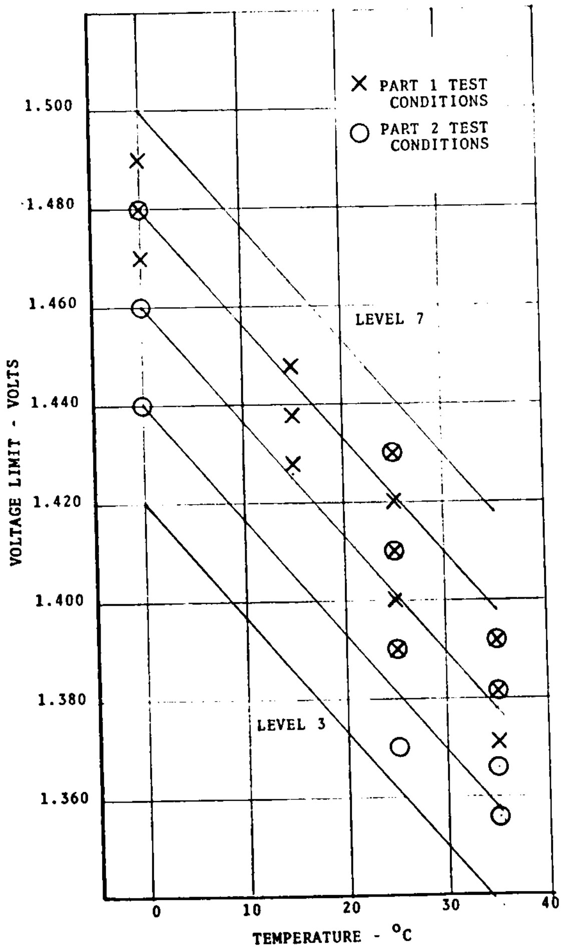
**PART I** - AT VARIOUS TEMPERATURES:

CAPACITY VS. VOLTAGE LIMIT
CHARGE-DISCHARGE RATIO VS. VOLTAGE LIMIT
FINAL CHARGE CURRENT VS. VOLTAGE LIMIT

**PART II** - AT VARIOUS TEMPERATURES:

CAPACITY VS. VOLTAGE LIMIT
CHARGE-DISCHARGE RATIO VS. VOLTAGE LIMIT
FINAL CHARGE CURRENT VS. VOLTAGE LIMIT
DIFFERENT DEPTHS OF DISCHARGE

Figure 3-12



TEST CONDITIONS AND NASA
BATTERY VOLTAGE LEVELS

Figure 3-14

TEST CONDITIONS

| | |
|---|---|
| CYCLE PERIOD | 108 MINUTES |
| DISCHARGE PERIOD | 35.7 MINUTES |
| CHARGE PERIOD | 72.3 MINUTES |
| MAXIMUM CHARGE RATE | 2.5 AMPERE |
| DEPTH OF DISCHARGE | |
| PART 1 | 18 PERCENT |
| PART 2 | 5 PERCENT |
| | 18 PERCENT |
| | 30 PERCENT |
| NUMBER OF CYCLES PER TEST CONDITION | |
| PART 1 | 28 to 62 CYCLES (AVG 43 CYCLES) |
| PART 2 | 26 to 52 CYCLES (AVG 40 CYCLES) |

CELLS IMMERSED IN TEMPERATURE CONTROLLED BATH, ± 1°C.

Figure 3-13

TEST SAMPLES

PART I

SIX, 6Ah GE P/N 42B006AB34 POLYPROPYLENE
(GAF WEX 1242) SEPARATOR SPRING 1974

PART II

SIX, 6Ah GE P/N 42B006AB34 POLYPROPYLENE
(GAF WEX 1242) SEPARATOR FALL 1975

ACCEPTANCE TEST DATA

CAPACITY AFTER 160 CYCLE
BURN IN (18% D.O.D., 110% CHARGE RETURN)

| | |
|---|---|
| PART 1 CELLS | 8.165 Ah AVG |
| PART 2 CELLS | 7.478 Ah AVG |

THIRD CYCLE CAPACITY (C/10 CHARGE C/2 DISCHARGE)

| | |
|---|---|
| PART 1 CELLS | 8.352 Ah AVG |
| PART 2 CELLS | 7.398 Ah AVG |

OVERCHARGE VOLTAGE AT .600 amp, 25°C

| | |
|---|---|
| PART 1 CELLS | 1.4458 Volts AVG |
| PART 2 CELLS | 1.4467 Volts AVG |

OVERCHARGE VOLTAGE AT .300 amp, 0°C

| | |
|---|---|
| PART 1 CELLS | 1.4825 Volts AVG |
| PART 2 CELLS | 1.4828 Volts AVG |

Figure 3-15

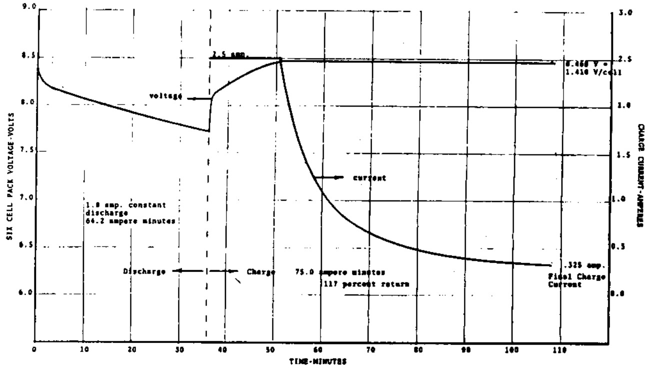
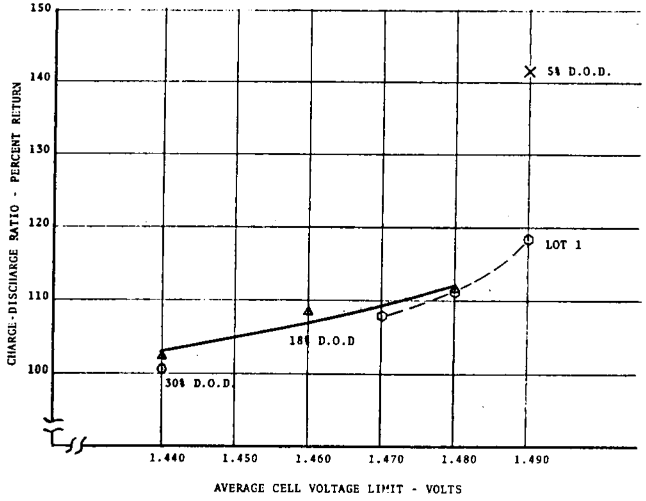


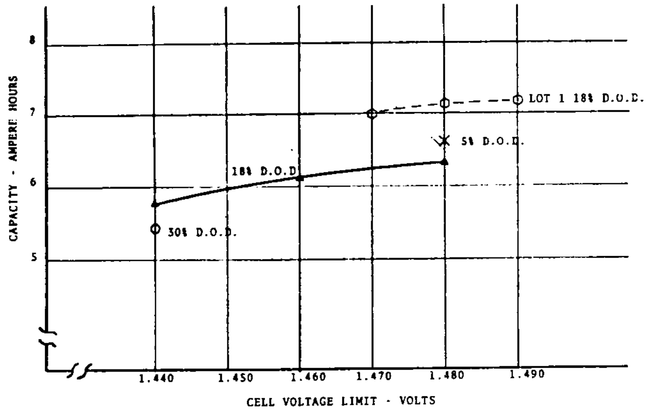
FIG. 2. TYPICAL CYCLE, 41st DISCHARGE, 42nd CHARGE
18% DEPTH OF DISCHARGE (D.O.D.), 25°C
8.460 VOLT LIMIT, (1.410 VOLTS PER CELL)

Figure 3-16



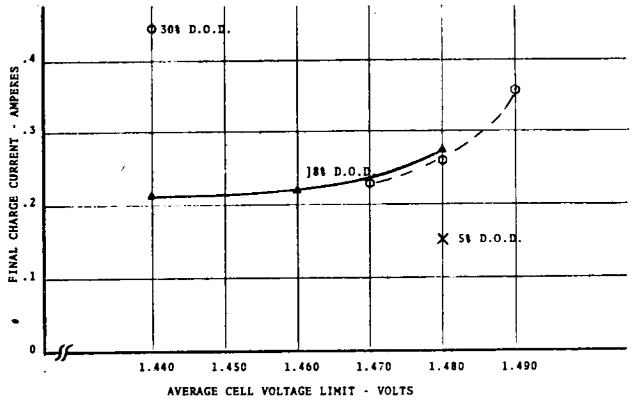
0°C PERCENT RETURN VS. VOLTAGE LIMIT

Figure 3-17



0°C CAPACITY VS. VOLTAGE LIMIT

Figure 3-18



0°C FINAL CURRENT VS. VOLTAGE LIMIT

Figure 3-19

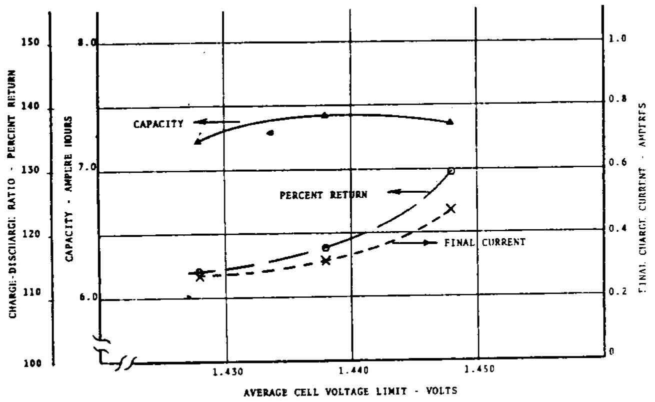
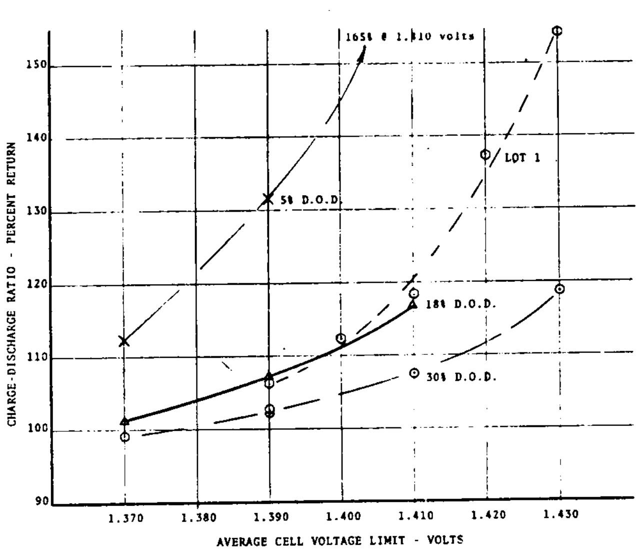


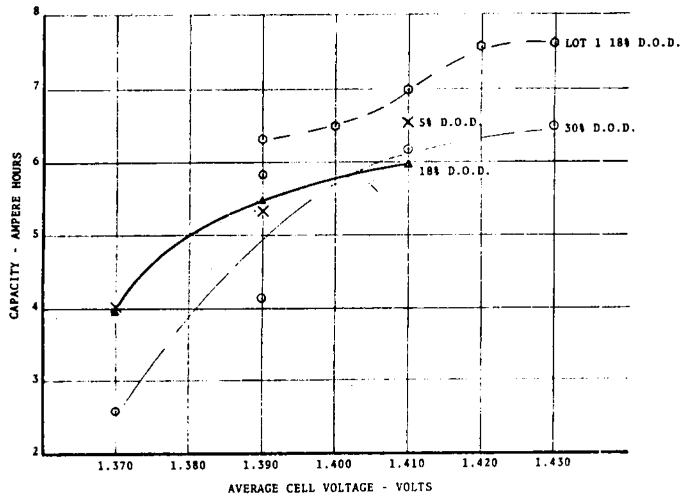
FIG. 6, 15°C CAPACITY, PERCENT RETURN & FINAL CURRENT VS. VOLTAGE LIMIT
LOT 1 CELLS ONLY

Figure 3-20



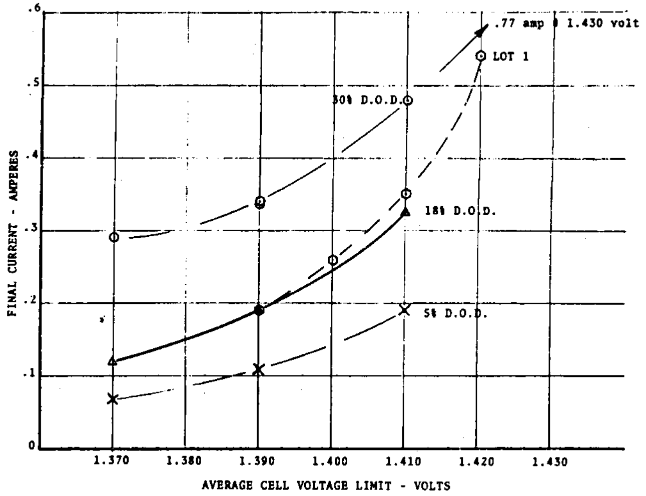
25°C PERCENT RETURN VS. VOLTAGE LIMIT

Figure 3-21



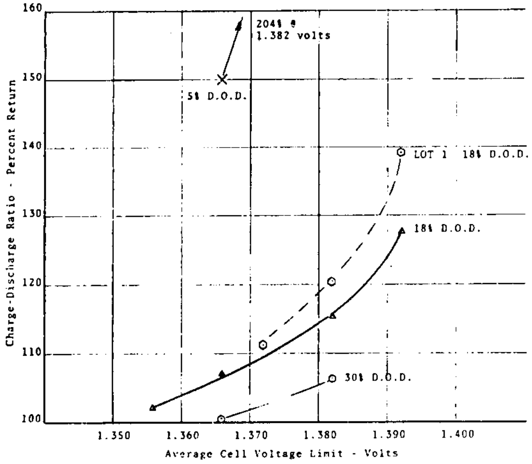
25°C CAPACITY VS. VOLTAGE LIMIT.

Figure 3-22



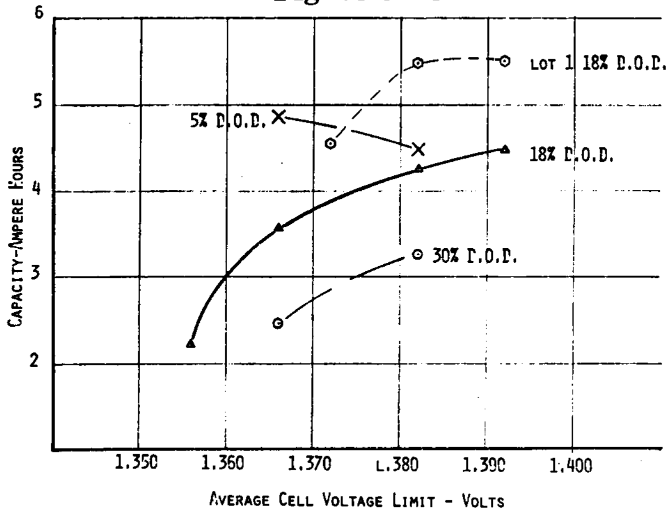
25°C FINAL CURRENT VS. VOLTAGE LIMIT

Figure 3-23



35°C Percent Return vs. Voltage Limit

Figure 3-24



35°C CAPACITY VS. VOLTAGE LIMIT

Figure 3-25

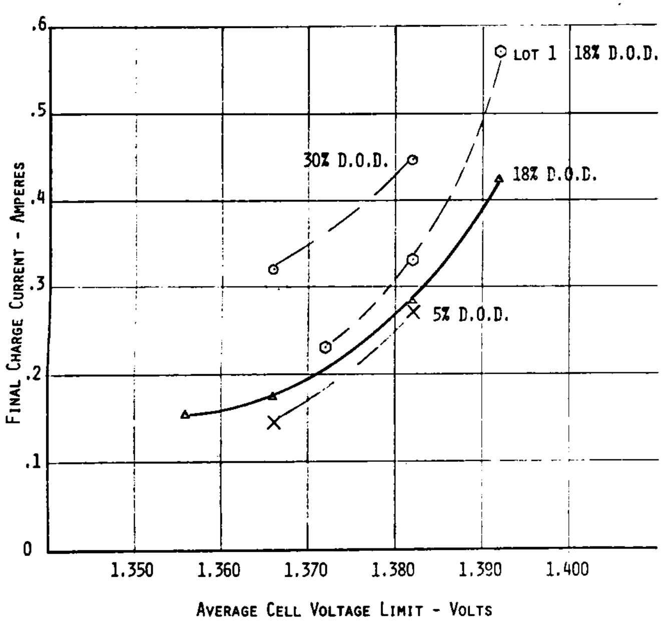


FIG. 12. 35°C Final Current vs. Voltage Limit

Figure 3-26

CONCLUSIONS

- BATTERY VOLTAGE LIMIT CHARGE METHODS WORK BEST AT TEMPERATURES BELOW 25°C.
- DECREASING THE VOLTAGE LIMIT MAY RESTRICT CAPACITY.
- DECREASING THE VOLTAGE LIMIT DECREASES CHARGE-DISCHARGE RATIO.
- DECREASING DEPTH OF DISCHARGE INCREASES PERCENT RECHARGE.

CORALLARY CONCLUSIONS

- INCREASING INITIAL CHARGE CURRENT INCREASES CHARGE-DISCHARGE RATIO
- INCREASING THE RATIO OF CHARGE PERIOD TO DISCHARGE PERIOD INCREASES THE CHARGE-DISCHARGE RATIO.
- THE SELECTION OF A PROPER TEMPERATURE COMPENSATED VOLTAGE LIMIT SHOULD CONSIDER:
  - SATELLITE ORBIT CHARACTERISTICS
  - CELL OPERATING CHARACTERISTICS
  - BATTERY OPERATING TEMPERATURE RANGE
  - DEPTH OF DISCHARGE RANGE
  - FINAL TAPER CHARGE CURRENT (FOR THERMAL DISSIPATION CONSIDERATION)

Figure 3-27

# IUE FLIGHT EXPERIENCE

S. Tiller
Goddard Space Flight Center

The IUE spacecraft was launched January 26 of this year into a synchronous orbit, and since that time it has passed through two 24-day solar eclipse seasons. The maximum umbrella or shadow period during an eclipse season is approximately 66 minutes in duration at the present time. I believe the predicted umbrella period for the ten solar eclipse season is up around 17 minutes.

During the shadow period, the spacecraft is powered by two 6-ampere hour nickel cadmium batteries. Each battery contains 16 standard cells and one-third electrode cell, and as Dave mentioned, they are manufactured by General Electric Company.

(Figure 3-30)

This is a list of the pertinent design parameters that were used in the design of the batteries for the spacecraft. After investigating several design iterations, a decision was made to fly two 6-ampere hour batteries over two 12-ampere hour batteries to reduce battery weight and size.

Six-ampere hour batteries are approximately 5.8 kilograms in weight and they take up approximately 280 cubic inches of space.

Since we had the biannual eclipse period of 24 days each, we had to specify certain constraints on the use of the batteries during the eclipse periods so that we could provide power to the spacecraft—164 watts of power, 82 watts per battery. And to do this, we had to specify a maximum depth of discharge at 80 percent at a 4-amp rate per battery.

(Figure 3-31)

This is a simplified diagram of the IUE power subsystem. This is a direct energy transfer system which operates at a bus voltage of 28 volts, plus or minus 2 percent. We have bus regulation during the sun periods through shunt dissipators.

When there is insufficient solar ray power, the spacecraft is powered from the batteries, through boost regulators, operating at a minimum efficiency of 90 percent. Each battery is controlled through individual charge controllers. We have a primary charge control system and a secondary charge control system.

The primary control system is controlled with a third electrode feedback loop, and the third electrode is loaded with a 300-ohm resistor. Whenever the voltage across the third electrode is below 150 millivolts, the charger charges the batteries at a 600 milliamp rate. As the third electrode increases from 150 millivolts to 240 millivolts, the current tapers from the 600 milliamps back to zero.

This system also incorporates a battery voltage plan. Whenever the batteries are cold for any reason and the battery voltage increases to 25 volts, the charge controller clamps the battery at 25 volts and will maintain it as long as the battery is cold. That is a 25-volt region.

There is some gray area between the time that the voltage controller takes over from the third electrode controller and vice-versa.

Secondary or back-up control mode of operation is accomplished through resistors switched in series between the battery and the main bus. Both the primary and secondary systems can be commanded from the ground. And also, we can turn the battery completely off line from the ground.

One of the resistors provides a high-rate trickle charge mode of approximately 300 to 500 milliamps, and the other resistor provides a low rate trickle charge from 100 to 300 milliamps.

The current level in the trickle charge mode is proportional to the voltage of the battery since it is in series with the main bus.

(Figure 3-32)

This is a curve that represents the current mode of the third electrode control circuit, as I previously mentioned. The 600 milliamps is provided up to the 150 millivolts and we have the taper from 600 milliamps back to zero whenever the third electrode gets up to 240 millivolts.

(Figure 3-33)

This is a simplified diagram depicting the mounting positions of the battery on the spacecraft. The batteries are mounted on the main equipment platform and they are mounted perpendicular to the outside periphery of the platform, and both are on the same radius with the center of the spacecraft.

I would like to note a couple points here. Two heat pipes are located on the under side of the main equipment platform, directly under the batteries, around the periphery of the main platform.

Also, the batteries are located adjacent to one of the thermal louvers that closes at temperatures below 0°C.

(Figure 3-34)

This is a typical battery recharge characteristics curve that was plotted from data acquired during the spacecraft eclipse season number 1, and this is day number 6 in the season.

As noted by the third electrode control circuit previously, the batteries start off on the main charger, providing 5-600 milliamps of charge current to the batteries until the third electrode crosses the approximately 150 millivolt point, at which time we start into the taper until we get down to—in this case, 100 milliamps.

In the operational control center of IUE, we have directives that specify that any time either battery exceeds a 25 degree point, and both third electrodes are above 150 millivolts, we place the batteries into the back-up modal charge or the low rate trickle charge. In this case, you can see after 11 hours of charge on the main chargers, we switched from the main chargers to the trickle load chargers.

There is shown here an eight-degree temperature delta between the two batteries and we believe that this delta is possibly caused by the position of the batteries to other components on the spacecraft, the positions of the batteries to the shunt dissipators on the spacecraft, and the fact that Battery Number 2, which is the colder of the two batteries, is located adjacent to the thermal luber and more surface area of the outside battery is exposed to deep space.

(Figure 3-35)

This curve was made from data acquired again during the solar eclipse season number 1. The battery discharge characteristics during a 66-minute shadow period, and as I said previously, the 66-minute shadow period is the maximum that this spacecraft has been exposed to so far.

This is approximately 72 percent depth of discharge. And the comment I would like to make at this point is in spite of the eight-degree delta between the two batteries, we have excellent load share between the two batteries. There is a difference of about .09 ampere hours at the end of the 66-minute period. One battery has approximately 4.2 ampere hours out and the other battery is 4.33 ampere hours out.

(Figure 3-36)

This curve is similar to the previous curves with the exception that this curve was taken from data from the eclipse season number 2. The same type of discharge curves except we have the 66-minute discharge at day 13—the same as the other curve.

There is one slight exception and that is that the spacecraft was allowed to discharge to four and a half amps during this time and we have a slightly larger difference between the capacity or the ampere hours out in delta between the two batteries.

(Figure 3-37)

This is a composite plot of data. End of discharge voltage versus day in eclipse, where we plotted data from an accelerated test conducted at Goddard in-house through six simulated eclipse seasons.

I would like to make one note here that Eclipse Season Number 1—during the accelerated test—was not started until after the batteries had been in operation for approximately one year of operation in a 24-hour orbit at 50 percent depth of discharge.

On this curve, to show some comparisons, we plotted the data from the spacecraft from Eclipse Number 1.

(Figure 3-38)

This, again, is a similar curve. In this case, we plotted both the first and the second eclipse season of the spacecraft and we have the data from the accelerated tests—eclipse season number 6, which should be the predicted level of the sixth season of the spacecraft or the trend. We believe that the sixth season can be predicted or the seasons three through six can be predicted from this type data.

(Figure 3-39)

Curves on this graph can be used to predict the average power available to the spacecraft from the batteries over the future eclipse seasons as related to the end of discharge voltage of the batteries or worse case conditions. The voltage curve in this case was plotted from 14 simulated seasons of data acquired from 12-ampere hour cells tested at Crane.

With this data, we calculated the available power to the spacecraft by using the boost regulation value of 90 percent minimum efficiency to the spacecraft. We have plotted the actual points of the spacecraft during the first and second eclipse seasons, but we don't believe that if you drew a straight line due to the two points that this is indicative of a trend, due to the fact that during the second eclipse season, the batteries were discharged at a harder rate. And we believe that this will be adjusted for future eclipse seasons back to the original design of the four-amp limit.

In conclusion, we feel that the data that we have so far, that we can predict that the spacecraft will operate over a three-year design life and a five-year design goal that was specified for the IUE spacecraft.

## DISCUSSION

GASTON: How do you treat the batteries during sun time? Are they in trickle charge and what temperatures do they see?

TILLER: During the solstice or sun time, the batteries are place in a low rate trickle charge or approximately 100 milliamps of charge and we specified through directives that unless there is some real requirement to use the batteries during this time, the batteries are to remain at the 100 milliamp low rate trickle charge mode.

GASTON: What temperature do they see during sun time?

TILLER: The outside battery operates approximately 12 to 15°C. The inside battery is approximately 16 to 20-some degrees. It still has the eight degree delta. The temperature varies in accordance with the attitude of the spacecraft, when the spacecraft is used for tests or experimentation and they go to high or low rate beta angles, both batteries falter, and I believe at that time, that they may get down to as low as eight degrees and 12 degrees or something in that area.

GASTON: Thank you very much.

GROSS: Gross, Boeing. Can you tell me, are the chargers—I mean—excuse me—the boost dischargers, are they slaved to force equal discharge currents out of both batteries?

TILLER: The batteries in this particular case operate independent of each other, except in the discharge mode. I am not sure I know the answer to that question. The boost regulators—maybe Floyd could answer that question. I am not familiar with that.

FORD: Yes, the batteries feed into a diode circuit. In other words, both batteries feed through diodes to a common point. So the boost, look for the common point. It has no way of controlling the current from each battery. So there is no force load sharing on discharge.

GROSS: However, the load sharing was quite close. What was the reason for that?

FORD: Well, one of our initial concerns after we got on orbit and found out we were going to be forced to operate with the eight-degree C differential, was what affect this would have on initial load sharing and obviously, the second question is, what affect it would have on the life—which we still are not sure 100 percent of the second part.

This is not—was not too suprising. The load sharing we see on discharge was not too surprising in light of the parallel data tests we had done where we had mix and match batteries as much as 20 degrees C. It just points out that the load sharing of the temperature characteristics of the battery in discharge is not that sensitive. So the voltage is not too sensitive to discharge. We do not see any real problem with this delta T so far. We are a little anxious about the five-year design goal and meeting its requirements.

GROSS: Another question is: where the heat pipes put under the batteries because of battery problems or because of general spacecraft considerations?

TILLER: The heat pipe is part of the general spacecraft design. It just so happens physically each battery was located over the heat pipes.

We still don't have the answer to the delta T. That is a little dilemma that we are still debating between the battery people and thermal people, which is usually a continuing argument.

GROSS: Yes, that one gets around quite a bit.

## 6 Ah AND 12 Ah IUE CELL DESIGN

- GENERAL ELECTRIC CELL
- DUAL, NICKEL-BRAZE, CERAMIC-TO-METAL SEALS
- PELLON 2505 SEPARATOR
- TEFLONATION OF NEGATIVE PLATE, LEVEL I
- CARBONATE REDUCTION PROCESS
- P.Q. PLATE WITH LIGHT LOADING
  GOAL: 10% REDUCTION IN LOADING
- HIGHER QUANTITY OF KOH
  GOAL: 4cc/RATED Ah

Figure 3-28

PERTINENT BATTERY DESIGN PARAMETERS

| | |
|---|---|
| AVAILABLE POWER TO SPACECRAFT . . . | 82 WATTS/BATTERY |
| MAXIMUM DISCHARGE CURRENT . . . . . . | 4 AMPS/BATTERY |
| DEPTH-OF-DISCHARGE. . . . . . . . . | 80 PERCENT |
| ECLIPSE PERIOD. . . . . . . . . . . | BI-ANNUAL (24 DAYS EACH) |
| WEIGHT. . . . . . . . . . . . . . . | 5.8 Kg/BATTERY |
| SIZE. . . . . . . . . . . . . . . . | 280 CUBIC INCHES/BATTERY |

Figure 3-30

### MANUFACTURING DATA

| | 6 Ah | 12 Ah | 12 Ah/2 |
|---|---|---|---|
| LOADING – POSITIVE AVERAGE | 12.72gm/dm$^2$ | 12.52gm/dm$^2$ | |
| NEGATIVE AVERAGE | 16.2 gm/dm$^2$ | 15.7 gm/dm$^2$ | |
| THEORETICAL CAPACITY – POSITIVE | 10.13 Ah | 21.23 Ah | 10.61 Ah |
| NEGATIVE | 18.19 Ah | 36.94 Ah | 18.47 Ah |
| FLOODED CELL TESTS – POSITIVE AVERAGE | 7.81 Ah | 15.5 Ah | 7.75 Ah |
| (ECT) NEGATIVE AVERAGE | 14.48 Ah | 29.2 Ah | 14.6 Ah |
| NEGATIVE/POSITIVE RATIO | 1.85:1 | 1.88:1 | |
| PRECHARGE SET (BY $O_2$ VENTING) | 2.84 Ah | 5.7 Ah | 2.85 Ah |
| ELECTROLYTE (31% KOH) | 4.17cc/ RATED Ah | 3.83cc/ RATED Ah | |
| DIFFERENCE: SEPARATOR SET OUT TIME (AVERAGE) | 39 SEC | 410 SEC | |

Figure 3-29

IUE SPACECRAFT POWER SUBSYSTEM

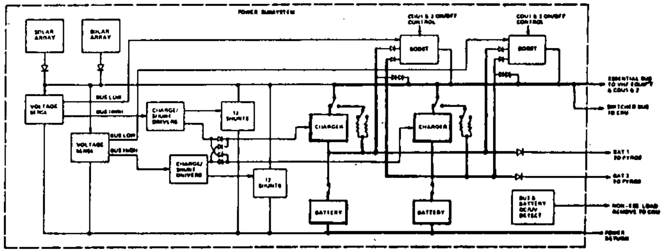


Figure 3-31

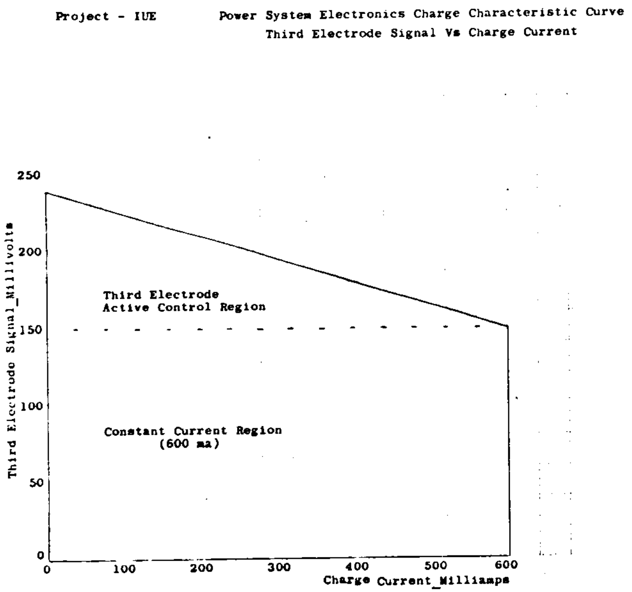


Figure 3-32

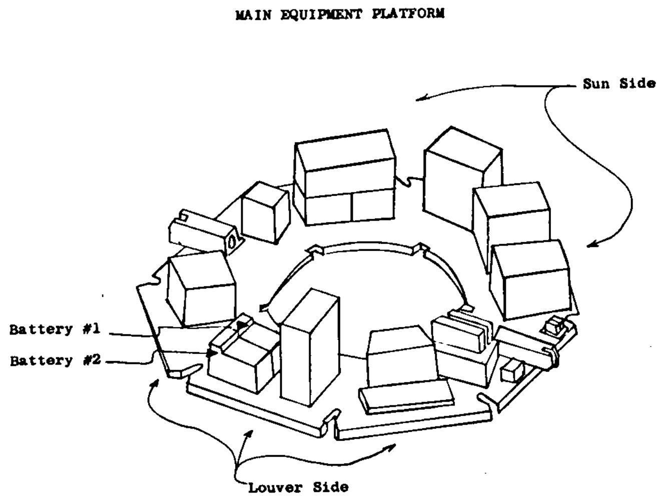


Figure 3-33

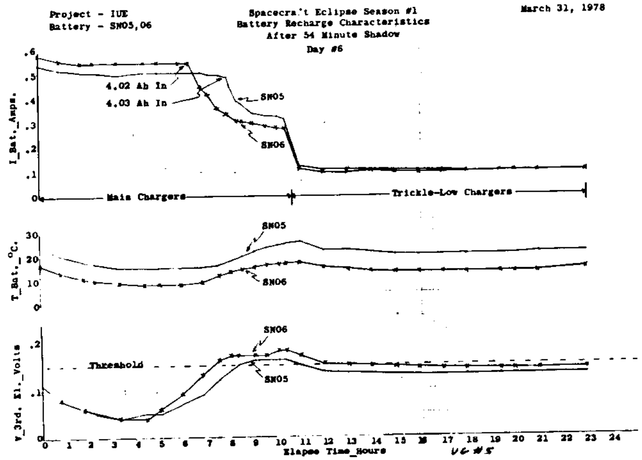
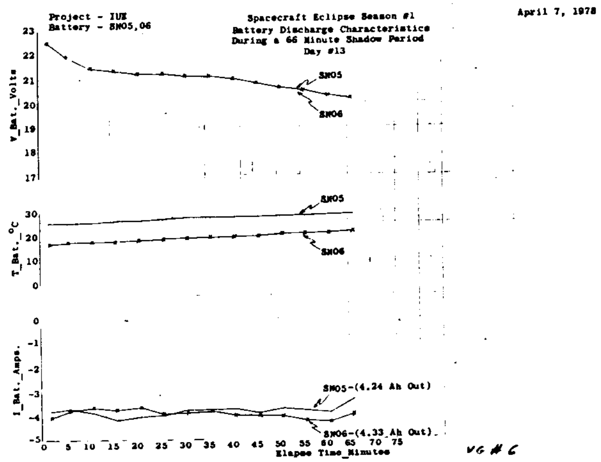


Figure 3-34



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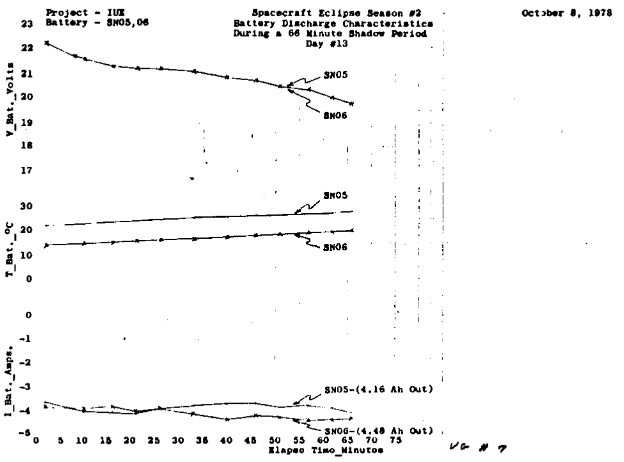


Figure 3-36

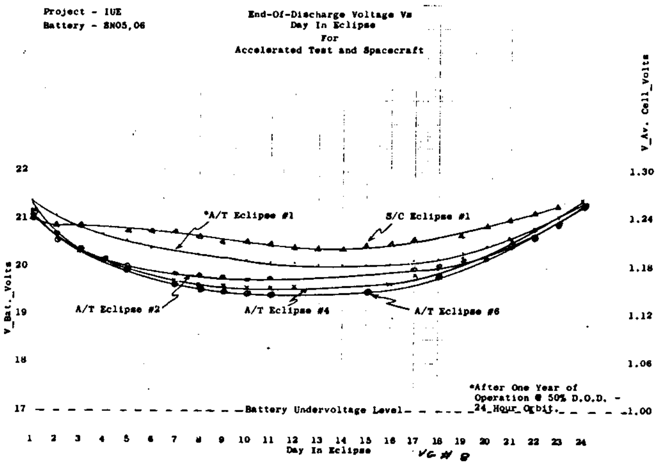


Figure 3-37

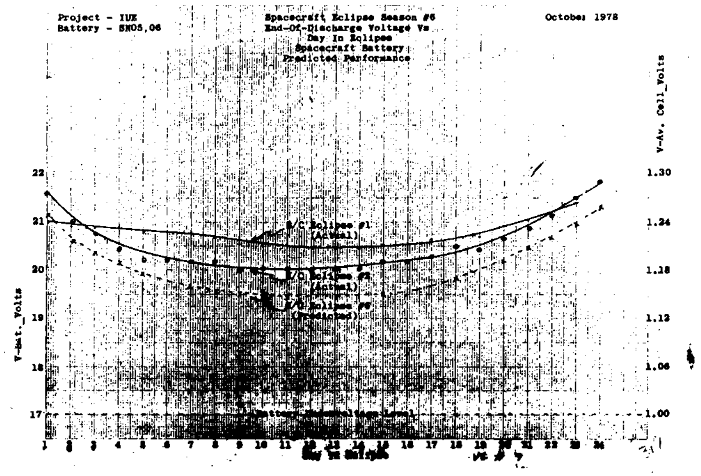


Figure 3-38

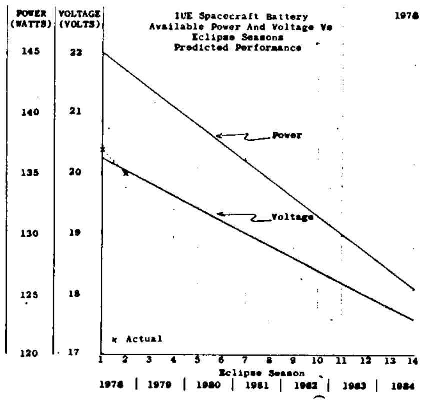


Figure 3-39

# VIKING FLIGHT DATA AFTER 24 MONTHS ON MARS SURFACE

J. Lear
Martin Marietta

What we would like to do today, ladies and gentlemen, gives you an update of the Viking landers after two years of operation on the surface of Mars. It is being presented today by myself and Al Britting, who is the Al pack leader at JPL.

(Figure 3-40)

This is the spacecraft, for the people who have not seen it too often, and the batteries sit in the compartment right under the seismologist right there.

(Figure 3-41)

This is the Viking mission sequence. Two spacecraft were launched in 1975, one on August 20th and the second on September 9th. The batteries are launched in a discharge condition. There are four batteries aboard each spacecraft, two-battery assemblies.

After leaving Earth, about 55 days into the cruise period, the batteries were charged by the orbiter. The orbiter is the mother ship that carries it along and then after it drops them off at Mars, it circles around and takes pictures for lander number 2 to come in on.

It was during this particular period of time that we found one of the chargers had failed on lander 2 and we had to make a procedure change in that particular part of the mission.

But during the 11-month cruise, the batteries basically remained in the discharge condition, with the exception of a few systems tests that we made in order to guarantee that all of the equipment was operating.

Prior to insertion, right here, the batteries were recharged again, and then we went into the Mars orbital insertion. But during this particular period of time, during the Mars insertion, the batteries are subjected to extremely high discharge rates.

We estimated it between 75 and 80 percent depth of discharge during the Mars insertion and touchdown. In actuality, it only came out to be about 55 percent depth of discharge through to touchdown.

(Figure 3-42)

Okay, this is basically the discharge control system. We have the four batteries, A, B, C, and D. Three batteries are on the bus at all times. One battery is being charged for an hour's period of time and then it goes onto the bus and another battery comes on and is recharged.

As I said, during the cruise period, the orbiter powered up the batteries, charged the batteries through this BPA and a separation, then two RTG's charged the batteries. So we have an eight-ampere hour battery on board and it uses a polypropylene separator and I will get into this a little bit later on.

As you can see, one battery is being charged; three batteries are on the bus reading the experiments.

(Figure 3-43)

This is a bar chart of some of the activities that took place during the cruise and during the lander operation. And A, B, C, and D relates to the batteries on board the spacecraft. As you can see, 8-20 was the launch date and 9-9 was the launch date for the second one.

At approximately 55 days into the mission, we did charge all four batteries up from the orbiter. And, again, like I said, we did discover that one of the chargers on lander 2 had failed.

We could narrow it down to several things. We never did isolate it. So we went to the redundant back-up charger and charged the batteries. At this particular time, we selected to float-charge one battery for the rest of the mission, the reason being that we would have to have one battery charged up in order to make the power transfer.

All of the batteries were in a discharge state. If we could not make the power transfer, the mission would be lost, so we kept a battery (we selected Battery "B" in each one of the landers) to be float-charged during the 11-month remaining cruise period to touchdown.

We did a capacity check on Battery "B" and on Battery "C" of lander 2 about 138 days out into the mission. This was during our housekeeping checks on equipment and equipment checks. We decided we would take one battery and find out just exactly how much capacity we did have in the battery.

Then we went through the housekeeping again. We charged them all up just prior to insertion and then went in for the touchdown. The batteries have been charged one hour on, four hours off, sitting on the bus.

(Figure 3-44)

We thought somebody might want to know what the depths of discharge were during the cruise period and during touchdown and all, so we got a little table here.

During the cruise check-out, we took the batteries down to like 25 percent depth of discharge. We ran six systems tests which amounted to about 20 percent depth of discharge and again, preseparation, 25 percent. Then in for the touchdown again.

We were sized for 75 percent depth of discharge. We went in at 50 percent depth of discharge on lander 1; 46 on lander 2. But since then, we have been doing some extended testing missions. Through the primary mission, the maximum depth if discharge we got to was 55. I think that was the biggest one. I think Al can elaborate on that a little bit later on.

On lander 1, we have like in excess of 489 cycles on the battery. On lander 2, we have 299. The discrepancy there is that lander 2 is in a different region of Mars and because of the cold winters and the warm summers, we sort of close up shop and go to sleep. Therefore, activity is reduced.

(Figure 3-45)

This is the battery. It is two batteries, actually. This is on one side; there is another one on the other side. It weighs 50.5 pounds and uses an eight-ampere hour GE cell, which I will get into a little later on.

(Figure 3-46)

Okay, here is the rundown on the battery. Two 24-eight-ampere hour batteries per assembly. Two battery assemblies for the spacecraft; it weighs 50.5 pounds each; they were heat sterilized for 54 hours at 233°F during the cruise. The orbiter supply, that is, C/15 charge rate and prior to insertion, we trickle charged all of the batteries at C/160.

In typical landing operations, we are doing a C/8 charge rate from the RTG's. On the ground, prior to acceptance tests and during the check-out of the spacecraft, we did have individual cell monitoring control that we could measure the voltages and the current. But in actual flight, all we have is battery and voltage temperature compensated cut-off.

(Figure 3-47)

Here are the characteristics of the cells. An eight-ampere hour weighs 273 grams; it has 23 $cm^3$ of electrolyte, and it uses polypropylene separator, which is FT-20140. I believe that it is not available anymore; I think Pete Voiesy at that time bought up all of the stuff and they have got it hid away someplace or other.

(Figure 3-48)

I will give you a little rundown on the capacity after launch. You will notice that it says minus 200 days and is being launched right here. This was the acceptance test. One month prior to spacecraft lift-off, we did another capacity check to determine exactly which capacity we had.

Okay, lander 1 is the solid line, and as you can see, we have degraded down from about 11 ampere hours to about 8.1 ampere hours. Lander 2 paralleled the thing right along until we got to the hot Martian summer. For 137 days, we were in excess of 80°F, and the efficiency of the battery and recharge and all of that fell off a little bit. We are reconditioning the batteries right now, and that is the discrepancy in the capacity right now. This is the first time that we reconditioned all four batteries.

We did four batteries here. These were the ban spreads for the capacity. And four batteries here, which was about 881, and I think Al can probably talk a little bit more about this particular thing.

We have two batteries that we have discharged. We have got like 50 percent of the capacity in the batteries right now.

(Figure 3-49)

Here is a typical lander 1 discharge characteristics. This is the cruise discharge that we made after 138 days, and we got 8.8 ampere hours out of the cells. End-of-life capacity is eight ampere hours. And here is 716 days, which was equivalent to a little over two years of surface life, 7.8 ampere hours.

The discharge rate was 1.45 amps and, as you can see, the temperature on the lander is about 45 degrees, while during the cruise period it is 78.

(Figure 3-50)

And lander 2. Same discharge rate. But you will notice the temperatures are a little bit different. The cruise was 85 and when we did the lander reconditioning, we were 62. We got four and a half ampere hours—645 days on the surface as opposed to 8.6 ampere hours or 135 days into the cruise.

Now we have another program ongoing at Martin, and it is called TELOPS. TELOPS is using the same batteries that were left over from Viking on their mission. It was Cell Number 24 and it has been stored in a discharged condition with each individual cell shorted out through a resistor, three and a half years at 40 degrees, and we recharged it up and did a capacity check on it; lo and behold, the thing came out to the 9.96 ampere hours, the same rate of charge and discharge that we did three and a half years ago.

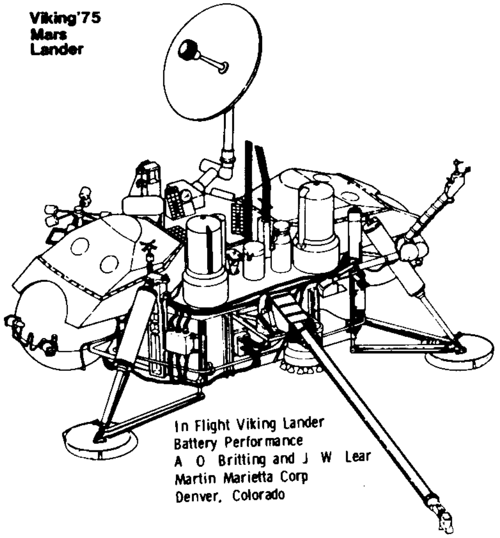
(Figure 3-51)

In conclusion, for the Viking lander we have operated three years with no failures on any of the four batteries that are sitting on Mars. The original mission was 90 days, so I think we are in about the third extended mission, but Al can talk on that in a couple of minutes.

Polypropylene separators, a standard cell, untreated negative plates, we did heat sterilize the cells and the batteries prior to the launch. We have operated 42 batteries in excess of 1,000 cells in the heat sterilizable regime that was required for Viking, with no failures.

We have two 24-cell batteries in the simulated Earth orbit, 25 percent depth of discharge, 25°C and that includes 5,000 cycles that we did at 40 degrees accelerated temperature tests. The test has just been terminated and we have not reduced all of the data, but it appears that this particular cell is a winner.

So from here, I will let Al give a little bit of a synopsis and some of the scientific stuff that we have taken on on Mars.



In Flight Viking Lander
Battery Performance
A O Britting and J W Lear
Martin Marietta Corp
Denver, Colorado

Figure 3-40

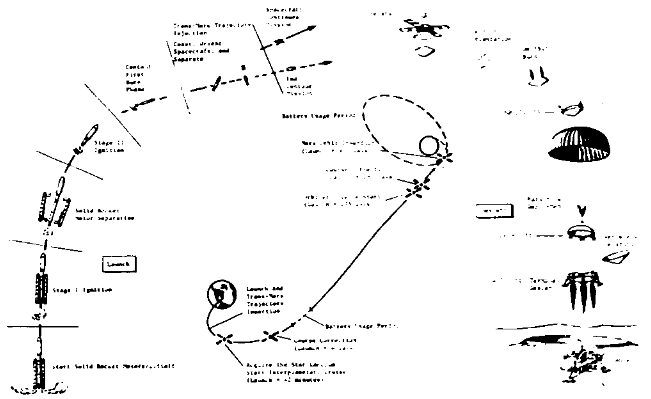
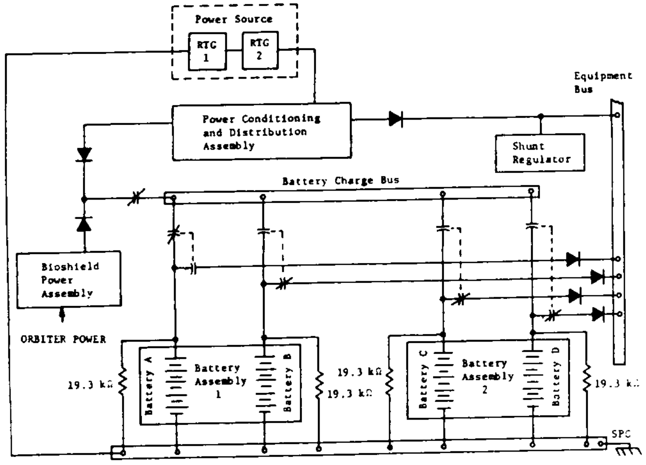


*Figure IV-1 Viking Mission Sequence*

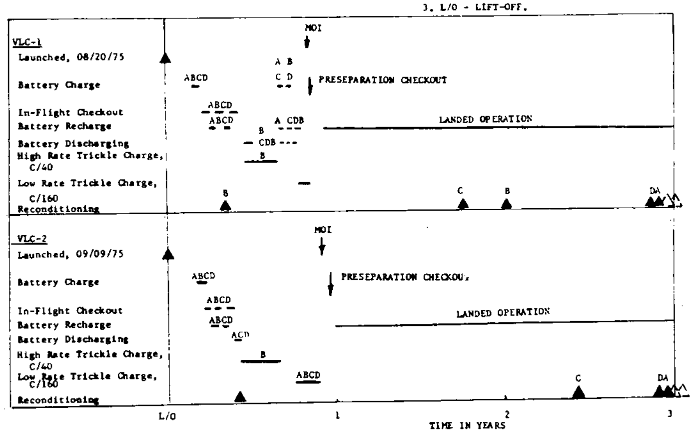
Figure 3-41



*Viking Lander Power System Block Diagram*

Figure 3-42

Note: 1. A, B, C, and D USED TO DESIGNATE BATTERIES.
2. MOI- MARS ORBIT INSERTION.
3. L/O - LIFT-OFF.



BATTERY OPERATIONAL DATA

Figure 3-43

BATTERY CYCLE LIFE

| Period | VL-1 | DOD | VL-2 | DOD |
|---|---|---|---|---|
| Cruise | | | | |
| Cruise Checkout | 1 | 25% | 1 | 25% |
| Subsystem Test | 6 | 20% | 6 | 20% |
| Mars Orbit Insertion | | | | |
| Preseparation Checkout | 1 | 25% | 1 | 25% |
| Preseparation | | | | |
| Preseparation thru Touchdown | 1 | 50% | 1 | 46% |
| Landed | | | | |
| Thru end of Primary Mission Sept 76 | 43 | 55% Max<br>10-20% Typ | 61 Nov 76 | 29% Max<br>10-20% Typ |
| Thru Conjunction Nov 76 | 65 | 23% Max<br>13-20% Typ | 8 | 5% Max<br>5% Typ |
| Thru Extended Mission Jun 78 | 308 | 40% Max<br>10-20% Typ | 211 | 42% Max<br>10-20% Typ |
| Thru Present (Nov 79) | 32 | 15% Max<br>5-10% Typ | 8 | 20% Max<br>10-20% Max |
| Thru Continuation Mission (Mar 79) | 32 | 15% Max<br>5-10% Typ | 2 | 22% Max<br>12-20% Typ |
| Total | <489 Cycles | | <299 Cycles | |

MARTIN MARIETTA

Figure 3-44

BATTERY CHARACTERISTICS

2 - 24-8AH Batteries/Assembly

2 - Battery Assemblies/Spacecraft

| | |
|---|---|
| Battery Weight | 50.5 lbs |
| Heat Sterilization | 54 Hours @ 233°F |

Charge Conditions

- Voltage/Temperature Control
- C/15 - In Cruise from V075
- C/160 - Trickle
- C/8 - Typical Landed Operation

Monitoring

- Temperature } Flight
- Battery Voltage } Flight
- Cell Voltage - Ground Only

MARTIN MARIETTA

Figure 3-46

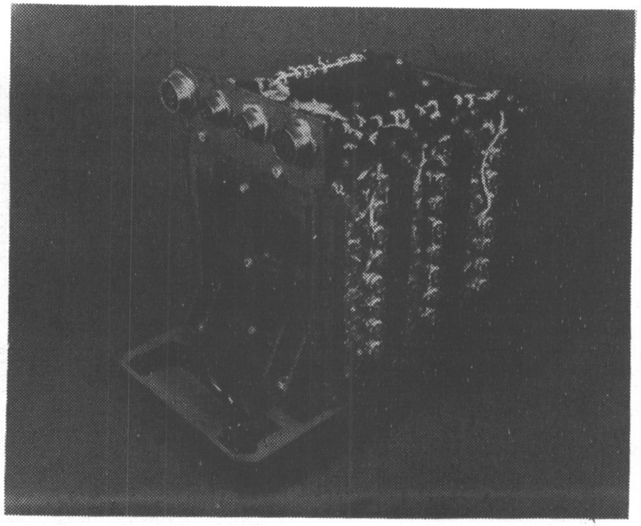


Figure 3-45

[illegible] *

| | |
|---|---|
| Cell Capacity | 8 A-h (Rated) |
| Cell Weight | 273 gm - Lot Average |
| Cell Size | 7.589 cm x 2.27 cm x 8.651 cm (including terminals) |
| Case Material | 304L Stainless Steel |
| Case Wall Thickness | 0.48 ± 0.05 mm |
| Insulated Terminals | Positive and Negative |
| Terminal Type | Nickel Post with Ceramic Insulator<br>GE - all Nickel-Braze |
| Auxiliary Electrode | None |
| Separator Material | Pellon FT2140 Nonwoven Polypropylene |
| Separator Thickness | 0.216 mm |
| Plate Pack Wrap | Pellon FT2140 Nonwoven Polypropylene |
| Case Liner | 0.127 mm Solid Polypropylene Sheet |
| Electrolyte | KOH |
| Electrolyte Concentration | 34% |
| Electrolyte Quantity | 21.5 to 23.5 cc |
| Plate Substrate | 0.101 mm Perforated Steel Sheet |
| Sinter Porosity | 80% Nominal |
| Number of Plates | POS 11<br>NEG 12 |
| Plate Size | 7.0 ± 0.03 x 4.9 ± 0.03 cm |
| Plate Thickness | POS 0.066 to 0.071 cm<br>NEG 0.078 to 0.081 cm |

* Viking Lander Spacecraft Battery
Final Report September 1976, MCR-76-321
Under Contract JPL GM 649000 Duane R. Newell

Figure 3-47

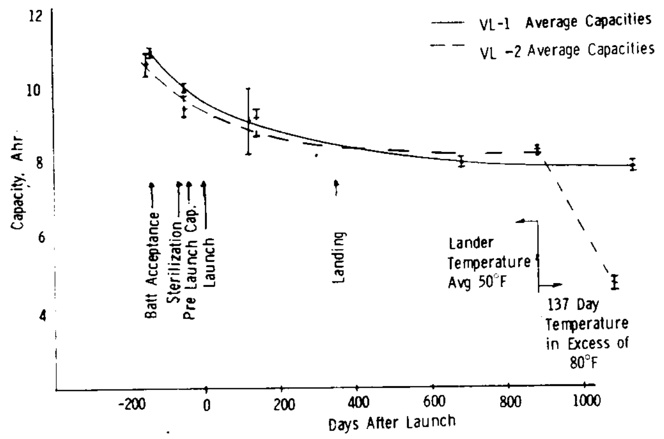
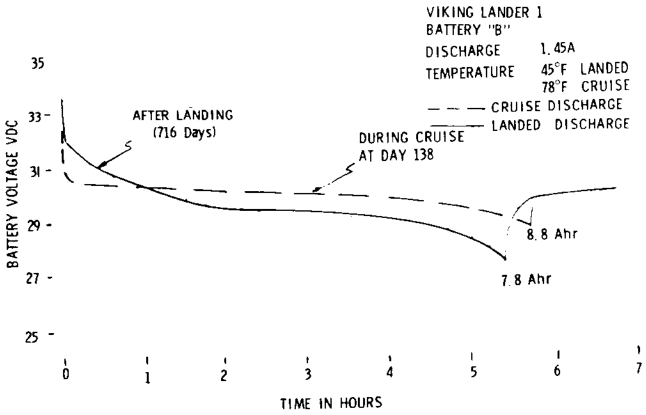
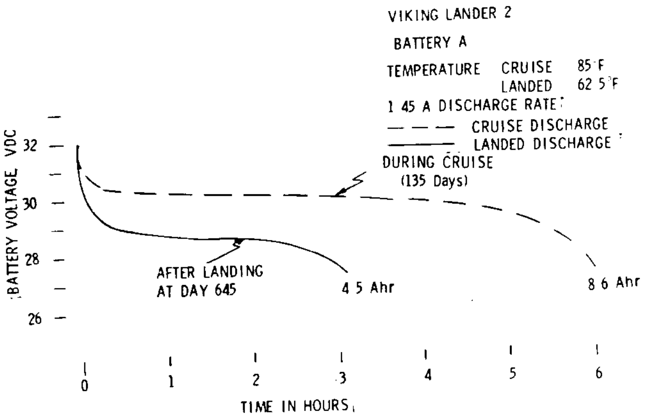


Figure 3-48



TYPICAL DISCHARGE CHARACTERISTICS

Figure 3-49



TYPICAL DISCHARGE CHARACTERISTICS

Figure 3-50

## SUMMARY

- o 3 Year Operation With No Failures
    - - 90 Day Operational Requirement
- o Cell Type
    - - Polypropylene Separator
    - - Standard Untreated Negative Plates
    - - Heat Treatment of Completed Cell Assembly
- o 42 Batteries Containing Over 1000 Cells Subjected to Viking Sterilization Requirements Without a Failure
- o Two 24 Cell Batteries Life Cycled In a Simulated Low Earth Orbit:
    - - Over 22,000 Cyles Achieved at 25% DOD, 25°C Includes 5000 Cycles at 40°C and 25% DOD

MARTIN MARIETTA

Figure 3-51

# SYNOPSIS OF VIKING FLIGHT DATA

A. Britting
Jet Propulsion Laboratory

Before getting into my picture show, John trapped me by saying I would say something a little more about the 50 percent degradation on the batteries on lander 2.

We went through a period where we didn't have access to the landers, particularly lander 2, and had some data collecting hardware problems, hardware failures, that we have since worked around. But we were stuck not being able to, number one, get data down from the lander, nor did we dare uplength without knowing what the configuration of the situation with the lander was, for quite an excessive period of time. And slowly through the Martian summer, the temperature was building up external to the lander and caused the internal lander temperatures to increase; hence, the 80°F and above (actually up to 88°F) exposure to the batteries.

One thing that, I guess, John didn't mention, the RTG's that supply the primary power to the lander have a peculiar trait where we must use all the power coming out of them somehow or they tend to overheat. So we have a shunt regulator scheme in the power subsystem that shunts the excess power to load banks that are located in the lander legs. That excess power is used for battery charging, but when battery charging is cut off for any reason (the batteries are full or we decide not to do any battery charging), that power must be shunted someplace.

Well, for the power not to be stuffed into the batteries, we have an automatic sequence temperature voltage sensing to cut off the charge to the batteries. One of the problems we had is that the batteries got warmer and the temperature caused the terminal voltage of each battery to go down, and since we are using a temperature voltage cut-off to sense when we should quit charging the batteries, we weren't getting to the point where we should be cutting off. So instead of shunting the excess power through the lander legs, we were stuffing the excess power (and it could be 10 to 15, and possibly even 20 watts) into the batteries on a one-hour charge cycle, cycling through the Batteries A, C, B, D, A, C, B, D; never allowing them to cut off for this 137-day period.

This had contributed to, I think, the problem that we are seeing here. I am not sure and I am not going to try to second guess; do we have a memory effect that we have created here? Do we have maybe a fail battery charger?

I do not think we have a failed battery charger. Do we have maybe a cell failed and the battery such that (well, it would have to be in all four batteries) the terminal voltage is lower and we can't get the cut-off to occur?

But we were stuffing anywhere from 10 to 15, maybe even 20 watts, into the batteries for this prolonged period of time, and this slowly did cause the battery to get warmer and the temperature of the voltage on the terminal of the batteries to get lower and lower to the point where it just kept on stuffing them.

Finally, what I did was to hook some additional loads on equipment bus to take that excess power away from being stuffed into the batteries, and we right away noticed the six-degree temperature drop on the batteries and then, lo and behold, November 22 we will be starting on Mars. As a result, the temperature on the surface kind of runs along fine and just shoots out to the point where now instead of being at 80 or 70 or 60, we are running in the range of upper 30's to about 50°F. With the lower temperature on the surface and a lower temperature internal to the lander, we are now in the last month seeing battery charge cut-offs and part of the conditioning of the batteries, which was a discharge to 27.3 volts or preselected voltage. And then a full recharge.

We did notice, and have continued to notice, that the terminal voltages are getting up in the area where we expect them to be, and we are seeing battery charge cut-offs not quite regularly yet, but I think as the temperatures get down a little bit lower, we will be seeing more cut-offs.

Our current plan right now is to do one more conditioning sequence on the batteries in January or February, someplace in that time frame. And I am hoping in the end, if the project will allow me, I would like to take one battery down on a time discharge instead of the preselected 27.3 volts that is built into the electronics right now just to see (we are calling our 27.3 volt point a 90 percent depth of discharge; it is kind of an arbitrary thing that we have selected). What might happen if we go ahead and just say, I will pick a six-hour time period, for example, and we discharge through a 19.3 ohm resistor, sensing the 27.3 volts across a resistor. I would just like to go ahead and take one battery all the way down and well, hopefully next year at this time, we can report the results. That, plus or four additional discharge tests.

[Ed. Note: At this point, Mr. Britting proceeded to show a series of photographs taken on the Viking Mars Mission; we were unable to include the photographs in these proceedings.]

## DISCUSSION

LEAR: I would like to thank Dwayne Newell and Cliff Ray for maintaining the records that we acquired this data from. There is a Viking Lander Battery Report out by Dwayne Newell under contract of JPL, and a lot of the facts that we presented here today is in the book. I think that you can probably, if you want the book, I think you can get it through Sam Bogner's office. I don't know if Sam still has copies of that book around or not.

So, again, I would like to thank them for maintaining the excellent records that they did maintain.

# RCA SATCOM IN ORBIT

# RECONDITIONING AND FLIGHT EXPERIENCE

J. Napoli
RCA

Presently, RCA American Communications has two communications satellites at geosynchronous orbit. They were designed to have an eight-year mission. They are called RCA Satcom F-1 and F-2.

The F-1 spacecraft has been in operation approximately three years in December. It has gone through six eclipse seasons and approximately 264 cycles of eclipse cycling, down to a depth of discharge of approximately 48 percent of actual.

Our second spacecraft, which is the F-2, will have three years of operation in March of next year. It has experienced five and a half eclipse seasons, with 242 cycles of eclipse cycling. And it also has a daily cycle of down to 24 percent DOD of actual, and so far we have accumulated 1000 cycles at that discharge depth.

The reason why we say five and a half eclipse seasons is because we actually launched in the middle of the eclipse in the middle of March. So we start counting in fractions here.

The battery parameters that we have, we are using GE ten-ampere hour cells. That is the actual case design. The rate is normally at 12 ampere hours. They actually deliver 14 ampere hours.

We are using teflonated negatives. We have 22 cells to a battery. We have three batteries per spacecraft.

We are going to show our first figure here, which is going to be a worse case temperature profile which is during the solstice period.

(Figure 3-52)

This is the F-1 spacecraft, and it shows you that the three batteries are operating at different temperatures at different times of day. This is strictly because of their physical location on the spacecraft itself.

I have taken a plot, which I don't have here, after two years of operation and have superimposed two years of 24-hour data of temperatures on top of the original day one data, and the temperatures are repeatable exactly to within a tenth of a degree. So we haven't seen any temperature degradation at all, either in our batteries or in our spacecraft system.

You can see that during the worst case temperature profile, it goes as high as about 28°C and cycles down to a low of about 12 degrees; it is less than that, about eight degrees.

During the winter solstice, the average temperature is somewhat cooler than that, averaging at about 12 degrees. Here, the average is approximately about 20 degrees over a daily period. This happens several months out of the year.

The available charge rates that we have on our spacecrafts are three. We have parallel charging battery management; we have a C/10 rate, which have a V-T clamp which causes the batteries to go into a taper charge when we reach a voltage temperature limit; and we also have a C/20 rate. These are C/20, C/10's are the nominal rates, nominal capacities; namely, 12-ampere hours.

The C/20 is the constant current with no V-T clamping. Then we have a C/60 trickle which we use during solstice maintenance periods.

We also have something that we are pretty much, I guess, pioneers in doing, and that is we do— in all the reconditioning, down to zero point zero one volts per cell twice a year. We do this by actually putting shorting resistors, one ohm shorting resistors across each cell. We do this approximately a week and a half prior to entering into the eclipse season so that we do try to recover our voltage degradation so that we do have the voltage when we need it during the peak eclipse season.

(Figure 3-53)

These are the typical battery reconditioning discharge characteristics when we put the one ohm resistor on. You can see that we start out at approximately 31, 32 volts and we come down to 0.01 volts per cell.

What we are looking at here is actually the terminal voltage of the battery. We don't have individual cell monitoring, but if you want to find out what the actual cell voltages were here, you would just divide it by 22 since we have 22 cells per battery.

What is interesting here is to note that the line with the dashes and the "x's" on it is our first reconditioning which we did in January 1978. It was done prior to the eclipse season because it was done as part of an overall in-orbit check-out test.

We noticed that the capacity that we received out of the battery at that time (which if you integrate that, comes out to be approximately 17 and a half to 18 ampere hours), is pretty much duplicated again after sixth reconditioning, which we performed in August 1978, which was our last reconditioning period. And that is depicted by the plot of the circles and the dots, I guess, as we come down here.

So we can see that for the most part, we don't see any significant or measurable increase or decrease in battery capacity after six eclipse seasons of reconditioning. This happens to be Battery 1. If you put the next slide on, I will show you what Battery 2 looks like, and this is the F-1 spacecraft.

(Figure 3-54)

Looking at both of them simultaneously, you can see how the two batteries compare. Again, this is the sixth reconditioning for F-2. So the voltages are holding pretty well. Again, we don't see any capacity loss at this time.

As we go to the next figures, we would like to show you what our end-of-discharge voltages look like.

(Figures 3-55 and 3-56)

On the main screen, we see the F-1 end-of-discharge voltage which rather than depicting it is just a single point just to show it as a straight line at a given voltage. This is the actual cell voltage corresponding to the battery terminal voltage.

You can see during the first eclipse season, and we are actually again discharging at a 48 percent DOD of actual. We have a first eclipse season at this point here. Our second was down here. Our third and fourth happened to be the same points. Our fifth season was in between the two. And our sixth, and most recent, was down at this level here which was approximately 1.181; I believe that is correct.

FORD: What's down on the X axis?

NAPOLI: There is really nothing. This happens to be the 21st day in the eclipse season or the peak eclipse period, so we are looking at voltage versus time and peak eclipse.

Again, this is really one point. I have just drawn it out as a straight line just to put something on a chart. You can see what the loads are. These are what our eclipse season loads were. I have some points missing, mainly because it is probably buried in the archives of our controls and I can't find it right now.

But you can see we have 5.61 during the third eclipse season; 5.7 during the fifth; 6.1 during the sixth. These were the average battery loads.

F-2, as I indicated, in addition to having the typical eclipse load, also has a daily discharge of down to about 24 percent DOD. You can see here that, after five and a half eclipse seasons, the end of discharge voltage is running very close to the F-1, which has a more benign operating environment since it doesn't have the daily discharge.

Again, there are some differences here, but again, these differences we don't seem to feel are really significant at all. In fact, the differences between the F-2 and F-1 appear to show that the F-2 and the discharge voltage is performing somewhat better than the actual F-1 because their values are higher.

These are average battery currents. I have taken the average of all three batteries. I don't have a chart of it here, but we have also looked at the load sharing between batteries and again, it is almost an immeasurable difference amongst all three batteries. They all seem to be contributing the same amount.

This is what our performance looks like in terms of end-of-discharge voltage. The question that comes up, and always has come up, really, is: how does reconditioning or does reconditioning improve performance? The only way you can really make this comparison is by looking at some standard yardstick. And looking at yardsticks, you have to try to get rid of all the variables and it is hard to do. Because if I tried to compare our cells, which are say in 1975, into inteflonated negatives against somebody else's cells, which maybe were manufactured in 1970, it is hard to really make a comparison.

However, I will show some data on the next figure which was provided in the paper that the Comsat had delivered at the 28th Power Symposium Conference in Atlantic City in May.

(Figure 3-57)

What I have done here, I have taken the INTELSAT IV F-2, F-3, and F-4 data and I have plotted it on the same plot that we have our end-of-discharge data. Now, this particular point here is the F-3 spacecraft which is running at 45 percent depth of discharge of actual. If these numbers are wrong, Comsat, I would like a correction, but I believe that they did run at 45 percent depth of discharge actual.

This was the fourth eclipse season and this is their end-of-discharge voltage during peak eclipse. This compares with the third, say our fourth eclipse season data point which is right up over here.

On their F-4 and F-2 spacecraft, you can see various data points over here. Now, this point down here should be the fourth eclipse season for the F-4. I am sorry, I take that back; that is correct as it is. I believe that is the fourth eclipse season for F-4. Right, and this is the sixth eclipse season for F-4. That is correct. What looks like a "6" is actually a "4" on that triangle with a dot in it.

So trying to get a comparison, again, it is difficult because of the variables, but the INTELSAT loads are between seven and eight ampere hours on discharge. Ours are slightly less, but we do go down the same depth of discharge and do have a newer cell. We do have a cell of different design in the fact that we use teflonated negatives. And we do have another thing which is important, too: the maintenance during solstice.

On the INTELSAT program, they maintain the batteries on open circuit and we maintain them on a trickle charge of C/60.

The real basic difference here is that we recondition down to 0.01 volts per cell and INTELSAT, I believe, does down to approximately 1 volt per cell.

This is how our performance compares against—well, I like to use the term "a yardstick" in the industry; in fact, it is an excellent data base. The Comsat data that they presented at that conference is really an excellent data base. And I appreciate Dean Maurer's ability to try to use that data for a means of prediction of spacecraft battery life. I think that is an excellent data base.

In trying to get some more data as a part of this comparison, I have been talking to Lieutenant John Capuli from SAMSO, who provided me with some NATO 3-A and 3-B data.

The NATO 3-A and 3-B program has an ideal depth of discharge of about 22 percent of actual. Their charging techniques are somewhat different. They have a sequence that they call "tri-sequence charging." So again, it is hard to make a one-for-one comparison here. But I will say that in terms of the depth of discharge, they are far more benign than we are, since we go down to 48 percent and they are at about 22 percent. They do recondition once a year because of temperature effects; they can only recondition once a year. They recondition down to one volt per cell.

(Figure 3-58)

Looking at the next figure here, we can see that this is the INTELSAT 3-A data point, end-of-discharge voltage during the fourth eclipse season. This is the 3-B data point during the fourth eclipse season. Again, these are down at 20 percent depth of discharge of rated.

Now the difference between 3-A and 3-B, as was explained to me, is that the 3-A batteries were not as fresh as they would have liked them to be when they put them in the spacecraft. They were maintained on extended cold storage for quite a while before actually being put into the spacecraft and launched; whereas, the 3-B batteries were quite fresh when they put them in. They were not sitting around in cold storage. As soon as they were manufactured, they were tested and put on a spacecraft and put into operation.

So that is what the differences appear to be—at least what SAMSO's explanation is, what the differences appear to be between the 3-A and 3-B performance.

In conclusion, it appears to me that the reconditioning on the cell level down to close to zero volts does at least improve performance at least in the early years of the spacecraft. Only time will tell if this performance will be extended out to our eight-year mission, and hopefully it will.

We are still trying to accumulate a large data base here, and we will be presenting more data as time goes on. Right now, I do feel that reconditioning down to that level based on the data that I have here is the way to go on future spacecraft design.

## DISCUSSION

DUNLOP: Since you use that data of ours, I would just like to make a couple of comments. I basically agree almost completely with what you said.

The data that we showed on the INTELSAT IV spacecraft that you showed up there after six eclipse seasons, that really goes on out to 12 eclipse seasons, to 14. And if you notice, what really happened is it sort of stays around that 1.16 to 1.15 volts per cell and then about the 12th season, starts dropping off. So we were lower in voltage than you are and we do attribute that lower voltage observed during eclipse seasons due to reconditioning.

We know from laboratory tests that if you do do the zero volt or the one volt reconditioning that you will get better voltage performance earlier in life.

The big question about reconditioning that still remains to be determined is what its effect is going to be after about five or six years in orbit.

But I agree with you that earlier in life, you certainly get a voltage improvement.

There seems to be a tendency for that voltage improvement to diminish with time.

The other point is that we were not reconditioning to one volt per cell. We were only reconditioning to 1.15 volts per cell, which is really not a very effective reconditioning level to go to. Either one volt or less is much better than 1.15.

The other thing is we did have those cells on open circuits for a few years, but we switched all the things over to trickle charge about two and a half years ago. So everything we have running has been on trickle charge for the last few years during storage.

NAPOLI: Thank you. The only reason why I didn't present your other data points beyond the six eclipse seasons was we are not that far in time.

MOORE: When you recondition a week and a half before the eclipse season starts, do you discharge each battery one time or do you cycle it a multiple number of times? And the same question for INTELSAT: do they just discharge once or a number of times before the season starts?

NAPOLI: As far as Satcom is concerned, we take one battery individually and we recondition that only once. We bring them down to that level and then we recharge them back up and then by the time we recondition all three batteries, we are a few days short of entering the actual eclipse season, so we only do it once. It may be, as time goes on, if the data base shows a degradation more than we like to see, then we may consider reconditioning twice to see if there is any noticeable effect.

The problem we have, of course, is this is a commercial spacecraft and we don't have the liberties of doing a lot of things that people in the battery field would like to do. It is not an experimental spacecraft; we have done it in ATS programs, for example, and we can't show all the data that the ATS people show. We just don't have those experiments on board.

DUNLOP: Just in answer to that question. We used to recondition twice, but we only do it once now. I would like to say one other thing. When we do the reconditioning now, we are out to 12-14 seasons, we are getting a lot of problems. We are trying to do deeper recharge reconditioning and we are running into shorts.

This is sort of along the same lines that we discussed yesterday. The cells, once they get to be up about six, seven years old, you start getting a fair amount of cadmium movements in the separator and into the separator and into the positive. You start seeing these partial shorts developing that were alluded to yesterday.

And now when we try to deep discharge reconditioning with a resistor across the whole battery pack, the problem is that we are running into individual cells dropping out and reversing, and the next problem is that when we try to charge them back up, sometimes they charge back up and sometimes they don't.

Now we have, in a number of spacecrafts, one or more cells that have shorted and in some cases, we haven't been able to get them to unshort.

Another problem we are running into, by the way, is that we are hitting high voltage on a lot of cells once they get beyond six years. You start seeing a lot of cells where the whole battery is pulled up in voltage and we are hitting voltage limits and having to curtail charges.

FORD: Joe, I would like to draw your attention back to two particular curves: one, you showed the voltage profile on reconditioning sequences; and the other, you showed the voltage end of dark at a particular eclipse over the several eclipses.

I note that there is a much smaller delta of voltage change-over reconditioning than the delta you are seeing from eclipse season to eclipse season. And recalling from discussion last year, or maybe the previous year at workshops, was some allusion to the fact that the voltage performance on discharge was becoming more and more rate dependent as a cell aid. I wondered if you would care to comment on that and maybe extrapolate in your own thinking how you can relate the reconditioning voltage to performance voltage as far as normal use during eclipse season.

NAPOLI: That is an interesting comment. The way I have looked at it is that when we go into this reconditioning discharge, we go into it at a very low discharge rate, namely, whatever the voltage is at the time (typically 1.4 volts divided by one ohm), so you are at about 1.4 amps of discharge rate.

Our actual load voltage during eclipse is at a higher rate. It starts out at about five amps and because we have a constant load on the spacecraft, as the battery voltage does down, the load is requiring additional current and that is also bringing the battery voltage down to some plateau.

I think this last voltage point that we saw here, that is actually down to the plateau level of discharge current which you get to rather rapidly during a six-ampere hour discharge rate, which you wouldn't be at a 1.5-ampere hour discharge rate. So I definitely think that the level of voltage that you get down to is certainly discharge rate dependent. And I think that, of course, the six-amp discharge rate, you are going to see a more severe degradation; but to the plateau level anyway.

I think what we have seen there, (hopefully, anyway), is the plateau level. I would like to see it stay at that level for the next six years.

LEAR: You were showing a comparison of the reconditioning of Comsat to yours, and Jim Dunlop made a comment about he only discharges down to 1.15 volts per cell. I was wondering what his rationale was for selecting that particular voltage.

DUNLOP: We started that 1.15 volt per cell in 1970. In 1969, 1970 is when that 1.15 volt thing was picked. The idea there was that you wanted to make sure you didn't reverse any cells. Now, actually that was a bad level to go to. We think that that 1.15 volts is not low enough to do an effective reconditioning.

The argument is (and it keeps coming up over and over again), if you do discharge a battery deeply, you want to get a good reconditioning, you have got to discharge it deeply. That has been well demonstrated by TRW in the last few years, and I think there is work at RCA which has well demonstrated the fact that a deep discharge reconditioning gives you better voltage performance on the next eclipse season.

The reason that you have to keep doing it over and over again is that the reconditioning is only a temporary effect, and so you have to keep doing it over again and over again to try and get the beneficial voltage performance.

We watch what everybody else is doing, so now we try and do deep discharge reconditioning on INTELSAT IV. Now what happens is we don't have the ability to put an ohm resistor across these cells like RCA does, which is a very nice way to do your discharge because you don't have to worry about reversing a cell. TRW, in the last few years, has been saying you can put a resistor across the entire battery and discharge it down. We have been trying to do that in the INTELSAT IV spacecraft, and the problem has been that we start reversing individual cells before we can discharge the whole battery down. They have got individual cells dropping out and going into reversal. These are on aged batteries, not on new batteries.

The big question now is not whether it is beneficial, not in terms of voltage performance, but how to do it in terms of not getting into this reversal phenomenon, so the idea of discharging a battery across one resistor is kind of a difficult thing to do, based on our experience, because you do get reversals occurring.

The other problem that you run into is that as the batteries really age, it is not clear whether you can do an effective reconditioning because you have got this partial shorting business going on with cadmium migration and it really doesn't allow you to do an effective reconditioning.

But the other point that Joe is making is that if you drop your current level way back, like if you drop back, you normally discharge at a seven-amp rate, and that really causes problems. If you drop back a quarter an amp rate, you might be able to do this, then you can discharge the battery a lot further before you start running into these problems that you see at the high rate.

GROSS: What was the design, the maximum depth of discharge for the batteries and the design mission duration?

NAPOLI: The design mission duration is eight years. Originally, the spec on the battery was not to exceed 65 percent depth of discharge. In actuality, we are operating down to 48 percent of actual and 58 percent of nominal.

GROSS: Did you make any determination of the effects of the daily discharges on the battery performance or the battery design depth of discharge limitation?

NAPOLI: I don't think I understand the question.

GROSS: What is the effect of the daily discharge?

NAPOLI: Well, I have shown the data here. The effect of the daily discharge is that we have an additional daily discharge of about 24 percent DOD on one spacecraft, in addition to the typical eclipse seasons.

Now, what that has done to us performance-wise, based on the data that I have shown here, it hasn't done anything. In fact, if you saw the F-2 and the F-1 data, you can see that they are running pretty much neck and neck where the end-of-discharge voltage is, during the sixth and five and a half eclipse seasons, respectively, on F-1 and F-2.

So we don't see any difference. In fact, earlier in the discharges during the, say, third and a half, second and a half, seems to be doing a little better than the F-1 spacecraft which has more of a benign operational experience now.

I guess benign is something that is to be defined here. What is more benign, to cycle once a day or to cycle 88 times a year? A lot of discussion could be made about that.

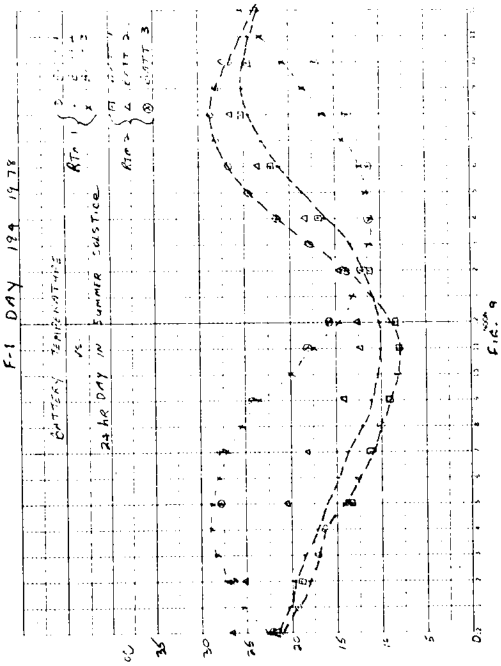


Figure 3-52

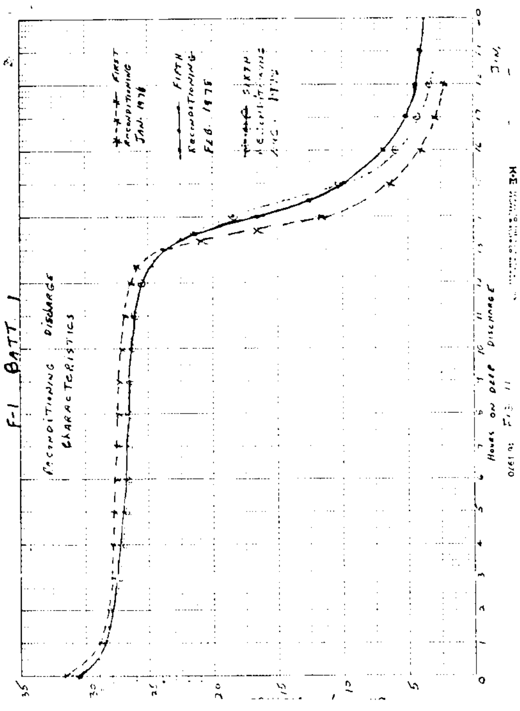


Figure 3-53

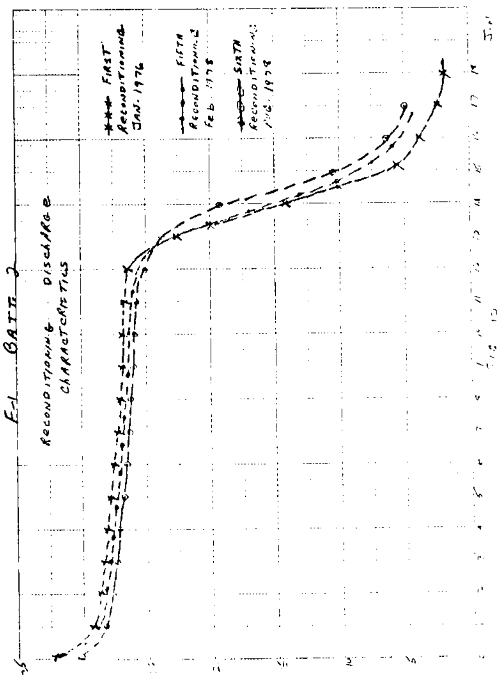


Figure 3-54

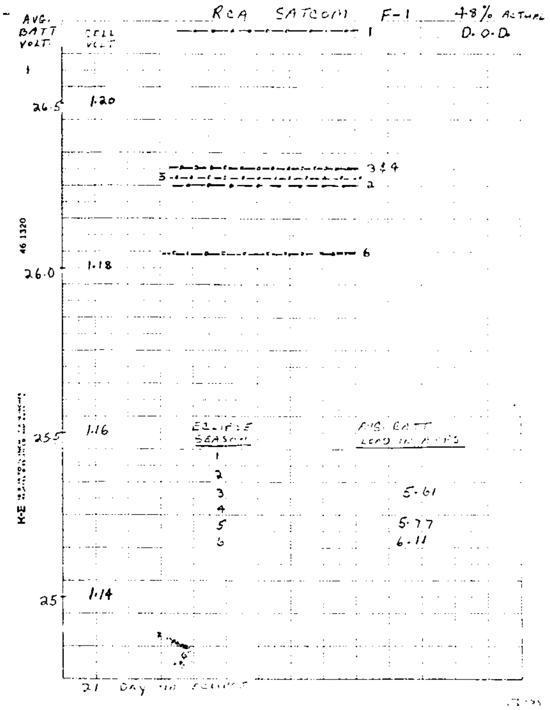


Figure 3-55

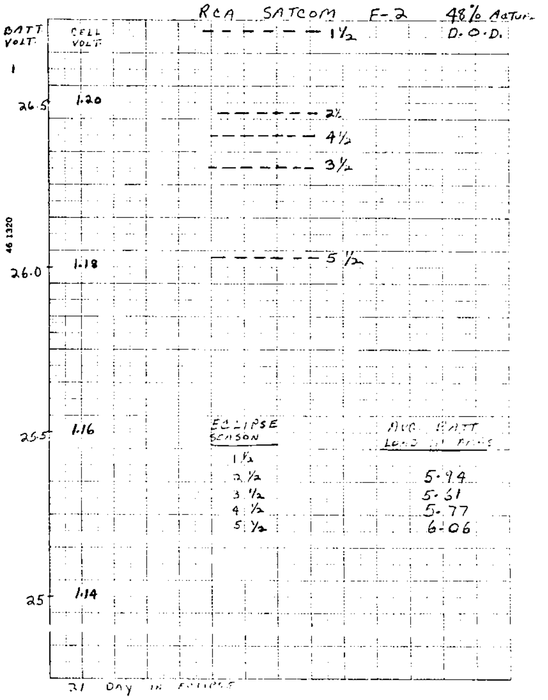


Figure 3-56

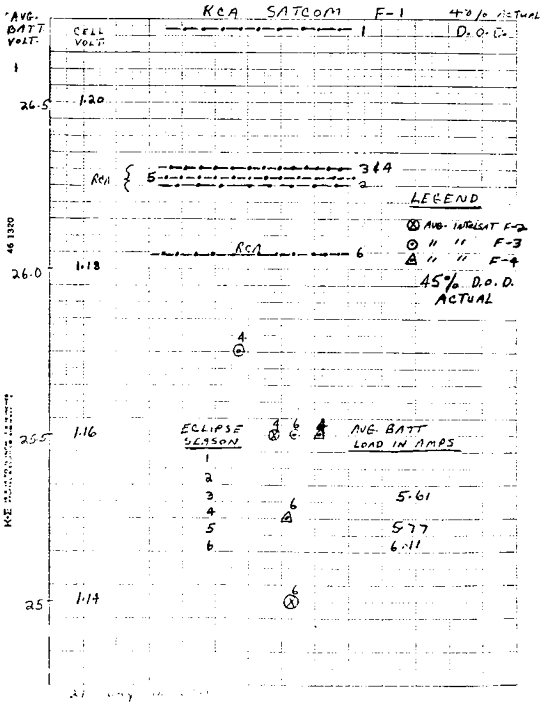


Figure 3-57

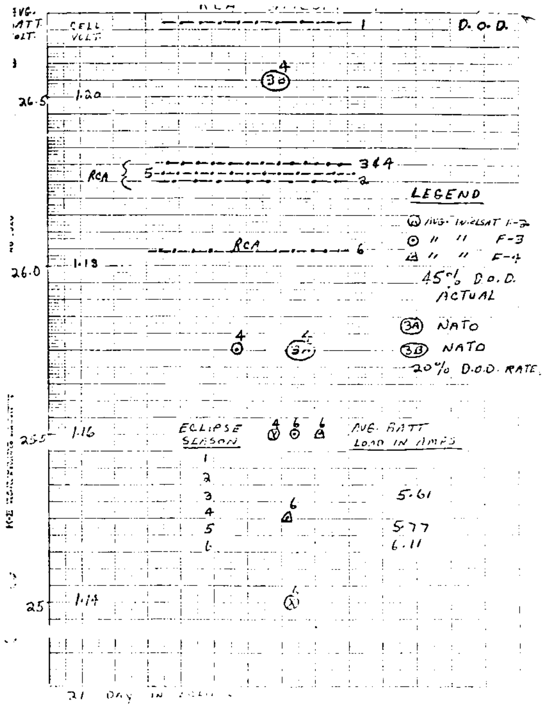


Figure 3-58

# CANADIAN TECHNOLOGY SATELLITE, AN UPDATE

J. Lackner
Defense Research Establishment

The title actually is Communication Technology Satellite, or CTS for short. Actually, I feel that some of the previous speakers have covered most of the material. This will only be a brief update on the performance because in the past two workshops, we presented the basic reconditioning philosophy and the design philosophy of the spacecraft. I will just try to point out one or two significant observations.

Although I should say that the spacecraft weight limitations in the short mission life of two years didn't allow us to have the optimum life design that RCA has and perhaps Hughes has. In fact, we possibly are doing several things we shouldn't.

First of all, as of the 17th of January, 1978, CTS did successfully meet its two-year mission life, and is now operating on its third year and there is a fourth year of operations planned.

What this points out is that we shouldn't allow short mission life design to compromise the long life characteristics that we know we should put into a battery because it just seems that the short mission life spacecraft end up extending for longer once they are in space.

So our two-year design life, which has been met, is now being extended to four years. Some of the operators are wondering why we are having battery problems.

One of the unique characteristics of CTS is that it operates half the year in the hot ambient of 18 to 30°F during the summer solstice and the other half of the year in the more ideal cold ambient of zero to 12, the winter solstice.

Now there is a definite fading in wattage and capacity during the summer solstice. One of our batteries, Battery "B," can get down to about as low as 20 percent DOD in the summer solstice. This is a function of the temperature dependence, the cadmium migration, and the self-discharge rate.

There is a little to no fading in capacity during the winter solstice, and the reconditioning is much more effective in the winter than it is in the summer. So if there is a temperature dependence or reconditioning, it definitely is better between zero and ten degrees than it is between 20 and 30.

During the noneclipse season, the batteries are subjected to a C/100 discharge rate and periods of open circuit stand of up to 18 hours a day. We don't have a trickle charge.

This has resulted in an increased self-discharge, particularly during the summer solstice season, where Battery "B" is self-discharging at approximately 100 milliamps per hour and "A" at about 35 milliamps per hour.

We have taken internal resistance readings of some cells on our simulated eclipse cycler which runs on the ground. Simulated eclipse cycler has now logged three and a half years real life and eight eclipse seasons.

The good cells on the eclipse cycler have 2.8 milliohms at the end of charge and 3.6 milliohms at the end of discharge; whereas, the poor cells have 5 milliohms at the end of charge and something like 23 milliohms at the end of discharge. So we have quite a variation in cell-to-cell which is reflected in voltage.

The other point that I wanted to cover is an allusion to the temperal affects that Dean Maurer talked about. We have noticed that if we discharge our simulated eclipse cycler at the C/2 rate, we can in 40 minutes get out 50 percent DOD to 1.25 volts. If we operate at our normal C/100, daily discharge rate, over 20 hours we come down to 1.25 volts and we only have taken out 20 percent DOD. So when you are comparing depth of discharge with rate, you have to take into account the time factor.

The batteries on the spacecraft now are giving, after two and a half years' operation and six eclipse seasons, 70 percent of nominal on Battery "A" and 50 percent of nominal on Battery "B" to our operational cut-off of 1.08 volts per cell. These are capacities that have been determined on reconditioning.

To try to get back to Joe Napoli's data, if we took our six eclipse seasons, the longest day, the minimum voltage we would have hit was 1.14 volts. That fits in with your data.

We do recondition down to 0.9 volts per cell, and at 0.9 volts per cell we are retaining 90 percent of rate on Battery "A" and six percent of rated on Battery "B."

With time, they spread in the low voltage capacity between 26.2, which is our minimal operational voltage, and 21.6, which is our cut-off voltage on recondition. That is equivalent to 0.9.

This degradation has been varied between 0.08 ampere hours at the start of life (that is, the difference between 26.2 and 21.6 is only 0.08), that means you have a sharp drop of voltage. And after two and a half years in orbit, that difference is now 1.3 amp hours.

On the simulated eclipse cycler on the ground, which is three and a half years old, that difference is now two amp hours.

So there is a definite shift to the lower voltage capacity.

In reference to parallel operation of the batteries, the batteries are hooked in parallel with isolating diodes, and we find that it is quite difficult to maintain a balance between the two cells, since they are at different geographical locations in the spacecraft and they are 12 hours out of phase as temperature, the same as Joe Napoli's. And we find that Battery "A" takes far more than "B."

# HCMM/SAGE TEST RESULTS

F. Ford
Goddard Space Flight Center

The two different spacecrafts I am going to talk about are part of the Goddard program called AEM, which stands for Application to Explore Mission. Basically, the concept was to develop kind of a standard bus for small satellites, something that could be carried on a scout vehicle to keep the launch costs fairly reasonable and also to carry maybe a single experiment.

The first mission of the AEM program was HCMM, and it stands for Heat Capacity Mapping Mission. Basically, it is mapping the thermal profile of the whole world.

SAGE stands for Stratospheric Aerosol and Gas Experiment. I think that is self-explanatory, but basically, it is part of the continuing effort to study the stratosphere concerning pollution with various types of gases, particularly Freon/Gas.

At the onset of the program, the idea was to try to implement the NASA 74 15,000 spec, using the manufacturing control document process that we have become familiar with, to set up configuration control through this documentation such that over a period of several missions, which it hopefully gets the same general performance out of battery characteristics and pretty well get it into a routine operation as far as self-procurement, battery testing, and flight performance, recognizing, in fact, that the in-flight application of the battery does change because each mission is in a different inclination, maybe a somewhat different altitude; but basically all of them are in a near earth environment.

The cell I am going to discuss concerns two procurement lots manufactured approximately four months apart. In fact, the HCMM activation date was in November of '76; activation date meaning, in this case, when electrolyte was added to the cell. The SAGE activation date was in March of 1977.

The parameters that are presented to you are what I refer to as the saliant features of the HCMM and the SAGE cell design. I might point out something here because I want to come back to it later on after I present some data, comparing the two groups of cells.

One is this fairly common use of negative-positive ratio parameter now, the 1.79 versus 1.47, and I would like to contrast that with what is shown in the line called utilization. That is the flooded capacity as percent of theoretical based on late pick-up.

(Figure 3-59)

I point out to you that the utilization of the positives in both of these cases came out to be very close. However, the utilization of the negative, while for practical purposes you may say that is not much of a variation, I happen to believe that that is one of the most important parameters that we have to deal with today in evaluating negative electrode performance for use in flight applications.

(Figure 3-60)

The two different lots were sent to the Naval Weapon Support Center in Crane. We had five cells out of each lot to do a life test on and the life test was, indeed, set up to try to simulate the electrical environment and to some extent, the thermal environment. But the thermal environment was a control in the engineering chamber, but the logical parameters are reflective of those that was to be used in each battery in each satellite.

The one exception here is that on the SAGE life test, the initial charge rate was set at two amps. This represented end-of-life current for one-year missions that would be available from the solar ray. We initiated the test with that charge rate in order to make sure that we could achieve energy balance under cyclic conditions, as the batteries had stabilized after some earlier cycling.

That was increased to a product of about three amps, which was like the beginning of life, the charge rate on the batteries during the early missions or during the beginning of life rate characteristics.

The batteries are used in a multiple V versus T charge control concept not unlike the ones that have already been discussed. I will show these for reference only.

(Figure 3-61)

In showing those, recognizing the complexity to it, but basically, the bus concept of the AEM on both spacecrafts have two sets of voltage limiters, which keeps the battery voltage constant as a function of temperature. The reason you see double levels there is because there is electronic offset to keep the two voltage limiters from having to try to track each other.

So one set of voltage limits go to the full operation and then the other set comes in. The test points that we used for life tests, as indicated on the previous test, was 20°C and it is about 1.43 volts per cell that we cycle these two packs at.

(Figure 3-62)

This figure is a summary of the HCMM life test, showing on this side cell voltage from 1.35 to 1.50. This is the nominal, about 1.43 volts per cell. On this scale is charge-discharge ratio from 100—1.1, 120, 130, up to 150. percent. And of course, this is cycle life in thousandths of cycles. For reference, there is 2000 cycles, 3000, 4000, 5000 cycles. Nothing particularly unusual about these characteristics, noting that the control lets us operate with about 1.1 C-to-D ratio in that particular orbit.

This indicates the first capacity test after six months of 2700 cycles, and we got 11.22 ampere hours.

I guess I should mention, as was indicated on the earlier figure, that this is an RS-10 cell. It was down-rated to a non-ampere hour cell because the loading was decreased slightly on these plates compared with that which EP had been using on the RS-10. As a result, we said, yes, you can derate it to a 9, but it still came in as a new cell in excess of 11 ampere hours. And it was still delivering in excess of 11 ampere hours after six months.

At the one-year period, we are down to approximately 10.2, but again, the capacity degradation here is nothing abnormal. We expect to see this. Bear in mind we are running these two packs of cells in parallel life tests, not parallel electrically. But they are being run simultaneously; one is about five to six months behind the other. About the time we saw this characteristic develop (and again, the voltage limit here), we started off with 1.34 volts per cell. We started seeing a sudden increase in the C-to-D ratio on the cells. We compensated for that by going to a lower voltage level which, in fact, we finally had to go up to 1.45, which was one of the lower curves I showed you in the eight levels, and brought the C-to-D back down and we have been sitting at that level pretty consistently. I believe that we are almost close to the two-year point on these cells.

The subsequent part of my talk is going to concentrate on the SAGE cells. I brought the HCMM cells in mainly as a point of comparison, because about the same time (approximately a year) we saw the C-to-D ratio take off on that group, we were approximately a thousand cycles in the life test on the SAGE cells.

(Figure 3-63)

Again, the same type of plot: recharge ratio, cell voltage limits, the dotted line here indicating the actual, the average control limit of the five cells. I mentioned earlier we start off with only two amp charge rate to indicate end of life conditions on the spacecraft. Actually about 800 cycles is indicated here. We up the charge rate to three amps. We were running approximately 800 cycles at a C-to-D of less than 1.05 or around 1.03 to 1.04. When we upped the charge rate, it had some effect, and shortly thereafter we actually saw the same characteristics of the C-to-D taking off.

Now we are charging with a current limit, not the potential, so if there is any change in cell voltage, the earliest and most significant manifestation of the change will be an increase in the overcharge.

This type of increase in overcharge would be prohibitive in a satellite because it has a very straightforward thermal design. It has a very finite limit on the amount of heat it can dissipate.

We let it go in this case until we got up to a C-to-D ratio of 1.6. What I have tried to indicate here is the type of cell voltage spread we were getting around the control limit. We have not altered the control limit. The load indicates the low cell in a five-cell group, and interestingly enough, it was not always the same cell. And the high is the same (the high cell in a group at that particular point), but that also was not always the same cell.

Generally speaking, the high tended to stay high and the low tended to stay low, but there were exceptions in a number of cases.

Obviously, we were somewhat anxious about this type of characteristics, and subsequent cycles out here are not shown. We went to a lower voltage level at 2400 cycles; we want to 1.412, which would drop you down to about this region. That brought down the C-to-D ratio, but it continued to increase, and at Cycle 2426 to get the C-to-D ratio down. Again we were using constraints that were available in the spacecraft charting system, so we were using the voltage limits. We went to the lowest voltage level, and we ended up at 1.393 volts per cell, at which they had been cycled at that time

Not shown here also is that it brought the divergence down, but we did continue to see cell voltage divergence among the five-cell group in its pack.

I mention the capacity checks that were run. I show you this one as a comparison of the six-month test point of the three groups.

(Figure 3-64)

There is only one cell running capacity on the HCMM cells, as indicated by this curve. We did that simply because that is a sequence we have set out. We run cells on different sequences—like Cell 1, I run the first six months; Cells maybe 1 and 2, I run the second six months; and keep doing that repeatedly until we get through all five cells over the life that we have set up the tests for.

But what I indicated here is that in the same relative time span, a little bit different orbit time, but basically the same depth of discharge, that the degradation on the SAGE cells was quite a bit more drastic than that we have seen on the HCMM cells.

(Figure 3-65)

The next figure is to give you an idea of what a typical cycle looks like. It certainly is not indicated to be absolute, but gives only the trend of the data, showing the high cell on discharge and the low cell on discharge. This is for cycle 4333, at which we are at that voltage limit which I indicated earlier of 1.39 volts per cell. I remind you this test is also being run at 20°C.

This shows you the general profile. There are only data points here, which tends to smooth this charge, but actually, it comes up, hits the voltage limit, and then what you are seeing is, in this region, the divergence of voltage while it is in the current taper region.

(Figure 3-66)

After that particular cycle, we decided to do another capacity test. We had done one at approximately 2700 cycles and found those cells to be low. Looking at the data more closely and watching the tests almost day-to-day then, we became a little more anxious about what was happening to the cells. So at 4344 cycle, we did a capacity discharge, and what this indicates is the range of cell capacity that we got. A high of 7.7 ampere hours and a low of 3.13 on C-2. This cell, too, was the same low cell on the previous cycle that I showed you, and in this case, this cell was also the high voltage on discharge.

But in the test regime, in the application that this is being looked at, this was (to put it very mildly) abnormal degradation.

At that time, we decided to remove the pack and life tests and try to do some further off-line evaluation of just what may be causing the problems with this particular group. Bear in mind the HCMM cells are still continuing at this time; at the time we did the special test they had over a year and a half and they were still running pretty close, as I showed you, at the end of the profile I presented earlier.

The special tests consisted of taking the pack off the life cycling and running an abbreviated portion of the initial evaluation tests that we had done at Crane on the two groups when they were first received. The initial evaluation tests that are referred to in the standard test, of which most of you on the distribution list get a copy of these little yellow reports that may have different flight programs, but the series of tests we do on all cells prior to putting them on life cycling.

One of those tests is a seven-day open circuit stand test which we have implemented, and we decided to go back and repeat that test. But what is summarized here is the data where the in-point data that you saw on the cycle I gave earlier for 4333, you see the actual discharge, capacity range. On the previous cycle, I showed the high and the low. This shows you the actual range (to eight-tenths of a volt) and the span and capacity we got at this point.

The cells were subsequently charged, end-of-charge voltage; now this is at room temperature. You notice we have got high cell voltage on these cell—at least on some of them, and some of them had to be terminated for that reason because they exceeded the voltage limits for a given period of time, which by the criteria we established previously constitutes removal from the charge.

We then allowed them to stand open circuit for seven days. Shown here in the two columns is the 24-hour reading on the voltages and the seven-day readings showing the drop-off in discharge

(Figure 3-67)

Also, this shows after seven days of $CO_2$ discharge the range of capacity we also got. Again, this indicates this C-2 certainly has a high leakage rate. I don't know that I can call it a short, but there is some mechanism causing this cell to lose capacity at some abnormal rate.

At the bottom, I presented the open circuit stand data for seven days during the initial evaluation test to give you an idea of how these values compared prior to life cycling or, in this case, at zero life cycle versus approximately 4300 cycles.

(Figure 3-68)

The discharge voltage characteristics of those cells after the seven-day open circuit stand are indicated here. But basically, it shows the voltage profile. Again, these are not very smooth plots, but just showing the general trend with the low cell C-2 and the high cell over nine ampere hours, which is the C-1 position of the cell, and, of course, the other cell in between here.

I think it suffices to say that the decision was made because of the early degradation of the one lot not to use them in a mission. It was an evaluation done by Boeing, the prime contractor, on an integration battery, and that battery is now being prepared for launch, I believe. The satellite will be launched in February.

The reason for presenting this is not so much in what is in the absolute value of the data, but to highlight a continuing problem, as I see it, of getting reliable space batteries. I don't know what the cause of the problem is. We are still looking at it; we don't have the answers. We hope to get to the bottom of it in the not-too-distant future because, obviously, this affects our planning for subsequent missions on this type of a program when we have several planned over the next four or five years.

But I leave with the question: what does it take to get repeatability out of the manufacturer? We certainly did not get it here. We had what we thought was the best configuration documentation control that we have ever implemented. It has worked in some cases, but it obviously is not 100 percent.

Now you talk about the cost of batteries, what it costs to get a good cell. The cost of a program is really hit hard when you get into a problem like this, particularly if it is schedule impact. Fortunately, this problem was identified in sufficient time that it will not impact the launch schedule of the mission. Had it impacted the launch schedule of the mission, the cost of this battery was trivial compared to the cost it would be to that mission to have to recycle the launch schedule.

## DISCUSSION

KILLIAN: Do you think that ampere hour meter charge control would help you with some of those charge problems on orbit charge control problems that you had, and do you think you will ever go to it?

FORD: First of all, this is life test, not on orbit. We haven't seen this in orbit. The HCMM is up there and I guess it is close to six months old. We see no real problem or significant changes, although we expect in a year's time, based on the life test, to have to adjust the voltage limit.

Addressing your specific point: in this case, for a satellite application and life test, we can do a lot of things because we have an infinite heat sink as well as the environmental chamber we are in. In this case, we looked at this performance in light of what the impact would be on the mission. It was a case where we are damned if we do and damned if we don't.

But we need the depth overcharge. Obviously we could do that to get more higher recharge. We could have kept that cell up in voltage. In fact, as long as we let that C to D run in the high range, we didn't get the drop-off in discharge voltage. But the consequence was that would be that the battery temperature in a satellite would probably get well over 35°C, even higher maybe. I don't know.

It was the thermal people who said they could not handle that much heat. The other way to go down in voltage limit, as we did in life tests, and actually show that the battery cells (one-cell capacity or all the cells to varying degrees) were actually losing capacity.

Off the cuff, I can't think of how an ampere hour meter would have resolved the dilemma we would be faced with if these were in a satellite up there flying today.

My general experience with what I call the onboard electronic meters has not been good. We are using onboard software ampere hour meters, if you can call it a term like that, where those satellites that have onboard computers are actually doing an on-line calculation. In fact, the satellite that has always recently launched has a very good onboard software program because they store it in tape recorders and the past pre-orbit history is always in a tape recorder when they identify to the experiment. They look at whatever they want to as far as the experimental checklist is concerned.

THIERFELDER: Have you done a failure analysis on these cells?

FORD: We are into that. We had at the same time, and not addressed here, another group of cells from SAGE that were here at Goddard under parametric test. Parametric tests look at the interaction of voltage levels, temperature, depth of discharge, and so on for other missions in general.

We had a similar problem on those cells. We took one apart and we have done analysis. We found a few peculiarities in it, but it was so preliminary that I would not want to go into it at this time. Maybe by the next workshop, I would like to discuss that, but we are in that process right now.

WERTHEIM: You indicated near the beginning of your presentation that you thought the negative utilization and the negative-to-positive ratio might be significant, but you did not follow that up. Do you want to comment on it now?

FORD: Well, yes. I was hoping someone would ask that question. If you look at this data on the surface, you can draw a number of conclusions. One of the conclusions might be, well, look at the HCMM cells. You have 1.8 negative-positive ratio and they performed relatively well compared with the ones that had the lower ratio.

That is a very shallow look at the cells. We have been looking at data over a period of time from different manufacturers, and one of the things that we see is that negative utilization bounces around for one or two reasons: either we don't know how to measure it adequately at this point, or it is really indicative of the process or something in the process. But the negative utilization is one of the most inconsistent parameters we are seeing from the data we are getting from manufacturers today.

We have seen a lot of effort and a lot of discussion on the positive electrodes. That has been in the previous workshops; it was at the electrochemical study this past fall. I am of the firm belief that if we are going to make a better nickel cad cell, we had better do something about the negative electrode because that is the factor right now that is giving us the biggest problem.

I don't deny the data that has been presented, the positive plate expansion. I am accepting that the electrochemical impregnation process on the positive is a vital one and that is the way we are going to be going in the very near future. But all I am saying is that if you take the technology of where we stand, that has not solved the problem with the negative and all this stuff we were talking about earlier (the reconditioning, voltage fade). A lot of this stuff can be attributed to electrolyte starvation. Once you get a wet cell, once you get more than enough electrolyte for the life of the cell that you have got, you still have a voltage fade; not a capacity fade, but a voltage fade. All evidence I have seen says that this is a negative electrode phenomenon.

BOGNER: You kind of hinted that that one cell was shorting. Is it shorted?

FORD: Well, having looked at the background, it is not a short. A short is a short is a short, okay? The cell is not shorted. There is a mechanism which has got a high self-discharge on it.

BOGNER: It is not losing its capacity on the stand? It is not there to begin with, is it?

FORD: Well, you don't have to have a shorted cell to lose capacity. You can have self-discharge for other reasons. You don't have to have a physical ohmic short. Now we have not opened that particular cell to—

BOGNER: It is usually the positive electrode that controls the self-discharge.

FORD: We happen to think there is—

BOGNER: I don't want to argue the point you are trying to make.

FORD: Well, we are still exploring the amount of impurities in the cell and what particular impurities are there at this point. We have not resolved that to our satisfaction.

BOGNER: What did the charge voltage on that particular cell look like?

FORD: The low cell on discharge was always the low cell on charge. The charge voltage would not come up on those cells. Now if you overcharged like to 160 percent, you could push the voltage up, but you still couldn't get it up to the nominal level we would expect to see.

BOGNER: Sounds like a problem we had on the Viking orbiter battery on a couple of cells.

FORD: It may very well be.

RAMPEL: I agree with your statement of negative electrode improvement, but I think it is important to consider that the nylon separator in the cell interacts with and also contributes to the lower voltage that you mentioned. Polypropylene, in some cases, generates a higher voltage.

FORD: On discharge?

RAMPEL: Yes, under similar circumstances, versus cycle life in, say, synchronous orbit, you can get similar cells where polypropylene would generate a higher voltage with the same negatives, same positives. So I think that the nylon separator is hydrolyzing, oxidizing, affecting perhaps both the electrodes. So it is just as important to do something about the separator as it is the negative electrode. That is the point I wanted to make.

FORD: I guess I won't argue the importance. What I am arguing now is the priority you put on the importance. What I would like to see from the manufacturer is a negative electrode that gives me better than 80 percent utilization at beginning of life. I think if we get that, we are going to find a negative electrode that will stay stable with life, which is really what we are talking about in a lot of this degradation phenomenon we are seeing as far as cell degradation with life.

RAMPEL: When you improve the negative utilization to 85 percent, say, or even 100 percent, what you are going to get as a consequence of that greater utilization is more cadmium migration and so on because of the greater activity of the negative electrode. To some extent, we have about 85 percent utilization in a negative electrode when a silver additive is applied, and in the presence of high concentrations of carbonates, you get more cadmium migration. So utilization of the cadmium is a delicate issue with the present separator systems.

FORD: Well, I think we are looking for scapegoats many times to blame problems on particular situations that don't exist. I think from my perspective on what is out there is the state of the art, that we are talking about 10 and 15 year batteries. The negative electrode has got to be improved. That is the bottom line.

SEIGER: The electrochemical impregnation of negative electrodes can indeed give you high utilization on weight gain in the active material, and that is by converting it to cadmium hydroxide, because one must be careful; there is a mixed deposit of cadmium and cadmium hydroxide.

In spite of that high utilization in excess of 90 percent and in some cases in excess of 95 percent, there is still a crystal growth and a redistribution of the active material. I have shown some slides here, I believe about two years ago, that showed that the immediate material laid down is laid down uniformly and has the particle size of about one micron. After about four rapid formation cycles, there is a redistribution that gathers in close to the negative electrodes and the crystal sizes are in the range of 8 to 10 microns. It will still fail.

Now, while you are sitting here and we have been listening now (we are in two days of it) of hearing test reports of seeing correlations, I see only one manufacturer reporting and he is reporting on a supportive program. We are not hearing from the manufacturers; we are not seeing any efforts or anything to support a stabllization program of the negative electrode. I agree with you, the problem is in the negative electrode; we have seen improved performance of positive electrodes; we have seen when we get rid of the cadmium electrode and put that electrochemically impregnated electrode in with hydrogen, we are now hearing and seeing much better results; and we are convinced that while we don't see any further improvements in cells made with electrochemically negative electrodes, the problem must, therefore, be in the negative. I concur.

However, the high utilization won't help. The problem still exists. Have you any indication of some support of such work?

RAMPEL: I think we ought to remember, though, that when we go to nickel hydrogen, we are looking at different separator systems and certainly not nylon.

## SALIENT CELL DESIGN/MANUFACTURING PARAMETERS

EAGLE-PICHER RSN-10 (9 Ampere-Hour)

| | HCMM | | SAGE | |
|---|---|---|---|---|
| | POSITIVE | NEGATIVE | POSITIVE | NEGATIVE |
| PLATE LOT I. D. | 1913 | 1393 | 1992 | 1416 |
| Ah FLOODED | 11.2 | 20.0 | 11.0 | 16.2 |
| PLATE LOADING (gm/in²) | 0.69 | 1.15 | 0.69 | 1.04 |
| THEORETICAL (Ah) | 12.11 | 28.13 | 12.11 | 25.69 |
| UTILIZATION (PERCENT) | 92 | 71 | 91 | 63 |
| NO. OF PLATES | 11 | 12 | 11 | 12 |
| AVG. THICKNESS (in) | 0.027 | 0.030 | 0.026 | 0.031 |
| ELECTROLYTE | 32 cc OF 31% KOH | | 32 cc OF 31% KOH | |
| NEGATIVE-POSITIVE RATIO | 1.79 | | 1.47 | |
| EXCESS NEGATIVE (Ah) | 8.8 | | 5.2 | |
| PRECHARGE-MEAS. (Ah) | 2.4 - 2.8 | | 2.2 - 2.7 | |
| SEPARATOR (12 MILS) | PELLON 2505 | | PELLON 2505 | |

Figure 3-59

## AEM PROJECT-BATTERY LIFE TEST

EAGLE-PICHER RSN-10 (9 Ampere-Hour RATED CAPACITY)

| SPACECRAFT | HCMM | SAGE |
|---|---|---|
| PACK IDENTIFICATION | 18 H | 18 I |
| LIFE TEST CONDITIONS | | |
| TEMPERATURE (°C) | 20 | 20 |
| DEPTH-OF-DISCHARGE (%) | 17 | 17 |
| ORBIT PERIOD | 1.76 hours | 1.64 hours |
| DISCHARGE RATE/TIME | 2.6 amps/36 min. | 2.0/45 min. |
| CHARGE RATE/TIME | 2.7 amps/60 min. | 2.0/52 min. |
| VOLTAGE LIMIT | #6/1.434 volts/cell | #6/1.434 volts/cell |

Figure 3-60

## AEM VOLTAGE LIMIT

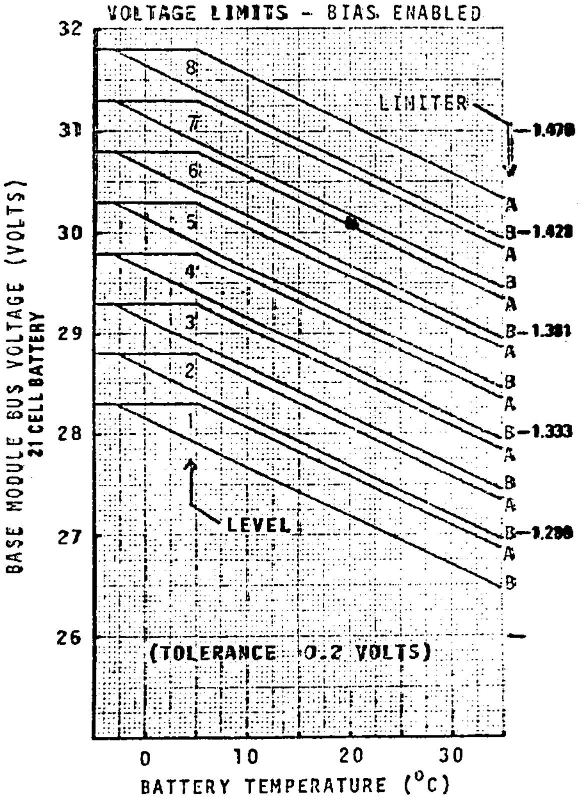


Figure 3-61

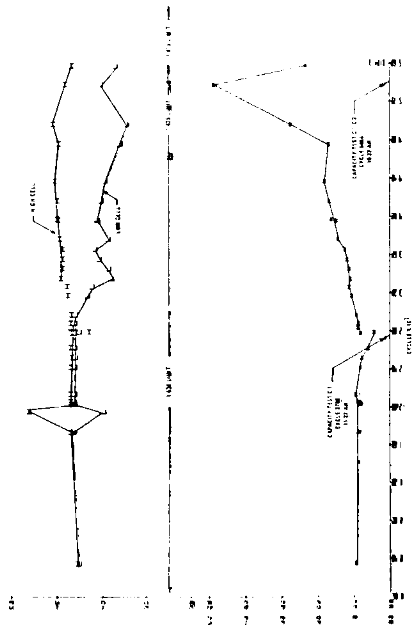


Figure 3-62

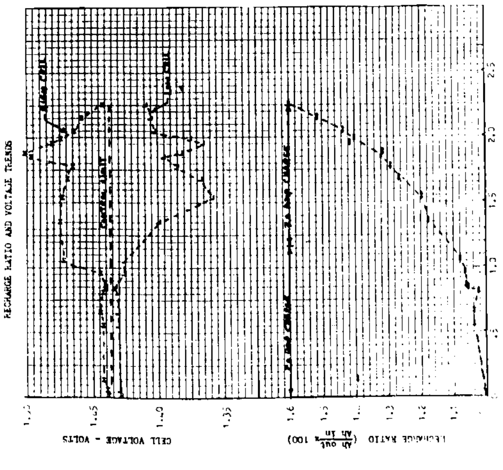


Figure 3-63

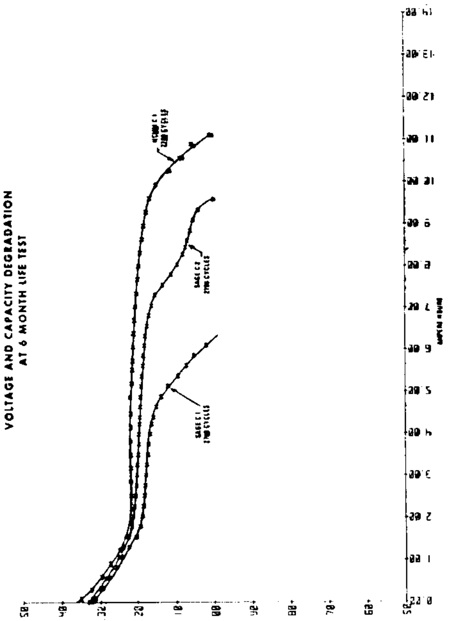


Figure 3-64

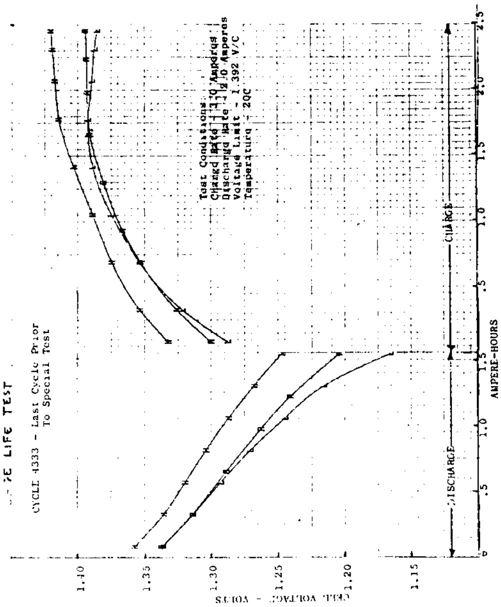


Figure 3-65

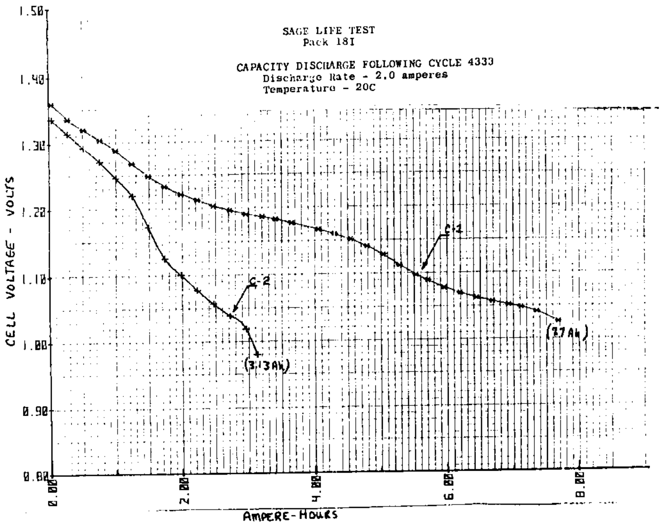


Figure 3-66

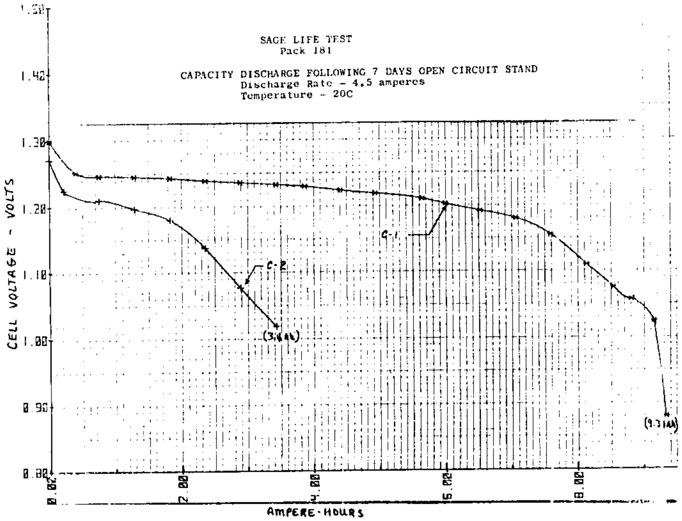


Figure 3-67

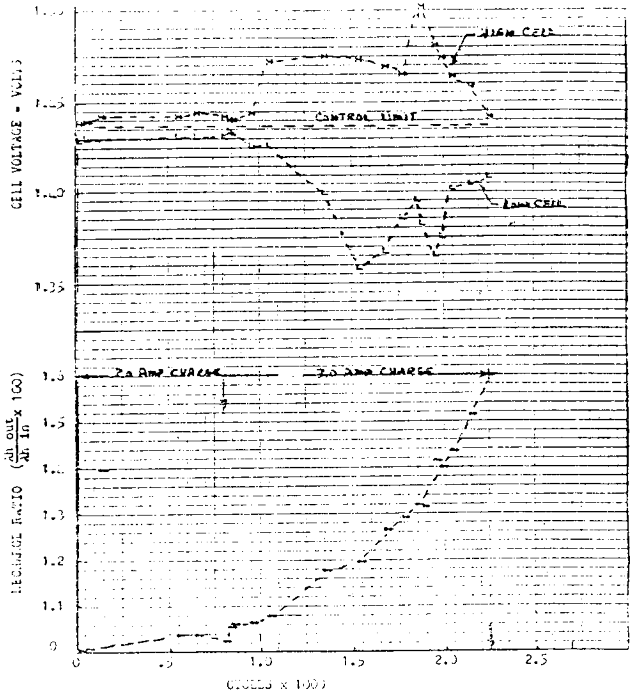


Figure 3-68

# MICROPROCESSOR CONTROLLED ADVANCED BATTERY MANAGEMENT SYSTEMS

T. Payne
Canadian Astronautics

The microprocessor, I don't think, is the answer to all of our problems, but in the process of doing some systems studies at the satellite level, we decided to take the approach that we were given the cells as they are. You buy the best ones you possibly can. What can you do to improve the energy storage system on the spacecraft?

So you see what you can do with the total system. On the next figure, I outlined the approach we have come upon. It is not completely unique. I know other people have been working on it, both here and in Europe. I intend to report the work we have done under contract with the Department of Communications in Canada in the past year and our approach to using the microprocessor.

(Figure 3-69)

The approach we have is to use the capabilities of an onboard microprocessor to monitor the state of the battery on a cell-by-cell basis and to compute the state of charge of each cell. The system will protect each cell from reversal; we have a scheme to prevent significant overcharge in each individual cell and to control reconditioning to zero volts per cell, and we have the capability of doing it at a dual rate. Whether or not that is an important feature, I am not sure.

(Figure 3-70)

The next figure shows the scheme that we are going to use as a proof of concept which will be a lab demonstration is to divide the system into what would be a flight operating system, which would have the battery management unit based on a particular microprocessor. As the relay switches, the battery is divided into cell pack modules, the battery discharge regulator, a constant current charger, and the peripheral items in our system, which include an array simulator, simulated load, and a supervisory system that can run the tests for us, which has all of these good things at the bottom that allow you to talk to the system and to get output from it.

(Figure 3-71)

The next figure shows where we are in the program right now. We have done the availability evaluation and done some reliability analysis from the design. We have done a proof of concept with detail design and we are within a week of starting initial testing. We expect to carry on in the next phase to detail design with packaging and type qualification of a prototype unit.

The extended testing will be done with both the breadboard that we are building now and with the QUAL units as they become available.

The higher limit elements are shown on the next figure.

(Figure 3-72)

We have, as I pointed out before, the regulator and the constant current charger; we have four modules and we are in the process of getting some cells similar to INTELSAT V type cells. We will substitute those as one of the cell packs for these commercial type cells that we are using now.

This system is an INTEL System that we are using, which is a microprocessor development system, which has a fair amount of flexibility. And it also allows us to put data onto floppy discs and interact by means of this terminal.

The analogue input, output board allows us to control the array simulator and the system load, and we can monitor the power going into that load and log that data as well.

(Figure 3-73)

The pack configuration that we are choosing is shown on the next figure. It is essentially an enhancement of the Satcom system where we have relays that we can switch into to recondition down to zero volts. We also have an additional pack let-down relay which allows us to get down to, say, normally one volt per cell during the initial parts of the recondition phase.

We also have an arming relay and then a set of shorting relays. These are the ones that provide protection against reversal and also can remove a cell from the circuit if it has failed in some manner.

The key to being able to do this is that battery discharge regulator, which is a boost regulator. We have changed the specifications that might impose on a regulator like that such that we can, in a 32-cell pack, fail up to three cells and operate down to one volt per cell and still maintain the output voltage of the regulators at the bus voltage. This gives you a fair amount of enhanced reliability. The software components are shown on the next figure.

(Figure 3-74)

This is a typical software. We have divided the software into two parts. The part on the left is the battery system supervisor, which is the part that you would actually have on the support system for testing the spacecraft. The other system is the flight operating system that would be embodied in the flight hardware. Between the two, you can visualize its limit in command links. These are just the normal things that you need to make a computer system work. And the flight operating system is divided into three different modes: (1) an operating mode (we have data scans, set points, and status switching); (2) a reconditioning mode that has different set points and relay switching, and (3) a parameter change mode that allows you to change the set points from the ground. This allows a considerable flexibility in the operation of the battery management system even while it is in orbit.

(Figure 3-75)

I will quickly go through some of the overall flowcharts for the modes which I have listed here. The first one is shown on the next figure. It is the operating mode's flowchart. There are no surprises. It just cycles through; scans; constructs a state picture of the state of the battery system, voltages, currents, and temperatures, which are monitored in each cell pack; implements cell reversal protection if one of the cells is within 10 millivolts of zero; and goes into the charging subroutine, which is shown on the next figure.

(Figure 3-76)

We use a constant current charger and charge up to a V-T limit, in much the same way as Floyd Ford has been describing, and several others have.

The difference here is that when we reach that V-T limit, we switch in the same relay that is the let-down resistor. That particular cell, then, cannot go into a significant overcharge state. That relay stays closed until all of the relays in the battery have closed and the total charger current can be set to a trickle charge state and then the switches can be opened.

We also monitored the pack temperatures and have a state of charge limit so that if there is an abnormal cell and the V-T is not operating properly, if the cell over heats, that particular cell is taken out of the high charge rate. Or if the state of charge limit for that cell is exceeded, we will remove it from the high charge rate.

(Figure 3-77)

The last chart I have, which is the reconditioning mode chart, which again uses the pack let-down release, goes through the status scan and monitors the cells to one volt. Then it closes individual cell let-down relays and reconditions the cells to zero volts. Then it reverts to the charging subroutine.

(Figure 3-78)

To show a comparison between a conventional system and our system, I have chosen a conventional system, the block diagram in the next figure. We have two out of three redundancy in the batteries, a series switch, and two discharge regulators which are in parallel. We have used these failure rates and a 30 percent depth of discharge. These criteria have been used, then, to calculate a reliability number versus time.

For this system, you compare it against the system shown on the next figure.

(Figure 3-79)

Up at the top, I have two battery discharge regulators. Only this time, they are not in parallel; they are both required to operate. One is slaved such that you take the same amount of energy out of each of these storage modules.

The criteria, though, are that only 29 of the 32 cells and associated switches must function in each battery; 50 percent depth of discharge; same switch failure rate, while we have a lot more switches in this pack module; and the same regular failure rate.

I used a cell failure rate that is time-dependent from some unpublic data that was provided to us by TELESAT and it also is a function of the depth of discharge.

(Figure 3-80)

So on the next figure I compare the reliability versus time as calculated using 50 percent depth of discharge for the advanced system and a 30 percent depth of discharge for the base line system.

Using this time-dependent failure rate, we integrate with respect to time and we see that this system has a fairly significant increase in reliability. We have done a bit of sensitivity now just by changing some of the failure rates and things like this.

Of course, if you have very, very reliable cells, there is no point in putting in these additional components. But this is, I think, a fairly reasonable failure rate which we have used. And there is a very significant improvement.

(Figure 3-81)

Using those two systems as a comparison, I have on the next figure done a rather quick and dirty comparison of the mass that you might expect to see for each of the systems and sized it out so that we needed approximately a 20 amp hour cell as a baseline. Because we need fewer cells, we get a weight advantage there. The pack hardware, including the relays, of course, weighs more for the advanced system. The discharge regulators are going to weigh the same for these systems, although they are not redundant in quite the same way.

We have implemented a rather unique discharge regulator that uses redundant switching elements in it and will have an extremely high reliability, quite a bit higher than I had used in this calculation.

What is interesting is that the advanced system is lighter, as well as has the higher reliability if you use the numbers which I have used.

(Figure 3-82)

In the last figure, I summarized some of the advantages which we see by this type of a switchable approach. We can eliminate cell reversal; we can cut back on overcharge stressing of the cells; we can charge at a higher rate because we are not going to over charge at that high rate; we monitor all of the cells continuously; and we have been able to remove one battery pack, basically, if you are going to go with the two-to-three redundancy.

If you use the numbers which we have used, you get a higher reliability by means of using the extra cells. There is no series switching. In fact, if the microprocessor (all of the relays) are uncommendable, you revert essentially to baseline system anyway.

We have this double contact configuration with an arming and then a switching relay so that during launch if there is any vibration-induced closures of the contact, the likelihood of having both close simultaneously is very remote.

Also, because we can go down to one volt per cell, we can use the useful capacity of the cell even if they have degraded in voltage with lifetime, as has been discussed. That means that you could do that even if you chose not to recondition.

We can use a higher depth of discharge because even if we have one weak cell and it continuously wants to go to zero volts and reverse, we can short it at that time and use the available capacity in the weak cell and then take it out of the circuit and continue discharging the rest of the batteries down to at least at a 50 percent depth of discharge; no possibility of reversal.

By using a boost regulator, we have a stable bus voltage and this wide variety of cell failure conditions, and we can protect against multiple cell failures.

## DISCUSSION

NIKLAS: Just what does your cell monitoring system consist of and what is the accuracy of it?

PAYNE: We are using an eighth bit accuracy. That means that we are monitoring the cell voltages from minus one to plus 1.56 volts and it is one part in 256. So it's about ten millivolts.

NIKLAS: Thank you.

ROGERS: What is the possibility of, say, a transient or an incorrect command telling a switching relay to switch across a charge cell? Even if it was rather remote, it would seem the consequences could be pretty bad.

PAYNE: Yes, you would blow the relay, I would imagine.

ROGERS: You would imagine. That would knock out your system if you had a bad cell, right?

PAYNE: Not necessarily. You would lose that switching function, but you would not necessarily fail the system. You would only fail the system if the cell itself had also failed open circuit. If it failed short, you would still have a usable system.

The best way to do this would be to do a complete Monte Carlo simulation of all the failure modes. We have implemented in our microprocessor system a check of the command being sent to the relays to ensure that it is a valid command and an allowed command.

One of the things you can appreciate is if you took off the connector which senses the voltage to one pack, it says, hey, all the voltages are zero. Close those six relays. You would short out the whole pack. Well, we have a software check to ensure that that doesn't happen.

But it is certainly something that we have to consider.

MOORE: You mentioned a stereo-rate a number of times and I have a couple of questions about that. One, what is it? Also, you said it was based on data provided by Telsat Canada?

PAYNE: Yes

MOORE: Are you saying it is based only on their data? Or did you include other data in arriving at that failure rate?

PAYNE: I can't discuss how they have derived that data, because I wasn't able to talk to the chapter providing it to me. If you want to know the numbers of failure rates, I have a figure on the numbers which I have used for those failure rates.

The initial analysis we did assumed the constant failure rate with time. The failure rates which we have used here they seem to straddle the point which we use, which was the order of $0.6 \times 10^{-6}$ per hour failure rate. This is the time-dependent failure rate which seems to show a slightly less reliable cell later on.

BADCOCK: One question: Did you include the reliability of the microprocessor in your calculations?

PAYNE: Yes, we did, but that is a very hard number to get out. We chose a fairly high reliability number for that. It is intended to be a redundant system, of course. I haven't really figured out a good way to get the reliabilities outnumbered. We have chosen one that does not impact the analysis all that much, basically.

LEAR: Mr. Payne, in your schematic, you said you could remove a cell if it was shorted or failed, but your schematic only showed that there was only a relay every other cell. Would you like to elaborate on that?

PAYNE: That is the arming relay which is every other cell. That is merely in ther so that you don't get this inadvertent contact closure during launch phase. You would probably close those arming relays after achieving orbit and leave them closed. Then, if you recall, down the side, ther is a relay across each cell which would be a dead short and another relay which has that let-down resistor and another contact.

IMAMURA: I just have a couple of comments. On the question of reliability, you have to conveniently break down into two parts. One is the battery cells themselves and electronics. And we have estimated the reliability more or less of flight configuration, including the processor ships, and we still could show the overall electronics. It is on the order of about five to ten times or more reliable than a given cell, whether you are talking about NICAD or silver zinc or any others.

So on paper, it could be shown quite readily what the reliability of the whole system is. Now, as to the comments that Tory had, it is hard to come up with a reliability number of failures. We take the position that the LSI chip could be considered part of the IC and possibly for reliability calculations, take a worse-case estimate of maybe one order less reliable; in terms of need time, it is inferior. Then calculate the reliability of the whole system. Still, it is a reasonable estimate.

PAYNE: Yes, that is using a different type of sensitivity analysis.

IMAMURA: Yes, it can be done. In fact, our system has been operating for over four years. You really don't have much problem with the microprocessor side; you have problems with the preflow circuits, like thickening conditioning circuits, and it is pretty much noise-immune from what Mr. Rogers was talking about. There is really no problem with the signal going through. You might have problems going—

PAYNE: That is with the systems operating. I agree with you, yes. It is the people poking their fingers in when it is—

IMAMURA: And software could take care of the problem of whether the signal is the right signal, going to the right relay.

PAYNE: Yes, that is the way we have implemented that.

IMAMURA: One question I have that relates to what John Lear asked. You really didn't have individual cell bypass or control according to your chart, is that correct?

PAYNE: Yes, there is individual bypass. I am sorry, maybe the—

IMAMURA: One line on your chart said the cells are hot-wired.

PAYNE: No, there is no series switching. You don't remove the cells; you short it out.

IMAMURA: I see.

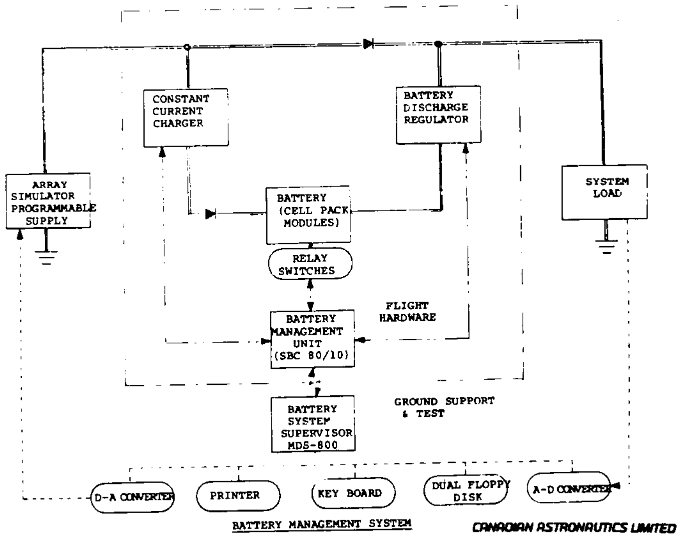
PAYNE: We aren't switching the cell out of the circuit; we just shorting it out.

IMAMURA: Thank you.

ADVANCED BATTERY MANAGEMENT SYSTEM

- Uses the capabilities of an on-board microprocessor to:
  - o monitor the state of the battery on a cell-by-cell basis
  - o compute the state-of-charge of each cell
  - o protect each cell from reversal
  - o prevent over-charge on each individual cell
  - o control dual-rate reconditioning to zero volts per cell

Figure 3-69



BATTERY MANAGEMENT SYSTEM

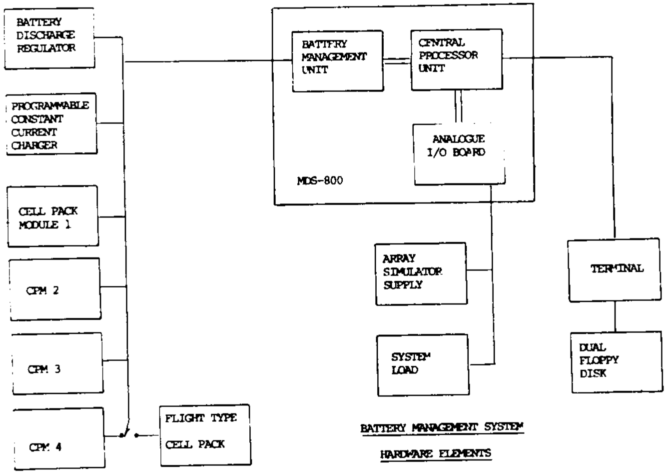
CANADIAN ASTRONAUTICS LIMITED

Figure 3-70

PROGRAM PHASES

| | |
|---|---|
| PHASE I | CONCEPTUAL DESIGN<br>- Component Availability Evaluation<br>- Reliability Analysis<br>- Preliminary Design |
| PHASE II | PROOF OF CONCEPT<br>- Algorithm Development<br>- Breadboard Hardware<br>- Initial testing |
| PHASE III-A | PACKAGING AND TYPE QUALIFICATION<br>- Hardware Design and Assembly<br>- Environmental Testing |
| PHASE III-B | EXTENDED TESTING<br>- With Breadboard<br>- With Qual Units |

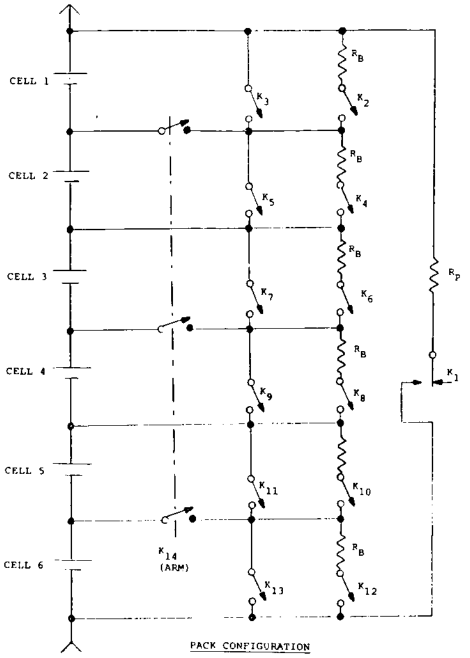
Figure 3-71



BATTERY MANAGEMENT SYSTEM

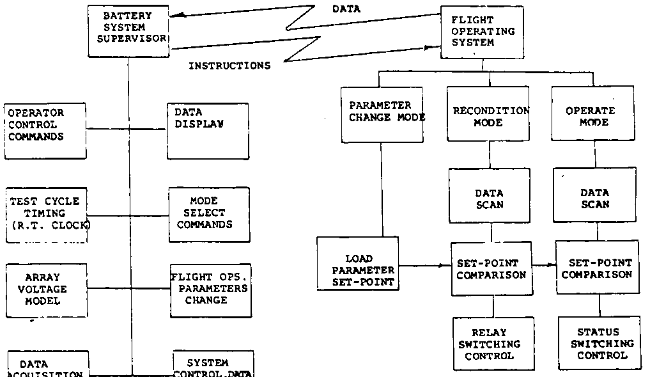
HARDWARE ELEMENTS

Figure 3-72



PACK CONFIGURATION

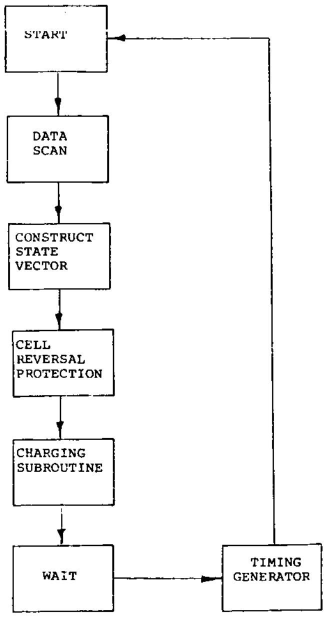
Figure 3-73



BATT II - SYSTEM SOFTWARE
DIVISION OF FUNCTIONS

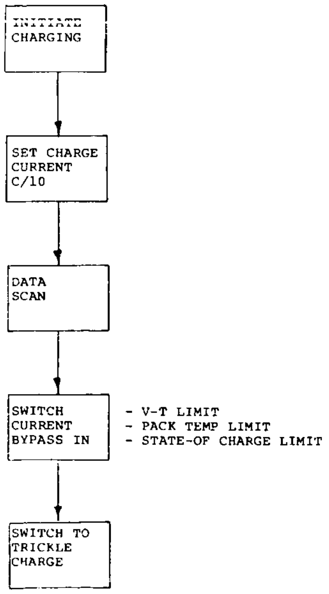
FIGURE 1

Figure 3-74



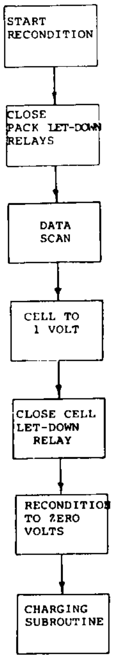
OPERATE MODE FLOWCHART

Figure 3-75



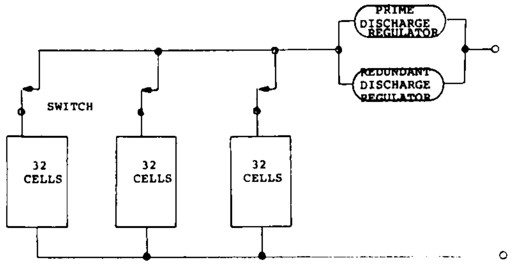
NORMAL CHARGE SUBROUTINE

Figure 3-76



RECONDITION MODE FLOWCHART

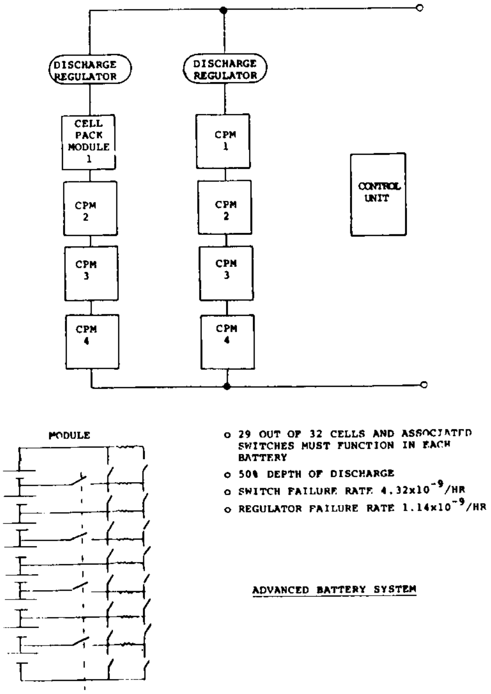
Figure 3-77



- o 2 OUT OF 3 BATTERIES MUST OPERATE
- o 30% DEPTH OF DISCHARGE
- o SWITCH FAILURE RATE 4.32 x $10^{-9}$/HR
- o REGULATOR FAILURE RATE 1.14 x $10^{-9}$/HR

BASELINE BATTERY SYSTEM

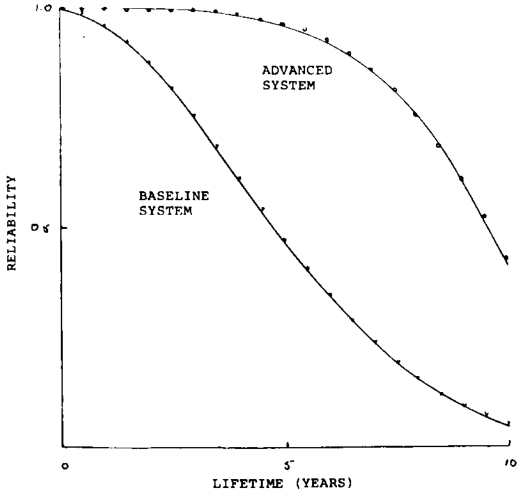
Figure 3-78



- o 29 OUT OF 32 CELLS AND ASSOCIATED SWITCHES MUST FUNCTION IN EACH BATTERY
- o 50% DEPTH OF DISCHARGE
- o SWITCH FAILURE RATE 4.32x$10^{-9}$/HR
- o REGULATOR FAILURE RATE 1.14x$10^{-9}$/HR

ADVANCED BATTERY SYSTEM

Figure 3-79



RELIABILITY AS A FUNCTION OF LIFETIME

Figure 3-80

MASS COMPARISON - TYPICAL SYSTEM

- first failure proof
- 600 watts load - 72 min. eclipse
- regulator efficiency 90%
- 50% D.O.D. nominal advanced system
- 33% D.O.D. nominal conventional system (to 50% with one battery failed)
- requires 17.5 A hr battery - consider 20 A hr as baseline

| | CONVENTIONAL (KG) | ADVANCED (KG) |
|---|---|---|
| CELLS 950 gm/cell | 94 | 62.72 |
| PACK HARDWARE Incl. relays | 16.93 | 26.33 |
| DISCHARGE REGULATOR | 16 Kg | 16 Kg |
| CONTROL BOX | - | 3 Kg |
| | 126.93 | 103.05 |

DIFFERENCE 18.88 KG = 41.54 LB.

Figure 3-81

## KEY ADVANTAGES OF THE SWITCHABLE APPROACH

### A) TAKES BETTER CARE OF CELLS

- o ELIMINATES DANGER OF CELL REVERSAL
- o PREVENTS OVERCHARGE STRESSING
- o PERMITS HIGHER RATE CHARGE IF DESIRED
- o MONITORS EVERY CELL CONTINUOUSLY

### B) BATTERY CONFIGURATION

- o ELIMINATES NEED FOR BATTERY PACK REDUNDANCY, RESULTS IN LESS WEIGHT
- o ACHIEVES HIGHER RELIABILITY WITH A SINGLE PACK PLUS SEVERAL EXTRA CELLS
- o ALL CELLS HARD WIRED IN SERIES - NO SERIES SWITCHING
- o DOUBLE CONTACT CONFIGURATION PREVENTS A SINGLE RELAY FAILURE FROM DISABLING A CELL

### C) BATTERY SYSTEM PERFORMANCE

- o IMPROVES PROBABILITY OF AVAILABLE BATTERY CAPACITY AS A FUNCTION OF LIFETIME DUE TO:
  - - IMPROVED SWITCHING REDUNDANCY
  - - IMPROVED UTILIZATION OF AVAILABLE CAPACITY AT END OF LIFE WITH THE DISCHARGE REGULATOR
- o CAN SAFELY USE HIGHER DEPTHS OF DISCHARGE
- o DELIVERS STABLE BUS VOLTAGE UNDER WIDE VARIETY OF CELL FAILURE CONDITIONS AND OPTIMIZES UTILIZATION OF REMAINING CELL CAPACITY
- o PROTECTS AGAINST MULTIPLE CELL FAILURES

Figure 3-82

# SESSION IV

# METAL HYDROGEN SYSTEMS

F. Betz, Chairman
Naval Research Laboratory

# AIR FORCE ELECTROCHEMICAL IMPREGNATION PROCESS RESULTS

L. Miller
Eagle-Picher

I would like to say one thing before I get into my paper here. I think it was inferred, or at least I thought this was said, that the battery manufacturer is insensitive to these problems. That is not the case at all. The Eagle-Picher and, I am sure, General Electric and some of the other suppliers put out quite a bit of effort doing research and development work trying to improve these cells and batteries for the battery industry.

We do operate under certain limits which probably are only known to us. For example, we talked about the negative electrode process and how we could improve that. We found in our studies that one way you could make consistent high utilization negative electrodes is to use fresh cadmium nitrate solution. However, obviously, this is a very expensive way to go; not only from the raw material cost because you are going to waste a lot more of that, but nobody in the world wants slightly used cadmium nitrate, particularly the guy who runs the city sewer system. So there is an additional cost there. But there are ways to do this if the industry is willing to pay the cost. It is not my decision. Let us just say the technology is available.

The purpose of this paper is to very briefly review the status of our Air Force Electrochemical Electrode Program. The objective of the program is to establish low-cost manufacturing technology and the commercial source for nickel alkaline batteries and cells exhibiting superior performance characteristics.

This superior performance is achievable as a result of the use of an advanced electrochemical impregnation process which was developed by the Air Force.

Electrode improvements include: one, reduce positive electrodes swelling, extending cycle life and depth to discharge capabilities; two, superior charge acceptance and active material utilization; three, reduce capacity of fading of cycle life; and four, a manufacturing process which is faster, easier to control, and produces a more uniform result.

The program was designed around and has evolved through specific phases. Phase one included design studies and the generation of documentation and engineering drawings. In Phase Two, prototype equipment was designed and assembled and tested to prove out design concepts. Phase Three, which we are now in, encompassed the major program efforts of actual construction of a production facility with the capacity of 7,500 each 50 amp-hour-size electrodes per production day.

The remaining two phases of the program, four and five, are associated with electrode cell and the battery production runs.

(Figure 4-1)

Under Phase Three, most of our efforts so far have been directed towards the policy process and the construction of the policy electrode portion of the facility. It is now approximately 95 percent complete. Actually, electrode production has been underway for approximately three months now. The block diagram presented in this figure demonstrates that this system comprises both continuous and batch type processing steps.

A continuous strip slurry process produces a uniform 30-mil-thick center with an 82 percent porosity. For more precise control, the strip is cut into 11-by-36-inch individual plaques for batch-type processing through the critical impregnation and formation operations.

It is planned that the final process steps consisting of spray wash, scrubbing, and inner-atmosphere drying will be again of a continuous nature.

The impregnation and formation steps are designed for an automatic operation. After the operator loads and seals 20 plaques into each tank, a button is pushed to start a preprogram sequence. Each impregnation tank is filled to a level equalling approximately 100 gallons of solution with continuous recirculation from the 800-gallon reservoir.

The solution temperature, concentration, and pH level are continuously monitored and automatically adjusted in the reservoir to maintain very tight tolerances. For example, the pH in the solution is controlled within ±0.1 units.

The precipitation current has been set at 0.35 amperes per square inch of plaque and with other processes where ampere is tightly controlled, a relatively linear relationship between impregnation time and impregnation level has been established.

The impregnated plaques are manually moved from the impregnation to the formation tanks and the automatic sequence continued with seven formation cycles.

(Figure 4-2)

In the electrochemical impregnation process the necessary plaque arrangement which forms multiple parallel circuits renders the precipitation current distribution a very important parameter for control. Eagle-Picher has solved this problem by employing a compensating resistor in line with each parallel branch, as shown in this figure.

The resistors are sized to assure that the resistance variations associated with the temporary plaque connections are very small compared to the overall circuit resistance.

In addition, by calibration of these resistors, it permits us to continuously and with some precision measure the current flow in each branch.

(Figure 4-3)

To date, more than 5,000 plaques have been processed with good results. The positive electrode characterization summary presented in Figure 4-3 here typifies these preliminary results.

The electrodes from processed plaques have been assembled into all of Eagle-Picher's nickel alkaline battery systems, including both vented and sealed nickel cadmium, nickel hydrogen, nickel iron and nickel zinc for evaluation.

In addition, electrodes have been subjected to what we call routine production high-rate formation stress tests to evaluate the center quality. Both electrical and physical performance and subsequent turn-down analysis results have been very encouraging.

This is a comment from the utilization of active material which show 90 percent at 25°C. Since this chart was put together, we have learned a little bit more about formation and that utilization now is probably closer to 100 percent.

## DISCUSSION

LEAR: In your opening statement you said that electrochemical impregnation reduces capacity fading. What percent of savings do you have and over what time period?

MILLER: Are you talking with respect to the cycle?

LEAR: Yes. Capacity cycle life, yes.

MILLER: Obviously, we do not have very many cycles yet. We just started this production some three months ago. Just from the preliminary results, the cells are showing less capacity fade than the similar chemical impregnated cell design.

SCOTT: In your earlier reports, I believe it said that you had decided that perforated steel sheet was preferable for a substrate and in later reports, I think I saw that you were using screen substrate. What is the story on that?

MILLER: We are using both. Some customers prefer the perforated substrate; others prefer the screen. So we are maintaining both processes.

ROGERS: In making 82 percent porosity with the slurry process, do you use any pour formers or anything like that to achieve that?

MILLER: Yes, we do. I think it is the same basic center process that we used on our Bell program.

MAURER: I would just like to modify that a little bit. The porosity in the Bell process on centering was controlled by the slurry components without a specific pour former, but we varied the ratio of CMC and percent nickel powder in the slurry to get to the high porosity. But there is not a specific pour form or anything in the mixture.

I would also like to comment a bit about the electrochemical negatives having a reduced capacity fading rate. You will remember that when Beauchamp presented the paper on the high temperature aqueous process back in '72, I guess it was here, he showed a curve that showed exactly that. The fading was much less, almost negligible.

BOGNER: I notice most of that was on positive electrodes. Do you have the same data on the negatives?

MILLER: No, at least I hope I indicated in the paper that to this point in the program, most of the effort has been directed toward the positive process.

RAMPEL: I do not have a question, but I have to add something to what I said just before lunch. I made a comment about a synchronous orbit with nylon and polypropylene separator. The data was private and I have gotten permission from Dean Maurer of Bell Labs to use it, and I want to make sure he has credit for that information.

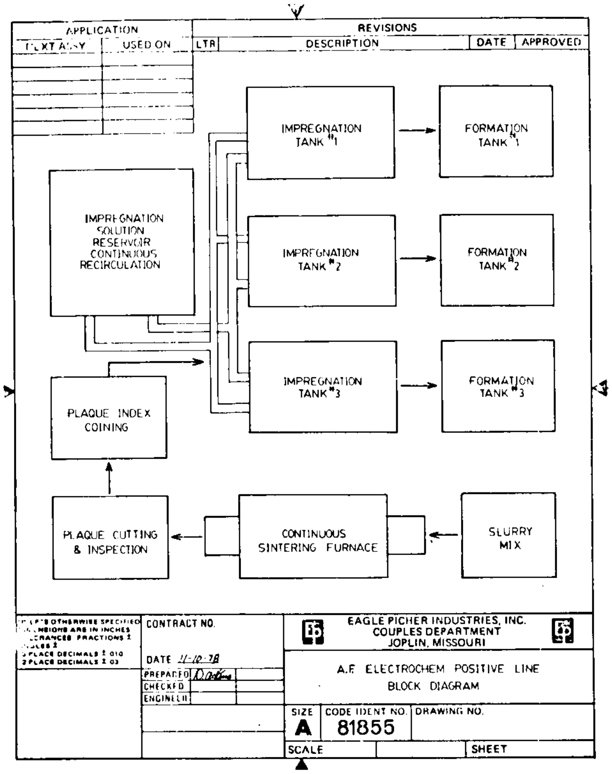


Figure 4-1

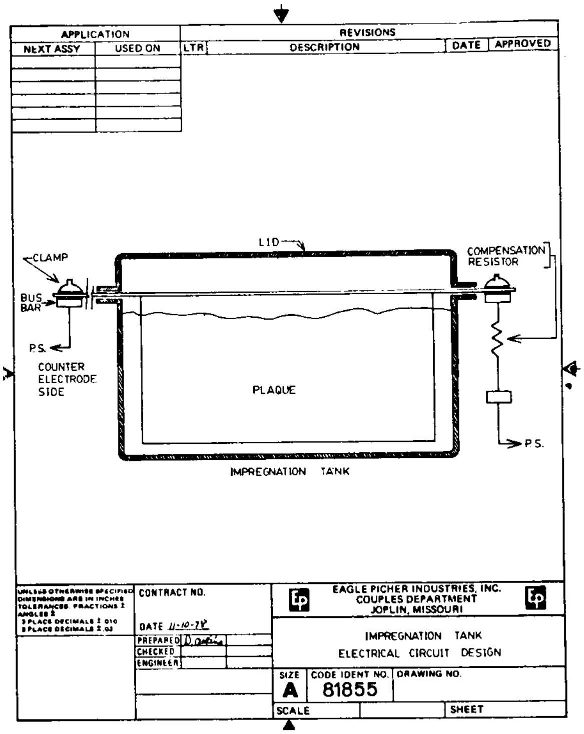


Figure 4-2

## POSITIVE ELECTRODE CHARACTERIZATION

### UTILIZATION OF ACTIVE MATERIAL

CHARGE 200% C/10, DISCHARGE C/2 TO 1.00 VOLTS
25°C 90% UTILIZATION, 0° 105% UTILIZATION

### DIMENSIONAL STABILITY

AFTER 400 CYCLES AT 80% DOD (APPROXIMATELY 3 HOUR CYCLE).
NO DIMENSIONAL CHANGE COULD BE MEASURED.

### LOADING LEVELS

ON 30 MIL THICK SINTER (82% POROSITY) 1.8 GRAMS/CC OF VOID VOLUME HAS BEEN ACHIEVED.

ON 100 MIL THICK SINTER (80% POROSITY) 1.6 GRAMS/CC OF VOID VOLUME HAS BEEN ACHIEVED (85% UTILIZATION AT 24°C).

Figure 4-3

# NTS-2 BATTERY AFTER 1 YEAR AND 3 ECLIPSE SEASONS

J. Stockel
Comsat

Ladies and gentlemen, this is just going to be a very short presentation, just more or less an update on the performance of the nickel hydrogen battery that is currently on board the NTS-2 Satellite.

As most of you know, or by now know, papers by both Fred and I over the last two years pretty much give the details of the satellite and the batteries, but just in general, it is a 14-cell battery; the satellite was launched in June of last year.

(Figure 4-4)

The first slide is just the three eclipse seasons. On the "Y" axis here, it is just the end-of-discharge voltages and along the bottom is the eclipse day. This satellite is in two shadow periods per day and we get about 30 days and we get somewhere like 60 shadows per season. It just completed the third eclipse season back in about July. That was the last eclipse season.

What you can see here is on the Season Number 1, which is the circle right here, when we started getting data for that first eclipse season, I think it was about the fifth or sixth day when we started getting power system data, and they did not have all the loads on it. By the time they got somewhere about here, about the 18th, 19th cycle, they did put the entire loads on and, of course, the battery voltage then dropped down here and continued on.

During the second eclipse season, we did have most of the loads on for the entire 60 revolutions. But unfortunately, by the time it got around to the third eclipse season, we were having trouble with the satellite and we never really did get the full load on. We only got down to right here, in the third eclipse season, which was about a 43 percent depth of discharge. This is 43 percent of the actual capacity of the cells, and the battery was measured at about 38 ampere hours or 20°C.

These points down here in the first and second seasons were about 60 percent depth of discharge. We took out somewhere like 22 ampere hours at this point. It is a constant power load, and with the constant power load, of course, the current is always increasing as we are going through the shadow.

Down at this point here, we had about 24-$\frac{1}{2}$ amps. That was our peak current, which is quite high. Right about here, we had about 18 amps of discharge current.

We did beat this battery around a little bit. Of course, during the early days when the satellite was still being maneuvered on station, I looked up one day, got my data and opened it up, and I found 14 big goose eggs which was once my battery voltage and by that time I was ready to pack everything in my boat and head for the sunset.

But what happened was that the oriented ray several times lost the Sun and drove the battery into reversal and we really did drive this battery into reversal. We did that a few times. You could only see the satellite, I think, about four or five hours a day, and the rest of the time there is no contact with it.

(Figure 4-5)

This next figure just is kind of a summary of what has happened since launch. Along the bottom are our revolution numbers, and you can see we started relaunch around in June of last year and the data then presents pretty much up to about a month or two months ago. This is up to around 850 revolutions. Up here at this top graph is the capacity in ampere hours.

The way we measure capacity on this battery is with strain gauges. We do have four strain gauges, two in each battery, and before launch, we did calibrate the strain gauge output in terms of capacity of the battery to one volt.

There is nothing really too much exciting here. It is just that this is the first eclipse season, and during the storage part of the eclipse season the capacity just sort of drifted up. We hit the second eclipse season; it started up here and we ended up down here, and it kind of drifted up again. In the third season, the same thing. And the voltages down here. This is the battery voltage. There are 14 cells in this battery. Most of this fluctuation is just due to temperature variations in the battery.

The loads seem to be just turned on and off quite frequently, and the temperatures jump around quite a bit. We happened to notice in that somewhere down around here, we find the high rate charge current all of a sudden comes popping back on and stays on for five or six hours and then goes off again. And then a while later, it is back on again. This does not seem to be affecting the battery, but it certainly is not the best thing in the world for it. It seems to be performing satisfactorily to date.

I think a lot of credit has to go to Fred Betz and the Naval Research Laboratory for finally getting this technology out of the hobby shop mode. I think there is going to be a real interest in this nickel hydrogen battery in the years to come.

## DISCUSSION

FORD: A question on the figure you left up there. I assume from what you have said that capacity is related to PSI readings of strain gauge?

STOCKEL: Yes, sir.

FORD: You are reading "four" and that represents an average of the four?

STOCKEL: No, one.

FORD: That represents one?

STOCKEL: That is all I can get.

FORD: If I recall correctly, back in some of the reports on nickel hydrogen, there was an indication of a pressure creep over the cycle life. And if you look at that top curve, it has a gradual upwards slope. Do you connect those two?

STOCKEL: Yes, you see a very gradual upward creep. Right now, I do not want to read anything into a one and a half ampere hour change in my strain gauge readings. The strain gauges that we put on this battery—it was the first time I did it and it can be done much better today. I am just not willing to say that really is.

ROGERS: On that point that Floyd just made, I was going to basically talk about the same thing. We have noticed gradual increases in pressure in almost every cell we have bothered to put a pressure gauge on, and it does actually relate to increasing its capacity. You can get the capacity out that the pressure would indicate you should get out of it; however, under normal discharge conditions, it is unavailable. So the measured capacity generally does not change much, but if you left it on like I did once for over a month on a dead short and measured the current, I got back every bit of capacity that the pressure increase (which was quite substantial) seemed to indicate. But it is not normally available as capacity, and you would not measure it in a capacity measurement such as you would normally do.

BADCOCK: Have you intentionally reconditioned these batteries?

STOCKEL: There is no reconditioning. Well, we did once, but not intentionally.

BOGNER: I do not understand how you reversed the battery. What drove it in reverse? If it is supplying the power—?

BETZ: When the satellite lost the Sun, the nickel hydrogen battery automatically supports the load until it is no longer able to do so and the bus full drops a little bit, the nickel cadmium battery would support the load. We had a back-up battery.

Now the booster was designed such that it would continue to try. So the nickel hydrogen booster continued to try to take current from a dead nickel hydrogen battery and put it on the bus and it just drove it down to zero volts. There were a few cells that were not goose eggs.

BOGNER: So it really was not reversed?

BETZ: Yes, some of the cells were.

DUNLOP: Just to finish that point off, when the boost regularly maintain their constant load of some type on the battery, it is just like taking a string of seven cells or 14 cells and putting a resistor across them. Eventually all the cells but one will be driven into reversal.

STOCKEL: I think the last data point we saw, we were drawing about four or five amps out of a two-cell battery.

DUNLOP: Yes, and so if you have got a two-cell battery, the rest of the cells are in reversal, you are still drawing current at four amps, right?

BETZ: Right.

DUNLOP: Okay. The second point is this: Several times we have mentioned this pressure increase. Joe does not want to make any comment on that because the strain gauge sensitivity or drift characteristics of the strain gauge are not fully known yet. But at the same time, it has been observed over the years, both with chemical and electrochemically impregnated electrodes, that with time there is a very slow corrosion process that does go on with the nickel sinter. That corrosion process has normally been related to what has been observed as an increase in capacity, and this capacity can generally be measured. In other words, if you see that pressure increase, you can generally discharge it down and measure a slight increase in capacity in cells that we have been looking at.

You do the same thing if you overcharge them excessively (generally, if you overcharge them for a very long period of time and push it up a little bit). It's the same idea as getting a little bit more charge into a positive electrode by excessive overcharging it (as Dean Maurer once talked about). Overcharging it for long periods of time at high rates, you may get the nickel to a slightly higher valence state, and when you discharge it, you do see slightly higher capacity.

What we normally do observe in the INTELSAT 4 and 4A type spacecraft is when we do recondition them down, we actually see a slight increase in capacity each year for the first two or three years in orbit. We attribute that to a corrosion mechanism.

HARKNESS: What is the anticipated mission life requirements of the battery? How many eclipse seasons?

BETZ: The original design life was a three-year minimum design mission. The portion of the payload, of course, is no longer there, so our loads are down; the battery will probably survive to ten.

ROGERS: Just a comment on the corrosion mechanism that Jim Dunlop just mentioned. If it was corrosion cells that we had, we would only have been able to get part of that capacity back, the part of it that relates the formation of nickel hydroxide from nickel, that is, plus two, would not be obtainable and you would keep the hydrogen.

We did not see that. That does not mean that it would not happen in other situations.

NAPOLI: I got a little confused there with the depth of discharge originally; before you reduced your loads, it was what, 80 percent?

STOCKEL: The depth of discharge before we reduced the loads was 60 percent.

NAPOLI: And now that you reduced the loads, it is what?

STOCKEL: Forty-three.

NAPOLI: And now that you reduced the loads, it is what?

STOCKEL: Forty-three.

SEIGER: I would like to continue on the point of how it rogers on this extra pressure. We went in detail on that at the Power Sources Conference. Yesterday we heard Dr. MacDermott relate that he found a precharge of nickel cadmium that was 2.2 times the increased capacity of the positive electrodes, and that sounds like it is a corrosion.

Now, with what I just heard you say, would it be correct to assume that your pressure increase, if you converted that to ampere hours, would be about equal to the increase of capacity of the positives? If that is so, then there is some active material that can be deposited (vacuum method or electrochemical) that would escape formation and can form as you charge and discharge a cell. So you can have an increase of the pressure. You can see that kind of pressure rise and it not be corrosion.

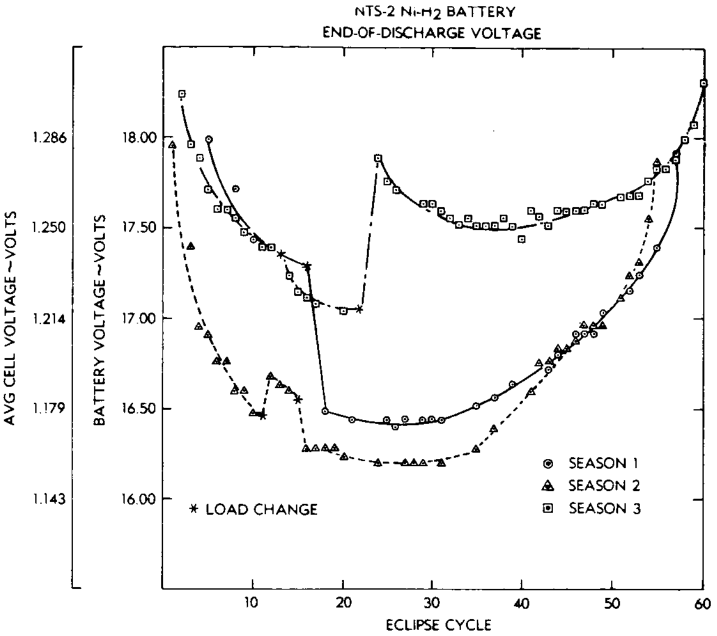


Figure 4-4

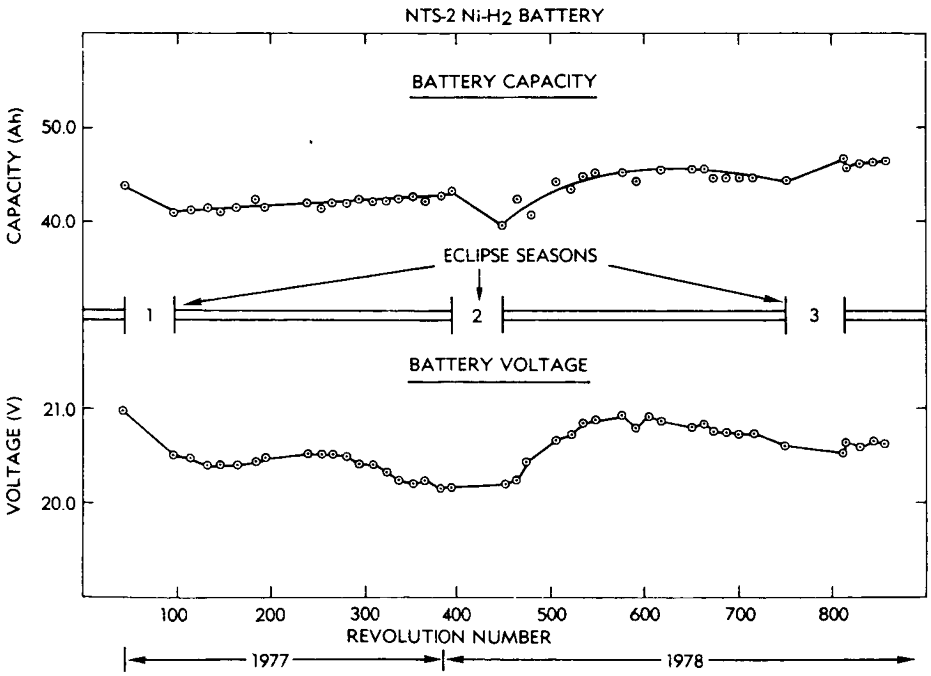


Figure 4-5

# USAF NICKEL HYDROGEN CELL

D. Warnock
USAF

I had originally thought that I might talk a little bit more about cell design, but I decided that that had been covered a couple of times this year by the Hughes people on the West Coast, and more recently I gave a paper at the Electrochemical Society Meeting in Pittsburgh. So I decided for those of you who are already pretty familiar with the cell design from these papers and technical reports that it might be of more general interest to talk about Air Force activity and nickel hydrogen in general and touch very briefly on what has been done in the past, but probably of more interest to most of you, give some indication of the kinds of things the Air Force might be involved in in the future.

(Figure 4-6)

I am not going to go over this chart in any detail, but it has some information, of course, which will be published in the proceedings and you may want to refer to it sometime in the future.

The activity goes back to about 1972 and it started out rather small, went through exploratory development, and then into advanced development, and it includes a space experiment which was done last year. I guess the bottom line is that the Air Force commitment in the nickel hydrogen area has grown continuously over the years. There has been a total input of a little over $2.5 million so far, and I do not think that that has peaked yet. I would estimate that we are probably about halfway through the total Air Force activity in nickel hydrogen. I expect several more years of continued activity, and some of the things that we are considering are part of the things that I will be talking about today.

Our confidence and enthusiasm in the system has been growing steadily over the years and, we think that we see a lot of potential for it in the future.

Most of the work thus far has been aimed at the development of 50 ampere hour cells. This is where you have one cell and a single pressure vessel, and I will contrast that later to the common pressure vessel approach, where you put a number of cells in a single pressure vessel.

(Figure 4-7)

Most of what I am talking about is individual pressure vessel cells or IPV cells. The work up until around mid-1978 has been primarily the development of that cell design. We put a great deal of time and effort into every aspect of cell design, working on the configuration. We have a complete computer model of the cell which includes a nodal thermal analysis of cell operation in various orbits. We spent an awful lot of time on things like electrolyte management, oxygen management, and thermal management. We have had some fairly interesting activity in developing new components such as a hydraulic seal terminal and a photochemically etched substrate for the negative electrode. We have spent a fair amount of time on how do you manufacture this thing. We have done the space experiment. We have developed a complete set of specifications. So we have pretty much completed the design and hardware development of a 50-ampere hour cell, and we are moving into a phase now where we will be building a substantial number of these cells, testing them ourselves, and passing them around to people who are potential users so that they can test them also. Hopefully, within a couple of years, there will be enough of the data base that people can consider seriously using these for operational missions.

The number of cells there, particularly the Navy 34 cells, actually should be 48. And over in the last column, GPS-6, the Air Force had been very interested in doing another experiment on global positioning systems, and that fell through last summer for lack of funding. But there still are a number of activities coming up.

(Figure 4-8)

This chart carries us a little bit into the future now. The first few bars in the upper left-hand corner, that first bar on IPV, is individual pressure vessel exploratory development, encompassing all of the programs that have been done so far. And the current IPV advanced development program is the one that we are in right now. And then there is the low earth orbit space experiment that was done last year.

The advanced development program, or at least the cell technology that has been developed in that program, will go this year into a manufacturing technology program. I have a separate chart on that later on. As you know, it was just reported that Comsat flew a nickel hydrogen battery on NTS-2 and the Air Force now has a memorandum of agreement with Fred Betz of the Navy whereby they will fly a nickel hydrogen battery on NTS-3. Again, I have a little more data on that later on.

Now, the next bar, the low earth orbit, geosynchronous earth orbit life test program, is a recognition that there is not a lot of long-term life test data on nickel hydrogen cells. I want to let you know that we are aware of the problem; we are sensitive to it; and we are seriously trying to figure out where to get the money and exactly how to go into a substantial ground test program on nickel hydrogen cells. I think that there may be some activity on that later on this year.

The last bar is a little less certain than some of the others. It is large cell development. It is a result of recognition that on some of the very large power systems that are being considered, 25 kilowatts and more, we would like to see larger cells sizes. We think that the present cell design can be scaled up to the range of 100 to 250 ampere hours. I sort of doubt that there will be a program in that area starting this year, but there could very well be some activity starting in that next year.

Then jumping back up to the top right-hand side of the chart, the CPV (common pressure vessel exploratory development) indicates that we plan to do an exploratory program looking at feasibility, advantages, and disadvantages of putting a number of cells in the same pressure vessel.

(Figure 4-9)

Now there are some problems associated with it in terms of electrolyte bridging and thermal control, possibly. There are also some advantages in reducing volume, reducing cost, and a very modest reduction in weight.

If that program should turn out well, then it would likely be followed by an advanced development program in going essentially through the same sequence that we have already been through on the individual pressure vessel. But that is a very "iffy" situation right now because we have not done that feasibility work.

(Figure 4-10)

Now to give some details on some of the bars on the bar charts. We did an experiment last year on which we were a piggyback experiment on another vehicle, and it was a low-orbit Air Force vehicle. We were not allowed to interfere with the primary mission of that vehicle and consequently there were some deficiencies in the amount of charge power available to us, the thermal set-up and so on and so forth.

But we did get 1733 cycles on the battery at seven percent depth of discharge; 26 cycles at 50 percent depth of discharge; occasional discharges from five to 40 amps; and one discharge at 75 amps.

Now, to the right of that, under the present nickel hydrogen low orbit design, I want to indicate that the design is capable of 6000 cycles a year, we believe, at 80 percent depth of discharge with all of those discharges occurring at 68 amps. So if you compare the right-hand and left-hand columns, you can see that what we actually did on our space experiment represented very mild conditions for the present design.

Our conclusions were that the battery performed well under very mild cycling conditions; performance was constrained mainly by vehicle electrical limitations and the fact that the experiment did not represent a good assessment of nickel hydrogen under low orbit conditions simply because the conditions were not rigorous enough.

(Figure 4-11)

Now that Hughes is starting to produce these cells in quantity this year, we have set up a program whereby we loan cells to the major aerospace companies for their evaluation. We are sending three cells to each company and each company gets to select the operating conditions that they are most interested in and do it under those conditions. The only thing that we have asked is that the data that results from these tests be shared among the participants and presumably will be made public, and I imagine some of that data may start showing up here at the workshop in the next year or two.

The first cells were shipped actually around the 16th to 18th of October, and I think that most of those have been received by the companies. You can see the nine participants listed at the bottom.

(Figure 4-12)

The manufacturing technology program that I have already mentioned has as its objective establishing a high-volume, low-cost production facility. The approach will be to use the cell design that has come out of the advanced development program. Whoever gets the manufacturing technology program will be required to describe in some detail exactly what his manufacturing methods are and to demonstrate that facility to other people who are interested in being manufacturers. Cells will be available to the qualified users.

(Figure 4-13)

This chart is a little bit out of date. A couple of things I will have to correct on it, but other than that, it is pretty much as shown.

On the third line down, it says "NTS-3 launch in September may use Air Force cells." That now is certain, since there is a memorandum of agreement. On the other hand, the statement that that would be done without a NICAD backup was the original idea. I understand that their plans have changed so that it would be done now with a NICAD backup, if it is done.

Is that still correct, Fred?

BETZ: Yes.

WARNOCK: And on the last line where it says "action required," that memorandum has been signed. Basically it provides that the Air Force will provide the cells and the Navy will design, build, and test the battery.

This also is possibly an out-of-date chart.

(Figure 4-14)

I would not pay too much attention to the numbers of cells or the kinds of test conditions that are mentioned here. But I guess the main point of the chart is that we are concerned about the lack of long-term test data. We are now in a position, since we are in cell production, to build cells and to get them on long-term tests. The exact conditions, the number of cells, we do not really know right now, but we are concerned about providing that kind of data, and hopefully sometime later this year we will be able to get some kind of program started to take care of that.

DISCUSSION

NAPOLI: Yes, to date, all the things that we have seen about the nickel hydrogen cell all seem to be very positive, and you did mention at some time there is going to be some chart or show of what the disadvantages are. Is there any a priori knowledge as to what the disadvantages are today of the nickel hydrogen cells, or is this the maker of the battery technology?

WARNOCK: I am rather hard-pressed to come up with disadvantages for it, but one that is fairly easily recognized is that the volume of the cell is larger than an equivalent capacity NICAD. They are one and a half to two times as large. If you have volume restrictions on your satellite, it would be more difficult to put in a nickel hydrogen battery because of volume restrictions than it would a NICAD. If you are not so restricted, then that is not a disadvantage.

In most of the other respects, you know, the advantages have been reported for a long time. You can bang these things into reversal; you can over charge them; the cycle life as a function of discharge seems to be greater; it is a very stable system. You have a depth of discharge indicator in measuring hydrogen pressure. So I am a little hard pressed to come up with disadvantages other than the obvious fact that it has a lower volume energy density.

NAPOLI: Approximately what is the volume, two to one ratio?

WARNOCK: It is like two to one, yes.

NAPOLI: Thank you.

FORD: Let me ask you a futuristic question. If you had to look into the crystal ball and suggest when the nickel hydrogen system will be an operational system, that is, if it is being considered in the early design phases and integral part of a satellite design program, what would you project today when that would be? What time frame?

WARNOCK: That is a very difficult question to answer, obviously. I would say that from a technical standpoint as soon as you get a data base that you are willing to count on, and it depends on whether you are satisfied with the two-year data base, you could consider operational use in 1981 or thereafter. Now, the actual amount of time that it takes to overcome the conservatism among program offices and being willing to accept a new technology or being satisfied with the size of the data base is another question. That is not really a technical question. I cannot answer that question. But I will say it will come somewhere after 1981, depending on the degree of conservatism.

DUNLOP: I can tell you one thing that may be of some interest to you, in answer to your question, Floyd. As you may or may not know, we are just about to complete Phase One of a program for nickel hydrogen INTELSAT V and at the end of this month, we are going to make a recommendation as to whether to go ahead with Phase Two and Phase Three. The Ford people may care to comment on that program since they are actually doing the work.

But we are in the process of finishing up a detailed design of the battery and of the cells to go into INTELSAT V, and they are scheduled to go into production about next month for that program. And if everything goes according to schedule, the cells will be built next year; the batteries will be fabricated next year; the prototype batteries will be fabricated to run through all the testing next year and there will be one year of auxiliary life testing to gain confidence for the user and then, hopefully, then we are going to be going into—if everything looks good by the end of 1979, we intend to go ahead and put them on F-4, 5 and 6 of the INTELSAT V spacecraft.

That is about the end of '81-'82.

WERTHEIM: Going back to Joe's question, if you went the common pressure vessel route, what kind of volume comparison for NICAD would you have then?

WARNOCK: It will become very comparable to NICAD on a volume basis, but in order to do that, you have to go to higher pressures. As you go to higher pressures, you will increase self-discharge and that may or may not be important to your application. In low orbit, the increased self-discharge at the higher pressures probably will not bother you. It certainly would be a greater source of inefficiency for synchronous orbit. But the volume of the cells will become quite comparable. It could, under some circumstances, be even better than NICAD, but roughly comparable.

STADNICK: Typically, in answer to Floyd's question, Hughes is considering using nickel hydrogen at least in conjunction nickel hydrogen and a nickel cadmium design in basically all new programs, and the intent is to use nickel hydrogen in those cases where it shows us a definite advantage.

BETZ: You are going to consider nickel hydrogen for all new programs, is that correct?

STADNICK: All new programs and, as in the case of INTELSAT V, if things show up where it indicates that we might need it on existing programs, there is a consideration there, too.

DUNLOP: What Don said, just to reenforce that, when we did the preliminary design of INTELSAT V, since we are using almost the same size ampere hour capacity cell, (it is almost a two-to-one), it is not quite a two-to-one, but it is somewhat bigger. Interestingly enough, typically where you pick up your volume is in the height of the cell. Your footprint does not have to change very much, and as a matter of fact, one of the criteria for that program on INTELSAT V is that you can make an almost minimum impact replacement of nickel hydrogen for the nickel cadmium, which means that you are using almost no modifications of your present spacecraft design and only minor modifications on your base plate, using basically the same footprint and basically the same thermal rejection criteria.

I think, Don, you are going to find one thing interesting. There is going to be a paper later on by Holleck which is going to show that the self-discharge and some of the performance at the high pressure, and it gives you some rather interesting results and the self-discharge really is not too bad, nor is the performance too bad at high pressure. We will show that to you a little later on today.

WARNOCK: The self-discharge will be higher at the higher pressure. Whether it is significant to the user or not is a different question. It may not be.

IMAMURA: Don, can you project on the cost of the cell per cell for a 50 ampere hour? The example is NTS-3, I guess. I do not know how many quantity or what the quantity of the cells are. I am apparently using Hughes' price, I guess.

WARNOCK: I believe I have a backup chart on that. If I do, I will try to get that for you. Yes.

BETZ: The cost to the Navy is very good.

WARNOCK: The cost to industry right now is very good also, if you are getting one from me, but if you are trying to buy one from Hughes, it is exorbitant.

WARNOCK: It is very quantity-dependent right now. These projections were made by Hughes based on their own manufacturing experience and information from cell vendors quoting against the present specs. It does not include the effect of the manufacturing technology program that I mentioned. In other words, this is the current cost. Now, when cells are made at this cost, they are really being made the way they were made in onesies and twosies throughout development. This is not a mass production type of cost here because there are no mass production facilities for them. They are still being made in small quantities, the way they were made during the development program.

But if you go to Hughes right now and ask for a quote on half a dozen cells, it is probably going to be 10 or $11,000. When we go to Hughes and ask for a quote on 25 cells, the cost tends to be maybe 4 or $5,000 a cell—all of this without benefit of the manufacturing technology program.

So I guess this is the best information that we have right now. I would expect that line to be displaced downward somewhat as a result of manufacturing technology programs. How much, I cannot say right now.

SLIFER: Since you did not mention it as a disadvantage, I assume that you consider the thermal problems with the nickel hydrogen cell equal to or less than the nickel cadmium?

WARNOCK: Yes. I hesitate to get into it and maybe I should not, but in some respects I think thermal arrangement on nickel hydrogen cells is somewhat better than it is on NICAD's, at least with respect to growth to higher capacity cells. For instance, we have a low orbit 50-ampere hour cell capable of 80 percent depth of discharge low orbit rates and thermally capable of doing that. To scale that to 100-ampere hour design is probably not very difficult with respect to thermal problems. I am not sure that that is really the case with the NICAD's, though. And I think you can probably talk about going beyond that before you get into the thermal problems. But it is basically related to the radial geometry of the cell as opposed to the prismatic geometry on the NICAD.

BETZ: Will the increased temperature, higher temperature operation, increase the migration of the negative electrode active material or deteriorate to separate it?

WARNOCK: I do not think I will answer that.

NAPOLI: I have a question on the cost chart again. I think I did not get a chance to review it adequately. You had ten for $8000, or was that $8000 if you bought them in ten-lot quantities? I am not sure what that means. Is that $8000, if you bought 10 cells, per cell? It is a per cell price?

WARNOCK: Right. Yes.

GANDEL: In talking about the thermal problems, when you go to the common pressure vessel, don't you anticipate that we are going to have that thermal management problem aggravated considerably?

WARNOCK: How do you mean that? Due to the heat rejection area available to you or due to increased sensitivity to thermal differences between cells?

GANDEL: No, I am just visualizing that if we have one large can containing the large stack, we are going to have that heat generation concentrated more than we have now, and also when that vessel increases in size, the available area for transmitting the heat is proportionately decreasing.

WARNOCK: I do not think we will have a problem. A couple of considerations: in the first place, if you increase cell capacity by increasing stack length, keeping the diameter constant, then you are increasing heat rejection area at the same rate at which you are increasing capacity, so you are not changing the heat rejection capability of the cell by adding capacity when you increase stack length.

The next part of your question is when you start to increase the diameter of the electrodes, then it depends on how you make your electrode. If you have a solid disk electrode, for example, and you start to increase the diameter of the solid disk electrode, then you start getting into a problem because you are increasing the heat generating volume in the electrode at a faster rate than you are increasing the heat rejection area at the perimeter of the electrodes. That is with a solid disk electrode.

If you have an annular electrode (that is, one with a hole in the middle of it), you increase the outside diameter. With the annular electrode, you can also increase the inside diameter so that you are keeping the distance between the inside diameter and the outside diameter more or less constant. When you do that, you are increasing the diameter at the same rate at which you increase heat rejection area at the perimeter, and again, you do not get into the problem.

So the computer studies that we have done have been based on having the same heat rejection capabilities in larger cell sizes that we already have in the 50-ampere hour size, which we know is adequate. So the studies that we have done have been based on maintaining that heat rejection capability by using the annular electrode.

## AIR FORCE NICKEL-HYDROGEN DEVELOPMENT

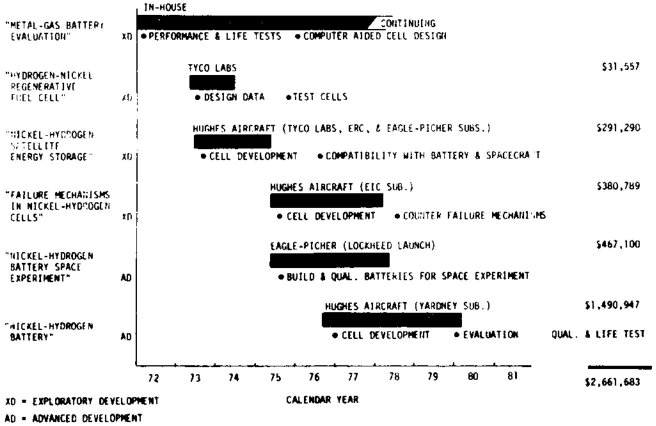


Figure 4-6

## NI/H2 BATTERY DEV. AND TEST SCHEDULE

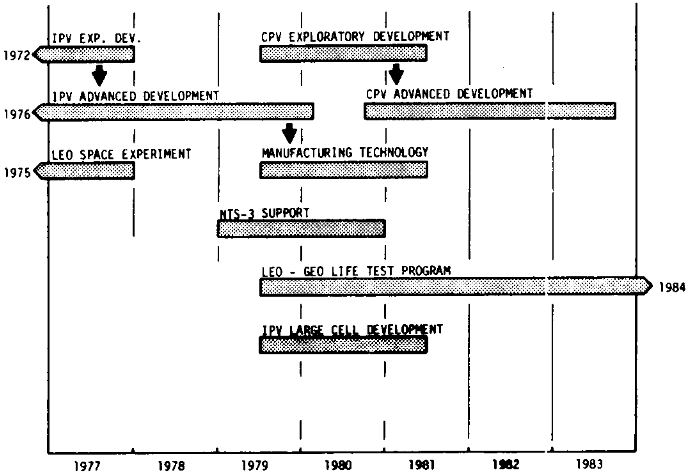


Figure 4-8

## STATUS

TRANSITION FROM DEVELOPMENT TO TEST AND APPLICATION

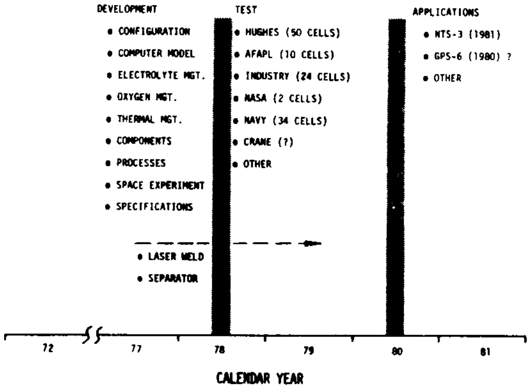
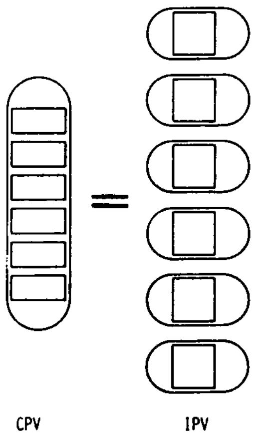


Figure 4-7

## COMMON PRESSURE VESSEL NI/H2 BATTERY



ADVANTAGES

- 50% VOLUME REDUCTION
- 25% COST REDUCTION
- 15% WEIGHT REDUCTION

PROBLEMS

- ELECTROLYTE BRIDGING BETWEEN CELLS
- ELECTROLYTE RETURN TO CELLS
- HIGHER PRESSURES (2X)

Figure 4-9

## NI/H2 BATTERY SPACE EXPERIMENT

o OBJECTIVE

- OBTAIN EARLY EXPERIENCE WITH A NI/H2 BATTERY UNDER LOW ORBIT CONDITIONS

o OPERATING CONDITIONS

| SPACE EXPERIMENT | PRESENT NI/H2 LOW ORBIT DESIGN |
|---|---|
| • 1733 CYCLES AT 7% DOD | • 6000 CYCLES/YEAR AT 80% DOD |
| • 26 CYCLES AT 50% DOD | |
| • OCCASIONAL DISCHARGES AT 5, 10, 20, 40 AMPS | • ALL DISCHARGES AT 68 AMPS |
| • 1 DISCHARGE AT 75 AMPS | |

o CONCLUSIONS

- BATTERY PERFORMED WELL UNDER MILD CYCLING CONDITIONS
- PERFORMANCE CONSTRAINED BY VEHICLE ELECTRICAL LIMITATIONS
- PERFORMANCE NOT ASSESSED UNDER NORMAL LOW ORBIT CONDITIONS

Figure 4-10

## NI/H2 CELL - INDUSTRY EVALUATION PROGRAM

- LOAN 3 PROTOTYPE CELLS TO EACH COMPANY
- COMPANY SELECTS TEST CONDITIONS
- DATA SHARED BETWEEN PARTICIPANTS
- FIRST CELLS SHIPPED 6 OCTOBER
- PARTICIPANTS:

| | | |
|---|---|---|
| BOEING | LOCKHEED | RCA |
| FORD | MARTIN-MARIETTA | ROCKWELL |
| G.E. | McDONNELL-DOUGLAS | TRW |

Figure 4-11

## NICKEL-HYDROGEN CELL MANUFACTURING TECHNOLOGY PROGRAM

OBJECTIVES:

ESTABLISH HIGH VOLUME, LOW COST PRODUCTION CAPABILITY

APPROACH:

AF/HAC CELL DESIGN

DESCRIBE AND DEMONSTRATE FACILITY TO QUALIFIED MANUFACTRUERS

CELLS AVAILABLE TO QUALIFIED USERS

Figure 4-12

## NTS-3 SUPPORT PROGRAM

- NAVIGATIONAL TECHNOLOGY SATELLITE SERIES DEMONSTRATES TECHNOLOGY FOR GLOBAL POSITIONING SYSTEM
- NTS-2 LAUNCHED IN JUNE 1977 USED COMSAT CORP. NI/H2 CELLS AND NI/CD BATTERY
- NTS-3 LAUNCH IN SEPTEMBER 1981 MAY USE AIR FORCE NI/H2 CELLS WITH NO NI/CD BACKUP
- DRAFT MEMORANDUM OF UNDERSTANDING PROVIDES:

| AIR FORCE WILL: | NAVY WILL: |
|---|---|
| • PROVIDE 16 CELLS BY JUNE 1979 | • DESIGN & BUILD BATTERY |
| • PROVIDE 32 ADDITIONAL CELLS BY JUNE 1980 | • PROVIDE BATTERY DESIGN AND GROUND TEST DATA |
| • PROVIDE SUPPORTING DATA AND ASSISTANCE | • PROVIDE ORBITAL OPERATION DATA |

- ACTION REQUIRED: AIR FORCE AND NAVY SIGN MEMORANDUM OF UNDERSTANDING

Figure 4-13

## LEO/GEO CYCLE LIFE TEST PROGRAM

o OBJECTIVE

DATA BASE ON NEW KIND OF BATTERY

o APPROACH

- 48 CELLS TOTAL
- 5 YEARS REAL TIME LEO TESTING (24 CELLS)
- 20 YEARS EQUIVALENT GEO TESTING (24 CELLS)
- 8 CELLS AT EACH OF 3 TEMPERATURES FOR BOTH ORBITS
- FAILURE ANALYSIS OF ALL FAILED CELLS
- COMPUTER COMPATIBLE DATA
- DOD/NASA BATTERY TEST FACILITY AT CRANE, INDIANA OR OTHER

o WILL PROVIDE

- PERFORMANCE, LIFE AND RELIABILITY DATA

Figure 4-14

# ACCEPTANCE TEST DATA ON HUGHES—USAF LIGHTWEIGHT NICKEL HYDROGEN CELLS

H. Rogers
Hughes Aircraft Company

I am going to be speaking about acceptance test data on 50-ampere hour lightweight nickel hydrogen cells. This work has been supported by the Air Force. Don Warnock, who just spoke, is the project engineer for the Air Force. Dr. Steven Stednack is the Hughes project manager.

These cells are the ones that Don has been describing. They are the Air Force-Hughes Pineapply Plate Design and have an integral wall wick to provide electrolyte return. The cells are manufactured by Hughes Aircraft and use Yardney positive electrodes. In the industry evaluation program, eight of these particular cells (and I am speaking about the same cells that have been distributed to industry) I am going to be talking about were distributed to the various companies Don listed.

(Figure 4-15)

This is a graph of the cell capacity versus the ambient temperature. Let me try to interpret this. I will describe the charge first. The C rate charge and what we do is we charge at the 50 ampere rate to what we call rollover, which is simply the decrease in cell potential caused by oxygen recombination and the negative temperature coefficient of the cell potential.

We use that as a means of determining some consistent state of charge. Then we discharge it at 70 amps to one volt.

Now there are two tests as numbered 1 and 2 at 20°C, and we got about 47 ampere hours roughly. We got the same number of ampere hours by charging at a C/10 rate for 18 hours and a C/2 discharge to one volt.

We then went to a change in temperature; we went up. You notice some decrease in capacity; and we got colder, you got a slight increase in capacity. Remember that the charge efficiency at C rate is not too sensitive to temperature, as it is at the lower rates.

An interesting point is up here where this was a 72 hour C/10 charge at zero degrees. That gave us a very large increase, about 30 percent, in capacity.

I should add that this is not the first time that we have seen that; we saw it on some early Bell process plates made by Tyco and, as I found out, this has also been seen by Bell Telephone Laboratories. It would be nice, however, if we could operate a cell under those circumstances.

(Figure 4-16)

This graph is simply what we call stabilization cycling which is a C/2 discharge and a somewhat smaller charge rate. The CD ratio there was 1.1, and for the entire time there was a very slight decrease in voltage, and the voltages in all cases were above 1.2 volts.

Now, we built some cells (these are not the same ones that I was just referring to; they are the next batch actually) that have asbestos separators and most have our zirconium oxide separator. We have got nine cells with the zircar and three cells with the asbestos and we have averaged these capacities.

Now, in a C/10 test (C/2, the conventional low rate test), the zircar separators did not do as well in capacity as the asbestos separators did. The second thing we noticed that at high rates, in our C rate charge and 1.4 C discharge, we got substantially decreased capacity of these cells. The second tests got even poorer.

(Figures 4-17 and 4-18)

This is from our failure mechanisms program. The major differences in these cells were that they used Air Force impregnated Eagle-Picher plaque. That was the dry sinter type plaque. Other than that, the cells are nearly identical.

You will notice that with the zircar and with the asbestos, at the low rate we got averages with identical capacities; and at the high rate, in this case, we got somewhat increased capacity. That is an interesting comparison.

## DISCUSSION

MAURER: I just wanted to comment on your comment that it would be nice to make use of that extra capacity. We, in fact, do on terrestrial batteries. That extra capacity is available at the 20-hour rate. If you charge at the 20-hour rate for at least 60 hours, you get that big increase in capacity at -18°C. We, in fact, used that as a qualification for shipment tests at Eagle-Picher.

And, by the way, if you have fouled up the higher temperature or the electrochemical impregnation process and allowed corrosion to occur, you will not get that capacity under those conditions. So we can use that particular test as a quality check on the impregnation. If you have had corrosion, it will not pass the test.

ROGERS: That is an interesting bit of information, Dean.

VAN OMMERING: You showed that the cells with the zircar had somewhat lower capacity before stabilization cycling. Did that change after stabilization cycling? And secondly, what do you think it is due to?

ROGERS: You are talking about now the lower capacity before. These cells have not yet had that stabilization cycling, or they are in the process. I am not sure which at this point. But we do not have that answer.

The only thing I guess I can report is (and I am not sure it is a direct answer to the question) we are doing some life testing now on the first batch of cells. The other four cells are in life test, and they do seem to stabilize out. The indication is that they are giving good performance at the 80 percent depth of discharge level, so that if the capacity had continued to decrease, you would not see that.

That is sort of an indirect answer, but they certainly are stabilizing out well.

VAN OMMERING: How did the zircar and asbestos cells compare on the 80 percent depth?

ROGERS: We are not doing any asbestos in that. This came from the second batch. The first batch of cells were only zircar separators.

ELIASON: Have you done any analysis of the cells yet, looking for anything like nickel migration or anything along that line?

ROGERS: No. We generally only analyze failed cells. We have taken apart a few where we did have a couple of problems that were not necessarily related to time degradation. We did have some which we just overcharged the hell out of them and we did see some blistering of the positives, which I guess is sort of expected. And we did see some migration of nickel materials. If you looked at the zircar separator, on the side facing the electrode, you did see a substantial amount of nickel; however, it did not go through the zircar. This is not something that is obvious. The stuff looked pretty porous. We also have seen a little bit of platnium on the other side, very small amounts. But we have never had the two cross, fortunately.

ELIASON: Does the nickel actually move beyond the surface of the nickel electrode, the active material of the nickel? I mean on a cross-sectional analysis of it, have you seen it migrate beyond the surface of the electrode?

ROGERS: We have not done a cross-sectional analysis. We had not actually gone through that complete analysis.

GASTON: Does Hughes plan to remain and manufacture for nickel hydrogen cells in the future? Or is this just a short-term arrangement?

ROGERS: We make them now. I do not really know how to answer that question. It really is not my area.

GASTON: I have a second question. Jim Dunlop mentioned INTELSAT V. Does Hughes plan to manufacture those cells for INTELSAT V, or do they have a different manufacturer?

DUNLOP: INTELSAT has two batteries companies which have licensed our technology, and we plan to use one of our two licenses to manufacture the cell. There are two battery manufacturers which have licensed technology.

GASTON: Could I just ask one other question? Then what essentially are the differences in design between the Air Force and the INTELSAT design?

ROGERS: Well, let me see. I think I can give the major ones. There is a geometric difference in the plate design. We have a hole in ours; they do not. They have a small hole in theirs; we have a big one in ours.

ROGERS: Ours is a complete circle; theirs has a cut-out for the electrode. That is a physical thing. There are probably two major things, I would say, that relate to electrolyte management. One is the difference in separator. The Comsat design uses asbestos, and we generally (except for a few test cells) use the zirconium-oxide separator. That makes a difference in gas in both the electrolyte management and in the oxygen management.

The second thing is that the presence of the wall wick, which serves to return electrolyte to the stack through the separators, is, I would say, a major difference in the electrolyte management in the cell.

The third thing I would add is that our cell is originally designed and is going to be used on low earth orbit. It is also suitable for synchronous. The Comsat cell was designed primarily for synchronous use.

GASTON: Just one final question. I do not know whether you can answer this one. What is the difference in cost between the two designs?

BETZ: You would have to ask the manufacturers, I guess.

WARNOCK: I want to get back to the question about whether Hughes will be manufacturing cells, because there is an answer on that, and I think that answer could be made public. Hughes has indicated that they intend to make at least some of the cells for their own use; that they will, in addition to that, be willing to make cells for any government use of the cells on any government program (NASA, Air Force, Navy). And that in addition to that, until there is an available second source for that design, they are not particularly interested in making them, but willing to make them for commercial users until there is a second source. They are not particularly interested in selling to commercial users as a business venture.

BETZ: I would just like to comment. I think that the documentation that has been developed on the program, though, is it true that other manufacturers could use that documentation to build cells?

WARNOCK: Domestic manufacturers. The technology is on the munitions list, which places restrictions on its export.

HARKNESS: On that one cycle where you chart for 72 hours and got that increase in capacity, did you ever repeat a cycle similar to that immediately following that and did you have a drop-off in capacity of that?

ROGERS: No, we did not repeat that. It was one test.

HARKNESS: Do you think if you repeated it right away following that, you would maintain that capacity, or you would have a sharp drop-off, or what?

ROGERS: I really do not know how to answer that. I do not really understand what causes that increased capacity. I can make a lot of guesses and I will not get you bored with that, but I do not really know. Therefore, I do not have any good way to predict it.

The only thing I can say is we did, a long time ago, find the same phenomenon and did find that it takes a combination of long-term charge at low rates to get it, as Dean, of course, also related.

FORD: Do you characterize the positive plates you are going to put in your cell to the extent of carbonate the positives may have in them at the time you get ready to assemble the cells? Do you determine the carbonate content of the positive electrode that you are going to put in your cells before you assemble cells?

ROGERS: We have not been. We have not up till now.

FORD: Is there any reason why you have not? Is this not an important factor?

ROGERS: I do not know how important a factor it is. Certainly an excessive carbonate would give us trouble in the cells. But so far, we have not noticed any effects of it.

FORD: I think there is pretty good evidence that positive plates do carry carbonate, and it is not a small amount. One of the things we see is that increase in carbonate level in electrolyte on cells has been extracted, and we are pretty certain it is coming from both the positive and negative; and some of the work E-P did back several years ago showed that there was a considerable amount of carbonate in positive electrodes when they were processed.

ROGERS: I think there also is a question, and I have seen some of the literature on it, on just how much effect carbonate has on the positive electrode. Certainly it does decrease electrolyte conductivity, and it is not something good to have. I certainly will take your suggestion as a good one.

LEAR: You made a statement earlier that you had a wicking type mechanism on the walls of the cell that would return the electrolyte back to the plate, is that correct?

ROGERS: That is correct.

LEAR: Have you done any long-term cycle life testing on this cell that shows that this phenomenon does work or this particular ribbing does work?

ROGERS: Yes. I guess the best example of that was, to show that work, was done on a boilerplate cell. We have other long-term testing on other cells, but what we had done was for other reasons. We had run a cell at a C/2.7 rate for three days. Of course, that kind of cooked the inside of the cell and evaporated the water of the electrolyte and the cell performance really started to go down the tube. So we simply let it sit for a few days and did not do anything else; we just let it sit. That performance came right back, and the only way that could have happened is by electrolyte coming back through that wick. It occurs, but it occurs slowly. The idea of it is that it is based on the fact that we do not expect evaporation out of the stack to take place very fast. As long as it is slow, the return mechanism is slow, but it is more than adequate to cover any losses.

I think the real question there is whether the capillary path is inadequate, which we think it is, and can the plates then pick up that electrolyte and use them to their fullest extent? So far, they appear to do so.

LEAR: Joe Napoli asked a question a while ago about the disadvantage of the cell. In my work at Martin Marietta with nickel hydrogen cells (these are old Eagle-Picher cells, Serial Numbers 13 and 14), I was running them in a simulated low earth 90-minute type of orbit. After 3000 cycles, they become electrolyte-starved, and it takes a vibration or a time period, like you just said, Dr. Rogers, for the electrolyte to get back into the plates in order for them to operate. But I did lose capacity and I did go into a high voltage condition.

ROGERS: Were these the semiprismatic type design?

LEAR: Round vessels.

ROGERS: Round vessels. And were these with chemically impregnated plates?

LEAR: I do not know.

ROGERS: A chemical. Well, our experience with those earlier nickel hydrogen cells that Eagle-Picher made with chemically impregnated plates was that, depending on the cycle and the particular plate batch, they could swell pretty badly, and of course would absorb electrolytes. So I do not really understand why they would have come back so well.

LEAR: I was operating them under C/2 charge and discharge at 25°C, 50 percent depth of discharge.

WARNOCK: We have been talking about the light return path, the electrolyte return mechanism. The wick that Howard is talking about is applied on the inside of the pressure vessel, except where the girth weld is made, and then there is an electrolyte bridge established around the girth weld right here.

The separators extend out from the stack and contact the wick. The wick is a two- to three-mil coating of zirconium oxide. It is porous; it is inherently wettable; it has been tested for its wicking characteristics; and it has been found to be more than adequate from a wicking standpoint. The separators are zirconium oxide cloth, which are inherently wettable and also have good wicking characteristics.

If you test a nickel hydrogen cell without some kind of electrolyte return mechanism (and we have all done this), you run a few cycles and you take the cell apart if it is a boilerplate cell, and you have got a pool of electrolyte down here and you have got a dry stack.

Now, depending on how you are cycling it, temperature and so on and so forth, you may get two or three thousand cycles out of that cell before you dry the stack sufficiently enough to kill it. But eventually, you are going to dry out the stack if you do not have any way of getting electroltye back. That is the way we ran cells for years. It was a race to see how soon you were going to lose your electrolyte. You might get 3000 cycles before your cell died. For a while, we were concentrating on methods of keeping electrolytes in the stack and we finally gave up on it. There are things that you can do, but they are not 100 percent effective. You are going to lose sometimes.

So we then started concentrating on getting the electrolyte back. And this mechanism is perfectly effective. It is not an attempt that falls short of the goal; it is something that works very effectively in returning electrolyte. You do not get any pool of electrolyte down here now. It all gets wicked back up and it all gets back into the stack.

As long as you keep that stack wet, I think you will be able to expect not 2000 or 3000 cycles, but 10,000, 15,000, or 30,000 cycles out of the cell, because I think that has been one of the primary reasons for failures in nickel hydrogen cells—the inability to get that electrolyte back. That is why I said earlier that we paid a lot of attention to electrolyte management. I think this is a very effective solution to that problem.

ROGERS: One comment I would like to make before Jim asks his question. Don is talking about low earth orbit cycling. In synchronous cycling you do not get the evaporation and condensation that does not return. It will return through vaporizing back.

DUNLOP: It is not the fact that it is low earth orbit or synchronous orbit, but the fact that you have to run a cell at about a 2-C rate to get the temperature between the stack and the wall high enough. I really do not think I want to go into this because we have a very good paper coming up about two more papers down the line, which is going to show 3000 cycles with all types of different reservoir wicks arrangements that we had done for us by E.I.C., which clearly shows the effect of, say, an 80 percent depth of discharge in the three-hour cycle. With an 80 percent depth of discharge in a three-hour cycle, there is absolutely no loss of electrolyte by this mechanism that Don was just talking about, up to 3000 cycles. There is an initial loss of electrolyte just by forcing some out of the stack.

After the initial loss or 3000 cycles, you do not see any. So this was shown clearly in the experiment. You know, Howard keeps saying, well, Comsat design, they are looking at a synchronous orbit. That is true, but it does not mean you cannot use it at low earth orbit. As a matter of fact, we have had the same cells that we built for NTS-2 running at low earth orbit at 50 percent depth of discharge have been running for hundreds and hundreds of cycles now. It really depends an awful lot on what depth of discharge you choose, and you really have to choose, I think, extremely deep depth of discharge in order to get an evaporation condensation mechanism to take place with any kind of a reasonable cell design.

Now, if you go back to a design that was made ten years ago, you may have such a big gap in there between your electrode stack and your wall that you are going to have a substantial temperature drop. If you look at any of the cell designs from 1974 on, you do not really—you have to do it at depth of discharge beyond 60 percent in order to get any evaporation, and that is in one hour. So you really have to start approaching over 1-C rates to see any evaporation condensation.

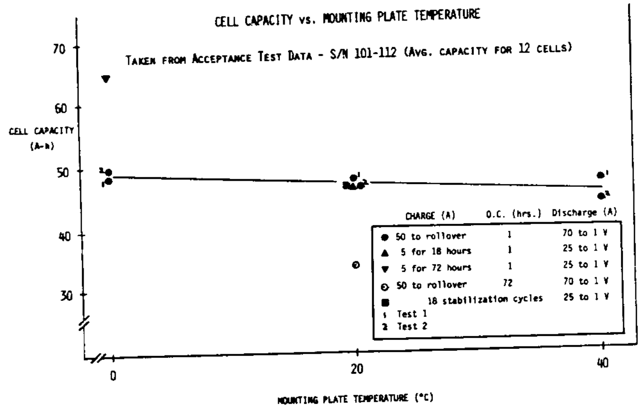


Figure 4-15

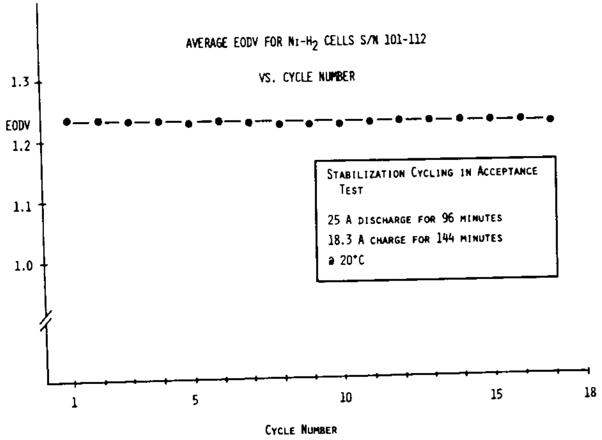


Figure 4-16

CAPACITY OF NICKEL-HYDROGEN ADVANCED DEVELOPMENT CELLS
WITH ZIRCAR SEPARATORS AND WITH ASBESTOS SEPARATORS*

HUGHES
HUGHES AIRCRAFT COMPANY

| | CAP. #1 | CAP. #2 | CAP. #3 |
|---|---|---|---|
| WITH ZIRCAR SEPARATORS (AVG. OF 9 CELLS) | 46.5 | 44.1 | 41.7 |
| WITH ASBESTOS SEPARATORS (AVG. OF 3 CELLS) | 50.6 | 49.3 | 43.4 |

TEST 1: 5 A CHARGE FOR 18 HOURS/1 HOUR OPEN CIRCUIT/25 A DISCHARGE TO 1 V.

TEST 2: 50 A CHARGE TO VOLTAGE ROLLOVER/70 A DISCHARGE TO 1 V.

TEST 3: SAME AS TEST 2.

* TESTS RUN AFTER FORMATION CYCLING BUT PRIOR TO STABILIZATION CYCLING.

Figure 4-17

CAPACITY TEST DATA

HUGHES
HUGHES AIRCRAFT COMPANY

FAILURE MECHANISMS PROGRAM VERIFICATION CELLS - RECIRCULATING DESIGN

| SEPARATOR | CELLS | CAPACITY - 20°C | |
|---|---|---|---|
| | | LOW RATE C/10 - C/2 | HIGH RATE C/1 - 1.4 C |
| IMPREGNATED ZIRCAR | 4 | 48.7 A-HR | 52.0 A-HR |
| ASBESTOS WITH RESERVOIRS | 2 | 48.7 A-HR | 52.4 A-HR |

Figure 4-18

# LIFE TEST OF Ni-H2 FLIGHT BATTERY

M. Gandel
Lockheed Missiles and Space Company

My talk today is going to be on the testing of the Air Force flight experiment battery, which the first figure here shows.

(Figure 4-19)

The battery is shown as it is mounted on a cooling plate, which has about ten gallons of watered glycol coolant going through it per minute. The battery is a 50 ampere hour, 21-cell unit, and it was flown last year as an Air Force experiment. Lockheed was the integrating contractor for the experiment.

Don went through the performance regime for the battery in flight, but because the flight was unable to subject the battery to its real capabilities, we offered to test it for Don Warnock and he was good enough to supply the battery. It has been on test since June.

(Figure 4-20)

This is a shot of the top of the battery, a better perspective of the cells. And we did add some voltage monitors and some thermocouples, which I will describe a little bit later.

The battery has been running since June. At this moment, I project we are somewhere over 2300 cycles, 90-minute cycles, to a 51 percent depth of discharge. That translates to a 44 amp discharge for 35 minutes, followed by a 30 amp charge. The recharge ratio is about 103 percent.

(Figure 4-21)

On this figure, I have shown the characteristic charge and discharge voltage. This shows a slight couple-of-minute open circuit periods between end of charge and beginning of discharge. We have been operating off of a selected cell with a cutoff voltage of 1.58 volts.

The other curve, the sawtooth, is temperature. On the right-hand side, I apologize for the minus signs before the temperatures. Those are plus degree

Celsius temperatures. Although pressure is not shown here, pressure is the inverse sawtooth of temperature and it is quite reproducible.

Let me just add this. This is a selected cycle and the temperature range is very typical, going between a low of about 12°C up to around 20°C.

(Figure 4-22)

Here I have tried to represent voltage degradation or spread as a function of the number of cycles. There is a discontinuity on the end-of-charge cell voltage because I began with a little higher voltage than my refrigeration system could stand. I should not say limitation of refrigeration system; I should say the limitation of the thermoconductivity of the battery. The cells are housed in aluminum castings. But before I go to that part, let me just go back to the chart here. Cell voltage has, for a long time, been controlled at 1.58 on the end of charge.

On the end of discharge we see some increase in spread between cells, although not too bad.

(Figure 4-23)

This shows some slight changes in temperature range to the course of cycling. It is not very significant.

(Figure 4-24)

At end of charge, we see the most severe gradients. Now, there is an elevation of the side view shown at the bottom with a 0°C, which is quite typical of almost all the testing, on the cold plate. We have thermal grease between the cold plate and the bottom of the battery. If it is zero on the cold plate, it is two degrees at the base of the battery casting and the top view shows some typical top-of-cell temperatures. This is locating thermocouples as close to the casting, as far down around the curvature of the top of the cell, as possible.

(Figure 4-25)

This is the same kind of a picture except this is the end of charge, which would be the min temperature.

We arrive at a charge-discharge regime that is 51 percent depth of discharge only because the limitations of controlling temperature on the battery.

Now, my cold plate might be dropped lower, but still, the limitation of conductivity down through that aluminum—so if I tried operating the battery at a higher depth of discharge, higher rates, then I am afraid I would move out of thermal control.

I think for a 1975 technology cell, these things are behaving beautifully, and we will continue running this battery until it just wipes itself out. Now, we have not done any reconditioning. We have only stuck with this regime.

I would just like to end by more of an analytical comment and say that I am bullish for nickel hydrogen, except that I fear that a reticent subsidized potential supplier might alter those cost predictions.

## DISCUSSION

FORD: What did you say the C to V ratio was on that test?

GANDEL: About 1.03.

GASTON: How does this 1975 design differ from the present prototype? I know it is a different manufacturer. I am aware of that.

DUNLOP: I did not do this, so I should let Don Warnock or somebody answer, but I am pretty sure, for one thing, that there is no wall wick.

WARNOCK: There are a number of differences. The flight experiment cells used asbestos separators, and currently our preference is zirconium oxide cloth. The flight experiment cells had both terminals on one end of the cell, probably not significant to its operation, but the present design has terminals on opposite ends. The '75 design did not have a wall wick, nor did the separators intentionally contact the inside surface of the pressure vessel, although there probably is some contact there.

The '75 design does not have the photochemically etched nickel foil substrate on the negative electrode. It uses a screen substrate. The '75 design was Inkenell 625 on the pressure vessel. We are now using Inkenell 718. The '75 design was compressed polymar seal, a Seigler-type seal, and we are now using a hydrolic seal terminal. There are some other minor differences, but those are the main ones.

FORD: In light of your comment about the thermal control, and you are doing this in a laboratory environment, what specific precautions or circumstances do you see that we have to start looking at in the thermal control of these things in a satellite environment? I am talking more than just where you were talking a passive, active system; but when you are looking ahead and saying well, the missions I am going to fly these on, you see that we have got to come up with more sophistication and thermal control than we have on NICAD batteries to achieve these depths to discharge in a flight environment?

GANDEL: Sure. By definition, when you say you are going to increase the depth to discharge and you are going to increase the heat generation per unit density, sure. We are going to have to do some real clever thermal design. But I do not see anything that frightens me.

BETZ: I think I would like to make a comment on that. I think the same problem would evolve with 50 ampere hour nickel cadmium cells as would evolve with 50 ampere nickel hydrogen cells.

LEAR: You said that voltage was termination cut-off of the cells during the charge cycle?

GANDEL: Yes. We have been up until now using one cell as the cut-off, and I have just given instructions to change that to a bettery level voltage.

LEAR: On your chart up there, you showed a very interesting end of discharge voltage spread. You are getting close to 1.10 or 1.0 volts.

GANDEL: Yes.

LEAR: Did you notice a decay in capacity as the voltages fell off?

GANDEL: Well, I am taking the same capacity out of each cycle, so I have no decay of capacity. If you ask me if I discharge for total capacity, would I see a decay, yes, I expect so.

STADNICK: I would like to address the thermal generation and the thermal management on the spacecraft in that the heat generated in a nickel hydrogen cell in synchronous orbit at 80 percent depth of discharge is approximately the same as in a corresponding NICAD. Consequently, you have no more heat to get rid of; you just have to change your mechanism of getting rid of it in that you do not have a flat pack anymore; you have individual cells. A radiator appears to work very satisfactorily and is a minimum encumbrance.

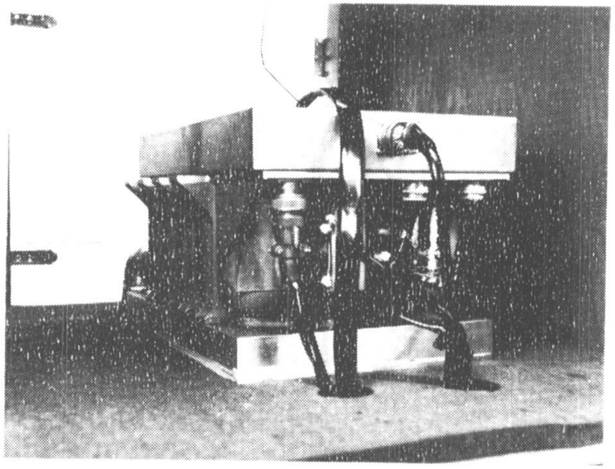


Figure 19

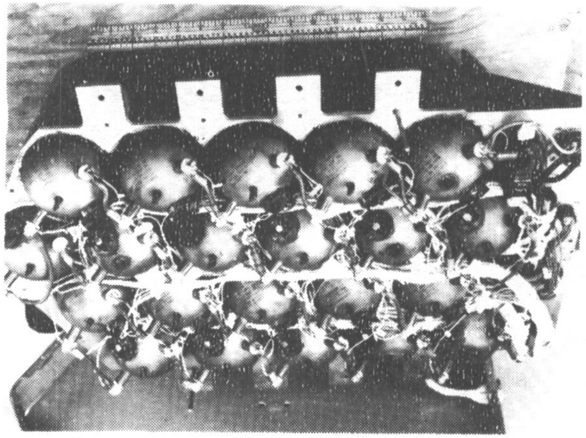
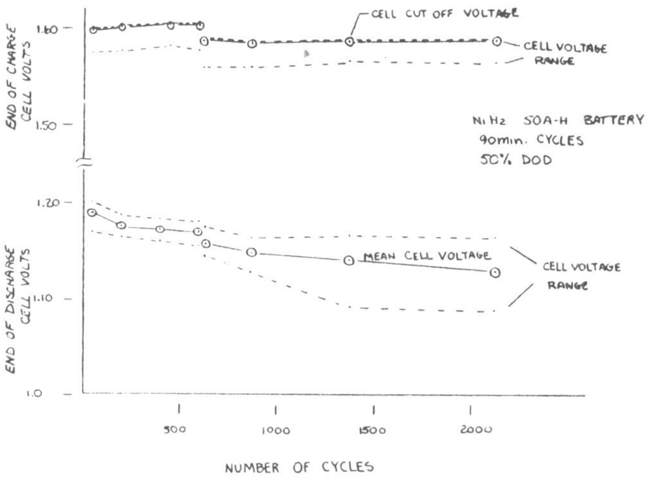


Figure 4-20



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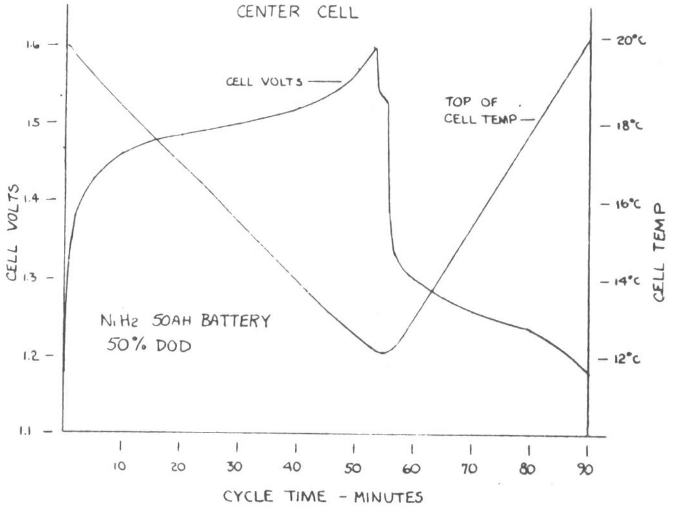

Figure 4-22

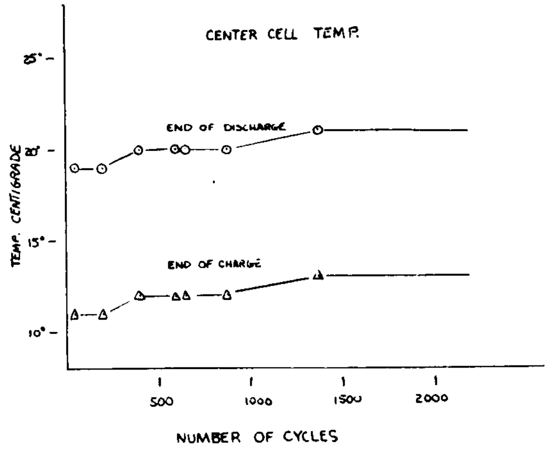

Figure 4-23

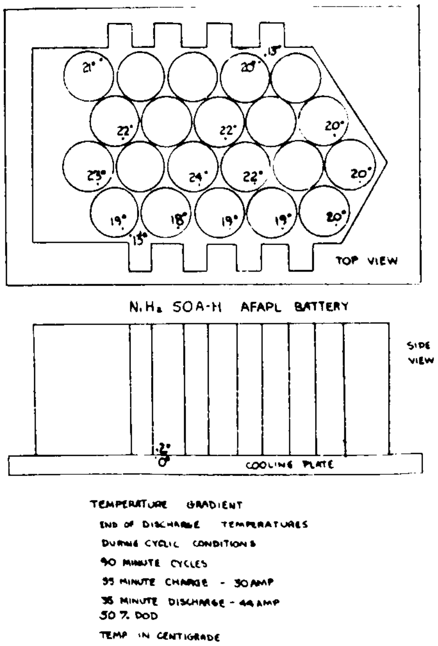

Figure 4-24

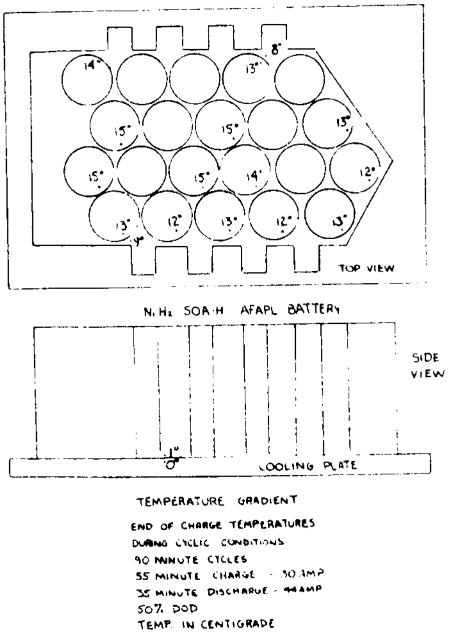

Figure 4-25

# CONFIGURATION ANALYSIS OF NICKEL HYDROGEN CELL

G. Holleck
EIC

(Figure 4-26)

I will present to you in a short summary the results of a program that we have carried out for an INTELSAT program for Comsat. The objective was to evaluate the significance of various stack configurations and components on the cycle life for nickel hydrogen cells for synchronous orbit use.

(Figure 4-27)

In previous work that we have carried out for the Air Force and Hughes, we have identified electrolyte management and oxygen management as the major actual and potential problem areas in nickel hydrogen cells which may lead to failure. And we have developed a practical solution which may modify the reservoir or wick or combinations, and especially the oxygen management also can be solved by appropriate stack configurations.

(Figure 4-28)

We have looked at various variables, and I have listed them here for you. We have looked at nickel oxide electrodes. There are two types: a Yardney and an Eagle-Picher electrode impregnated by the Bell process. Both are electrochemically impregnated electrodes, I think. It is generally accepted that electrochemically impregnated electrodes are superior, so we did not test any chemically impregnated electrodes.

We have looked at a hydrogen electrode of our own making, of two different platinum loadings, as separators, asbestos and potassium titanate. We have looked at two stack configurations, and I will illustrate quickly for you then, to remind you of what this means.

We have looked at the reservoir; we have made stacks with and without reservoirs; and we have operated cells at two different pressures. As you know, energy densities are strongly dependent on the stack cell pressure, and so we wanted to examine this parameter also.

(Figure 4-29)

Here is a typical back-to-back configuration. It is shown here with reservoir structures in the back of the nickel oxide electrode. The standard configuration would just leave out these components here.

(Figure 4-30)

The next slide shows you a recirculating arrangement. Here you have a single electrode cell components with the hydrogen electrode separator; nickel oxide electrode and a reservoir in the back of the nickel oxide electrode. In this configuration, the oxygen evolved, the nickel oxide electrode is recombined, migrates through the gas space, and is recombined at the hydrogen electrode of the next cell subunit. So on continued overcharge, you do get a migration of water, in this case, downward in the cell stack. And we have a wick which closes the circuit to prevent such a movement and returns the water.

(Figure 4-31)

Here, I am summarizing for you the test conditions that we have used. The cycle regime, the three-hour cycle regime at 1.2 hour discharge, 1.8 hour charge to 80 percent depth of discharge, the research ratio was initially 1.15 and then we lowered it to 1.10; the temperature was 10°C; the average cell capacity was about 14 ampere hours. We monitored a number of parameters: cell voltage, electrode potential, cell pressure, cell capacity, displaced electrolytes by draining the electrolyte from the vessel, stack temperature, and periodically the measured self-discharge rate of the cells.

(Figure 4-32)

This shows you a typical cycle, voltage on charge and discharge, and naturally jostling your pressure change. And here is the temperature difference between the cell stack and the outside pressure wall. You have the low heat generation on charge, and this peak is due to the overcharge. As I have mentioned, we have used this as the reason to cut back our recharge ratio from 1.15 to 1.1, which still leaves a small peak, but not this high. You can cut it actually further back, and then the temperature would just run smoothly into the discharge temperature.

(Figure 4-33)

This gives a summary of the capacity data that we have measured and periodically we have discharged the cells all the way to determine their total capacity and this is the data that I am showing here. In between, there were cycle 2, 80 percent depths, so there naturally you would get the same capacity out each time.

These cells were cycled 3000 cycles, and except for the cells with a potassium titanate separator here (we will get to this), all cells completed this cycling without failing, so this is to be considered as a mimimum number of cycles they would have gone on.

Now, let us look at some specific things. The general feature: these capacities increase during the first 100 cycles and then slowly decrease over the next 3000 or 2900 cycles. From this, you can also see the various configurations. Yardney and Eagle-Picher designate the electrodes and asbestos separator, KT separator, and the loading of the platinum electrodes and the presence or absence of the reservoir and the different pressure information.

The failures of the cells with the potassium titanate were due to the inability of the potassium titanate separator to withstand the fairly high mechanical forces that are exerted onto the separator by oxygen gas bubbles, both during overcharge for example, or the later part of charge. An analysis of these cells showed that in all cases, the separator was pressed aside and you had a postchitous in the separator and eventually the failure mode of the cells was a soft short by some loose surface particles of the nickel oxide electrode, using these holes or open areas in the separator to make a soft short circuit.

Aside from the fact that maybe that is not surprising anymore, but that the cells actually completed these 3000 cycles, I think the most interesting aspect is that there is hardly any difference between these cells in the results. These cells are really, really different in many respects, and especially, for example, with respect to electrolyte. The cells that have no reservoir have significantly less electrolyte than the cells that do have the reservoir.

Suffice it to say there is very little difference. It does not show up. The only thing that does show up and seems to be significant is that the two cells that we have tested at higher pressures have a higher capacity. I might specifically mention that Cell 11 is a duplicate of Cell 1 and Cell 12 is a duplicate of Cell 7, so these cells are identical except for the fact that they are tested at different hydrogen pressures.

(Figure 4-34)

Here I have given you some selected voltage and pressure data. Let me just point out here the end of discharge voltage; that is the end voltage of 80 percent depth cycle. You see there is some decrease in the end of discharge voltage, but it is not a very significant decrease. What is also interesting is that there is no real pattern to relate these variations with cell configurations. Initially one might attribute a slightly lower voltage to the low platinum hydrogen electrodes here of Cells 2 and 4. In the end, after 3000 cycles, you cannot really see any such difference anymore.

With respect to the pressure, the cell pressures have increased slightly. Well, they have increased generally between the 16th cycle, for example, the early cycles, and the 3000th cycle. That is in agreement with what we have also heard before. There is an increase in cell pressure. It is not a very large increase. If you discharge the cell at the normal rate, the low end pressure will also be higher; but if you then continue discharging the cell at low rates to zero volts, the pressure actually does come down to the precharge pressure.

(Figure 4-35)

I mentioned before we have also measured the self-discharge rate of the cells periodically, and we have found that rate of self-discharge is first order in hydrogen, and that means it is directly proportional to the hydrogen pressure. You can therefore express the change in hydrogen pressure by such an equation, and this rate constant here is what I have plotted here, evaluated here. What we have found is that fresh cells initially have a self-discharge rate which is higher than a cell which has been cycled. You have a decrease in rate constants, about a factor 2 difference, here after 500, 1500 cycles, and then it increased again somewhat and stayed more or less there.

The self-discharge rate of all the cells was quite uniform and independent of cell configuration, so with respect to the self-discharge, it does not matter whether you have a reservoir or you do not have a reservoir. And if you look at the rate and compare these rates with diffusion rates, you will find that the rate is not limited by diffusion in the electrolyte. It is a reaction between the hydrogen and the nickel oxide electrode.

(Figure 4-36)

During this cycle testing (and I show this just to give you some feeling for the ruggedness of this battery) at about 1500 cycles, that is about halfway through this test, we had some difficulties with the cycling equipment and the cells did overcharge and overcharge and this shows 170 percent over charge at the C/2 charge rate. This did not do any harm to any of the cells, and I have shown you in the earlier data that they continued the next 1500 cycles. If you look at any of the voltage or capacity data, you could not tell where this extended overcharge and overdischarge had occurred.

Here I have a summary sheet of some of the electrolyte data measurements that we have made. These test cells had valves at the bottom that allowed you to periodically drain the electrolyte that was expelled from the stack, and this reflects these measurements. Initially, you collect a considerable amount of electrolyte which is displaced from the cell stack, and after about—well, I have listed it here to 1000 cycles—we have continued to do this measurement, and there was no electrolyte expelled from the stacks anymore; and that applied to any, with or without separators, of these cells.

(Figure 4-37)

Here I have shown you roughly how much electrolyte is in these cell stacks. It is quite an insignificant difference between the cells without and with reservoirs—about two-thirds here from this. I think in view of this, at least I find it particularly interesting, that in this cycling regime this does not show—did not show up in the capacity as voltage test data.

(Figure 4-38)

So let me come to an end and say we have demonstrated 3000 discharge cycles. This is not, I think, the end; it is the end of this program, but not the end of the cycle life of nickel hydrogen cells. We have to conclude that for at least the synchronous orbit cycling regime, the configuration does not appear to be critical; high-pressure operation appears to be beneficial and suitable components include certainly both electrochemically impregnated plates that we have tested and both high and low platinum loading anodes. What is an important factor for the anodes is not only the platinum loading, but they have to have good oxygen combination capabilities, which both of these have. But this is a factor to look for when one looks at suitable anodes. And those asbestos separators seem to perform very well.

## DISCUSSION

VAN OMMERING: I think that I would like to add just a few comments to what Dr. Holleck has said, just to see what all this data means for the future INTELSAT programs and how we are going to make our design selection. I guess he put all the conclusions right up front there. Just to reiterate them, there is really no major difference between the different cell configurations as far as electrolyte loss, voltage performance, and capacity performance are concerned.

But one other point that Dr. Holleck brought out that is very important is that cells with reservoirs, whether it is back-to-back or recirculating, do give you quite a weight penalty because there is an added amount of electrolyte in the cells, as well as the weight of the electrolyte reservoirs themselves and other components. It would also increase the physical size of the cell somewhat. So on the basis of all this, it looks like for INTELSAT programs—especially, of course, for synchronous applications—we are just going to stick with the conventional design without reservoirs, with a reasonable amount of electrolyte, no recirculating design or anything.

One other interesting point is that this test was done at 80 percent depth of discharge with a discharge in 1.2 hours. The kind of temperature gradients that we came up with, as Dr. Holleck showed, were something on the order of 5 to 6°C from the center of the stack to the pressure vessel wall. Just imagine what would happen with the cell designs if you would do this 80 percent depth of discharge in, say, 35 minutes. You see, that is still the temperature difference which probably would not exceed something like 10°C between the stack and the pressure vessel wall. So there is a strong indication that each of those designs will do quite an adequate job in low earth orbit, and presently Comsat labs are testing these out and the results to date seem to indicate that that conclusion is valid.

STADNICK: I would just like to mention that these are boilerplate cells and that in a real flight, the coldest place in the cell is not immediately adjacent to the stack; it is in the ends of the cell. And I am sure you take that into account in your analyses.

HOLLECK: These are boilerplate cells, yes. Now, I might mention, though, that the gap between the plates and the pressure vessel in those boilerplate cells was actually larger than what is used today in actual cells.

MILLER: You may have shown this in your data and I missed it, but did you not have to pay some sort of voltage penalty by going to the one milligram loading on your negative?

HOLLECK: Well, in the voltage of the initial fresh cells you see about 20 or 30 millivolts difference in the voltage. During the cycling, this is wiped out by other effects, changing in the nickel electrodes and what have you so that it does not show up. Yes, there is some polarization difference.

FLEISCHMAN: My question follows on that. With the lower platinum loading, it seems to be a negligible penalty that you are paying; is that now your recommendation for loading?

HOLLECK: Well, I think that if you are strictly looking for performance, my recommendation is ten milligrams. If you are making a trade-off between performance and cost, then it depends on what type of parameter you put in. It is very difficult to make such a thing without adequate assumptions on what your cost is doing to you.

SEIGER: When you showed the difference in the stack weight with electrolyte, were those differences due entirely to the reservoir itself? Was all the difference in the reservoir and in the reservoir in the wicking arrangement, the recirculating arrangement?

HOLLECK: Yes, but if you look at electrolyte weight, there is a little bit more to it than that. Even if you do use reservoirs, that does not necessarily mean that you have to put in more electrolyte. And if you look at the electrolyte weight of a cell, it depends on what you do. If you take a fresh cell, you vacuum impregnate it. It will absorb a certain amount of electrolyte after draining, and if you then seal the cell and you operate it under whatever conditions, a fraction of this electrolyte will be displaced and will end up in the bottom of the vessel. This electrolyte is a useless ballast, so unless you take this electrolyte out prior to sealing, it is in there and adds weight without adding benefit or performance.

LEAR: You did not explain, or maybe I missed it, what you used for termination to determine the capacity on the capacity data chart.

HOLLECK: One volt discharge, one volt cell.

LEAR: One volt per cell on discharge, but charge of 1.6?

HOLLECK: There was no voltage limit on charge. We, in this case here, returned 110 percent of what we took out.

LEAR: Of the capacity?

HOLLECK: Yes, but I think if you do not have that number in practical operation, you can use pressure, but I personally think that even more sensitive and better than pressure would be temperature. The temperature rise at the end of charge is a very sensitive measure of when your charging process becomes inefficient.

LEAR: What charge rates did you use?

HOLLECK: This was C/2. It is 1.8 hour charge from 80 percent; it makes C/2.

BADCOCK: Would you clarify the statement about self-discharge? Did you mean that the electrolyte is always saturated with hydrogen when you talked about diffusion, or diffusion to the membrane or to the separator, rather?

HOLLECK: No, if you consider self-discharge and you look at what is the mechanism of this, you could think that maybe diffusion of hydrogen to the nickel electrode or into the nickel electrode pores is the right determining factor. If that were so, then you might think that adding a wet reservoir onto the nickel electrode should slow down your rate of self-discharge because it definitely slows down the gas transported to this electrode. But we are in a completely different rate range. It is much slower than diffusion. Diffusion would be ten to a hundred times faster than what we measured.

## Ni/$H_2$ CELLS FOR SYNCHRONOUS ORBIT

OBJECTIVE:

EVALUATE SIGNIFICANCE OF:

- STACK CONFIGURATION
- COMPONENT SELECTION

Figure 4-26

FAILURE MODES:

- ELECTROLYTE MANAGEMENT
- $O_2$ MANAGEMENT

SOLUTIONS:

- RESERVOIR
- WICK
- STACK CONFIGURATION

Figure 4-27

### Ni/$H_2$ CELL VARIABLES

| | | |
|---|---|---|
| 1. | NICKEL OXIDE ELECTRODE: | YARDNEY<br>EP, BELL |
| 2. | $H_2$ ELECTRODE: | EIC 10 MG PT/CM$^2$<br>1 MG PT/CM$^2$ |
| 3. | SEPARATOR: | ASBESTOS<br>POTASSIUM TITANATE |
| 4. | STACK CONFIGURATION: | BACK-TO-BACK<br>RECIRCULATING |
| 5. | RESERVOIR: | PRESENT<br>ABSENT |
| 6. | MAXIMUM CELL PRESSURE: | 34 ATM<br>68 ATM |

Figure 4-28

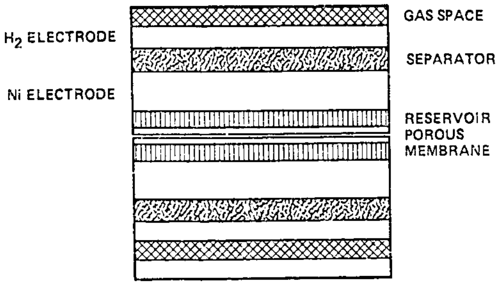

Figure 4-29

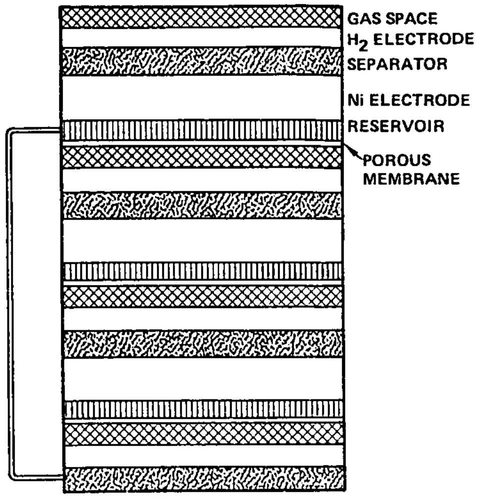

Figure 4-30

TEST REGIME

Discharge - 1.2 hr
Charge - 1.8 hr
DOD - 80%
Recharge Ratio - 1.15-1.10
Temperature - 10°C
Average Cell Capacity - 13.75 Ah

MONITORED PARAMETERS

Cell voltage
Electrode potentials
Cell pressure
Cell capacity
Displaced electrolyte
Stack temperature
Self-discharge rate

Figure 4-31

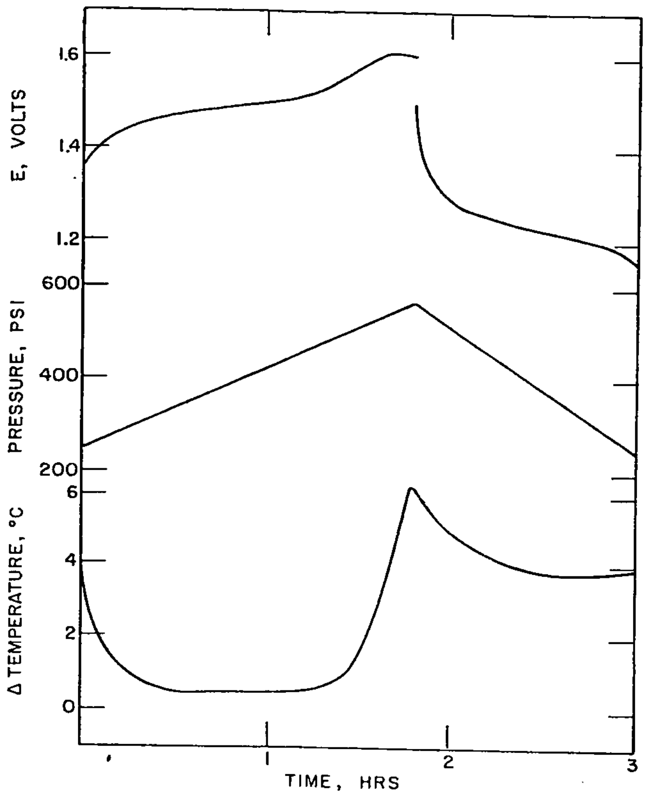

Figure 4-32

Ni/H$_2$ Cells, Capacity Data

| Cell No. | Pos. Electr. | Sep. | Negative Electrode mg Pt/cm2 | Conf. | Res. | $P_{MAX}$ ATM | Cell Capacity Ah (to 1V) Cycle | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | 0 | 15 | 96 | 500 | 1000 | 2000 | 2500 | 3000 |
| 1 | Y | A | 10 | b | Yes | 34 | 13.5 | 14.7 | 15.5 | 14.6 | 14.3 | 13.2 | 12.5 | 12.5 |
| 2 | Y | A | 1 | b | Yes | 34 | 13.5 | 14.1 | 15.0 | 14.6 | 14.3 | 13.6 | 12.9 | 12.8 |
| 3 | EP | A | 10 | r | Yes | 34 | 15.3 | 15.6 | 15.9 | 15.3 | 14.7 | 12.7 | 12.2 | 11.9 |
| 4 | Y | A | 1 | r | Yes | 34 | 14.5 | 15.3 | 15.6 | 15.5 | 15.2 | 14.8 | 14.4 | 14.6 |
| 5 | EP | A | 10 | b | Yes | 34 | 13.9 | 14.7 | 15.7 | 13.2 | 13.0 | 12.7 | 12.3 | 11.7 |
| 6 | EP | A | 10 | b | No | 34 | 12.7 | 12.9 | 13.3 | 12.4 | 12.1 | 11.8 | 11.6 | 11.5 |
| 7 | Y | A | 10 | b | No | 34 | 14.1 | 15.3 | 15.4 | 14.6 | 14.4 | 13.8 | 13.1 | 12.7 |
| 8 | Y | KT | 10 | b | Yes | 34 | 14.4 | 14.3 | 14.0 | - | - | - | - | - |
| 9 | Y | KT | 10 | b | No | 34 | 13.8 | Failed | | 13.6 | 13.8 | 14.4 | 13.5 | - |
| 10 | Y | KT | 10 | r | Yes | 34 | 13.3 | 13.5 | 14.4 | 13.2 | - | - | - | - |
| 11 | Y | A | 10 | b | Yes | 68 | 12.9 | 15.9 | 16.1 | 16.1 | 15.5 | 14.9 | 14.4 | 14.2 |
| 12 | Y | A | 10 | b | No | 68 | 13.2 | 15.8 | 15.7 | 15.2 | 15.0 | 14.5 | 14.6 | 14.4 |

---

*Identical configurations: 1 and 11
7 and 12

Figure 4-33

## $Ni/H_2$ CELL, VOLTAGE AND PRESSURE DATA

| Cell No. | Pos. Electr. | Sep. | Negative Electrode mg Pt/cm$^2$ | Conf. | Res. | $P_{MAX}$ atm | End Discharge V Cycle 16 | End Discharge V Cycle 3000 | Pressure Atm Cycle 16 | Pressure Atm Cycle 3000 |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Y | A | 10 | b | yes | 34 | 1.17 | 1.08 | 36.5 | 45.6 |
| 2 | Y | A | 1 | b | yes | 34 | 1.13 | 1.08 | 34.5 | 42.6 |
| 3 | EP | A | 10 | r | yes | 34 | 1.18 | 1.07 | 37.2 | 41.7 |
| 4 | Y | A | 1 | r | yes | 34 | 1.14 | 1.11 | 38.8 | 45.2 |
| 5 | EP | A | 10 | b | yes | 34 | 1.17 | 1.07 | 43.5 | 36.4 |
| 6 | EP | A | 10 | b | no | 34 | 1.17 | 1.13 | 34.7 | 35.4 |
| 7 | Y | A | 10 | b | no | 34 | 1.17 | 1.11 | 39.1 | 45.9 |
| 8 | Y | KT | 10 | b | yes | 34 | 1.15 | - | 41.1 | - |
| 9 | Y | KT | 10 | b | no | 34 | 1.12 | - | 42.2 | - |
| 10 | Y | KT | 10 | r | yes | 34 | 1.16 | - | 37.4 | - |
| 11 | Y | A | 10 | b | yes | 68 | 1.17 | 1.15 | 74.1 | 77.1 |
| 12 | Y | A | 10 | b | no | 68 | 1.19 | 1.15 | 74.8 | 81.6 |

*Identical configurations: 1 and 11
7 and 12

Figure 4-34

## SELF-DISCHARGE PARAMETERS FOR 14 AH $Ni/H_2$ CELLS

$$\log P = \log P_0 - \frac{K\,RT}{2.3V}\,t$$

| Cell No. | Pos. Electr. | Sep. | Negative Electrode mg Pt/cm$^2$ | Conf. | Res. | $P_{MAX}$ atm | $K\cdot10^5$ mol atm$^{-1}$ hr$^{-1}$ Cycle 0 | 500 | 1500 | 2500 | 3000 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Y | A | 10 | b | yes | 34 | 2.1 | 1.02 | 0.94 | 1.50 | 1.30 |
| 2 | Y | A | 1 | b | yes | 34 | 1.5 | 1.04 | 0.95 | 1.66 | 1.28 |
| 3 | EP | A | 10 | r | yes | 34 | 1.8 | 1.00 | 0.91 | 1.51 | 1.16 |
| 4 | Y | A | 1 | r | yes | 34 | - | 0.91 | 0.83 | 1.69 | 1.16 |
| 5 | EP | A | 10 | b | yes | 34 | 3.0 | 1.76 | 1.09 | 1.43 | 1.76 |
| 6 | EP | A | 10 | b | no | 34 | 2.0 | 0.73 | 0.63 | 1.32 | 1.61 |
| 7 | Y | A | 10 | b | no | 34 | 2.0 | 0.82 | 0.87 | 1.31 | 1.10 |
| 8 | Y | KT | 10 | b | yes | 34 | 1.8 | - | - | - | - |
| 9 | Y | KT | 10 | b | no | 34 | 2.7 | 0.92 | 0.92 | (24.3) | - |
| 10 | Y | KT | 10 | r | yes | 34 | 2.8 | - | - | - | - |
| 11 | Y | A | 10 | b | yes | 68 | - | 0.94 | 1.00 | 1.31 | 0.56 |
| 12 | Y | A | 10 | b | no | 68 | 1.5 | 1.06 | (2.59) | 1.16 | 1.03 |

*Identical configurations: 1 and 11
7 and 12

Figure 4-35

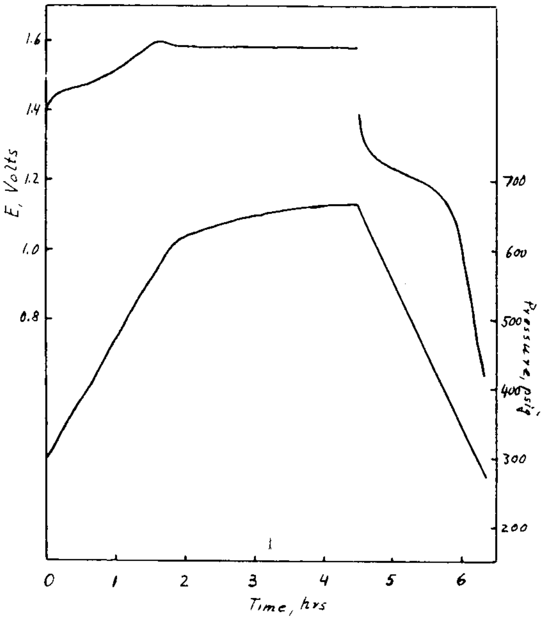

Figure 4-36

Ni/$H_2$ CELLS, ELECTROLYTE DATA

| | DRAINED ELECTROLYTE ($CM^3$) | | | | | |
|---|---|---|---|---|---|---|
| | CYCLE NO. | | | | | ELECTROLYTE IN STACK ($CM^3$) |
| CELL | 0 | 16 | 96 | 500 | 909 | |
| NO RESERVOIR (6, 7, 12) | 1.17 | 0.1 | 0.17 | 0.33 | 0.03 | 33 |
| WITH RESERVOIR BACK-TO-BACK (1, 2, 11) | 2.43 | 1.37 | 0.33 | 0.23 | 0.07 | 52 |
| WITH RESERVOIR RECIRCULATING (3,4) | 1.6 | 0.15 | 0.4 | 0.05 | 0.05 | 58 |

Figure 4-37

## CONCLUSIONS:

- DEMONSTRATED 3000 DEEP CYCLES
- CONFIGURATION NOT CRITICAL FOR SYNCHRONOUS ORBIT
- HIGH PRESSURE BENEFICIAL
- SUITABLE COMPONENTS:
  - ELECTROCHEMICAL CATHODES (YARDNEY, EP)
  - ANODES, 10 AND 1 MG PT/$CM^2$ (EIC)
  - ASBESTOS SEPARATORS

Figure 4-38

# COMMON PRESSURE VESSEL BATTERY PERFORMANCE

B. Otzinger
Rockwell

(Figure 4-39)

During the course of the last year, we conducted several tests on two common pressure vessel type nickel hydrogen batteries. So the purpose of my presentation today is to describe some of the tests that we have conducted and to show you some of the results we got.

The purpose in doing these tests is that we wanted to evaluate the performance of these units. There are two problem areas that we want to investigate or to take a look at. These were not necessarily solutions to the problems in these areas, but more investigative, sort of to get our feet wet, you might say, or get familiar with some of the problems that we might anticipate. These are not the only problems, but they are two that we selected.

The first one is self-discharge through the electrolyte leakage paths, and the second one is electrolyte loss due to water vapor transfer.

We had Eagle-Picher put together two batteries. The four-cell ten amp hour battery was designed with the intention of exploring number one, a self-discharge through electrolyte leakage paths. The second unit had a two-cell 20 amp hour battery. It was designed to investigate electrolyte loss due to water vapor transfer.

(Figures 4-40 and 4-41)

The test that we conducted with the four-cell unit involved a charge retention test and then a synchronous eclipse season. In the two-cell unit, what we plan on doing there is temperature differential synchronous 80 percent depth of discharge. We have run about 11 cycles so far on that temperature differential, and they are simply calibration runs, so I think I will just dispense with any further discussion on that particular unit. Figure 4-40 shows the results of the charge retention test, and Figure 4-41 shows the results of the synchronous eclipse season cycling test.

(Figure 4-42)

Taking a look at the units here, this is a four-cell unit, and you can see that we have it put into a resealable laboratory thick wall type enclosure, or pressure vessel. The other unit, the two-cell unit, was fabricated much as you would fabricate a light type, a lightweight configuration, and that is all welded shut.

(Figure 4-43)

Taking a look at the four-cell unit, the way it is constructed or the solution, you might say, to the self-discharge through electrolyte leakage paths was sort of a crude one at the time. This unit is about a year and a half old. We are a little late getting it tested, actually.

The important point here is that the solution was to provide a gap of 80 mils between the stack and the wall. Now, you can see there is a cross-hatch cylinder in here. That cylinder is made of stainless steel in order to aid in the transfer of heat. You notice this cross-section here, here, and here. That is Plexiglas, pieces that are put in to give us a half-inch stand-off between the four stacks.

Now, I will be talking about the stacks so if you will remember that they are counted one, two, three, four, going up, and that in the bottom,—they stand in the bottom. These up on top are pretty much isolated from the structure.

(Figure 4-44)

This is a description of the four-cell unit. It is rated at ten amp hours. Typically, we are getting 8.8 amp hours repeatedly. Those are the voltages that we were getting. Pressure range charge, about 410, 140 discharged per volume, and there is about a liter. Positive electrode plates, we have ten plates there; eleven negative; about 75 square inches for the electrodes. Separator materials are asbestos about 11 mils thick. Spacers—this is a gas spacer, probably propylene—concentration of electrolytes, about 1.3, and quantity is running in the neighborhood of 138 cm$^3$ and about 180 grams.

The first thing we did was to conduct a charge retention test to see to what extent the simple approach of just providing physically tortuous paths for the electrolytes to bridge. You can see how that might have affected self-discharge.

What we did there is we charged for an ampere 18 hours, and then we allowed an open circuit stamp for 72 hours, and then we did a five amp discharge to a four-volt cut-off. We had four cells; that is equivalent to our one volt per cell. Our results were that we had a pressure decay there of from 410 down to about 310 over the 72 hours. Then we did a discharge and found that we developed a 5.6 amp hours.

Doing a calculation on retention basis percentage, we have retained 76 percent and on a capacity basis, about 64 percent.

Last year at the battery workshop, Dr. Holleck presented the paper on the relationship of pressure decay with respect to charge retention. A little later, I will show you a comparison of that.

(Figure 4-45)

This is a comparison now. Dr. Holleck, of course, had a single cell unit, whereas we have a common pressure vessel, but you will notice the striking similarity. The comparison of percentages are in the same ballpark, which in a way is kind of surprising, because we did actually develop some self-discharge there. But they did compare rather favorably.

(Figure 4-46)

I am getting a little ahead of myself here, but I need to do that in order to demonstrate a point here. You will notice that our limiting cell on our reference cycle is the one just ahead of charge, then. It was 100 percent depth, just ahead of charge then, and you will see that our limiting cell was either three or four.

Then if you jump to our synchronous cycles here, you will notice that four is always a low cell. However, when we conducted a charge-in, you will notice that Cell 2, one of the better performing of the cells, was the lowest and indicated it had suffered more self-discharge than the other cells.

So then the conclusion here is that our pressure decay is probably questionable as a criterion for common pressure vessel type batteries.

Taking a look at this data, it was not entirely conclusive that the kind of charge retention we saw here would debilitate the operation of the battery in a practical type application, so we thought we would take a chance and go ahead and run it on a synchronous eclipse season and see if there would be any noticeable effects on running that type of a mission. Since on the synchronous, we have relatively long periods of trickle charge in between the eclipse discharges, we thought something might show up.

(Figure 4-47)

So our cyclic eclipse season, the test parameters there, rather quickly, we discharge the C/1½. One thing I did was since we were achieving repeatedly about 8.8 amp hours instead of ten, I rerated for the purposes of conducting this test, and called it an 8 amp hour unit, so that when we started running our 80 percent depth, we would not very quickly get into difficulties.

(Figure 4-48)

We simulated 46 cycles; the results were that we got good energy balance, as indicated by end of charge pressure, end of charge voltage, and the capacity on the 47th cycle where we did 100 percent depth to verify that we had been getting good energy balance.

(Figure 4-49)

We will dispense with this one rather quickly. This simply shows a typical simulation pattern that we use for synchronous eclipse seasons. Notice, this is the eclipse days running down this way and back up that way; and this tells you the durations. Again, these are the discharge parameters. I do not think there is anything unique there.

This is what we achieved when we ran the cycling. We started out all right, but coming back up on the back side, when we started to back away from the depth of discharge, the battery, as you can see, did not come back on up the other side, as you would anticipate. That is what is stated here, that it did not recover after the max. This is our maximum depth right here, 72-minute depth.

Some of the conclusions that we reached were that C/40 trickle was sufficient to maintain charge and replace self-discharge losses based on this data up here. Cells 3 and 4 did not support the load due to electrolyte loss with cycling. Harking back to what was said earlier, the very things that we did or were done at that point in time to reduce the probability of electrolyte shorting, that is, giving the 80 mil gap between the stack and the wall, was our own doing. The stack dried out. If you remember the numbering of cells, Cells 4 and 3 are on the top of the stack and the Cells 1 and 2 down toward the bottom, maintained enough electrolyte that they kept right on functioning.

Referring back to Figure 4-48, in the charge voltage range, you can see it is reasonably tight and end of pressure range was relatively good. Our capacity on the 47 cycles were around 7.6. So, like I say, it was kind of interesting, though, to see that at C/40 we did not have any trouble with the electrolyte leakage. That does not seem to be a problem. But we sure suffered on the electrolyte loss. There are probably three different ways it can happen. As Dr. Halleck pointed out in one of his papers, one of them would be vapor transfer. We took a look at that. What I did is I drained some of the electrolyte out of the cell and we did a chemical analysis on it. Now we should have about 31 percent KOH and it came out about 28.4; I do not know if that is within experimental error or not; it tends to indicate, though, that we were getting some vapor transfer since the solution was somewhat diluted.

The other things that could more than likely happen was we just had displacement of electrolyte during charge of displacement of the electrolyte with the hydrogen evolution. That is more than likely the chief mechanism in how the electrolyte was lost.

So I think this graphically shows you what will happen if you do not have some method of electrolyte management in that stack. This is a much more difficult problem because you cannot put a wall wick in and put the individual cells up against the wall and short them out. We will have to get clever; probably reservoirs and/or internal wicks will probably be needed in order to make this type of unit work.

## DISCUSSION

THORNELL: On your electrode analysis, what percentage carbonate did you pick up?

OTZINGER: We did not check on it, but we were very careful in taking out. We immediately put it in a sealed container and got it right over to the chem lab.

THORNELL: I mean from the plates.

OTZINGER: That I do not know. We did not check the carbonate. We probably should have, but we were in kind of a hurry. I had this done just before I came out here and I told them do it as fast as you can.

LEAR: I just have one question. What other types of failures of a common pressure vessel could one expect, other than loss of electrolyte, that would cause the cells to fail?

OTZINGER: In that fashion, I have an awful lot of discharge data; I just do not want to bore you with a whole lot of data. I think we have something like 150 graphs. What else could have caused that? Well, I suppose if we had gotten some contaminants in there, we may have run into this kind of a problem. One thing that I am going to do with this unit is to reflood it and draw the vacuum down and so on and make sure we get all the gases and so on out and refill it with fresh hydrogen.

There is a possibility that at Rockwell they may have allowed air in there, some amount of air. So there is a possibility that that could, you know, cause a problem somewhat similar to this.

NICKEL-HYDROGEN COMMON PRESSURE VESSEL BATTERY PERFORMANCE

PURPOSE: EVALUATE PERFORMANCE OF TWO CPV BATTERIES

PROBLEMS:
1. SELF-DISCHARGE THROUGH ELECTROLYTE LEAKAGE PATHS
2. ELECTROLYTE LOSS DUE TO WATER VAPOR TRANSFER

BATTERIES TESTED: EAGLE-PICHER, 4 CELL, 10 A-H BATTERY
EAGLE-PICHER, 2 CELL, 20 A-H BATTERY

TESTS CONDUCTED: CHARGE RETENTION AND SYNCHRONOUS ECLIPSE SEASON
TEMPERATURE DIFFERENTIAL WITH SYNCHRONOUS 80% DOD

Figure 4-39

CHARGE RETENTION TEST

TEST PARAMETERS:

- O CHARGE 1 AMP FOR 18 HOURS (62°TO 71°F)
- O OPEN CIRCUIT STAND FOR 72 HOURS
- O DISCHARGE 5AMP TO 4 VOLTS CUT-OFF (64°TO 70° F)

RESULTS:

- O PRESSURE DECAY, 410 TO 310 PSIG
- O DISCHARGE CAPACITY, 5.60 AMP-HOURS
- O RETENTION, PRESSURE $\frac{310}{410} = 76\%$

  CAPACITY $\frac{5.6}{8.8} = 64\%$

CONCLUSIONS:

- O PRESSURE DECAY QUESTIONABLE CRITERIA FOR CPV BATTERY
- O RETENTION SATISFACTORY FOR SYNCHRONOUS ECLIPSE SEASON TEST

Figure 4-40

SYNCHRONOUS ECLIPSE SEASON CYCLING TEST

TEST PARAMETERS:

O DISCHARGE C/1.5 = 5.3A     C/D RATIO = 1.3/1
CHARGE C/10 = 0.8A     MAX. DOD = 80%
TRICKLE C/40 = 0.2 A     TEMPERATURE = 60° F TO 80° F

O SIMULATED 46 CYCLE GEOSYNCHRONOUS ECLIPSE SEASON

RESULTS:

- O GOOD ENERGY BALANCE MAINTAINED (EOC P, EOC V, CAP.)

BATTERY

- O END-OF-DISCHARGE VOLTAGE DID NOT RECOVER AFTER MAX. DOD

CONCLUSIONS:

- O C/40 TRICKLE SUFFICIENT TO MAINTAIN CHARGE AND REPLACE SELF-DISCHARGE LOSSES
- O CELLS 3 AND 4 DID NOT SUPPORT LOAD DUE TO ELECTROLYTE LOSS WITH CYCLING

Figure 4-41

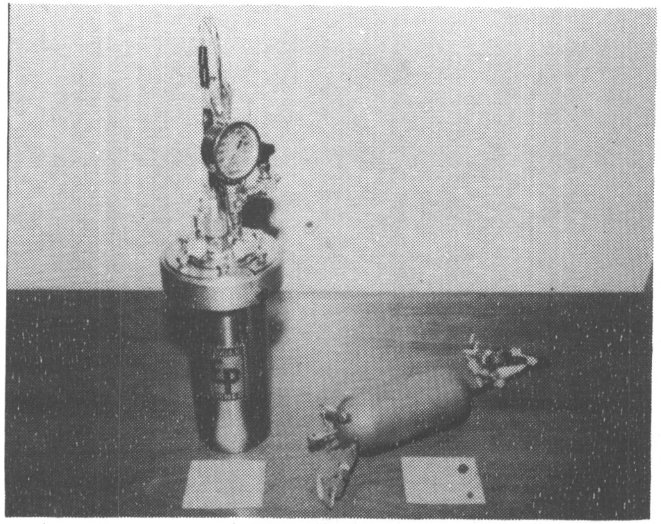

Figure 4-42

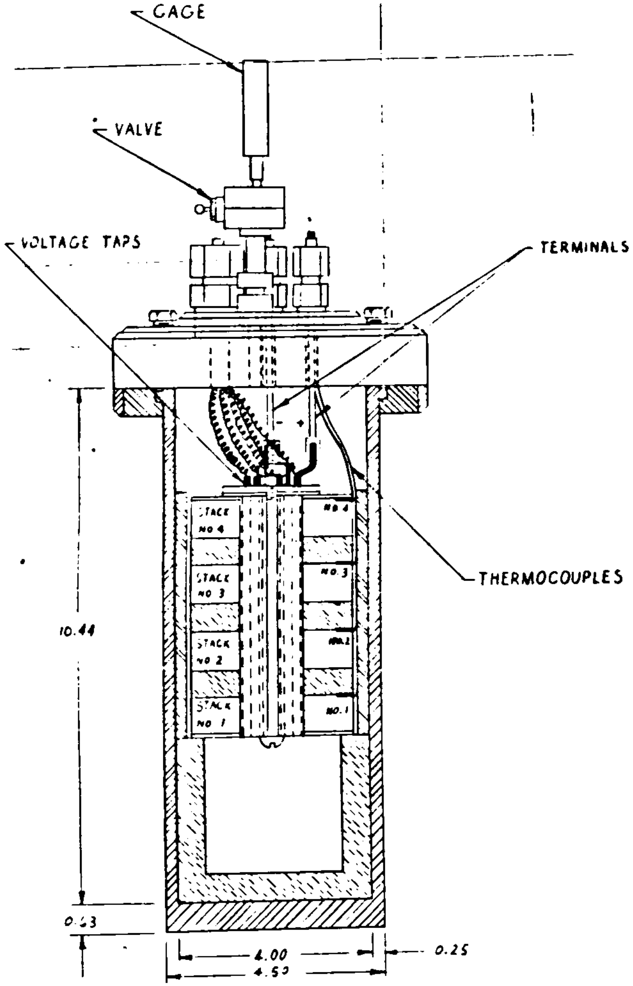

Figure 4-43

**Eagle-Picher CPV Type Nickel-Hydrogen**
**Boilerplate Battery**

•

**Description**

| | |
|---|---|
| **Number of Cells:** | |
| **Capacity:** | |
| 1. **Rated** | **10 A-H** |
| 2. **Typical** | **8.8 A-H** |
| **Voltage:** | |
| 1. **Charged O.C.** | **5.6 Volts** |
| 2. **Nominal Load (9A)** | **5 Volts** |
| **Pressure Range:** | |
| 1. **Charged** | **410 psig** |
| 2. **Discharged** | **140 psig** |
| 3. **Free Volume** | **1012 cc** |
| **Positive Electrode:** | |
| 1. **Plates** | **10** |
| 2. **Total area** | **75 Sq. In.** |
| 3. **Plate thickness** | **0.030 In.** |
| 4. **Impregnation (AF Bell Process)** | **Electro-Chemical (EC)** |
| **Negative Electrode:** | |
| 1. **Plates** | **11** |
| 2. **Plate thickness** | **0.009 In.** |
| **Separator:** | |
| 1. **Material** | **Regenerated Asbestos** |
| 2. **Thickness** | **0.011 In.** |
| **Gas Spacers:** | |
| 1. **Material** | **Poly Propylene** |
| 2. **Thickness** | **0.025** |
| **Electrolyte:** | |
| 1. **Concentration** | **Sp. Gr. 1.300** |
| 2. **Quantity** | **138.5 cc/180 gm** |

Figure 4-44

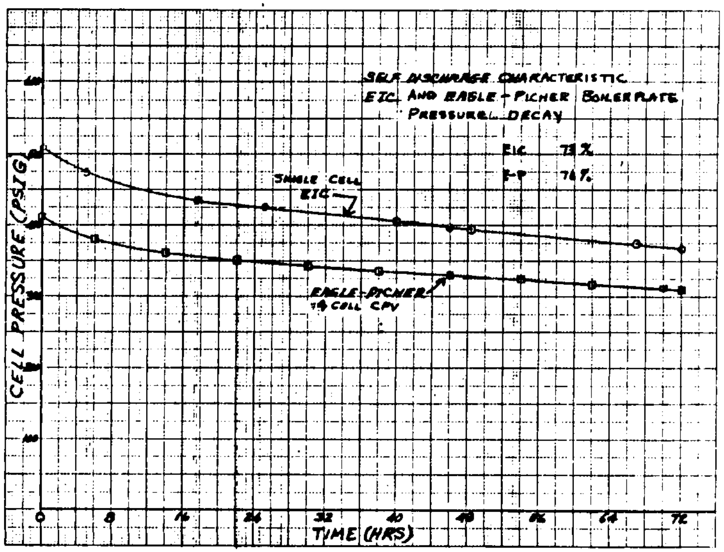

Figure 4-45

Ni-$H_2$ SYNCHRONOUS ORBIT
CHARGE/DISCHARGE PARAMETERS
FOR 8 A-H CPV BATTERY

| ECLIPSE DAY | | DISCHARGE DURATION (MINUTES) | FULL CHARGE AT 0.8 AMPS (HRS.) | (MIN.) | TRICKLE CHARGE AT 0.2 AMPS (HRS.) | (MIN.) |
|---|---|---|---|---|---|---|
| 1 | 46 | 8 | 1 | 10 | 22 | 42 |
| 2 | 45 | 15 | 2 | 10 | 21 | 35 |
| 3<br>4 | 44<br>43 | 30 | 4 | 20 | 19 | 10 |
| 5<br>6<br>7<br>8 | 42<br>41<br>40<br>39 | 45 | 6 | 30 | 16 | 45 |
| 9<br>10 | 38<br>37<br>36 | 53 | 7 | 40 | 15 | 27 |
| 11<br>12<br>13<br>14 | 35<br>34<br>33<br>32 | 60 | 8 | 40 | 14 | 20 |
| 15<br>16<br>17<br>18<br>19 | 31<br>30<br>29<br>28<br>27 | 66 | 9 | 32 | 13 | 22 |
| 20<br>21<br>22<br>23 | 26<br>25<br>24 | 72 | 10 | 24 | 12 | 24 |

DISCH. @ C/1.5 = 5.3 AMP.

FULL CHARGE @ C/10 = 0.8 AMP.

TRICKLE CHARGE @ C/40 = 0.2 AMP.

Figure 4-47

CELL VOLTAGE AT CUT-OFF

| DISCHARGE CYCLE | CELL VOLTAGE<br>CELL 1 | CELL 2 | CELL 3 | CELL 4 |
|---|---|---|---|---|
| REFERENCE | 1.163 | 1.066 | 0.888 | 0.900 |
| CHARGED STAND | 1.173 | 0.674 | 1.110 | 1.045 |
| SYNCH. CYCLE 14 | 1.185 | 1.215 | 1.125 | 0.896 |
| SYNCH. CYCLE 35 | 1.194 | 1.212 | 0.934 | 0.620 |

Figure 4-46

ENERGY BALANCE

SIMULATED ECLIPSE SEASON CYCLING

| | |
|---|---|
| EOCV (RANGE | 4.401 TO 4.442 VOLTS |
| EOCP (RANGE) | 403 TO 424 PSIG |
| CAPACITY CYCLE 47 | 7.60 AMPERE-HOURS |

Figure 4-48

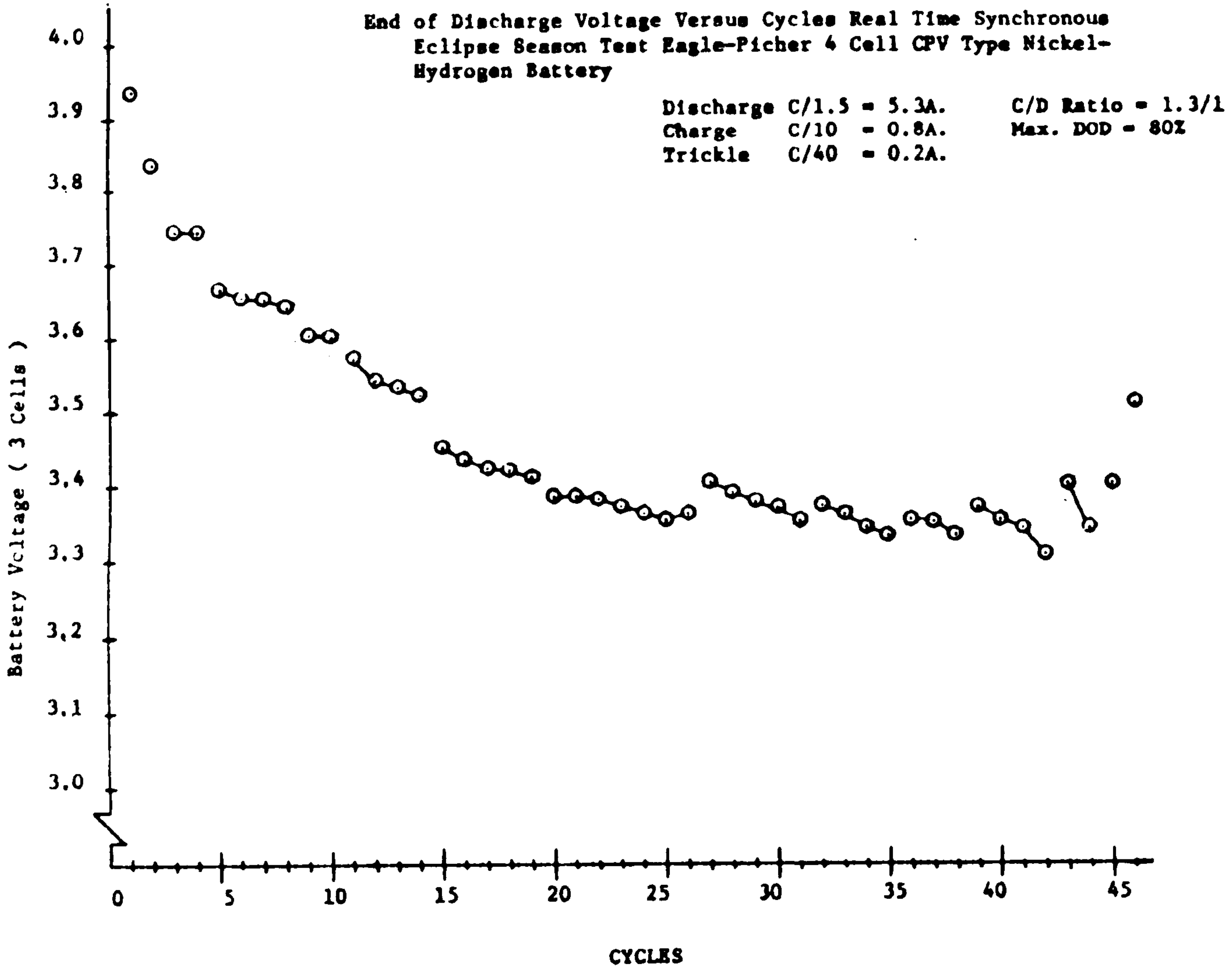
End of Discharge Voltage Versus Cycles Real Time Synchronous Eclipse Season Test Eagle-Picher 4 Cell CPV Type Nickel-Hydrogen Battery
Discharge C/1.5 = 5.3A.
Charge C/10 = 0.8A.
Trickle C/40 = 0.2A.
C/D Ratio = 1.3/1
Max. DOD = 80%
Battery Voltage ( 3 Cells )
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
0
5
10
15
20
25
30
35
40
45
CYCLES

Figure 4-49

# SILVER HYDROGEN BATTERIES

G. Holleck
EIC

Since we just talked about nickel hydrogen cells, let me first mention this is a short summary of the main findings of a program that we have carried out for the Air Force. It naturally cannot go into all the factors, but I will try to at least mention the major parts.

(Figure 4-50)

You can look at a silver hydrogen cell. It's very similar to a nickel hydrogen cell where you use a center silver electrode instead of the nickel electrode and the general cell design may be quite similar, let us say, like a stack, as you have in the nickel hydrogen cell with cell plates of this type. The second configuration that we looked at is a voltage design where the electrodes go around the interior part of the pressure vessel.

As to the placement of the cells, the nickel electrode versus silver electrode will give you a higher energy density, and this is the objective of the whole thing. It has some of the common problems that you have in nickel hydrogen cells, such as electrolyte management and oxygen management, and it has some additional problems that you do not have in the nickel hydrogen cells, and those are associated with the relatively high solubility of silver oxide in the potassium hydroxide.

So typically such a cell stack would consist of silver electrode, an absorber layer, a membrane (for example, something similar to what is commonly used in silver zinc cells), and another absorber layer and the hydrogen electrode.

(Figure 4-51)

This summarizes the cell reaction, and similar to the nickel hydrogen cell, you should expect the cell to be insensitive to overcharge and cell reversal. One item that I might point out: there is a change in the water participation in the reaction. For example, on charge, there is an overall change of one-half water per electron consumed on charge. The actual changes at the individual electrodes are larger than this because at the silver side on charge, you have a net gain of half water and on the hydrogen side on charge, you have the loss of one water.

(Figure 4-52)

The general approach was to utilize what we know about nickel hydrogen cells, and since no fundamental difficulties were epxected, we intended to use known, established components such as sintered silver electrodes. They are used in silver zinc cells. Membranes as they are used there; the NASA membrane, Permion membrane, and Viking was a cellulosic membrane. Look at the effect of these parameters and, in addition, the number of membrane layers and the amount of electrolyte as through the variables.

(Figure 4-53)

This just quickly shows you a typical cycle, a charge. As you remember, a two-step charge and two-step discharge; at higher rates the first step of the discharge tends to disappear and smear out and the pressure naturally goes also just up and down. On the bottom, you have a temperature change which is similar to the nickel hydrogen. It is somewhat more complex, which is not obvious from this figure.

The cycling regime used initially was a sawtooth type cycling regime. It is close to a user application, and I just show it because it was used for the data, but there is no particular significance in this.

(Figure 4-54)

We built 16-cell stacks. These were 15 ampere hour 8 and 15 hour cells, and don't go to the trouble to figure out these configurations. These were stacked cells of the configuration. The upper one I showed you before. All of these cells failed very rapidly, and they failed in a common mode by short-circuiting the silver shorts. Often such a short would disappear again on charge, and in some cases the cell could be cycled quite extensively after this. For example, here we had after 23 cycles such a short, and it self-healed itself and cycled another 28 cycles.

But to sum it up, all of these cells failed relatively early and the common failure mode is short-circuiting by silver.

(Figures 4-55 and 4-56)

In order to eliminate the problem of short-circuiting, you would like to have a larger overlap of the membrane at the end of the stack. Now, in a packed-in configuration, you are limited because that would ruin your thermal management.

In a rolled configuration, like this, it allows you to overlap the separator membranes considerably without ill effect onto the thermal management because it is out of the range.

We built such cells, and here it did not even take that long to get in trouble. Right away, as you can see, if you look, for example, at the capacities here (which are a very low rate), on the formation we are already charging. We did not achieve the capacity to a two and a half volts cut-off that we expected, except in two cells, which had the NASA separator.

Those are here, 2 and 8 and here. Now what is going on here? We identified the problem to be an electrolyte management problem, and specifically what was happening was that the silver on charge, the silver side dried out.

(Figure 4-57)

Here I show you a charge-discharge curve, typical charge-discharge curve. (A) Here is a cell where the capacity is limited by the silver electrode. You have the two-step charge and discharge. (B) is a cell that is limited by electrolyte; not by total electrolyte amount, but by drying out on the silver side in this case. The voltage goes up before the silver electrode is completely charged, and if you now reverse the cells to discharge, you get enormous polarization and then as you continue on, it recovers and goes down.

(Figure 4-58)

We investigated this aspect further, and, as I have mentioned, we identified as the problem area, electrolyte transport through the separator membranes as the critical parameter. I have summarized here for you the various transport processes that do occur and that all have to be considered in the cell. We have measured each of these parameters individually; I have presented this data before. Then this confirms that electrolyte transport through the membrane is the critical factor and that of the four membranes that we have tested, only the inorganic-organic NASA separator is suitable for use in silver hydrogen cells.

(Figure 4-59)

We have built a third set of cells. This uses in all cases the NASA separator, except in some cases where it uses no separator at all (well, no membrane at all). We have test cycled these cells for 500 cycles, and we have analyzed data. What we can conclude from this is that if you do this, the cells will cycle, and the most important factor in influencing the capacity or the energy output after 500 cycles are the amount of electrolyte; cells with, let us say, two asbestos separators show better performance than those with one layer, and those with no layer or in some cases also one will fail. The Kt, for example, here has a lower electrolyte retention than one asbestos. This is not enough.

The other thing that was of importance was the orientation of the NASA separator. The NASA separator is an impregnated and surface-coated asbestos-type material, so the membrane coating is on one side, this is indicated by the arrow here. Preferentially, the membrane coating should point to its hydrogen electrode, but you do need an electrolyte absorber layer between this membrane and the hydrogen electrode.

(Figure 4-60)

We have carried out an extensive analytical effort in determining the various parameters that affect energy density and design parameters. The most important parameter is silver electrode utilization for the rate energy density, and the utilization of silver electrodes is strongly carbon density dependent. Therefore, you can expect from such a cell that the energy density is strongly rate dependent.

You see here this goes anywhere. This is about 66, 35 watt hours per pound, all the way up to 110 pounds at the CO weight rate. So it is very strongly dependent on rate, and if you have an energy density quoted to you, you had better ask also at what rate this applies.

(Figure 4-61)

I have summarized some data that we have developed. This shows you, for example, the energy density, a plot of gravimetric energy density against volumetric energy density for a load design here. The points are for three layers in the hole of the open surface, for four layers in the hole, and I give you here also the maximum pressure and the length to radius ratio. Now length, in this case, is from the beginning of the hemispheric lens to the radius. You see the maximum is about here. We are considering only practical cells, which, I think, are only between this limit indicated here, mainly indicated by the length to radius ratio. The cells up here come very long and skinny and they become impractical. In this area here, these are cells of similar shape, length to radius dimension, as you have in the present nickel hydrogen cell.

(Figure 4-62)

So, concluding, I would say that silver hydrogen cells are feasible and that energy densities between 65 and 100 watt hours per kilogram (roughly half of this per pound) can be obtained, and the rate is the most important factor here. You can expect certainly over 500 cycles, and we have in one cell (I forgot to point it out) exceeded 1000 deep discharge cycles. These 500 cycles cells we had terminated there without failure.

Electrolyte management is critical, and in this context the most important factors are the nature of the separator system because of the characteristic transport parameters and the amount of electrolyte that you have overall and on each side of the separator of the membrane.

## DISCUSSION

LEAR: Is temperature as sensitive on termination of a charge, as sensitive in this cell as it is in the nickel hydrogen cell?

HOLLECK: I have not really looked at it. We did not have thermal couples integrated into the cell stack. As a matter of fact, I should take this back. We did, but the circular test cells that we had, had one single layer in the pressure vessel here, and so they had very good thermal contact. We did consider this analytically, and what you have to look at, if you take several layers, the innermost layer has to dissipate its heat through the other layers and the gas spaces. This limits you to within acceptable limits at the C/1½ or the fairly high rate that was required for this particular cell application. You can tolerate only three or four layers. You cannot go to more layers or you run into thermal problems.

LEAR: What time frame do you see these operational, and what is the cost of the cells?

HOLLECK: Well, I do not know what time frame they will be operational because, at the moment, I think nobody is doing anything with them. And secondly, with the cost, it is the same thing. You cannot really put a cost on something that is not developed. Where they would be useful, I think, is for a specialized application where you need a higher energy density than obtainable with hydrogen and where you do not need the exceptionally long cycle life that you have with nickel hydrogen. So if you need high energy density and up to 1000 cycles, it is fine. If you are looking for 10,000 cycles and 15-year life, I would still go with the nickel hydrogen.

BETZ: I might comment the energy density looks to be a little better perhaps than silver zinc or about the same, wouldn't you say?

HOLLECK: Well, I have not actually compared them, but I think silver zinc must be also as good.

BETZ: At the same rates, but with the cycle life added.

HOLLECK: Oh, the cycle life is much better. You see, you have the same system. The differences are the silver zinc has actually a higher voltage than the silver hydrogen, so you get more energy from this. But, as I understand it, today silver zinc cells do not go over 200 cycles, if that much.

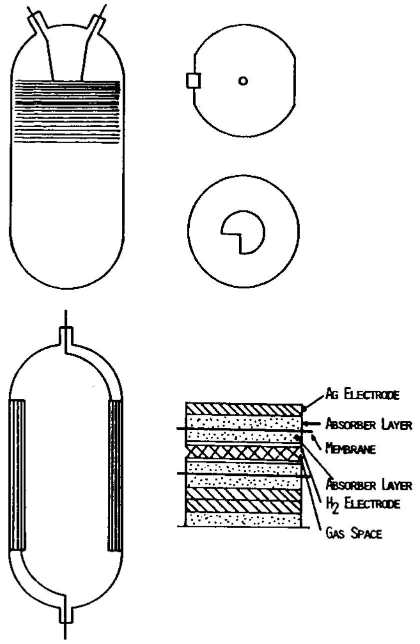

Figure 4-50

CELL REACTIONS

Charge

Ag Electrode: $2Ag + 2OH^- \rightarrow 2e^- + H_2O + Ag_2O$

$Ag_2O + 2OH^- \rightarrow 2e^- + H_2O + 2AgO$

$H_2$ Electrode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

$2Ag + 2H_2O \rightarrow 2H_2 + 2AgO$

Discharge

Reverse of Charge

Overcharge

Ag Electrode: $2OH^- \rightarrow 2e^- + 1/2\,O_2 + H_2O$

$H_2$ Electrode: $1/2\,O_2 + H_2O + 2e^- \rightarrow 2OH^-$

$$\left(\begin{array}{l} 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \\ 1/2\,O_2 + H_2 \rightarrow 2H_2O \end{array}\right)$$

Reversal

Ag Electrode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$H_2$ Electrode: $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

Figure 4-51

LIST OF TEST VARIABLES

| | Abbreviation |
|---|---|
| 1. Membrane material | M |
| a. NASA | $m_0$ |
| b. Permion 2193 | $m_1$ |
| c. Permion 2291 | $m_2$ |
| d. Visking | $m_3$ |
| 2. Plate thickness (Ag) | T |
| a. T (0.025 cm) | $t_0$ |
| b. 2.5 T | $t_1$ |
| 3. Number of membrane layers | N |
| a. 1 layer | $n_0$ |
| b. 2 layers for NASA or Perion 2193<br>3 layers for Permion 2291 or Visking | $n_1$ |
| 4. Amount of electrolyte | E |
| a. Low (2 and 3 abosrber layers for $t_0$ and $t_1$, respectively) | $e_0$ |
| b. High (3 and 5 absorber layers for $t_0$ and $t_1$, respectively) | $e_1$ |

Figure 4-52

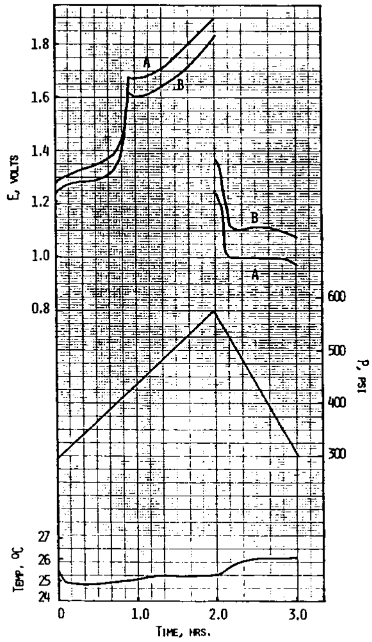

Figure 4-53

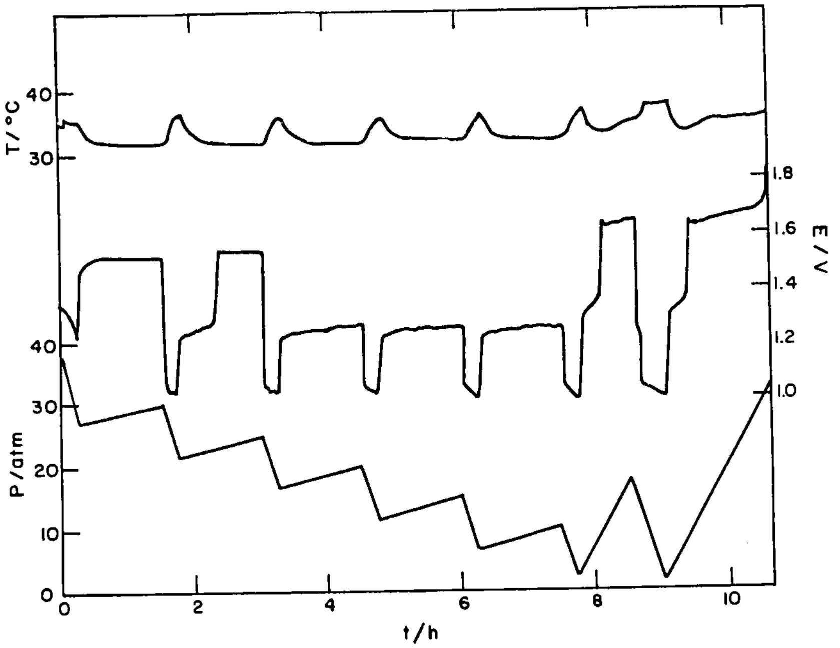

Figure 4-54

TEST RESULTS OF STACKED $Ag/H_2$ CELLS

| Cell No. | Configuration | Cycles to Failure First | Second | Total |
|---|---|---|---|---|
| 1 | $t_0\ m_0\ n_0\ e_0$ | 25 | - | 25 |
| 3 | $t_0\ m_1\ n_0\ e_0$ | 21 | 7 | 28 |
| 5 | $t_0\ m_2\ n_0\ e_0$ | 7 | - | 7 |
| 7 | $t_0\ m_3\ n_0\ e_0$ | 1 | 14 | 15 |
| 9 | $t_0\ m_1\ n_0\ e_0$ | 1 | 1 | 2 |
| 11 | $t_0\ m_1\ n_0\ e_1$ | 14 | 1 | 15 |
| 13 | $t_0\ m_1\ n_1\ e_0$ | 1 | 1 | 2 |
| 15 | $t_0\ m_1\ n_1\ e_1$ | 29 | - | 29 |
| 2 | $t_1\ m_0\ n_0\ e_0$ | 37 | - | 37 |
| 4 | $t_1\ m_1\ n_0\ e_0$ | 8 | - | 8 |
| 6 | $t_1\ m_2\ n_0\ e_0$ | 1 | - | 1 |
| 8 | $t_1\ m_3\ n_0\ e_0$ | 23 | 28 | 51 |
| 10 | $t_1\ m_1\ n_0\ e_0$ | 27 | - | 27 |
| 12 | $t_1\ m_1\ n_0\ e_1$ | 34 | - | 34 |
| 14 | $t_1\ m_1\ n_1\ e_0$ | 23 | 4 | 27 |
| 16 | $t_1\ m_1\ n_1\ e_1$ | 23 | 19 | 42 |

Figure 4-55

TEST RESULTS OF ROLLED $Ag/H_2$ CELLS

| Cell No. | Configuration | Formation Charge(1) Capacity (Ah) to 1.7V | Formation Charge(1) $E_{max}$ (V) | Pretest Charge(2) Capacity (Ah) to 1.7V | Pretest Charge(2) $E_{max}$ (V) | Drained KOH ($cm^3$) Formation Charge | Drained KOH ($cm^3$) Pretest Charge | Test Cycles to Failure |
|---|---|---|---|---|---|---|---|---|
| 17 | $t_0\ m_0\ n_1\ e_0$ | 8.0 | 1.73 | 6.6 | 1.74 | 5 | 1.5 | 48 |
| 19 | $t_0\ m_1\ n_1\ e_0$ | 3.2 | 2.30 | 7.0 | 1.77 | 6 | 2 | 1 |
| 21 | $t_0\ m_2\ n_1\ e_0$ | 1.0 | 1.84 | 6.8 | 1.75 | - | 1.5 | 6 |
| 23 | $t_0\ m_3\ n_1\ e_0$ | 5.2 | 1.86 | 6.4 | 1.74 | 7 | 1.5 | 21 |
| 28 | $t_0\ m_1\ n_1\ e_1$ | 2.8 | 1.80 | 7.0 | 1.82 | 6 | 7 | 2 |
| 30 | $t_0\ m_0\ n_1\ e_1$ | 7.9 | 1.73 | 7.6 | 1.72 | 4 | 1.5 | 65 |
| 31 | $t_0\ m_2\ n_1\ e_1$ | 1.4 | >2.5 | 7.0 | 1.92 | 9 | 4.5 | 2 |
| 32 | $t_0\ m_3\ n_1\ e_1$ | 2.9 | 2.08 | 7.0 | 1.75 | 5 | 3 | 9 |
| 18 | $t_1\ m_0\ n_1\ e_0$ | 18.5 | 1.73 | 17.0 | 1.77 | 3 | 2 | 47 |
| 20 | $t_1\ m_1\ n_1\ e_0$ | 11.1 | 2.41 | 10.5 | >2.5 | 9 | 4 | 0 |
| 22 | $t_1\ m_2\ n_1\ e_0$ | 8.6 | >2.5 | 6.8 | >2.5 | 11 | 6 | 0 |
| 24 | $t_1\ m_3\ n_1\ e_0$ | 7.8 | >2.5 | 17.8 | 1.75 | 5 | - | 1 |
| 25 | $t_1\ m_0\ n_0\ e_0$ | 19.2 | 1.73 | 15.7 | 1.75 | 5 | 1 | 520(3) |
| 26 | $t_1\ m_2\ n_0\ e_0$ | 5.8 | >2.5 | 8.9 | >2.5 | 11 | 4 | 0 |
| 27 | $t_1\ m_3\ n_0\ e_0$ | 9.0 | 2.24 | 17.6 | 1.76 | 7 | 7 | 0 |
| 29 | $t_1\ m_1\ n_1\ e_1$ | 10.2 | 1.88 | 17.1 | 1.80 | 9 | 9.5 | 2 |

(1) Total charge input 8.5 Ah for thin and 19.9 Ah for thick Ag electrode cells.

(2) Total charge input 8.6 Ah for thin and 21.6 Ah for thick Ag electrode cells.

(3) Discontinued without failure.

Figure 4-56

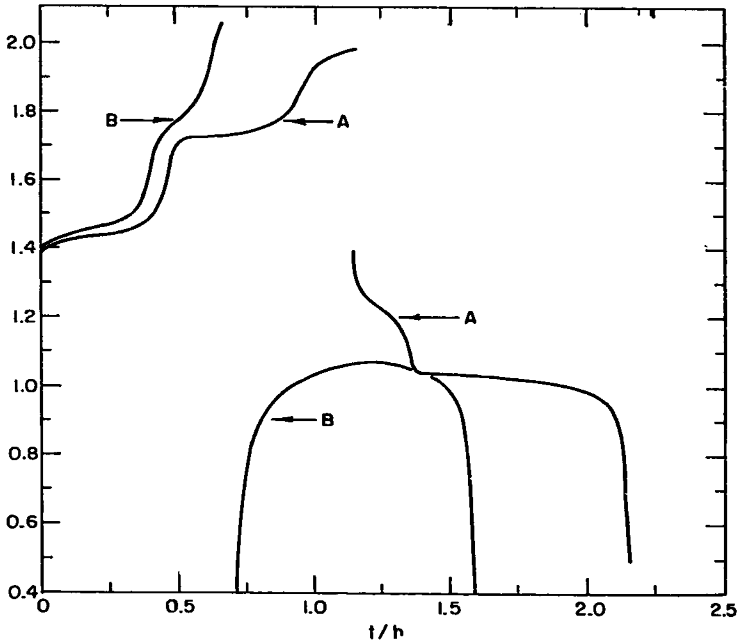

Figure 4-57

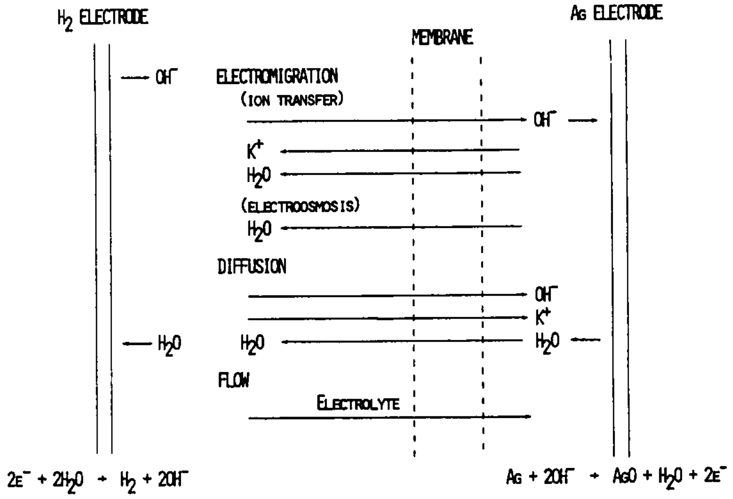

Figure 4-58

Capacities of Rolled $Ag/H_2$ Cells

| Cell No. Configuration | Capacity (to 0.8V) Ah Prior to Cycling | Cycle 104 | Cycle 514 |
|---|---|---|---|
| A-1 -(1 A/NASA)+ | 14.55 | 13.82 | 11.72 |
| A-2 -(1 KT/NASA)+ | 14.55 | 13.97 | 12.42 |
| A-3 -(2 A/NASA)+ | 16.05 | 16.28 | 14.35 |
| A-4 -(2 KT/NASA)+ | 15.15 | 11.03 | (13.65) |
| A-5 -(1 A/NASA)+ | 15.00 | 14.87 | 12.95 |
| A-6 -(1 KT/NASA)+ | 15.75 | - | - |
| A-7 -(1 A/NASA/1 A)+ | 16.20 | 11.55 | 11.72 |
| A-8 -(1 KT/NASA/1 KT)+ | 13.95 | 12.42 | 10.94 |
| A-9 -(1 A/NASA)+ | 16.35 | 13.13 | 11.46 |
| A-10-(2 A/NASA)+ | 15.75 | 17.33 | 15.23 |
| A-11-(1 A)+ | 14.85 | 13.97 | - |
| A-12-(2 A)+ | 16.05 | 16.45 | 11.99 |
| A-13-(NASA)+ | 13.05 | 11.72 | - |
| A-14-(3 KT/NASA)+ | 16.20 | 17.33 | 15.84 |
| A-15-(1 KT/NASA/+/wick | 16.20 | 14.52 | 10.67 |
| A-16-(NASA/wick/NASA)+ | 16.05 | 16.62 | 14.18 |

Figure 4-59

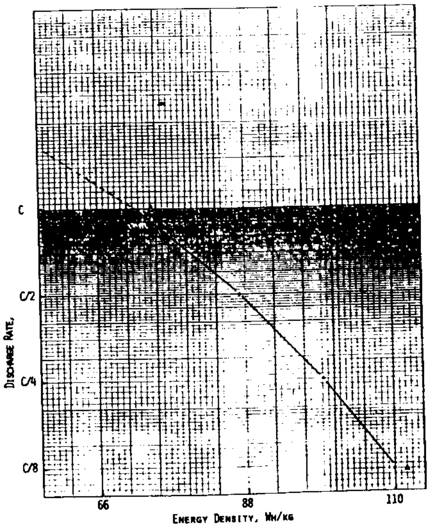

Figure 4-60

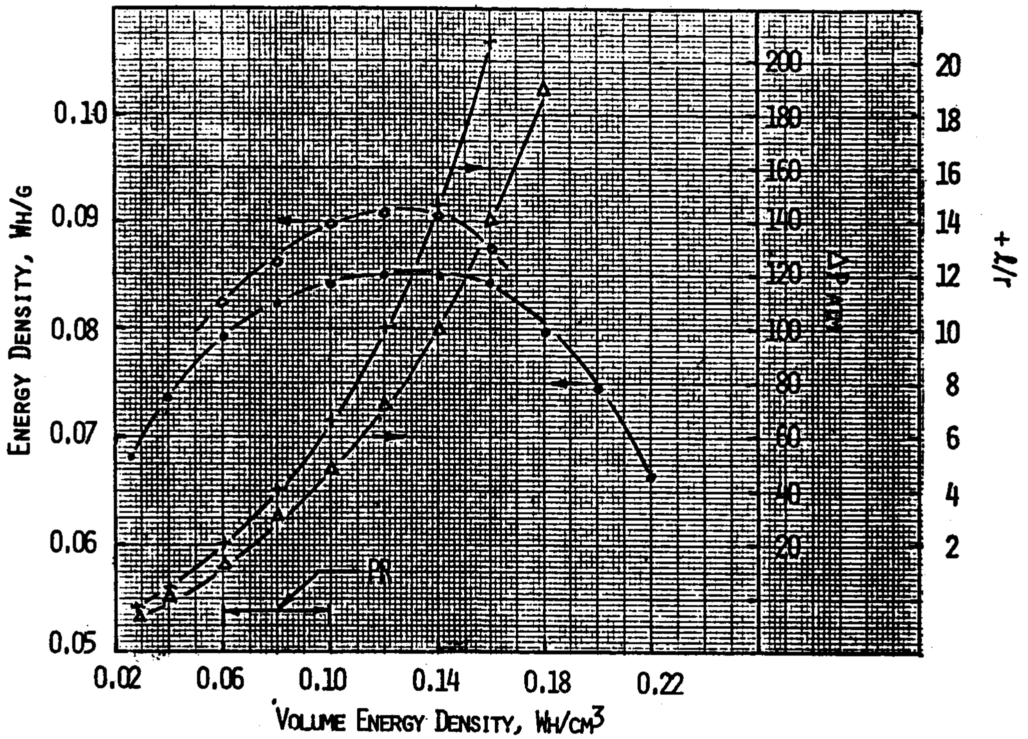

Figure 4-61

# CONCLUSIONS

A /$H_2$ CELLS ARE FEASIBLE

ENERGY DENSITY:

- 65 TO 100 WH/KG
- ~500 TO 1000 DEEP CYCLES

ELECTROLYTE MANAGEMENT CRITICAL

- NATURE OF SEPARATOR SYSTEM
- AMOUNT OF ELECTROLYTE

Figure 4-62

# SILVER HYDROGEN VOLTAGE/PRESSURE PERFORMANCE

C. W. Koehler
Ford Aerospace Company

I am going to talk a little bit about silver hydrogen and some pressure data.

(Figure 4-63)

We wanted to determine four things: first was the self-discharge characteristics at 1000 and 2000 psi; second, state of charge parameters; third, trickle charge rates; and also compare these results with nickel hydrogen.

We purchased four cells from Eagle-Picher, and this is the cell stack.

(Figure 4-64)

The cell stack is made up of two gas electrodes and one positive silver electrode. Between the gas and the positive electrode, there are two astropower separators whose functions are anode and cathode electrical isolation for electrolyte transportation and storage and prohibiting active material migration from the positive to the negative electrode.

There are also two fuel cell asbestos reservoirs whose functions are to store the electrolyte for the positive plate reaction requirements. The electrolyte was 30 weight percent KOH. And there are also two hydrogen gas screens on the back side of both gas electrodes.

We ran two cells at 1000 psi, and prior to the self-discharge test we ran two capacity measurements to verify that they were four amp hour cells and to determine what pressure changes occurred between the fully charged cell and the fully discharged cell.

(Figure 4-65)

As you can see, the pressure drop there is fairly linear except for the first few hours.

(Figure 4-66)

The second two sets of cells we ran at 2000 psi, or approximately 2000. What is happening here is that the voltage is going from the silver 2 oxide potential to the silver 1 oxide potential at about 100 hours. Again, the pressure change is fairly linear, except for the first few hours.

(Figure 4-67)

I did some calculations to determine the state of charge of the silver hydrogen at 1000 and 2000, and I used some data from Dr. Halleck in his presentation in 1977 here. I estimated 1000 psig, and he might want to comment on that later.

Some people have said that that line should be closer to the 2000 psig silver hydrogen cell, and he might want to correct me on that.

(Figures 4-68 and 4-69)

I then calculated some trickle charge rates required to keep the battery at the fully charge state. Again, I used some data from Dr. Halleck. What this says here is that at a constant trickle charge rate, a silver hydrogen battery can add up to one-half the gas volume—and I say gas volume of the nickel hydrogen battery of the same capacity, and also that for a given battery pressure a silver hydrogen battery can have twice the open circuit storage life of the nickel hydrogen cell, which is what I just said there.

There was some talk earlier today about volumes and areas and baseplate areas and that type thing. We did a quick calculation here, and based on the INTELSAT V nickel cadmium battery and the INTELSAT V nickel hydrogen battery, we normalize these areas and volumes (the nickel hydrogen volume, and I mean these are the outside dimensions; not the actual heart or volume, but the outside dimensions of the battery itself). The nickel hydrogen has 3.6 times that of the nickel cadmium battery, and a silver hydrogen battery of the same capacity would have a volume of about twice that of the nickel cadmium. On the baseplate area, the nickel hydrogen battery has approximately two times the area of that of the NICAD battery, and a silver hydrogen battery would have approximately one and a half times the baseplate area.

## DISCUSSION

GANDEL: If you equalize the pressures, what would happen to your volume comparison?

KOEHLER: If you ran both batteries at the same pressure? Is that what you you are saying? Is that the question?

GANDEL: If your nickel hydrogen was of the same pressure as your silver hydrogen, how would the volume comparisons come out?

KOEHLER: I am not sure, but the thing there is that the trickle charge rate required to keep the nickel cadmium battery would be higher, much higher than that for the silver hydrogen battery. Or in other words, the open circuit storage life would be less for the nickel hydrogen battery.

If you ran them both at the same pressure, that comes out at the energy densities, and I am not sure what the ratio is there. Do you know, John or Bob?

KOEHLER: I cannot answer that question.

GASTON: When you are dealing with a very small capacity cell like four amp hours, do you have any weight advantage over nickel hydrogen versus silver hydrogen? Of course now, the pressure vessel and the inactive component come in a very large portion, so I think for small cells like that you might not find any big difference between nickel hydrogen and silver hydrogen.

KOEHLER: On a weight basis, you might be right. But sometimes your satellite does not have the volume for a large battery like the nickel hydrogen battery. So there you would want the silver hydrogen.

ROGERS: I would make one comment on that last remark. One of the problems of nickel hydrogen (and I cannot see any reason why it does not apply to silver hydrogen) is that small cells are really not particularly useful as long as they are single cells. I am not talking about multiple within a pressure vessel. Below about 20 ampere hours, we generally do not think about nickel hydrogen, at least not at this time. I think silver hydrogen would suffer from the same thing, so I do not see the comparison.

KOEHLER: The purpose or reason for ampere hour cells is just to get the trend data. There are no plans of using a four amp hour cell at this time.

ROGERS: My actual question I had is why are you discussing nickel hydrogen and silver hydrogen. You are comparing them and I do not see them as comparable in the sense that the mission that each would be—are you really considering silver hydrogen for a synchronous mission?

KOEHLER: John just reminded me that we have cycled silver hydrogen cells through—what, 5000 cycles, John? John can comment better than I can on that.

ARMANTROUT: There is a paper that Ron Haas and I authored. I do not know if you have seen it. We discuss a cell that we did. It was ICEC, San Diego. Now, that was just a boilerplate type cell, and the purpose of that test was to evaluate the separator system. Of course, in that paper we discuss having to recharge the cell and things like that. But the purpose of the test was to evaluate the separator system, so I refer you to that for some of the history. We think it is feasible and it is a long-term replacement. All the technology that has been developed for nickel hydrogen is directly transferrable as far as pressure vessel is concerned to a large degree.

HOLCOMB: I might add that in the introduction paper I gave yesterday, in our program in silver hydrogen (which unfortunately there is not a paper on today), we are in the current stage of trying to finalize cell design at the 50 amp hour capacity size. The intent of that program is to follow very much in the footsteps of the way the Air Force is approaching the nickel hydrogen cell. That is, we are going to fabricate a number of these cells and make them available to industry probably in the 1980 time period for industry to test and evaluate for their own particular applications.

We have with the cells successfully tested similar numbers of cycles, roughly 1000 cycles at reasonably the same energy densities that you are talking about.

STADNICK: Isn't the amount of hydrogen that is generated during the charge of, say a 50 ampere hour cell the same for a nickel hydrogen as for a silver hydrogen cell ?

SIEGER: Yes, the quantity of hydrogen generated for the same capacities is obviously the same, the same number of most. What we are dealing with as a major difference in volume between the two systems are the sizes of the positive electrodes, and in silver hydrogen they will be smaller and will weigh less.

Now, you can take that additional volume and you can make the cells smaller or you can operate at a different pressure.

STADNICK: But that typically means that it is smaller only by the difference in the weight times the volume of the electrodes, which in either a silver hydrogen or a nickel hydrogen cell that I am familiar with, most of the volume is not occupied by the positive electrodes; perhaps ten or 15 percent of the volume is occupied by the positive electrodes. Even if you were to cut that in half, you would lose perhaps five or six percent in equivalent volume running the cells under equivalent pressures. Consequently, I find it difficult to understand the volume efficiencies that were quoted for the nickel hydrogen versus the silver hydrogen cells.

SIEGER: I do not know where it comes from, but I have been doing the comparison studies of the two systems, and it is amazing how the little difference in thickness makes such a difference in volume of the nickel hydrogen—of the silver hydrogen compared to the nickel hydrogen. It comes out not so much volume, but really weight. There is a big weight difference.

I have not looked at my figures to see where it comes from, but there are differences.

HOLLECK: Let me just make a comment to this first. Yes, there is a significant weight difference, but I tend also to think that volume difference is insignificant. The small difference in volume that you address from the silver electrode is more than offset by the increase in electrolyte that you need to keep the cell operating properly over what you have in the nickel hydrogen cell. But that was not really my main point.

I have a question. You made some comparisons between nickel hydrogen and silver hydrogen. Do you remember which of my rate constants you used, the one for fresh electrodes or the one for cycled electrodes ? They are almost a factor or two different.

KOEHLER: You are talking about the charge rate curve ?

HOLLECK: The self-discharge that you have shown. You compared the self-discharge rate between nickel hydrogen and silver hydrogen.

KOEHLER: Right.

HOLLECK: And you used, I think, for the nickel hydrogen data that I had presented.

KOEHLER: Yes, I used the equation that you had in your paper.

HOLLECK: Yes, but in this paper that I have presented, I showed that the self-discharge rate of fresh cells was almost twice as high as of cycled cells. I was wondering whether you remember which data you used for the comparison on the chart ?

KOEHLER: I have got your paper right here. I will check it.

HOLLECK: We have also found in our measurement that silver hydrogen cells do have a lower rate of self-discharge than nickel hydrogen cells. I do not know in quantitative terms; they behave somewhat less proper with respect to the rate constant and so on than do the nickel hydrogen cells. I do not know how to interpret the rate determining process in those cells.

I have one other question. Did you cycle these cells or similar cells to what you showed for extended time, and if so, at what type of rate and did you use voltage limits on charge?

Let me tell you why I am asking that and that may make it easier also, because I found that at least at the higher rate, the C/1½ for example, two astropower separators are already too much. The transport rate through two astropower separators is not enough to maintain continuous cycling at high rates unless you put a voltage limit into your charge.

KOEHLER: Those were fresh cells. We did not cycle them.

ARMANTROUT: There was a voltage clamp.

KOEHLER: No, there was not. We charged at the C over 20 rate for 21 hours. That is all.

ARMANTROUT: I will just comment. In the cell that we cycled for 5000 cycles, we did have to impose a voltage clamp. So your comment is true.

VAN OMMERING: I think I might be able to shed a little bit of light on that volume question. Maybe it is not quite fair to compare on a one-to-one basis the somewhat optimized silver hydrogen design and the INTELSAT V nickel hydrogen design because the INTELSAT V nickel hydrogen design, as was said earlier, is really designed to minimize the impact on the spacecraft, and it is not really optimized in terms of volume and energy density as well as it could be. You might be able to do about 50 percent better in terms of volumetric energy density on the nickel hydrogen battery if you designed the spacecraft around it from the ground up rather than what we are doing now. So when you look at it that way, I guess silver hydrogen is just slightly better than nickel hydrogen on the volume basis, but not tremendously. Nickel cadmium is about a factor two to three better than either one of those.

PALANDATI: I have got two questions. One is, do you also use the NASA/Lewis separator system in your cell designs? And the second is I think you mentioned that you have about a 30 percent concentration in your electrolyte. In most silver zinc cells, I find they usually run about 40 to 44 percent concentration. I was wondering why you used 30.

KOEHLER: I am not sure what the NASA separator system is, but it is the same? Astropower separator is the same, then. The 30 weight percent—

ARMANTROUT: We just have not studied anything other than that.

KOEHLER: It just seemed like a good one to use.

SILVER-HYDROGEN HIGH PRESSURE TEST OBJECTIVES

- DETERMINE SELF DISCHARGE CHARACTERISTICS AT 1000 AND 2000 PSIG
- DETERMINE STATE OF CHARGE PARAMETERS
- DETERMINE TRICKLE CHARGE RATES
- COMPARE RESULTS WITH NICKEL-HYDROGEN BATTERY CELL

Ford Aerospace & Communications Corporation

Figure 4-63

4 Ah SILVER-HYDROGEN CELL ELECTRODE STACK CONFIGURATION

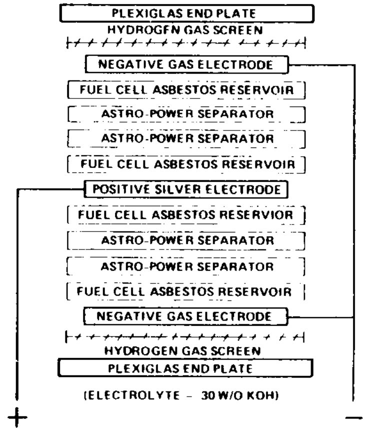

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Figure 4-64

4 Ah SILVER-HYDROGEN CELL SELF DISCHARGE CHARACTERISTICS AT 1000 PSIG

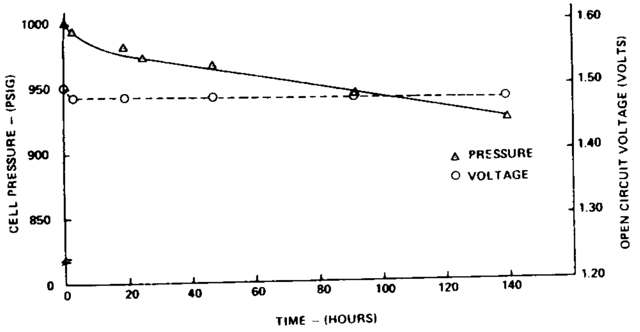

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Figure 4-65

4 Ah SILVER-HYDROGEN CELL SELF DISCHARGE CHARACTERISTICS AT 2000 PSIG

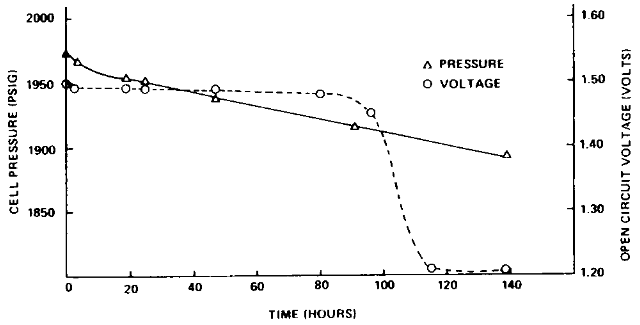

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Figure 4-66

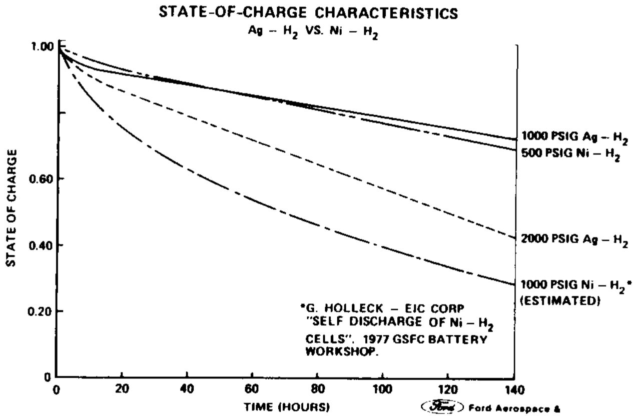

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Figure 4-67

## SILVER-HYDROGEN HIGH PRESSURE TEST CONCLUSIONS

- FOR A GIVEN TRICKLE CHARGE RATE, A SILVER-HYDROGEN BATTERY HAS HALF THE GAS VOLUME OF A NICKEL-HYDROGEN BATTERY OF THE SAME CAPACITY
- FOR A GIVEN BATTERY PRESSURE, A SILVER-HYDROGEN BATTERY HAS TWICE THE OPEN CIRCUIT STORAGE LIFE AS THAT OF A NICKEL-HYDROGEN BATTERY

Ford Aerospace & Communications Corporation

Figure 4-68

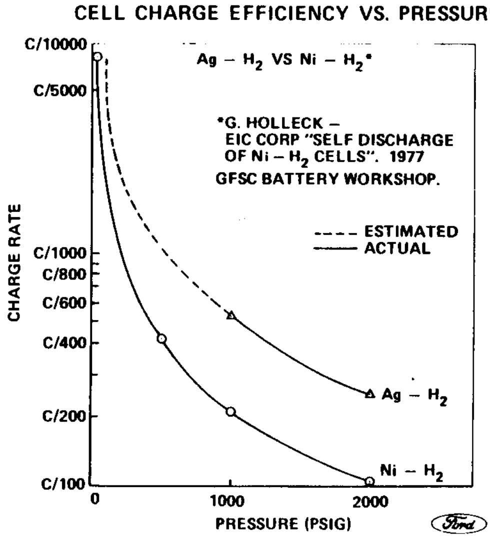

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Figure 4-69

# SESSION V

# LITHIUM CELL PROGRAMS, APPLICATIONS, AND SAFETY

L. Holcomb, Chairman
NASA Headquarters

# NASA LITHIUM CELL APPLICATIONS

G. Juvinall
Jet Propulsion Laboratory

I'd like to mention at the very outset that this a general summary of the NASA programs given by Harvey Frank during the summer lithium battery workshop. Harvey can't be here today, and I'm sort of pinch-hitting for him this morning.

During the course of the presentation, I would like to touch briefly on the advantages of the systems and describe some of the Nasa missions as are presently envisioned and on down through LDEF shuttle and high man balloon applications.

Insofar as advantages are concerned, I don't want to dwell on that, in that I think we're all aware of the advantages which can accrue from the increased energy density of the lithium systems. Suffice it to say that volumetric and gravimetric energy densities could probably be extended to be four times the silver/zinc, and in addition having a tolerance of low temperatures.

(Figure 5-1)

A representative probe operation is represented by the Jupiter situation here. One has the altitude and atmospheric pressure axes on the left and a schematic series of events as the probe enters. Most scientific instruments are not put on until just subsequent to parachute deployment, and then during a brief interval of essentially coming on down in a parachute through the atmosphere, the objectives of the mission are accomplished.

(Figure 5-2)

This is an artist's conception. That was sharp enough; it should have been included here on the entry probe with the type of chute design I would assume, in this case, for the Jupiter situation.

(Figure 5-3)

This is a brief summary of the Galileo mission. I would call this one a mission because it is well established. The other things that I will mention are considered strictly studies at this point. The purpose, of course, of Galileo is to gather data on the atmosphere of Jupiter. This spacecraft will be launched from the shuttle with the probe and have a three-year cruise period and then drop the probe into the atmosphere as the spacecraft orbits the planet.

There are two possible functions of the battery in this case: one is memory protection for the CMOS devices; the other one is the main power supply, which is about 500 watts, I guess, at this time. And, of course, the needs for lithium, again, are the life, weight, simplicity, and an advantage I did not mention before, which is apparently going to be a relatively reasonable cost. The leading candidate system here, of course, is the lithium sulfur dioxide.

(Figure 5-4)

More in the realm of planning now, there's a possibility of a Saturn orbiter dual-probe mission, and this would gather data on the atmospheres of Saturn and one of its moons, namely Titan. This is very similar in some ways to the Galileo mission, with the exception of the seven-year cruise time. The functions of the batteries, again, are very similar, as are the other parameters here. Being further off in the '80s, I would suspect that Lithium thionyl chloride may be a very active candidate at that time.

(Figure 5-5)

Another study involves the Uranus-Neptune fly-by with probes, again similar in the logistics to Galileo. This is getting further out. This is considered to have maybe a ten- to fifteen-year cruise depending on the trajectory. Again, candidate systems would be lithium sulfur dioxide and possibly at this late date, again, lithium thionyl chloride.

(Figure 5-6)

A rather interesting mission that's in the planning stages now would be a Mars sample return. The unique character of this mission, of course, is to get a sample of Martian soil and return it to Earth for analysis. Again, it would be launched from a shuttle, have a one-and-a-half-year cruise time, orbit the planet, and eject the lander capsule. The lander would be in two parts, one being the ascent vehicle, which would return either directly to the Earth or via an orbiter after the sample is obtained. The talk of it now is for a lithium thionyl chloride system for that one.

(Figure 5-7)

Here's a little better illustration, I think, of the sample return process that really sums up, very rapidly I think, what I've just been saying.

(Figure 5-8)

This one's an artist's conception of the two-piece lander, with the ascent stage seen taking off.

(Figure 5-9)

A rather interesting mission, I think, in concept at least is the Mars airplane. The objective here would be to cover a larger area of Mars than a Viking mission was able to do, not only photographically but also for deployment of instrument packages. Again, the spacecraft would be launched from the shuttle, have the typical one-and-a-half-year cruise time, and the lander ejected from the spacecraft and descending. The difference would be that the airplane would be deployed with the parachutes, and then begin following terrain features to implement the cruise.

This would be a main power plant in conjunction with a dc motor on the airplane. This would involve rather large possibly lithium thionyl chloride cells, analogous maybe to some of the large cells that are being developed by Joe McCartney's group in NOSC San Diego.

(Figure 5-10)

This is an artist's conception of the Mars airplane. To give an idea of the size of it, they were talking about a thirty-foot wingspan and speed of about 200 miles per hour.

(Figure 5-11)

The airplane would follow various features of the terrain, as illustrated on this slide, and hopefully make use of some of the cruise missile technology which we have now in order to lay out the course and follow it successfully.

(Figure 5-12)

There have been studies done on tradeoff versus the electric power system versus the hydrazine engine. I would say that this study was done by a specialist in packaging. There may be some optimism here.

One can see how the energy density certainly affects the effective range of the airplane. It clearly outranks the hydrazine option.

(Figure 5-13)

Moving on into the LDEF missions, there's a little different approach to it here. The purpose of the LDEF is to provide a facility for conducting a variety of experiments, and these range from various space processing applications, materials, pure scientific endeavors, and so on. The LDEF will be launched from the shuttle, put into Earth orbit, and then experiments can be exposed to the space environment for periods up to eleven months.

The plans are to return the LDEF to the shuttle and then back to the Earth. The function of the batteries in this case would be to serve as individual power supplies as required for any of the 70 experiments that will be on board. These will be self-contained, not only powering the experiment but doing our own data acquisition.

Again, needs for lithium would be volume, weight, and cost. Lithium $SO_2$ might well be used on the first LDEF, and further downstream, the thionyl chloride may well be in the lead position.

(Figure 5-14)

This is a picture of the LDEF. The structure is about 14 feet in diameter by 30 feet long, and each experimenter would be assigned a tray or a bay in the structure. Each one would be 3 feet by 5 feet by about 1 foot deep.

(Figure 5-15)

This is a view of the experimenters' trays. The large black box here would be a data processor control assembly; the small box is a tape recorder. Lithium batteries would probably be mounted at the bottom back of the side of it.

(Figure 5-16)

Another application would be in the shuttle launch research vehicle. The functions of this vehicle would be to test new engines and get aerodynamic data and test new materials for reentry. I haven't had access to any real specifics about the power systems that might be used yet, but apparently it would be 28 volt and in the order of magnitude of 20 amp-hours.

(Figure 5-17)

This is an interesting acronym: payload assist module (PAM). The purpose of the payload assist module is to increase the payload weight by having essentially a booster unit installed in the shuttle and then inject the payload into a higher Earth orbit. Again, it would have its own power supply separate and apart from the shuttle.

Now, this is distinguished from the integrated upper stage (which I'll get to in a moment) primarily by size.

(Figure 5-18)

This one, of course, has smaller battery requirements. Candidate systems for this one, of course, are silver/zinc nylon and perhaps advanced lithium systems later.

I believe the integrated upper state used to be called the interium upper stage, but the acronym remains the same. Again, the function of this thing is to increase payload weight and consequently the flexibility of the missions, which will be launched in the '80s and '90s.

The IUS must contain its own power supply, quite separate and distinct from the shuttle. The numbers that are being bandied about now are 24 volt, 180 amp-hour units for the first stage, and 24 volt, 10 amp-hour units for the second stage. Again, silver/zinc, perhaps followed up by lithium thionyl chloride.

(Figure 5-19)

This is a picture of the integrated upper stage being deployed from a shuttle.

Additional applications include life support systems, extravehicular mobility units, and so on. I'm simply not going to dwell on the details of this unit. I think the point of interest here is that we're considering about a 17 volt, 18 amp-hour battery unit for this application.

(Figures 5-20 and 5-21)

In addition, there's a man-maneuvering unit which is being considered. This involves actual mobility by any of the gas jets. Fundamental electric power for the unit, of course, could well be a small lithium battery.

(Figure 5-22)

In launch vehicle applications, we're now considering the solid rocket boosters which are fastened to the shuttle, of course, to aid in the launch. But batteries are needed here in order to destruct the system in the interest of range safety and in the case of a malfunction and also for beacons for retrieval of the solid rocket booster upon landing.

Requirements call for 28 volt units and a capacity, again, of about 18 amp-hours. Lithium carbon monofluoride is perhaps the leading candidate now. It may well give way to the lithium thionyl chloride later.

(Figure 5-23)

This is a picture of the solid rocket booster unit. Again, there's no point in dwelling on this. It will be in the notes. The battery, in all probability, will be in the unit down here.

(Figure 5-24)

The space shuttle, of course, will make use of these, in that this shows the relationship of the solid rocket boosters attached to the shuttle and the external tank.

(Figure 5-25)

Finally, we're getting down to applications in research balloons, and typically these are more academically oriented studies ranging all the way from cosmic ray studies, gamma ray, optical, UV, astronomy, infrared, atmospheric sciences, magnetospheric, and down to micrometeorite studies.

These are supported by the National Scientific Balloon Center, which is in Palestine, Texas. It's a private nonprofit organization which contracts with the government.

(Figure 5-26)

This picture will perhaps give a feel for the type of experiment, the type of launch situation one is faced with here and the supporting ground unit.

(Figure 5-27)

The batteries on balloon flights are used for five primary functions: pointing, telemetry, command, control, and then, of course, powering instrumentation. Typical sizes run in the range of 30 amp-hours, and a typical battery would be 28 volts.

(Figure 5-28)

In conclusion, I would like to reemphasize the attractive features of the lithium systems: being lightweight, compact, having potentially a long life, and usefulness over a wide temperature range. The benefits to NASA would include an increased payload weight and consequently, an increased cost-effectiveness to the customer. The increased payload weight should also involve more flexibility for design as far as the payload people are concerned.

There appear to be numerous applications for them and a very strong incentive to resolve the remaining problem areas and qualify lithium batteries for flight. Now, I've dwelt quite a bit on lithium thionyl chloride, and this keeps coming up again and again. I think this is a reflection of a feeling that, although there are a lot of problems remaining to be solved, I think the solutions will be coming along.

There is a tremendous expenditure of funds and work by DOD, and it would certainly seem profitable to NASA to assume a complementary role here and build on the DOD technology.

## DISCUSSION

LEUPOLD: The airplane you're going to fly, that was on what planet?

JUVINALL: That would be Mars.

LEUPOLD: Mars. Is there enough air up there to sustain flight for an aircraft like that?

JUVINALL: Apparently so. That worried me, too. When I first heard about the concept, I asked the same question. Apparently they have done studies that, with the kind of wing area we're talking about, they would be able to pull this thing off.

KRAUSE: Maybe I should address this to Lee, perhaps, not Gordon, and that is: what are NASA's real plans with respect to the amount of resources that they're going to devote to lithium battery development in consideration of all these possible applications?

HOLCOMB: I believe on the first day I gave an overview, and the funding level was indicated on that chart. It was rather small. We're talking about a technology program that's probably only about $200,000 this year. We'll be funding the development flight qualification of battery packs, and I believe that through these applications there will probably be more funding going into the lithium area in the near future than in our technology program, because we're going to be building heavily on what the DOD has done in this area.

I would like to see NASA get a role in the technology area; however, I believe a lot of progress has been made to this point in time. There will be a paper later this morning describing what limited activities we plan this year, but I do not anticipate technology funding growing much over a few hundred thousand dollars in the next year or so.

GASTON: You mentioned before an application where the lithium cell might be used for range safety. Has it actually be used already?

JUVINALL: Not to my knowledge. I'll defer if anyone here is aware of a situation and I'm not.

HOLCOMB: To date, the only application of lithium batteries that NASA has flown was for experiment power, one on the Skylab and one on the Apollo-Soyuz mission. Both of them, I believe, were camera power.

GASTON: Thank you.

GROSS: The lithium carbon monofluoride battery for the Boeing cruise missile is planned for range safety, for destruct.

MIKOWSKI: One of the problems with lithium has been its low current output. What progress has been made in overcoming that deficiency?

JUVINALL: Well, there's one vendor on the scene now who claims that they can get up to relatively high rates, even to the point of, perhaps, in propulsion systems. As a proprietary thing, I am not privy to whatever they've done there, but if their claim can be substantiated, I would say there's been some progress.

## REPRESENTATIVE JUPITER ENTRY PROBE OPERATIONS SEQUENCE

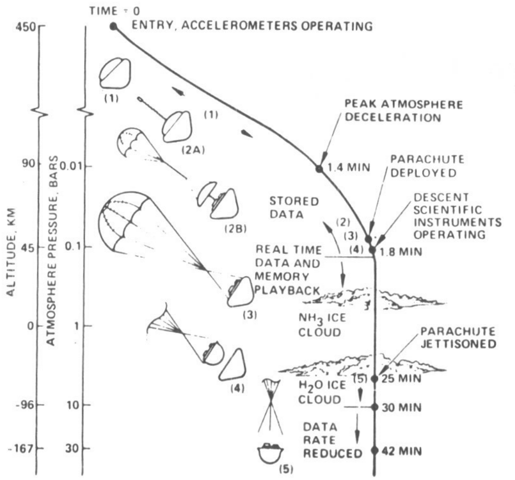


Figure 5-1

## GALILEO MISSION

- PURPOSE: GATHER DATA ON ATMOSPHERE OF JUPITER
- DESCRIPTION: LAUNCH SPACECRAFT FROM SHUTTLE WITH PROBE. 3 yrs CRUISE. PROBE ENTERS ATMOSPHERE AND SPACECRAFT ORBITS PLANET
- FUNCTION OF BATTERIES:
  - a) SPACECRAFT: MEMORY PROTECTION FOR CMOS DEVICES IN THE EVENT OF SHORT TERM POWER OUTAGES, $P_{max} = 5W$, FOR 1 to 2 sec INTERMITTENTLY
  - b) PROBE: MAIN POWER SUPPLY, $P_{max} = 500W$, E = 400 W-hr
- NEED FOR LITHIUM: LIFE, SIMPLICITY, WEIGHT, COST
- CANDIDATE SYSTEM: $Li\text{-}SO_2$

Figure 5-3

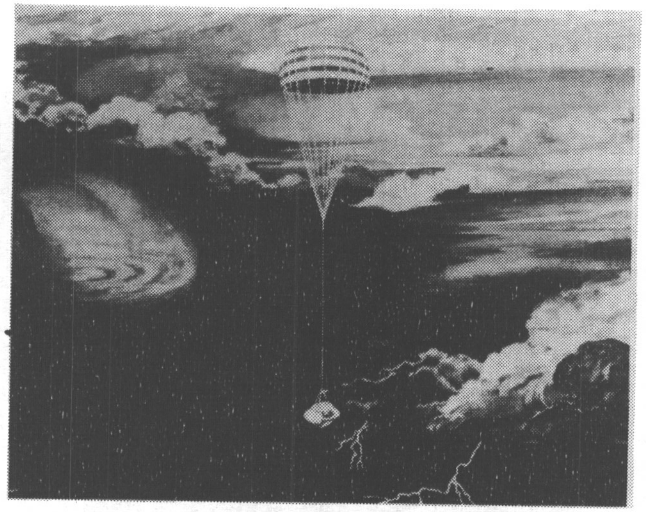


Figure 5-2

## SATURN ORBITER DUAL PROBE MISSION

- PURPOSE: GATHER DATA ON ATMOSPHERES OF SATURN AND ONE OF ITS MOONS, TITAN
- DESCRIPTION: LAUNCH SPACECRAFT FROM SHUTTLE WITH 2 PROBES. 7 yr CRUISE. PROBES ENTER RESPECTIVE ATMOSPHERES AND SPACECRAFT ORBITS PLANET
- FUNCTION OF BATTERIES:
  - a) SPACECRAFT: MEMORY PROTECTION SIMILAR TO GALILEO
  - b) PROBES: MAIN POWER SUPPLIES SIMILAR TO GALILEO
- NEED FOR LITHIUM: LIFE, SIMPLICITY, WEIGHT, COST
- CANDIDATE SYSTEMS: $Li\text{-}SO_2$, $Li\text{-}SOCl_2$

Figure 5-4

## URANUS-NEPTUNE FLYBY WITH PROBES

| | |
|---|---|
| • PURPOSE: | GATHER DATA ON ATMOSPHERES OF URANUS AND NEPTUNE |
| • DESCRIPTION: | LAUNCH SPACECRAFT FROM SHUTTLE WITH 2 PROBES<br>SPACECRAFT FLYS BY PLANETS AND DEPLOYS PROBES |
| • FUNCTION OF BATTERIES: | |
| a) SPACECRAFT: | MEMORY PROTECTION SIMILIAR TO GALILEO |
| b) PROBES: | MAIN POWER SUPPLIES SIMILIAR TO GALILEO |
| • NEED FOR LITHIUM: | LIFE, SIMPLICITY, WEIGHT, COST |
| • CANDIDATE SYSTEMS: | $Li\text{-}SO_2$, $Li\text{-}SOCl_2$ |

Figure 5-5

## MARS SAMPLE RETURN MISSION

| | |
|---|---|
| • PURPOSE: | GATHER SAMPLES OF MARTIAN SOIL AND RETURN TO EARTH FOR ANALYSIS |
| • DESCRIPTION: | LAUNCH SPACECRAFT FROM SHUTTLE. 1 1/2 yrs CRUISE. SPACECRAFT ORBITS PLANET AND EJECTS LANDER CAPSULE. CAPSULE GATHERS SAMPLE AND TRANSFERS IT TO ASCENT VEHICLE. ASCENT VEHICLE RETURNS DIRECTLY TO EARTH OR VIA ORBITER TO EARTH |
| • FUNCTION OF BATTERIES: | MAIN POWER SUPPLY FOR LANDER $P_{max} = 800W$, $E = 3160$ W-hr |
| • NEED FOR LITHIUM: | WEIGHT, LIFE |
| • CANDIDATE SYSTEM: | $Li\text{-}SOCl_2$ |

Figure 5-6

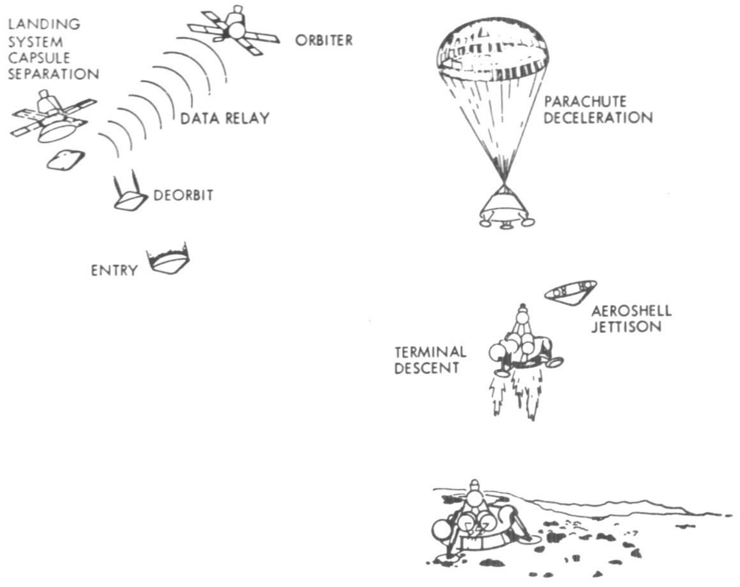


Figure 5-7

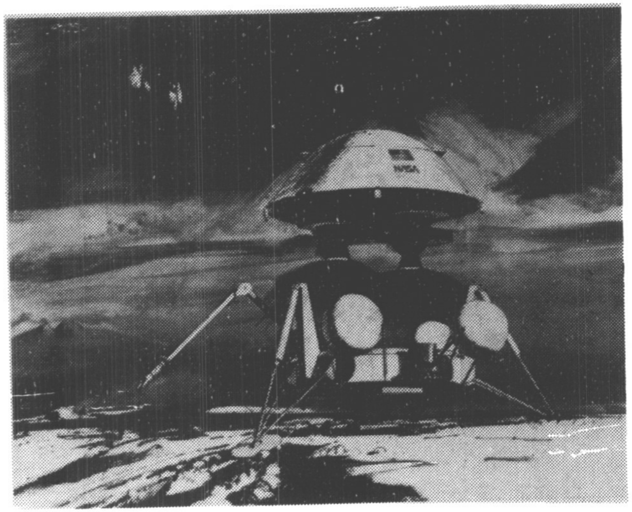


Figure 5-8

## MARS AIRPLANE MISSION

| | |
|---|---|
| • PURPOSE: | COVER BROADER AREA OF MARS THAN IN VIKING MISSION. AIRPLANES WILL TAKE PHOTOGRAPHS AND DEPLOY PACKAGES CONSISTING OF SEISMOMETERS, MAGNETOMETERS, METEOROLOGICAL, AND GEOCHEMICAL ANALYSIS INSTRUMENTS AS WELL AS PENETRATORS AND MINI ROVERS |
| • DESCRIPTION: | LAUNCH SPACECRAFT FROM SHUTTLE. 1 1/2 yr CRUISE. SPACECRAFT ORBITS PLANET AND EJECTS DESCENT SYSTEM CONTAINING AIRPLANES. AIRPLANES DEPLOYED WITH PARACHUTES AND BEGIN TERRAIN FOLLOWING CRUISE |
| • FUNCTION OF BATTERIES: | MAIN POWER PLANT IN CONJUNCTION WITH d.c. MOTOR FOR AIRPLANES, $P_{max}$ = 11 kW, E = 90 kWh |
| • NEED FOR LITHIUM: | WEIGHT, LIFE, COST |
| • CANDIDATE SYSTEM: | $Li\text{-}SOCl_2$ |

Figure 5-9

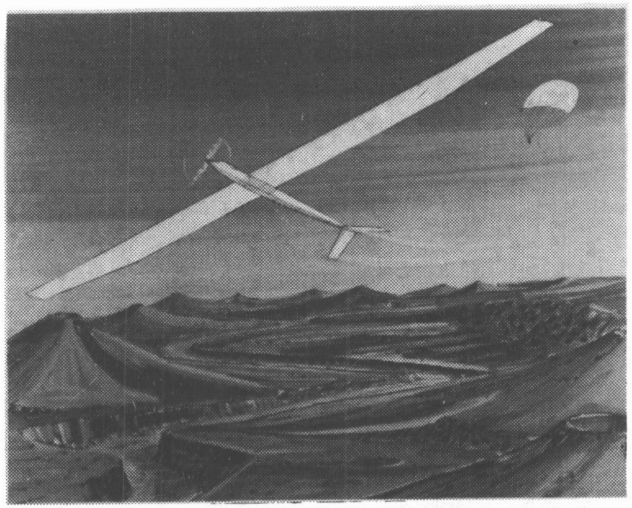


Figure 5-10

MARS AIRPLANE

LOW - ALTITUDE TERRAIN FOLLOWING MISSION

(ADAPTATION OF CRUISE MISSILE TECHNOLOGY)

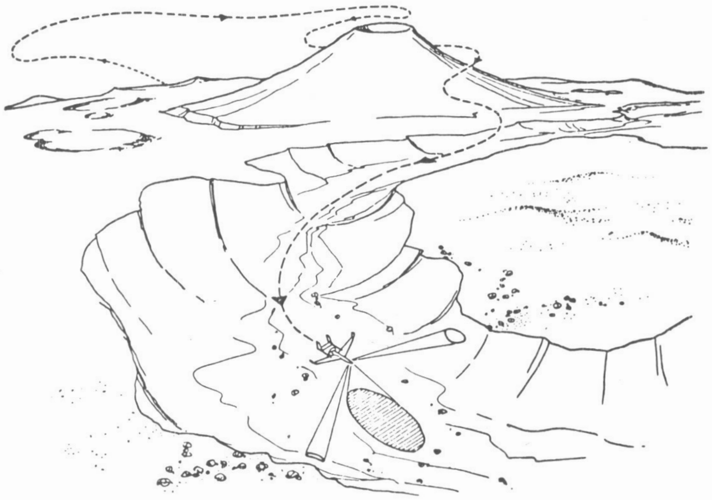
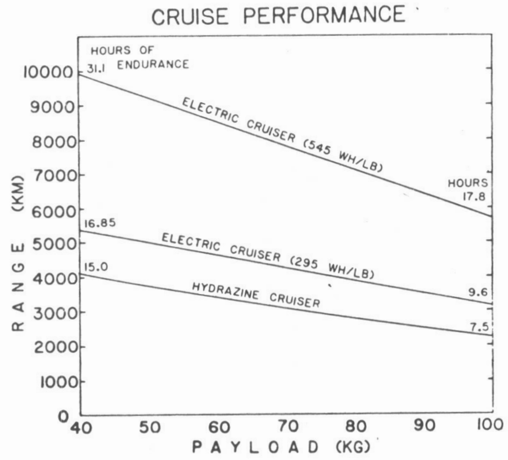


Figure 5-11



| | | | |
|---|---|---|---|
| AUW | 300 KG | PROP EFFICIENCY | .85 |
| WING SPAN | 21 M | HYDRAZINE ENGINE CRUISE SFC | 4.85 |
| WING AREA | 20 M² | ELEC. MOTOR EFFICIENCY | .85 |
| CRUISE ALTITUDE | 1 KM | AUX. POWER CONSUMPTION | .4 KW |
| LIFT/DRAG AT 300 KG | 27.75 | | |

Figure 5-12

## LDEF MISSIONS

| | |
|---|---|
| • PURPOSE: | TO PROVIDE A FACILITY FOR CONDUCTING A VARIETY OF EXPERIMENTS IN SPACE IN SUCH AREAS AS FIBRE OPTICS, THERMAL COATINGS, SOLAR PLASMA, MATERIALS etc. |
| • DESCRIPTION: | LAUNCH LDEF FROM SHUTTLE AND PLACE IN EARTH ORBIT. CONDUCT EXPERIMENTS ON LDEF FOR PERIODS UP TO 11 MONTHS. RETURN LDEF TO SHUTTLE AND THEN TO EARTH |
| • FUNCTION OF BATTERIES: | TO SERVE AS INDIVIDUAL POWER SUPPLIES AS REQUIRED FOR ANY OF THE 70 EXPERIMENTAL PACKAGES |
| • NEED FOR LITHIUM: | VOLUME, WEIGHT, COST |
| • CANDIDATE SYSTEMS: | $Li-SO_2$ FOR 1st LDEF. $Li-SO_2$ OR $Li-SOCl_2$ FOR 2nd LDEF |

Figure 5-13

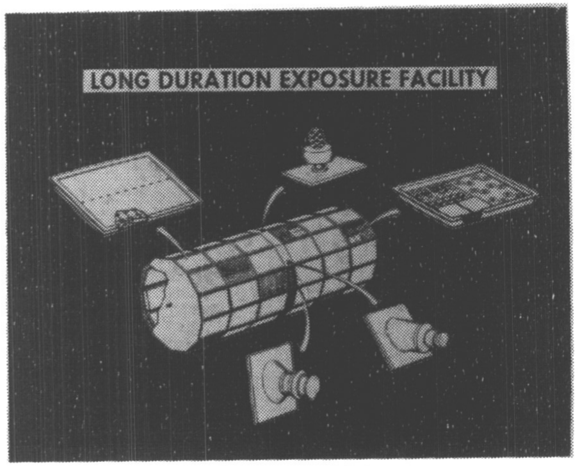


Figure 5-14

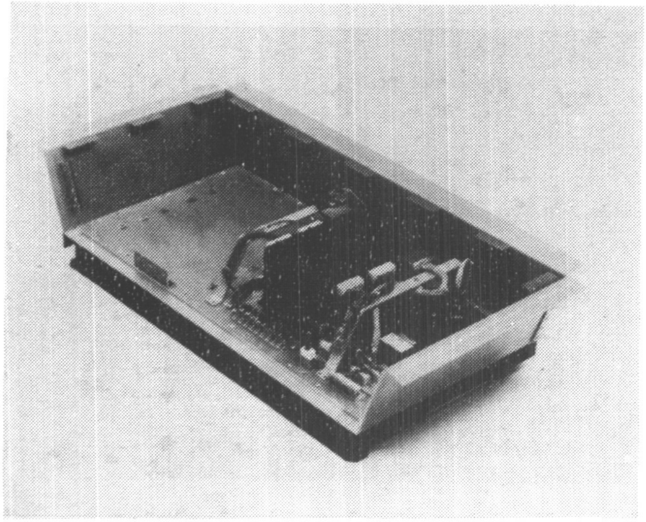
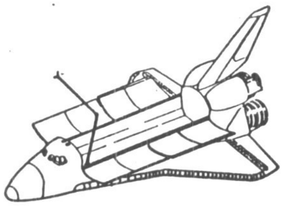


Figure 5-15

SHUTTLE LAUNCHED
RESEARCH VEHICLE (SLRV)

BATTERY
28 VOLTS
20 A.H.



FUNCTIONS
1 Test new engines
2 Gather aerodynamic data upon re-entry
3 Test new materials for re-entry

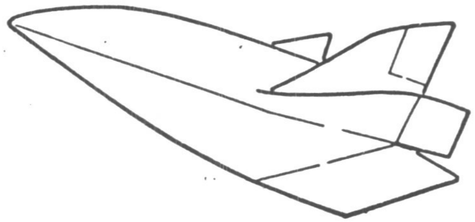


Figure 5-16

## PAM FOR SHUTTLE

| | |
|---|---|
| • PURPOSE: | THE PAM ENABLES INCREASED PAYLOAD WEIGHT OF EARTH ORBITING SPACECRAFT TO BE LAUNCHED IN THE 1980's AND 1990's |
| • DESCRIPTION: | THE SPACECRAFT IS INSTALLED IN THE IUS WHICH IN TURN IS INSTALLED IN THE SHUTTLE. THE PAM LAUNCHES THE SPACECRAFT FROM THE SHUTTLE WHILE IN EARTH ORBIT TO A HIGHER ORBIT |
| • FUNCTION OF BATTERIES: | THE PAM, LIKE THE IUS, MUST CONTAIN ITS OWN POWER SUPPLY SEPARATE AND APART FROM THE SHUTTLE. THE PAM IS SMALLER THAN THE IUS AND HAS CORRESPONDINGLY SMALLER BATTERY REQUIREMENTS |
| • NEED FOR LITHIUM: | WEIGHT |
| • CANDIDATE SYSTEMS: | Ag-Zn NOW, PERHAPS Li-$SOCl_2$ LATER |

Figure 5-17

## IUS FOR SHUTTLE

| | |
|---|---|
| • PURPOSE: | THE IUS ENABLES INCREASED PAYLOAD WEIGHT OF PLANETARY AND OTHER SPACECRAFT TO BE LAUNCHED IN THE 1980's and 1990's |
| • DESCRIPTION: | THE SPACECRAFT IS INSTALLED IN THE IUS WHICH IS IN TURN INSTALLED IN THE SHUTTLE. THE IUS LAUNCHES THE SPACECRAFT FROM THE SHUTTLE WHILE IN EARTH ORBIT |
| • FUNCTION OF BATTERIES: | THE IUS MUST CONTAIN ITS OWN POWER SUPPLY SEPARATE AND APART FROM THE SHUTTLE. THREE 24 V, 180 Ah UNITS REQ'D FOR THE 1st STAGE AND SIX 24 V, 10 Ah UNITS REQUIRED FOR THE 2nd STAGE |
| • NEED FOR LITHIUM: | WEIGHT |
| • CANDIDATE SYSTEMS: | Ag-Zn NOW, PERHAPS Li-$SOCl_2$ LATER (COULD SAVE 50 kg) |

Figure 5-18

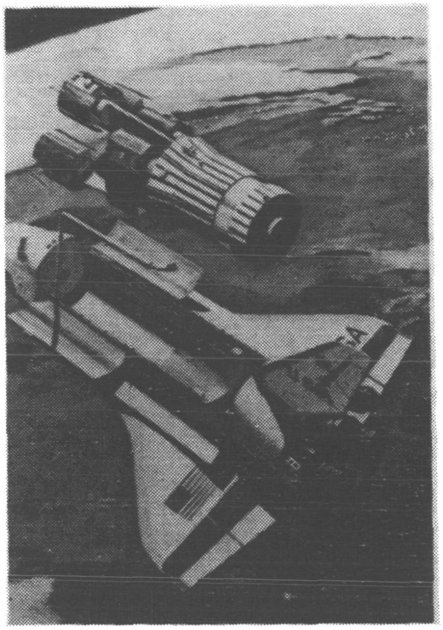
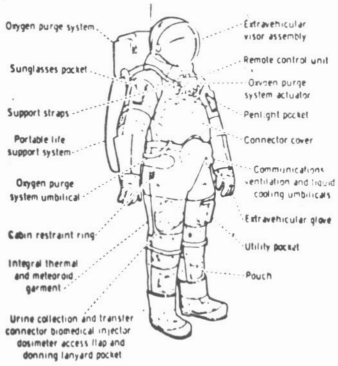


Figure 5-19



BATTERY

17 VOLTS

18 A. H.

Figure B-1.- Extravehicular mobility unit.

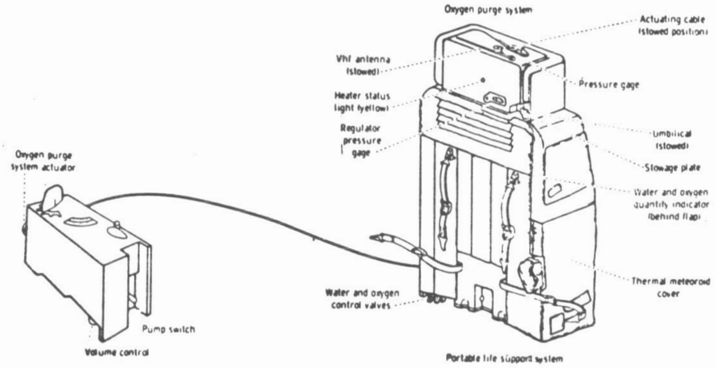


Figure B-2.- Portable life support system.

Figure 5-20

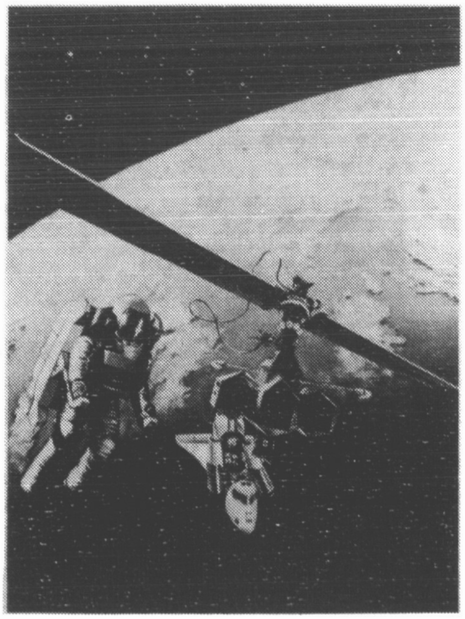


Figure 5-21

## LAUNCH VEHICLE APPLICATIONS

| | |
|---|---|
| • PURPOSE: | RANGE SAFETY AND LOCATION AIDS FOR SOLID ROCKET BOOSTERS (SRB) |
| • DESCRIPTION: | THE SRB IS DESTROYED IN THE EVENT OF A MALFUNCTION. THE SRB IS RETRIEVED UPON LANDING |
| • FUNCTION OF BATTERIES: | BATTERY TRIGGERS AN ARMING DEVICE TO DESTROY THE SRB IN THE EVENT OF A MALFUNCTION. BATTERIES POWER TRANSMITTER AND ALSO FLASHING LIGHTS ON SRB AFTER LANDING.REQUIREMENTS CALL FOR 28±4 volt UNIT, WITH CAPACITY OF 18 A. H. |
| • NEED FOR LITHIUM: | VOLUME |
| • CANDIDATE SYSTEMS: | Li-CF NOW, PERHAPS Li-$SOCl_2$ LATER |

Figure 5-22

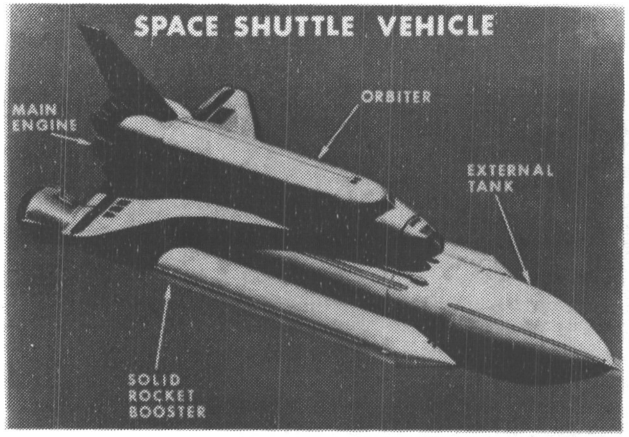


Figure 5-23

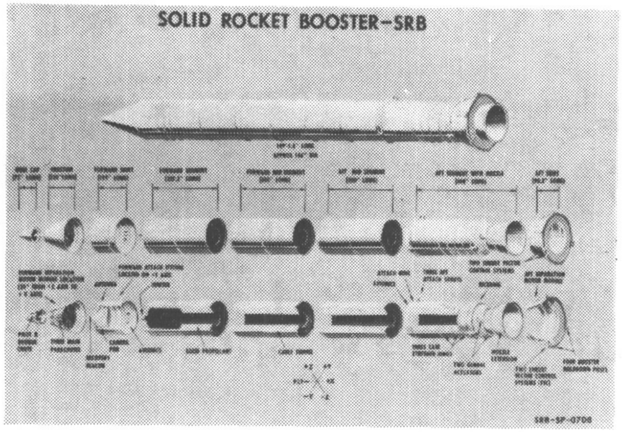


Figure 5-24

TYPES OF RESEARCH FOR WHICH BALLOONS ARE USED

- COSMIC RAY STUDIES
- GAMMA RAY AND X-RAY ASTRONOMY
- OPTICAL AND ULTRAVIOLET ASTRONOMY
- INFRARED ASTRONOMY
- ATMOSPHERIC SCIENCES
- MAGNETOSPHERICS
- MICROMETEORITE PARTICLES

Figure 5-25

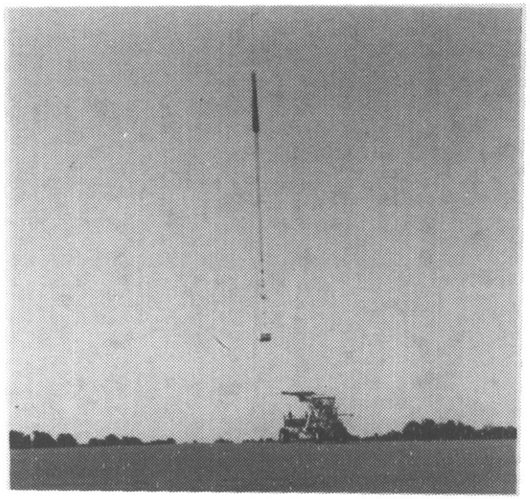


Figure 5-26

## FUNCTIONS OF BATTERY POWER SUPPLIES ON BALLOONS

- POINTING
- TELEMETRY
- COMMAND
- CONTROL
- INSTRUMENTS

## TYPICAL SIZE OF BALLOON BATTERIES

- VOLTAGE 28 VOLTS
- CAPACITY 30 A. H.

Figure 5-27

## CONCLUDING REMARKS

- ATTRACTIVE FEATURES
  - a) Lightweight
  - b) Compact
  - c) Long Life
  - d) Wide Temperature Range
- BENEFITS TO NASA
  - a) Increase Payload Weight
  - b) Increase Cost Effectiveness of Missions
- NUMEROUS APPLICATIONS AS DESCRIBED HEREIN
- STRONG INCENTIVE TO RESOLVE REMAINING PROBLEM AREAS AND QUALIFY Li BATTERIES FOR FLIGHT

Figure 5-28

# U.S. NAVY LITHIUM CELL APPLICATIONS

F. Bowers
Naval Surface Weapons Center

I've been asked initially to tell you a little bit about a group that we have to discuss lithium battery problems within the DOD and government. Several years ago, the Joint Logistics Chiefs (the Army, the Navy, and the Air Force) formed a panel on batteries and fuel cells, the purpose of which was to streamline development of batteries within the DOD and to avoid duplication of effort.

Now, about eighteen months ago, with all the problems that were coming up in the use of lithium batteries, it was decided that it would be a good idea to form, within that charter from the Joint Logistics Chiefs, a group of people who would meet on a quarterly basis to discuss problems associated with the use of lithium batteries.

We meet regularly. We have representatives from all of the services, plus the FAA, DOT, and NASA, and it is a group where we can kind of let down our hair and discuss mutual problems. The chairmanship of this group resides with the Army, and there is a secretary who will be alternated between the Air Force and the Navy.

My purpose in being here today is to discuss Navy applications, but I've expanded this somewhat to also describe the approach that the Navy is taking in the control of the introduction of lithium batteries into the fleet.

(Figure 5-29)

These next couple of slides are going to merely list the applications that we actually have in the fleet at the present time and those that are under development, and the purpose is to show you not only the applications but to give you some idea of where they are being used, and also to give you some idea of the discharge rate.

I purposely left off the designation of some of these things, largely for security reasons. But to start off, we have two radios. The first one here I'd like to describe a little bit. This is a radio that is used on board life rafts on surface vessels, and it has two "D" size cells.

Now, one would not think that two "D" size cells could be any particular problem, but this radio was designed with two separate cells so that you could use a Leconche cell with a lithium cell or a mercury cell with a Lithium cell; you could get everything all screwed up. So as a net result, we are now taking and putting those two "D" cells into a tube.

This second is actually two radios that are both powered by the Army BA-5590. Both of these are what we'd call moderate discharge rates, and to avoid any conflict, what I've done at the bottom of those figures is, I've defined what we consider low, moderate, high, and very high rates. These are lithium sulfur dioxide.

Next we have a display terminal that is really a device that assists with respect to maps and overlays and that sort of thing. In other words, the Navy has to find its way sometimes, and this is a device that helps it do that.

Then we have a laser that is under development. Actually we have two, but I've just listed one because they're very similar.

This is a land mine using lithium vanadium pentoxide. We have a transponder here that has 50 "D" cells in series, and one of the things that we ran into here was that the people that were developing this thought it might be a good idea to get this transponder back every once in a while and test out the battery and then replace individual cells.

This is a mobile target that is an underwater device that is used in training sailors in the use of torpedoes. On this one, we have had a couple of safety problems involved with lithium sulfur dioxide.

(Figure 5-30)

Here we've listed three sonobuoys, and actually in this, there is a group of some five buoys, at least some of which, I believe, are now in the fleet. This gives some idea of the size of cells that are being used and some idea of the rates of discharge.

This jammer is an interesting device. That is a group of series-connected "D" size cells that is being discharged at the 40 minute rate. When we came into contact with that, the people that were developing this had thought that if they only took half of the energy out of it (in other words, discharge it only for 20 minutes), that it would make it safer.

They do have cooling available, and this is one thing that the Navy has pretty much as a regular thing. We can cool these batteries so that it does permit us to use lithium batteries in ways that might be unsafe or impractical for other people who are using them.

In the jammer, it is intended to use cooling, and this is a device that won't be recovered.

Then we have a computer, and this is a computer for divers that has two small "AA" cells.

This is a retrofit for a mine that is now in the fleet, and we're developing a lithium battery for that, and it will permit us to upgrade that mine.

Finally, these two are lithium thionyl chloride, and just give some idea of the direction that we may be going. Here we're looking at propulsion, as far as lithium thionyl chloride is concerned.

Now, with the wide disparity of uses of lithium batteries within the Navy and the possibility of things happening that we would not like to happen, the Navy has started to control the use of such batteries within the fleet, and we have in the final stages of preparation a Navy Instruction that contains guidelines, and I'd just like to briefly describe what we're doing.

(Figure 5-31)

What we first do, and we'd like to see this done as early as possible in the development phase, is to submit a description of the device and the battery through official channels to NAVSEA Systems Command, the safety office there.

The Navy, in developing batteries, is different than the other services. The responsibility for the battery and its safety resides with a project manager of the item that is being developed. So therefore, any description that is submitted has to be submitted through the proper channels.

The next thing is: the battery and the intended use are evaluated then for safety to see whether there are any problems, and the evaluator submits a formal report to the user. In this report, we attempt to warn the user (if there is any need for warning) of the possible safety hazards and also to try and keep the user abreast of the latest safety guidelines.

(Figure 5-32)

Now, the next two figures just give some of the guidelines that we are using. We have developed a system of color coding for use in the Navy, so that the battery will be marked to indicate principally the cathode material that is used. Not all lithium batteries are the same, as we know.

Also, we are using the consolidated hazardous marking system symbol that we have to put on all chemicals in the Navy.

We are requiring at the present time that cells be hermetically sealed; this is a must. We are also requiring that cells contain vents, and we prefer that the vents be placed in the bottom of the cells, the reason being that if they're placed on the side, you run a possibility of the diameter of the cell increasing if a cell vents, and then you run the possibility of jamming in the tube, as we use tubes to contain some cells in some designs.

We like to see fuses and diodes. We recognize that in not all cases are either one practical. We prefer to see them. Where we're using individual cells or a few cells in a tube, for example, we prefer to see cells that are not the same size as the more conventional cells. What I'm thinking of here is the interchangeability of flashlight cells with lithium cells in some applications.

Now, one of the age-old things that we run into in development of batteries is: every engineer likes to get his hands on cells and he knows more about making a battery than the battery manufacturer does. This is axiomatic, and we all recognize that battery manufacturers are somewhat incompetent, but we prefer, in the Navy, to allow the battery manufacturers to make the batteries. We think that just maybe they might be able to do a better job than some of us can do in the laboratory.

(Figure 5-33)

The next figure continues, and in the event of any safety incidents, we have channels in the Navy, as they do throughout all government, for notification of any safety incidents that occur.

We want to use batteries to be discharged immediately, and in some cases we are going to deep-six batteries in the Navy, particularly if we're off the continental shelves where they cannot be recovered. In some cases, with a one-shot device, we lose the device anyhow, but we don't plan to have any large-scale dumping of batteries and that sort of thing.

On land, the batteries will be gathered together at a central location for discarding as hazardous chemicals.

The next is kind of a general catch-all guideline that just says be sensible in the handling of lithium cells.

Finally, our batteries in the Navy will be transported by the latest DOT guidelines.

## DISCUSSION

BENNETT: I was wondering, in all of these applications that you have been using them in, whether you found any problems with cell mismatching either in series or parallel configurations, especially at end-of-life conditions, or are the manufacturing and quality control standards close enough that that really isn't a problem?

We have not used lithium batteries widely in the Navy, but we do have some in the fleet, and so far as I know, the mismatch has not been a problem.

MIKOWSKI: You made a comment about the batteries having hermetically sealed units, yet they have vents. That sounds a little contradictory. Would you care to explain that a little bit more, please?

BOWERS: All right. In the early stages of development of lithium batteries, the seal was variable. The next step was to go to a hermetic seal, which was welding the cover in place.

Now, under various uses and primarily when the batteries are discharged at high rates, the internal pressure builds up to a point where, if you did not provide some means of opening the cell, it would explode. So manufacturers in general have a vent that is usually a coined part of the metal case that is weakened by coining and opens up, and once the vent opens, it remains open permanently.

Now, when a cell opens up, we consider that that cell has failed, and we in the Navy have some particular problems with venting. If at the time of venting in the use of sulfur dioxide cells, we know that we have methane gas, we have cyanide, and we have sulfur dioxide, and it doesn't take very much sulfur dioxide in the air to cause one to cough and sneeze. So in confined spaces like submarines, the venting of lithium sulfur dioxide and lithium thionyl chloride, where venting would produce sulfurous acid and hydrochloric acid, can be a problem. It avoids the cell exploding, however.

PALANDATI: I'm curious. You mention that the batteries have to be evaluated by a group. Just what sort of evaluation are you talking about now? Do you also include hazards tests in your evaluation of a battery? In other words, if I were to suddenly come up and say, "I've got a 100 ampere-hour lithium battery, and we would like you to evaluate it," would part of the evaluation require a hazards test?

BOWERS: What the evaluation is at the present time is taking the data that is available from the developer and determining what he has done with respect to investigating the particular application that he has and to determine if he is using this in what has been typically an unsafe way and whether he has incorporated what we consider to be the latest safety devices in the design of his cells and batteries. The safety evaluator does not perform any tests.

PALANDATI: I see. Thank you.

CHODOSH: Mr. Bowers, you mentioned before that you prefer to have the vent on the bottom of the cell. I'd appreciate it if you'd elaborate on that as to what is the specific advantage. I think you mentioned that if you have the vent on the side, there's a possibility of jamming in a tube, and I presume that you mean that with the vent on the bottom of the cell, this eliminates any possibility of jamming.

BOWERS: That, plus the fact that also if you have the vent on the side of the tube, it makes it more difficult if you have to pot the cells in.

CHODOSH: Well, that's a function of the specific design, isn't it?

BOWERS: This is right, and that's why I said we preferred to see the vents in the bottom rather than the side.

CHODOSH: Okay, but the words "prefer" and "mandatory": are they synonymous?

BOWERS: Obviously not. If you look them up in the dictionary, you'll find that they are different.

CHODOSH: Thank you very much. I have one other question. You mentioned a list of applications and, I think except for the last two the ones that preceded those were all $SO_2$ applications.

BOWERS: Not all of them. One was—

CHODOSH: One was a vanadium pentoxide.

BOWERS: Right.

CHODOSH: I stand corrected. And the period of time that the $SO_2$ cells have been used in a hermetic configuration is approximately what time period, would you say?

BOWERS: We've had lithium cells in the fleet for roughly two years.

CHODOSH: Two years hermetic, and your experience has been satisfactory, I presume?

BOWERS: Not in all cases. In most cases.

CHODOSH: Thank you.

MARINCIC: I'd like to make a comment first-a very brief one-on the last paper. Somebody wants to fly a plane on Mars, and he needs 550 watt-hours per pound out of the battery, if I understand it correctly. Well, we have spent a lot of money up until 1972 to make $SO_2$ cells with 115 watt-hours per pound. Then we spent about three years and several millions of dollars to get to about 185 to 200 with lithium thionyl chloride. You hope, with $200,000 per year, to double that so that NASA can fly the plane? You really are not coming anywhere near the money needed to finance that kind of undertaking, because 550 watt-hours per pound probably will not ever be reached.

The next comment that I want to make is that I like your guideline number 8. You don't allow anybody to drill holes in the cells. Why don't you sometimes talk to the Army? You know, they are the first ones who started drilling holes in cells.

And then a question about the vent. Most of us will probably remember the case (we don't want to mention companies here) when somebody made a "D" size cell with a vent, a very good one. Then they put 25 of those into a tube and potted them in epoxy to make them hermetic.

After that, they were not vented anymore, and they blew up. So you'll have to make up your mind whether you want the vent or not. And the question is: the question of vent has been imposed upon the battery manufacturers because you started off with pressurized cells. Have you ever thought of having a battery that just doesn't blow up so it doesn't need a vent? That means that you are eliminating those batteries out of consideration because you insist on venting whether it's needed or not.

BOWERS: I would suggest that you missed one of the guidelines, and that was number 5, which says: "Let the lithium battery manufacturer make the batteries."

MARINCIC: I think that's a good idea.

TAYLOR: For the benefit of the listeners, of course, they may have been confused when Nikola said 115. He meant to say 150 for lithium $SO_2$ in terms of energy density, but anyway, that's by the way.

What I want to do is take up two points. One was this question of potting cells, high rate discharges, and venting. I suggest that yes, you really do leave the construction of the batteries to the manufacturer, because when you discharge any cell at a high rate, you're obviously going to generate a high temperature, and I don't care whether it's lithium $SO_2$ or any other system, it will eventually blow up. So I suggest, in fact, since you're dealing with high power batteries, that you put in methods for cooling the system during high rate discharges. It's a sensible and essential precaution for any system.

The second point I want to make is that I couldn't help hearing the statement, as I think probably everybody else did, about cyanide. There has been a report by Versar in two stages. The second part of that report did clearly state that there is no cyanide generated in the advanced lithium $SO_2$ cells, which are nigh pretty much routinely produced by the Mallory Company, for example.

BOWERS: Unfortunately, we don't know whether we are getting the advanced or the old stuff that you guys put out.

## LITHIUM BATTERIES FOR NAVY APPLICATIONS

| DEVICE | NUMBER & SIZE OF CELLS | DISCHARGE RATE* | IN-WATER |
|---|---|---|---|
| RADIO | 2 "D" | M | NO |
| RADIO | BA 5590 | M | NO |
| DISPLAY TERMINAL | 3 "D" | M | NO |
| LASER | 12 "C" | H | NO |
| MINE | 2 ½ "A" | L | NO |
| TRANSPONDER | 50 "D" | L | YES |
| TARGET | 13 SMALL "D" | H | YES |

*L 24 HOUR, M 10-24 HOUR, H 4-10 HOUR, VH - < 4 HOUR

Figure 5-29

## PROPOSED NAVY SAFETY PROCEDURE

1 – SUBMIT DESCRIPTION OF DEVICE AND BATTERY THROUGH OFFICIAL CHANNELS TO NAVSEA SYSTEMS COMMAND SAFETY OFFICE

2 – BATTERY AND INTENDED USE ARE EVALUATED FOR SAFETY

3 – EVALUATOR SUBMITS A FORMAL REPORT TO THE USER

Figure 5-31

## LITHIUM BATTERIS FOR NAVY APPLICATIONS (CONT.)

| DEVICE | NUMBER & SIZE OF CELLS | DISCHARGE RATE* | IN WATER |
|---|---|---|---|
| BUOY | 6 "C" | H | YES |
| BUOY | 10 "C" | H | YES |
| BUOYS | "C", "D" | H M | YES |
| JAMMER | 27 "D" | VH | YES |
| COMPUTOR | 2 "AA" | M | YES |
| MINE RETROFIT | 75 "DD" | L | YES |
| HEDB | 1000 Ah | H L | YES |
| PROPULSION | >100 Ah | VH | YES |

*L >24 HOUR, M 10-24 HOUR, H 4-10 HOUR, VH 4 HOUR

Figure 5-30

## PROPOSED NAVY GUIDELINES

1 - BATTERIES MUST BE MARKED TO GIVE
    A. ELECTROCHEMICAL SYSTEM PLUS COLOR CODING
    B. WARNING AGAINST MISUSE
    C. CONSOLIDATED HAZARDOUS MARKING SYMBOL

2 CELLS MUST BE
    A. HERMETRICALLY SEALED
    B. CONTAIN VENTS (PREFERRABLY IN THE BOTTOM)

3 - DESIRABLE
    A. APPROPRIATE FUZES
    B. DIODES

4 WHERE EVER POSSIBLE USE CELLS THAT ARE NOT INTERCHANGEABLE WITH CELLS USING OTHER ELECTROCHEMICAL SYSTEMS.

5 LET LITHIUM BATTERY MANUFACTURERS MAKE THE BATTERIES.

Figure 5-32

# PROPOSED NAVY GUIDELINES (CONT.)

6 – NOTIFY APPROPRIATE AUTHORITIES WHEN SAFETY INCIDENTS HAVE BEEN EXPERIENCED.

7 – DISCARD DISCHARGED BATTERIES IMMEDIATELY AND BY PROPER PROCEDURES. DON'T LET DISCHARGED BATTERIES ACCUMULATE.

8 – WHETHER FRESH OR DISCHARGED, LITHIUM BATTERIES ARE NOT TO BE PIERCED, CRUSHED, BURNED, INTENTIONALLY DROPPED, CANNIBALIZED, DISMANTLED, MODIFIED, OR OTHERWISE CARELESSLY HANDLED NOR SHALL THEY BE SHORT CIRCUITED, CHARGED OR USED IN ANY WAY OTHER THAN THEIR INTENDED USE.

9 – TRANSPORT IN COMPLIANCE WITH APPROPRIATE DOT REGULATIONS.

Figure 5-33

# SHUTTLE PAYLOAD REQUIREMENTS AND IMPLEMENTATION PROCEDURE

J. Scheller
NASA Headquarters

A couple of explanatory notes here to start with. When we say "shuttle," as the first speaker explained, the shuttle is the basic workhorse of our space transportation system launch vehicle, our manned, reusable system. There are other elements of the space transportation system besides the shuttle, namely the interim upper stage and also the Spacelab.

The other point I wanted to make introductory-wise was that this presentation will cover the safety requirements to fly on the space transportation system.

(Figure 5-34)

This is the payload safety-related documentation. The top item is a Headquarters document. That's the parent document that contains mandatory requirements. We'll have more specifics on this document in the next couple of vugraphs, and we also have some handouts of this available for you if you'd like it. They're right up here, and you can get those at your convenience, whenever Lee thinks an appropriate time is. There are 150 copies there, so I think that'll be enough to go around.

This Headquarters document is officially issued; it's an official document. A revision is expected to be made early next year, at which time it will be converted to a NASA handbook and assigned a number. I don't believe there are any significant changes forthcoming in this revision from a battery standpoint.

The second document is a Kennedy Space Center document. This also contains requirements; however, these are just a few additional requirements that are unique to ground service equipment, ground support equipment, and ground operations.

The third item is a JSC document issued number 13830. It has a JSC number and it's issued by JSC, but it's a jointly prepared document by JSC and Kennedy Space Center. It delineates the respective roles of these two centers in implementing the requirements of the first two documents. This is done in a common coordinated fashion so we have a consolidated approach to the assessment review function, which is the role that NASA takes relative to the safety question, and this document delineates the way in which you get approval for flight.

JSC plays the role of the flight operator: they look at the flight hardware design and flight operations. Kennedy Space Center looks at the ground support equipment design and ground operations. This document is not released yet. It should be released soon. We'll talk, a little bit further on the next couple of charts, with respect to these implementation procedures.

The last document is a guidelines handbook. It's issued out of JSC. It was put together by JSC with support from the rest of the government and industry both, and it is not a requirements document. These are optional guidelines; they're not mandatory. They delineate practice in the safety realm from prior space missions.

The battery part of this document was recently revised in response to comments and critiques that were made out of Lee Holcomb's group, especially, and a lot of you folks, I'm sure, contributed to the information that's incorporated in this revision. I'll have a chart on this revision to the battery section later on.

We did add specific coverage on lithium batteries and some special design considerations. It was released in September. I had hoped to have copies available to hand out; I'm sorry, I don't have them now. They're in the mail and should be arriving down in Washington today, and if I can arrange it, I'll run back down and bring them out here for you later this afternoon before you break up. If they don't arrive in today's mail, you can order them as shown below.

(Figure 5-35)

This delineates who does what. It's similar to the Navy paper that was just presented in a lot of respects. The role that we take at NASA is to put the burden, responsibility-wise, on the payload organization. That's the spacecraft supplier and you know, of course, with the batteries as part of his cognizance.

The burden of assuring safety of the payload is placed on the payload organization, and that organization has to verify to NASA, to the STS operator, that they've complied with the requirements in the document we talked about earlier.

In the role that NASA plays as the STS operators, we obviously interface with the payload organization and perform the review that's noted, evaluate the data that's generated, and also look at interactions among mixed payloads on a given mission.

(Figure 5-36)

This document shows the mandatory requirements. There are 26 of them, covering things such as the general guideline that no single point failure shall cause a hazard. We also have specific battery-related paragraphs on structural design, pressure vessel design, electrical system design, and the release of hazardous or corrosive materials.

I won't read the entire chart to you, but we are available to assist you in your interpretation of these requirements, and interpretation, you know, is necessary from time to time. We talk a little bit about waivers there, under Paragraph 5.0.

The guts of the implementation process, from the assessment review standpoint, come under Paragraph 5.2, which talks to systems safety, where we have, you know, the analysis reviews and compliance data submittals.

I would just pause momentarily on the bottom bullet, which is "Safety Verification Methods." These require NASA concurrence, so when you show that my battery, my device, is indeed safe and meets your requirements, we require that you provide verification of how you do it. In many cases this can be done analytically or based upon prior experience. In other cases which are newer technology-wise, we'll want to see some test data. I just would touch on that point. I think the gentleman from the Navy also has a similar point.

(Figure 5-37)

Now, this chart talks to the implementation procedure; how you get your safety approval. This is done through a series of formal meetings between us and the payload organization. There are as many as four of these review meetings which are spaced out throughout the development program of the payload, as the center of the chart talks to.

The implementation procedure will be available soon. That was the third document on the first chart, the earlier chart we were talking about. That has data requirements, formats, and more specifics in it. From the safety review, these formal review meetings do involve, you know, formal minutes, agreements, action items, open items, and payload hazard reports.

(Figure 5-38)

As an example, this chart talks to one of our earlier phase safety reviews. This is the phase zero safety review. We look for the data to be submitted in advance of the meeting, the payload description as the gentleman from the Navy showed that they're looking for; then the next two items talk against note 2. These are the payload. Basically, we've mechanized or procedurized, for standardization purposes, the forms that are used for the payload hazard analysis, and those forms are attachments to the implementation procedures document.

The next bullet talks to the mode of working the safety analysis, and there is the reference to the other document on the earlier chart which talks to hazard groups. That document is available. That is the guidelines handbook.

I won't read the rest of the chart. Some of it repeats what we had on the previous chart.

(Figure 5-39)

This is a chart that Bob Bragg at JSC (Johnson Space Center in Houston) prepared for me to display. I won't attempt to talk to it. This reflects the revision to the battery section of the payload safety guidelines handbook, and you can see that it does pick up on lithium batteries, which we had neglected in the original issue of the document, and it's regrouped, reformatted; it's easier to read, and has added some specific design considerations, many of which you'll recognize.

## DISCUSSION

MOORE: I have one question and two comments I want to make. In the first place, John, I'd like to know what your organizational relationship to Bobby Miller is.

SCHELLER: We're on the same team. I'm in the office which reports directly to the Associate Administrator for Space Transportation Systems, John Yardley, in Washington. It's NASA Headquarters. Bobby Miller is our lead safety man at JSC, and at Kennedy Space Center it's Jim Swet in the implementation of these.

We work very closely with Bobby, and as a matter of fact, I'm up here at Bobby's request, to cover this session for him.

MOORE: I had two comments which I think are important. One of them is that you said no single point failures will be tolerated for the shuttle that create hazardous conditions. That requirement, it's that no combination of two failures may create a hazardous condition, and this has a big impact on the payload community.

SCHELLER: Whether it's one or two?

MOORE: The requirement for the shuttle is that no combination of two failures or human errors may create a hazard. It has to be more than two failures away from a catastrophic condition.

SCHELLER: That's a good question. The document does talk to this, and I'll try to clarify that. You're talking to the catastrophic failure which would wipe out the whole mission: you know, we'd lose the crew, lose the orbiter, not be able to get back down—something of that mode. For failures which would be of that realm, the catastrophic realm, yes, that's correct. We require that you be able to survive two failures, two malfunctions or two procedural errors in that case. That's in the area of, like, upper-stage or kick-stage motors firing in the payload bay, which would blow the back end off the shuttle.

Off hand, I don't think that would apply to the battery realm. There we do require, you know, that it be able to survive a single failure without creating a hazard. That's a good question.

MOORE: I think it applies to the batteries because batteries have a potential of exploding or, if they're vented, they have a potential of venting corrosive fluids within the payload bay. So there's a lot of questions about whether those are singles or doubles.

SCHELLER: I see. That's quite a pivotal point for battery designers. Yes. Well, have you talked to Bobby Miller about that?

MOORE: Sure.

SCHELLER: What does he say?

MOORE: Oh, I've just talked in general. I'm still trying to find out what the requirements are.

SCHELLER: Well, I guess if it could blow a hole in the side of the shuttle and prevent reentry, it would fall in the catastrophic realm, so if it's a big boom or a little boom, that's judgmental. If it's a big boom, yes, you would have to be able to survive two failures.

MOORE: I'm bringing this up because I think that everyone in this group has to be aware of that.

SCHELLER: Yes.

MOORE: I had one other comment I wanted to make that I think has to be clarified. Department of Defense payloads are not reviewed directly by NASA; they're reviewed by a safety review team that's Department of Defense, who then certifies to NASA.

SCHELLER: Yes?

MOORE: A lot of people here are going to be DOD if they have the impression they're going to be reviewed directly by NASA. I just thought it should be clarified.

SCHELLER: Yes, that's correct. DOD puts the NASA technical payload requirements, this document, on their payload contractors. This document is currently an attachment to SAMSO Regulation 127-4, and it's being incorporated into a new mil standard—Mil Standard 1575, which DOD is going to put on their payload contractors and which will incorporate these very same requirements.

We have delegated responsibility and authority to DOD to do a self-certification of their payloads, that's correct, but these same requirements do apply.

Now, one possible elaboration on that point: DOD can, at their option add their own requirements as long as they're of a more stringent polarity. So the general proviso is that these documents do get put on verbatim on DOD payload contractors, as well as any other mil standards DOD wants to put on their payload contractors. If there's any difference between the two, the more stringent applies.

That was a good question. Any other questions?

BENNETT: Again, pertaining to the single point failure mode: has there been any final decision as to whether there will be a need for single cell protection in series strings to prevent the opening of that string in case of a cell vent and dry-out where that could be a case where you would have a mission failure if that's your primary power source?

SCHELLER: Chuck, I'm sorry, but I'm going to have to pass on that technical question. Lee, do you have an answer?

HOLCOMB: Well, I think, in the discussion we've had earlier in this regard, the section of the safety guidelines that are associated with diode protection and fusing are optional. They are just that: they are guidelines, but they are not mandatory. The mandatory document doesn't specify that directly.

BENNETT: Thank you.

SCHELLER: But if you're acquainted with Bob Bragg, Bob can clarify that for you. I'd suggest that this "Revised Guidelines on Batteries" may talk to it further, too.

LACKNER: You mentioned in one of your requirements that you require an absorbent material in the head space?

SCHELLER: Well, that, sir, is not a requirement. That's a guideline; it's a suggestion. It's one way of resolving that hazard potential.

LACKNER: Do you know anyone who's worked around trying to resolve that particular guideline?

SCHELLER: You mean incorporated that sort of foam in the ullage head there?

LACKNER: Right.

SCHELLER: I don't know. You see, I'm not involved in the technical part of it. I'm just trying to talk, you know, broad requirements, the general requirements in our policy approach towards the safety. I can't answer your question, in short.

LACKNER: While I think it's very desirable, I'm just sort of wondering if it's technically feasible.

HOLCOMB: The LDEF battery and also the SRB battery pack, I believe both of those, which are two ongoing programs, do not include that provision in the battery design. However, I believe there are people working on trying to develop that.

SCHELLER: I'm not trying to avoid your question. Thank you very much, Lee. Does that satisfy the gentleman's question?

LACKNER: Not really.

SCHELLER: Well, I'd like to refer you to Bob Bragg or Barry Trout at JSC, and if you want to copy this, Bob Bragg's extension—the last four digits—are 6491. It's Bob Bragg, and the area code and the three-digit prefix to that extension are (713) 483. Please do call Bob. I'm sure he can clarify it further.

PAYLOAD SAFETY DOCUMENTS

- • NASA HQ SP&R - "SAFETY POLICY AND REQUIREMENTS FOR PAYLOADS USING THE SPACE TRANSPORTATION SYSTEM (STS)," DATED JUNE 1976 (NHB NUMBER TBD).
- KSC K-STSM-14.1 - "LAUNCH SITE ACCOMMODATIONS HANDBOOK FOR STS PAYLOADS," DATED MARCH 14, 1978.
- JSC 13830 - "IMPLEMENTATION PROCEDURE FOR STS PAYLOADS SYSTEM SAFETY REQUIREMENTS" (JOINT JSC-KSC DOCUMENT) (NOT YET RELEASED).
- JSC 11123 - "STS PAYLOAD SAFETY GUIDELINES HANDBOOK," DATED JULY 1976.
  •(BATTERIES SECTION REVISED SEPTEMBER 1978.)

REQUEST DOCUMENTS FROM

DOCUMENTATION MANAGEMENT/JM 61
L. B. JOHNSON SPACE CENTER
NASA
HOUSTON, TEXAS 77058

• HANDOUT AT WORKSHOP.

Figure 5-34

SP&R DOCUMENT

- INTENT - TO PROVIDE THE OVERALL STS SAFETY POLICIES AND REQUIREMENTS
- RESPONSIBILITIES (PARAGRAPH 3.0)
  - PAYLOAD ORGANIZATION
    - ASSURES SAFETY OF ITS PAYLOAD
    - VERIFIES COMPLIANCE WITH SP&R TECHNICAL REQUIREMENTS
  - STS OPERATOR
    - INTERFACES WITH PAYLOAD ORGANIZATION
    - REVIEWS PAYLOAD FOR ADEQUATE SAFETY IMPLEMENTATION
      - EVALUATES SAFETY DATA GENERATED BY PAYLOAD ORGANIZATION
      - PROVIDES CONCURRENCE/APPROVAL OR OTHER DISPOSITION TO THE PAYLOAD ORGANIZATION'S SAFETY ACTIVITIES
    - ASSURES INTERACTION AMONG MIXED PAYLOADS AND BETWEEN PAYLOADS AND STS DOES NOT CREATE HAZARDS

Figure 5-35

SP&R DOCUMENT (CONTINUED)

- TECHNICAL REQUIREMENTS PARAGRAPH 5.1)
  - 26 REQUIREMENTS
  - INTERPRETED AND IMPLEMENTED ON A CASE-BY-CASE BASIS.
  - STS OPERATOR ASSISTANCE IN INTERPRETATION AND IMPLEMENTATION IS THROUGH JSC/SPIDPO AND KSC/SAFETY.
  - JSC POINT OF CONTACT FOR SAFETY IS MR. B. MILLER/NS2 713/483-2901.
  - KSC POINT OF CONTACT FOR SAFETY IS MR. J. SWEAT/SF-SOO 305/867-4317.
- WAIVER REQUESTS (PARAGRAPH 5.0)
  - APPROPRIATE ONLY IF TECHNICAL REQUIREMENT CANNOT BE MET AS IT APPLIES TO A SPECIFIC HAZARD.
  - TO BE SUBMITTED AS SOON AS NEED IS IDENTIFIED.
  - WAIVER REQUEST FORM IS IN THE IMPLEMENTATION PROCEDURE.
- SYSTEM SAFETY REQUIREMENTS (PARAGRAPH 5.2)
  - DEFINES BASELINE POLICY AND REQUIREMENTS FOR IMPLEMENTATION TASK.
    - SAFETY ANALYSIS (PARAGRAPH 5.2.1)
    - SAFETY ASSESSMENT REVIEWS (PARAGRAPH 5.2.4)
    - SAFETY COMPLIANCE DATA (PARAGRAPH 5.2.5)
  - SAFETY VERIFICATION METHODS REQUIRE NASA CONCURRENCE.

Figure 5-36

SAFETY ASSESSMENT REVIEWS (PHASE REVIEWS)

- FORMAL MEETINGS WITH THE PAYLOAD ORGANIZATION
- DEPTH AND NUMBER OF REVIEWS DETERMINED BY PAYLOAD HAZARD POTENTIAL
- SCHEDULE FOR REVIEWS
  - ESTABLISHED BY PAYLOAD ORGANIZATION AND COORDINATED WITH STS OPERATOR
  - FOR PLANNING PURPOSES
    - PHASE 0 - CONCEPTUAL PHASE OF DEVELOPMENT
    - PHASE I - PRELIMINARY DESIGN REVIEW STAGE
    - PHASE II - CRITICAL DESIGN REVIEW STAGE
    - PHASE III - PAYLOAD DELIVERY
- IMPLEMENTATION PROCEDURE CONTAINS DATA REQUIREMENTS FORMAT AND OBJECTIVES
- SAFETY REVIEW MINUTES ISSUED BY STS OPERATOR
  - AGREEMENTS
  - OPEN ITEMS (NOTE 1)
  - ACTION ITEMS (NOTE 1)
  - PAYLOAD HAZARD REPORTS

NOTE 1 - WILL BE TRACKED BY STS OPERATOR AND WILL REQUIRE FORMAL CLOSEOUTS

Figure 5-37

PHASE 0 SAFETY REVIEW

- DATA REQUIRED AT MEETING (PRIOR TO MEETING PREFERRED)
  - PAYLOAD DESCRIPTION AND OPERATION
  - PAYLOAD SAFETY MATRIX (NOTE 2)
  - HAZARD LIST (NOTE 2)

- PRELIMINARY SYSTEM-LEVEL SAFETY ANALYSIS PERFORMED - IDENTIFIES
  - HAZARD GROUPS INHERENT WITHIN PAYLOAD SUBSYSTEMS (JSC 11123)
  - THE ASSOCIATED HAZARDS
  - APPLICABLE SP&R TECHNICAL REQUIREMENTS

- SAFETY REVIEW MEETING
  - STS OPERATOR EVALUATES DATA
  - STS OPERATOR AND PAYLOAD ORGANIZATION AGREEMENT ON
    - BASELINE HAZARD IDENTIFICATION
    - APPLICABLE SAFETY REQUIREMENTS
    - SCHEDULE AND NUMBER OF ADDITIONAL SAFETY REVIEWS

- SAFETY REVIEW MINUTES
  - OPEN ITEMS
  - ACTION ITEMS
  - PAYLOAD SAFETY MATRIX
  - HAZARDS LIST

NOTE 2 - PAYLOAD SAFETY MATRIX AND HAZARD LIST SUMMARIZE AND REPORT RESULTS OF PRELIMINARY SYSTEM LEVEL SAFETY ANALYSIS.

Figure 5-38

NASA Lyndon B. Johnson Space Center

Engineering and Development Directorate

| REVISED PAYLOAD SAFETY GUIDELINES | EP5 | |
|---|---|---|
| | B. J. BRAGG | 11/6/78 |

SECTION 3.4.1.2 BATTERIES

MAJOR MODIFICATIONS

- REORGANIZATION
  - CATEGORIZED FAILURE MODES
  - GUIDELINE CONSIDERATIONS LISTED WITH SPECIFIC FAILURE MODE
- SEPARATE LISTING OF PRIMARY AND SECONDARY BATTERIES
- NEW COUPLES WITH POTENTIAL PAYLOAD APPLICATION
  - LITHIUM-ORGANIC ($Li-SO_2$, $Li-CF$)
  - LITHIUM INORGANIC ($Li-SO\,Cl_2$)
  - ZINC-OXYGEN
  - SILVER-HYDROGEN
- ADDITION OF SPECIFIC DESIGN CONSIDERATIONS
  - HERMETICALLY SEALED CELLS
  - ADSORPTIVE/DETONATION SUPPRESSION MATERIAL IN HEADSPACE
  - DIODE PROTECTION AGAINST REVERSAL AND CHARGING
  - THERMAL SWITCHES
  - FUSES/CIRCUIT BREAKERS
  - OPERATING AND HANDLING PROCEDURES

Figure 5-39

# NASA'S LITHIUM CELL TECHNOLOGY PROGRAM

G. Juvinall
Jet Propulsion Labratory

I should mention again that I'm filling in for Harvey Frank in a sense. This is also the contents of a presentation that he gave at the NASA Battery Workshop last summer. I hope today to just very briefly point out the areas in which the various centers are working, and I shall not attempt to go into any detail on the kind of work that they're doing and the experimental details involved.

I would like to go down through Ames Research Center, Goddard Space Flight Center, Johnson Space Center, Lewis Research Center, Marshall Space Flight Center, and the Jet Propulsion Laboratory. Then I'll touch briefly on '79 programs in the areas of safety, thermal, life, and high rate, and these will be peculiar to JPL.

(Figure 5-40)

The Ames Research Center activities in lithium for '78, include the objective of supporting the Galileo mission, and their approach has been, to my understanding, a major emphasis on life testing in lithium sulfure dioxide cells. This presentation is scheduled to be given later by Duane Dugan of ARC.

(Figure 5-41)

The Goddard Space Flight Center objectives have been to develop improved batteries for balloon flight experiment power systems, and I think probably secondarily to identify a low-cost, high-performance battery for use on the get-away program. The approach has been to perform characterization tests on lithium sulfur dioxide cells and to package lithium sulfur dioxide cells in 28 little batteries in the range of 8 to 40 amp-hours. Also, some investigation of a large lithium thionyl chloride cell for possible application to the get-away program.

(Figure 5-42)

The Johnson Space Center activity's objective has been to obtain performance data for selected applications. The approach has been parametric testing of 30 amp-hour cells and of 25 amp-hour cells.

(Figure 5-43)

At Lewis Research Center, the Objective has been to develop an improved secondary battery, and the approach has been investigation of sodium beta alumina anode structures and investigation of soluble sulfur cathodes.

(Figure 5-44)

At Marshall Space Flight Center, they've been interested in supporting shuttle system development, and the approach has included qualification tests on lithium carbon monofluoride batteries and performance of environmental tests on 28 volt, 18 amp-hour units.

(Figure 5-45)

At JPL, the objectives have been twofold: to demonstrate a 300 watt-hour per kilogram primary battery by fiscal year '82, and a 200 watt-hour per kilogram secondary by fiscal '82. The approach there has been to study applications of primary lithium batteries as a first step, and that report is soon to be out; define the shelf life of reserve lithium thionyl chloride cells; evaluate performance and safety of small primary lithium sulfur thionyl chloride cells (these are Altus Corporation cells); and take a look at and establish the feasibility of secondary lithiums.

(Figure 5-46)

Now, these objectives relate specifically not to the JPL work on the idea of a remotely activated lithium battery. This supports the objective of defining the shelf life. Not finding data available for the stability of thionyl chloride over a long term, this was undertaken by Harvey Frank. Also, the objective at JPL is to provide data which will aid in gearing cells to specific applications in the areas which I mentioned previously this morning.

(Figure 5-47)

Now, the approach on the thionyl chloride stability has been the accelerated life tests on samples, namely, examining the stability of the thionyl chloride at elevated temperatures, develop an Arrhenius plot, and extrapolate over a long term (it's quite an extrapolation, but it gives us an idea, certainly) to get an idea of the shelf life.

(Figure 5-48)

This is a summary of some of Harvey's data. The line is formed from an integration analysis of the points marked by the circles. This is up to 50 days' storage. The X's were added later, up to 150 days' storage data, and superimposed on top of the graph.

(Figure 5-49)

From the plot, there's an empirical function, on which I won't go into any great detail, but it enabled him to come up with a very quick prediction of the order of magnitude of shelf life that one might expect.

(Figure 5-50)

He concluded—but as I say, being aware of the degree of extrapolation involved—that we had a handle on a decomposition rate of the thionyl chloride and projected about 12 percent decomposition after ten years. He does not anticipate severe degradation in performance after ten years' storage. The results may well apply also to the active lithium thionyl chloride cells.

(Figure 5-51)

Additional work Harvey's done at JPL has been involved in taking a look at some of the Altus cells. These are simply a quick way of looking at representatives of the kind of data that he's been obtaining. The initial buy on these cells was 200 units, so this is only one slide to give you an idea of the kind of characterization work that he's been doing with it. I don't think it's anything startling, but we are beginning to get a data base on the cells.

(Figure 5-52)

This is a comparison of their high and low range cells at the C/2 rate, and other data has been temperature on the output of the cells, a feel for the temperature capabilities.

(Figure 5-53)

The other aspect of taking a look at the Altus cells has had to do with the safety claims of the vendor, and as I mentioned earlier, this is a vendor who claims to have made significant advances in the safety and performance of lithium cells. So we were concerned with short circuit testing and also forced reversal tests. So far, there's no venting, nor has there been any explosion.

There will be another buy of larger cells in the 20 to 50 amp-hour range, and then we'll be getting some data on those.

(Figure 5-54)

The final part of JPL's activity has been looking into secondary lithium cells, and right now we're looking into the lithium titanium disulfide system primarily.

(Figure 5-55)

This figure gives a little more detail of the exact cells that we're looking at. There are 10 cells involved in the buy; they were supplied by EIC (in the 5 to 6 amp-hour range) and are anticipated to have a cycle life of 100 to 200 cycles, operating voltage about 2.1 volts. Maximum charge rate, C/5; maximum reduced charge rate, C/2.

(Figure 5-56)

The JPL plans for '79 include abuse tests of the larger Altus cells, as I mentioned earlier, in the 20 to 50 amp-hour range on both short circuit and reversal. There will be calorimetric studies where we try to determine the heat rate, evolution rate, of lithium thionyl chloride cells as a function of the discharge rate and make this data available to the packaging people.

(Figure 5-57)

In terms of life, there will be some accelerated storage life tests of the lithium thionyl chloride cells under both light loads and pulse loads, and in the high rate area, looking at new cathode substrates, half cell measurements.

## DISCUSSION

MALACHESKY: I'd just like to make the one comment that we people from Exxon have been making for a couple of years now: don't use lithium perchlorate in a lithium secondary battery. We have shown in papers and other ways that lithium perchlorate in a secondary lithium battery is a definite safety hazard and should not be used even by people in development cells. It's dangerous.

JUVINALL: Thank you.

GROSS: I would recommend that you don't put full faith in the Arrhenius curve to determine life of lithium thionyl chloride cells and that you conduct real time tests.

JUVINALL: I think we all agree with you. I think that was a way of getting a handle on it as a first go at it.

CHODOSH: Are there any extrapolated costs for the Altus cells in larger quantities and are they reasonable for your applications?

JUVINALL: I really don't know the cost figure on it. I do know that the thousand amp-hour unit, which the Naval Ocean Systems Center has been working with, goes now for about $1,000 a cell. That's the only data point I have on it.

BENE: Any particular reason why you didn't mention the effort in lithium cell development at Langley, and number two, have you guys measured the start-up characteristics of the Altus cells?

JUVINALL: To answer your questions in reverse order, the start-up characteristics of the Altus cell have not been checked as such at JPL yet. In regard to your first question, I have really no answer for it. There is no reason it was not mentioned except I simply had no information on it. You probably should ask Harvey about that.

HOLCOMB: We recognize that Jim at Langley has done quite a bit on the LDEF program. It was just an omission.

JUVINALL: Yes.

## ARC ACTIVITIES FY 78

- OBJECTIVE
  - SUPPORT GALILEO MISSION
- APPROACH
  - MAJOR EMPHASIS ON LIFE TESTING OF
  - Li-$SO_2$ CELLS
  - PRESENTATION TO BE GIVEN BY D. DUGAN OF ARC

Figure 5-40

## GSFC ACTIVITIES FY 78

- OBJECTIVES
  - DEVELOP IMPROVED BATTERIES FOR BALLOON FLIGHT EXPERIMENT POWER SYSTEMS
  - IDENTIFY LOW-COST, HIGH-PERFORMANCE BATTERY FOR USE ON GET-AWAY PROGRAM
- APPROACH
  - PERFORM CHARACTERIZATION TESTS ON Li-$SO_2$ CELLS
  - PACKAGE Li-$SO_2$ CELLS IN 28V BATTERIES IN THE RANGE OF 8 - 40 Ah
  - INVESTIGATE LARGE Li-$SOCl_2$ CELLS FOR POSSIBLE APPLICATION TO GET-AWAY PROGRAM

Figure 5-41

## JSC ACTIVITIES FY 78

- OBJECTIVE
  - OBTAIN PERFORMANCE DATA FOR
  - SELECTED APPLICATIONS
- APPROACH
  - PARAMETRIC TESTING OF 30 Ah CELLS
  - PARAMETRIC TESTING OF 25 Ah CELLS

Figure 5-42

## Le RC ACTIVITIES FY 78

- OBJECTIVE
  - IMPROVED Li SECONDARY BATTERY
- APPROACH
  - INVESTIGATION OF Na/$\beta$ ALUMINA ANODE STRUCTURES
  - INVESTIGATION OF SOLUBLE SULFUR CATHODES

Figure 5-43

## MSFC ACTIVITIES FY78

- OBJECTIVE
  - SUPPORT SHUTTLE SYSTEM DEVELOPMENT
- APPROACH
  - COMPLETED QUALIFICATION TESTS OF Li-CF BATTERIES
    - PERFORMANCE AND ENVIRONMENTAL TESTS
    - 28V, 18 Ah BATTERIES

Figure 5-44

## JPL ACTIVITIES FY 78

- OBJECTIVES
  - DEMONSTRATE 300Wh/Kg PRIMARY BATTERY BY FY82
  - DEMONSTRATE 200Wh/Kg SECONDARY BATTERY BY FY82
- APPROACH
  - STUDY APPLICATIONS OF PRIMARY Li BATTERIES (REPORT TO BE PUBLISHED SOON)
  - DEFINE SHELF LIFE OF RESERVE Li-$SOCl_2$ CELLS
  - EVALUATE PERFORMANCE AND SAFETY OF SMALL PRIMARY Li-$SOCl_2$ CELLS (ALTUS CORP.)
  - ESTABLISH FEASIBILITY OF SECONDARY Li CELLS

Figure 5-45

## OBJECTIVES

- Primary Technical Objective—establish stability of $SOCl_2$ over the long term for reserve and active Li-$SOCl_2$ cells
- NASA Applications

a) Planetary probe missions
b) Exploration of Mars
c) Shuttle applications
d) Launch vehicle applications
e) Scientific balloon flights

Figure 5-46

## APPROACH

- Accelerated life tests on samples at elevated temperatures
- Arrhenius plot of ln rate vs $\frac{1}{T}$
- Extrapolate life over long term at ambient temperatures

Figure 5-47

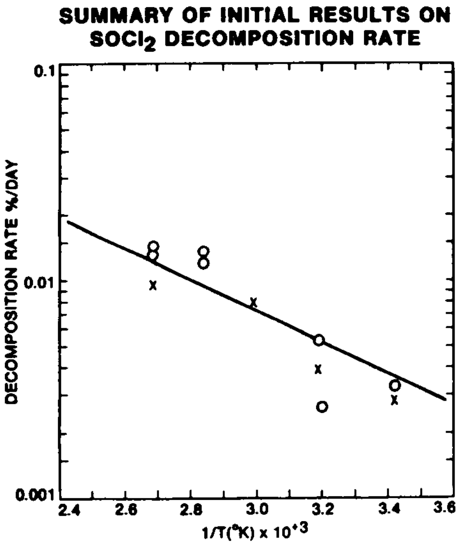


Figure 5-48

## CONCLUSIONS

- Established decomposition rate of $SOCl_2$ as a function of temperature
- Project 12% decomposition after 10 years of storage at ambient temperatures
- Do not anticipate severe degradation in performance of reserve type Li-$SOCl_2$ after 10 years' storage
- Results pertinent to active Li-$SOCl_2$ cells

Figure 5-50

## EMPIRICAL EXPRESSION FOR $SOCl_2$ DECOMPOSITION RATE

$$\ln(\%/\text{DAY}) = -0.12 - 1605.09 \left(\frac{1}{T}\ {}^{\circ}\text{K}\right)$$

%/DAY = % LOSS OF $SOCL_2$ PER DAY

T = ABSOLUTE TEMPERATURE, °K

Figure 5-49

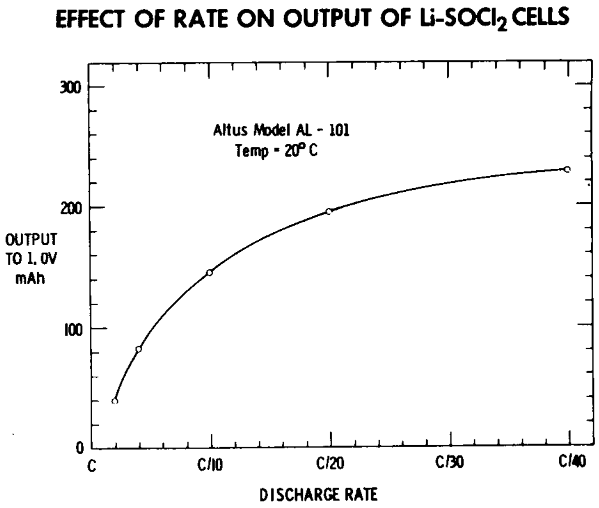


Figure 5-51

## COMPARISON OF HIGH AND LOW RATE Li-SOCl$_2$ CELLS

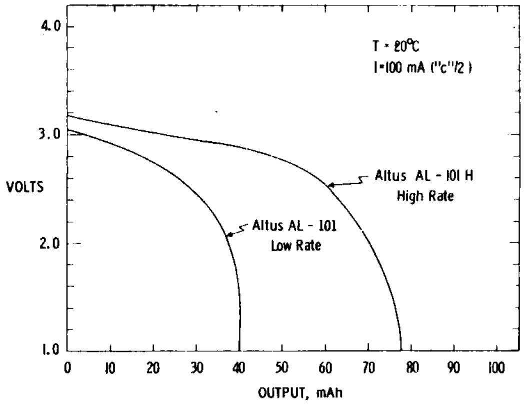


Figure 5-52

## ABUSIVE TESTING OF Li-SOCl$_2$ CELLS

### ALTUS MODEL AL-101

A. SHORT CIRCUIT TEST
- PLACED ON DEAD SHORT
- MAXIMUM CURRENT . . . . . . . . . . . . . . . . . . . . . . 1.25 amp (6.25 "C")
- TEMP RISE. . . . . . . . . . . . . . . . . . . . . . . . . . . 47°F
- NO VENTING AS PER WEIGHT CHECK
- NO EXPLOSION

B. FORCED REVERSAL TEST
- DISCHARGED AT 100 mA ("C"/2) to 0 volts
- REVERSED AT 100 mA ("C"/2) FOR 3.5 hr (350 mAh)
- MAXIMUM REVERSE VOLTAGE . . . . . . . . . . . . . . . . -0.2 volts
- MAXIMUM TEMP. . . . . . . . . . . . . . . . . . . . . . . . 70°F
- NO VENTING AS PER WEIGHT CHECK
- NO EXPLOSION

Figure 5-54

## EFFECT OF TEMPERATURE ON OUTPUT OF Li-SOCl$_2$ CELLS

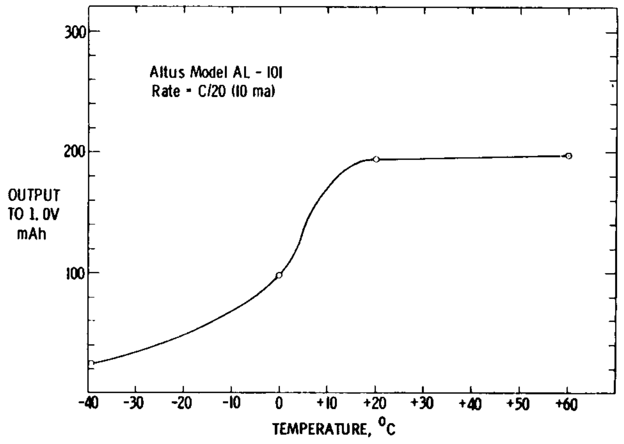


Figure 5-53

## DESCRIPTION OF SECONDARY LITHIUM CELLS

| | |
|---|---|
| • ANODE: | LITHIUM FOIL |
| • CATHODE: | TRANSITION METAL SULFIDE SUCH AS $TiS_2$, $VS_2$, OR $VCrS_2$ |
| • ELECTROLYTE: | LITHIUM SALT SUCH AS $LiAsF_6$, $LiClO_4$, OR $LiAlCl_4$ |
| • SOLVENT: | NON-AQUEOUS SOLVENT SUCH AS PROPYLENE CARBONATE, METHYL ACETATE, TETRAHYDOFURAN, OR DIMETHYL SULFOXIDE |
| • REACTION: | $Li + MS_2 \underset{\text{CHARGE}}{\overset{\text{DISCHARGE}}{\rightleftarrows}} LiMS_2$ |
| • THEORETICAL ENERGY DENSITY: | 900 - 1100 w-hr/kg |

Figure 5-55

## INITIAL DEVELOPMENT OF SECONDARY LITHIUM CELLS

| | |
|---|---|
| • CONTRACTOR | E. I. C., NEWTON, MASS. |
| • NUMBER OF CELLS | 10 cells |
| • CONFIGURATION | SPIRAL WOUND, "D" SIZE |
| • DESCRIPTION | |
| ANODE | Li |
| CATHODE | TiS$_2$ |
| SOLVENT/ELECTROLYTE | PROPRIETARY |
| • DELIVERY DATE | August 1978 |
| • ANTICIPATED CHARACTERISTICS | |
| CAPACITY | 5 - 6 A. H. |
| ENERGY DENSITY | 110 - 175 W-hr/kg |
| CYCLE LIFE | 100 - 200 cycles |
| OPERATING VOLTAGE | 2.1 volts |
| MAXIMUM CHARGE RATE | "C/5" |
| MAXIMUM DISCHARGE RATE | "C/2" |

Figure 5-56

## PROGRAMS AT JPL FY 79

- SAFETY
  - ABUSE TESTS OF ALTUS Li-SOCL$_2$ CELLS (20 TO 50 Ah)
    - SHORT CIRCUIT
    - FORCED REVERSAL
- THERMAL
  - CALORIMETRIC STUDIES
    - MEASURE HEAT EVOLUTION RATE OF Li-SOCl$_2$ CELLS AS FUNCTION
    - OF DISCHARGE RATE
- LIFE
  - ACCELERATED STORAGE LIFE TESTS OF Li-SOCl$_2$ CELLS
    - LIGHT LOADS
    - PULSE LOADS
- HIGH RATE
  - INVESTIGATE NEW CATHODE SUBSTRATES
    - HALF-CELL MEASUREMENTS

Figure 5-57

# U.S. ARMY LITHIUM CELL APPLICATIONS

A. Legath
AECOM

I'm going to talk about the how and the why the Army is applying lithium batteries and the where. Before I get into details, we are committing ourselves quite heavily to the use of lithium batteries in new equipment, equipment that will be going into the field anywhere from FY '80 and thereafter. Our philosophy is to guide our users, the equipment designers, to use battery packs rather than single cells. We prefer 6, 12, and 24 volts, although you'll see some exceptions.

The idea of battery packs gives us the flexibility of going into other electrochemical systems within the same black box configuration. For example, being quite cost-conscious these days, many of our primary batteries have rechargeable counterparts. Thereby, for training, the rechargeable battery can be used and the primary battery used for fielding. This would be a cost-effective measure.

I'll go into details on the battery types that we're considering.

(Figure 5-58)

The first one shown, a 3-volt battery BA-5567, is a single-cell battery. It's to replace a two-cell mercury-type battery which is used in a number of night vision equipments, and some off the new night vision equipments on the drawing boards will also use it. The objective here is to provide a full low-temperature capability.

At the present time, with the mercury battery, with many of these night vision devices used in the Arctic, the user keeps the battery in his pocket someplace under his outer clothing and a cable comes out to his equipment. We don't like that; the soldier doesn't like that.

Typically, this battery is used anywhere from 10 to 50 milliamps. It's a rather small battery. It measures about an inch in diameter and roughly an inch high.

Another comment on the 3-volt 5567. It will probably be competitive costwise with the mercury battery that they're using.

In the 6 volt category, the first two batteries shown, the BA-5100 and the BA-5200, are both replacements for present batteries. The BA-5100 is a replacement for a mercury-type battery also used in night vision equipments and in some NSA equipments. The BA-5200 is the lithium equivalent of the BA-200, a very familiar 6 volt lantern battery.

Although the configuration of the BA-200 would allow four lithium cells in this battery pack, we have designed it with only two, and the two-cell lithium battery does the same that the zinc/carbon battery does. The reason for designing it with two cells is very deliberate. If we parallel cells, we insist diodes be used in either the battery or the circuitry. Had we put four cells in this battery, we would have had to have put diodes in the battery.

The BA-5847 is shown here, but it really hasn't gotten off the ground to date. It'll be a two-cell battery, a two "D" cell battery, also for some of the night vision equipments, the TAS-4 and -5 are night vision equipments. The AN/PRS-7 is a very old mine detector that's in the Army system, and the Army is updating it. It currently uses a mercury battery.

The 9 volt category: the BA-5090. I might mention, in our nomenclature scheme, BA, your primary batteries, 5000 series, will all be lithium-type batteries. If you go down the line, the 4000 series is magnesium; there are only two in the system; 3000 are the alkaline manganese dioxide; 2000 used to be low-temperature types which we've eliminated. The 1000 are the mercury batteries.

So if we were to make a zinc/carbon battery, for example, equivalent to the 5847, it would be 847.

The 9 volt battery, BA-5090, is a lithium version of your common familiar 9 volt transistor radio battery. In the military system, there are three available right now: the BA-90, which is zinc/carbon; the BA-1090, which is mercury; and the BA-3090, which is alkaline $MnO_2$.

At the present time, the major equipment is using the BA-3090, getting fairly good low-temperature performance. The BA-5090 would allow the user to go lower in temperature for his operations.

The BA-5599 was designed for night vision equipment, the AN/PAS-7, and another customer came along with equipment known as the COU, which is a cable order wire unit. It's a piece of test equipment for telephone lines.

The PAS-7 started life with a zinc/silver oxide rechargeable battery, which was hung on the soldier's belt and a cable went up to the equipment which he holds up here. When it was subjected to user tests, the user made two comments: we don't want the battery hanging on the guy's belt, and we don't want a rechargeable battery. The lithium battery will take care of both of these comments.

It is used in a high-rate situation, current varying between 1.6 and 2 amperes. At this current, we're quite concerned about high temperatures, high ambient temperature and high cell temperature.

To overcome or to satisfy our concern, the battery has a thermostat within it, such that when it senses the temperature going up, if I recall correctly, at about 160, the thermostat opens; the battery won't operate the equipment anymore. The soldier that has it has a spare with him; he has to replace batteries.

We've done this to avoid cell venting or worse.

In the 12 volt category, the first battery shown, the BA-5598, is shown for a number of equipments here, both Army and Marine Corps: the AN/PRC-25, which we're going to have to scratch from the list, the PRC-74, the -77. The PRC-77 will be the major user for the 5598.

Now, the PRC-77 presently uses a magnesium battery which sits underneath the radio set in its battery box. It's about 9-1/2 inches long. Our first approach to a lithium battery for that set was what, for convenience, I'll call a full-size battery—a battery 9-1/2 inches long that fits under the radio set in the battery box.

In this design we had two parallel sections: 10 cells, two parallel sections of 5 cells each section. Because we could not get at the equipment, diodes would have to be put within the battery. That was one constraint.

The present magnesium battery operates the radio set about 50 hours; the lithium would double that in a full-size version. We're not so sure the user would know what to do with a $100 battery, because we're told he throws the battery away and gets a new one every time he goes out on a mission. He is used to the 50-hour battery.

We've cut the battery in half. The 5598, then, is half of the 9-1/2 inch original battery. It provides the 50 or 60 hours that the present magnesium battery operates.

Now, in the radio set, we envision the user would put two batteries in his radio set: one in operation, one as a spare to fill up the whole volume that he had there. This battery is going to be evaluated under field conditions this winter in Alaska.

The other equipments, the PPS-15 that currently uses the magnesium battery, will use the 5598 when it becomes more widely available in the field. Similarly for the GRA-114 and the PSN-6. The Marine Corps, likewise, will switch over to the 5598 when it becomes available.

The 5588 exists only on paper. We will be awarding an R&D contract very shortly for the development of this battery. It will be a five-cell battery. The major intention is the AN/PRC-68, which is a radio set developed some years ago by Magnavox for the Marine Corps. Both the Marine Corps and the Army are going to use this set. This will be a high-volume item.

The Navy will also use the PRC-68. They're going to use it on shipboard. They're not going to use the lithium battery on shipboard; we're going to develop a NiCad battery to do the same job in the same configuration as the lithium battery. This, then, will also make a NiCad battery available to the Army and Marine Corps for training purposes.

The 24 volt applications: the BA-5557 for an equipment that we call the DMD or digital message device. This equipment is used primarily by the Army field artillery people. It uses a nickel cadmium battery in it now. The artillery people are very unhappy with it: every two hours the battery has to be replaced, which means they have to have a steady supply line of batteries going back and forth between charging stations and the equipment.

The 5557 will give them more than a day's operation, and it'll overcome this back-and-forth situation that, for fielding, the Army is quite negative about.

The BA-5840: this is a big battery, probably the biggest one that we would envision at this point in time, roughly 4 by 12 by 6 inches high. This will be on the order of 15 ampere-hours for equipment that require higher currents for longer times.

The BA-5590 is one of the first batteries that we designed. It's designed with two 12-volt sections; thus, the user can either put it in parallel for 12 volts or in series for 24 volts. The initial equipment that this was designed for has since gone by the board. I guess it got caught by the austerity cut.

New equipment, though: the Vinson, the MX-9331, and the Bancroft under the Marine Corps side will be the major users. The other users will be secondary users for this particular battery.

One other comment on the design of these batteries: they must all be fused, obviously with the exception of the 3 volt cell. But all other batteries that we anticipate using in the Army system will be equipped with replaceable fuses.

## DISCUSSION

OTZINGER: Are these all cylindrical cells or do you have some prismatics in there?

LEGATH: They're all cylindrical.

OTZINGER: Are you planning to get into prismatic cell development at all?

LEGATH: We have no plans along that line right now, no.

OTZINGER: You know, space would be improved considerably. That's why I was just wondering if—

LEGATH: It would, it would.

OTZINGER: —if you had anything planned at all in that direction.

LEGATH: No, we haven't even considered rectangular cells.

CHODOSH: Just a quick comment. On the 5840, it's rated at 24 ampere-hours, as I recall, not 15.

LEGATH: At one time, Stew, we were talking about 15.

CHODOSH: Oh, okay.

MARINCIC: Why do you insist on putting a diode on cells in parallel? If you're talking about cells that change voltage with the depth of discharge, then I can see the point, but if you are talking about either liquid sulfur dioxide or thionyl chloride, you really don't need that. Thermodynamically and by experience, these cells have the same open circuit voltage regardless of the depth of discharge; Therefore, you can hook up in parallel a cell which is 99 percent discharged with a brand new one. They will not do anything to each other, and when you begin to drain the current out of the parallel stack, only the new one will supply the current because with the discharge at that point, the internal impedance in the used one goes down.

So you really don't need the diode at all in parallel stacks of these cells that have constant open circuit voltage regardless of the depth of discharge.

LEGATH: I would agree with you when you say putting a fresh cell in parallel with a 99 percent discharged cell: the impedance of that cell, you're not going to get any current through. But we're talking primarily where you might have a good fresh cell, 100 percent, and another fresh cell 90 percent and perhaps we're being ultraconservative and overly safety conscious, but at this stage of the game, this is the direction we're going in. As we gain more experience, we may drop diodes.

MARINCIC: I have to reemphasize this: it's thermodynamically impossible to do anything by one cell to the other in these two categories of cells. It only makes sense if you are putting in a diode to prevent somebody from charging it with the external power source. That is the only case where I can see you would need a diode—to protect your cell against the charging by an external power source, but not by another stack of cells.

LEGATH: I understand your point, but as I say, perhaps we're being ultraconservative and going overboard on safety consideration. As we gain more experience, we may drop the diodes.

LEUPOLD: Who's building your batteries for you? Are you constructing all these yourself or are the different manufacturers building them?

LEGATH: No, we're not constructing the batteries that I described. PCI has made batteries, Mallory has made batteries, and Honeywell has indicated an interest to get into the market. Now, for production quantities, we had one production contract of 3,000 batteries (I'm quoting this production) a little over a year ago. PCI had that one. PCI just was awarded another contract for the BA-5590, and very shortly there'll be another production contract for the 5598, and I expect four bidders.

LEUPOLD: One other comment: When they manufacture the batteries, do they manufacture them under a performance spec that you put out?

LEGATH: Yes, the performance spec that our Material Readiness Command put out.

LEUPOLD: And they do all the testing of the batteries and they present you with the information, and then you review that to meet this performance spec, is this correct?

LEGATH: There's both contractor testing and government testing. Contractor testing is witnessed by DCASS and by Ft. Monmouth people.

HIRSCHLER: You were talking about the high-rate discharge of a 9-volt cell which you discharged at 1.6 to 2 amps. What does that constitute in terms of c rate, this high rate discharge?

LEGATH: Well, that would be about the four hour rate—three to four hour rate. It's a "D" cell, the "D" cell in that battery.

BENNETT: Can you tell me how long you have actively had hermetically sealed cells in the field?

LEGATH: I'd say we had hermetically sealed cells in Alaska three years ago, and another group went up to Alaska last year. Because of administrative problems, they weren't used in Alaska last year; they're going to be used this year.

BENNETT: Question: Have you had any in other than low-temperature storage conditions—say, in more tropic or semitropic environments—and have you gotten any data back?

LEGATH: In the field? No. Only spec testing, four-week, 160. That sort of thing.

BENNETT: Okay, thank you.

LEGATH: Now, the batteries that were delivered to Alaska last winter, a year ago this past October, were not in low-temperature storage over the summer. They were in what we call casual storage, a warehouse.

BENNETT: That's still different from casual tropics, though.

LEGATH: Oh, definitely, definitely, yes. There's no experience with tropical storage.

SLIFER: What's the weight of the 5840 battery?

LEGATH: That's going to run about ten pounds, I imagine. Stew, do you have any figure on that?

CHODOSH: Nine to ten.

LEGATH: Nine to ten pounds, yes.

## LITHIUM BATTERY APPLICATIONS

| VOLTAGE GROUP | TYPE | ARMY USE | OTHER SERVICES |
|---|---|---|---|
| 3 Volts | BA-5567/U | AN/TVS-2,4,5<br>AN/PVS-2,4,5 | |
| 6 Volts | BA-5100/U | Night Vision Devices | NSA (COMSEC Equip) |
| | BA-5200/U | Lanterns | |
| | BA-5847/U | AN/TAS-4,5<br>AN/PRS-7 | |
| 9 Volts | BA-5090/U | Lt Wt Doppler Set<br>PEWS | |
| | BA-5599/U | AN/PAS-7<br>COU | |
| 12 Volts | BA-5598/U | AN/PRC-25,74,77<br>AN/PPS-15<br>AN/GRA-114<br>AN/PSN-6 | Marine Corps (AN/PPS-15) |
| | BA-5588/U | SUT-AN/PRC-68 | Marine Corps (AN/PRC-68) |
| 24 Volts | BA-5557/U | DMD | |
| | BA-5840/U | AN/TRN-30<br>AN/TAS-6<br>AN/UIH-6 | US Air Force (Dual Band Beacon) |
| | BA-5590/U | VINSON<br>MX-9331<br>BCS<br>PLRS<br>REMBASS-1<br>TA-978/G | US Air Force (GPS)<br>Marine Corps (AN/PRC-104)<br>Marine Corps (VINSON, MX-9331, Bancroft) |

Figure 5-58

# HAZARDS OF LITHIUM THIONYL CHLORIDE BATTERIES

J. M. Parry
A. D. Little

I want to talk this morning on two quite different topics. Their only relation is that they are pertinent to lithium thionyl chloride battery safety. One of these is a hazards anylysis of a system (risk assessment, if you wish), a formal approach that's been used in nuclear engineering and predicting of oil spills and things like this. It's a formalized approach to getting an assessment of the degree of risk associated with the use of any particular system.

The other is a small piece of chemistry related to the explosions that can occur with lithium thionyl chloride systems. I'd like to start with the chemistry.

While there's a lot of work that's been done looking for levo species in the discharge process of lithium thionyl chloride cells, as far as I can see in the literature, nothing very specific has been identified. But there's one circumstance in which I think we've been overlooking something that's rather obvious, and this is what happens to an anode limited cell when it's in reversal.

I think we have distinct prospects in the thionyl chloride system of driving the lithium anode to a potential where you decompose the passive film that makes this cell possible. I think that, obviously, with small electrodes operated in the laboratory and you're discharging the lithium, you can't polarize it far enough to break down the lithium chloride film. It involves pushing the electrode to more than 4 volts positive to a lithium reference.

But if you look at the real world and look at a cell where you can isolate some of the products through a high resistance or isolate some of the active material through a high resistance, and you force that cell into reversal, you can get the potential going far enough, and although there's a high resistance involved with that active material, it's still an equipotential electrode, so you drag that material with you to the point where you can begin to break down the lithium chloride film.

Once you've got a free lithium surface, then all sorts of very highly energetic reactions can take place. Most of them are going to generate passive films again, lithium chloride or lithium sulfide, but I think as these break down electrochemically and are regenerated chemically, you're producing a lot of heat. Eventually you get to a point where you have thermal runaway and an explosion.

(Figure 5-59)

So to emphasize the point I'm trying to make, let's take this as a summary. I think in reversal in a practical cell (particularly the large cells), you can push the anode to a point where you've got potentials greater than 4 volts.

Under these circumstances, the protective film of lithium chloride can break down, and the lithium metal can undergo more energetic reactions.

Now, it's perhaps difficult to believe that you can push the lithium electrode that far, that you can get polarizations as much as 4 volts. With proper acknowledgment to EIC, it has been reported in the literature.

(Figure 5-60)

We see here where a reference electrode has been used in a relatively small cell. You can trace the anode potential at this point coming up to nearly plus 4 volts against the lithium reference. And this is a cell that eventually exploded.

Now, it's not going to be an instantaneous thing when the anode reaches 4 volts. You have a fair amount of lithium chloride to consume; you've got the thick film; you've got the thin film, which is the passivating layer; and, as I say, if you get a free lithium surface, there's an ensuing chemical reaction which regenerates a passive film. So you see all these spikes. They appear in the cell potential here, but since the reference electrode failed, the actual voltage of the anode was not tracked.

But you see these spikes associated with the breaking and re-forming of the film until eventually you generate enough heat to possibly create local melting, and then have that followed by an explosion.

There's some other minor evidence that contributes to this concept. With cathode limited cells in reversal, the temperature increase is a lot less than with anode limited cells in reversal.

So I put that out as an idea. It might be controversial, it might be totally wrong, but let's see what comes of it.

The second topic I wanted to talk about was an approach towards formalizing the risk assessment associated with thionyl chloride batteries. What we're going to get to is really just the first step of risk analysis.

(Figure 5-61)

We'll end up with a fault tree of this sort, which attempts to link all the factors that could contribute to catastrophic failure. I'll be coming back to this in a while.

(Figure 5-62)

The concept of the fault tree analysis is that it provides a logical and graphic representation of the various combinations of possible events which can cause a predefined undesired event. In this case, our predefined undesired event is an explosion or perhaps disventing.

(Figure 5-63)

The important thing about generating the fault tree is that you can see the interrelationships, if any, of several events that, again, bring you to the point of the occurrence of the undesired event.

(Figure 5-64)

The fault tree structure can be used to determine the significance of fault events and the probability of their occurrence, given a significant data base. That concept of the data base is a very important one. It's one that we are lacking at the moment for the lithium thionyl chloride system. We're just seeing widespread use of these batteries, and I think it's imperative that orderly data gathering be carried out so that when the time comes for greater deployment of these systems, we can make a significant assessment of the degree of risk involved in using the particular battery.

(Figure 5-65)

In view of the preliminary nature of the fault tree I'm going to put up in a moment, I'd like to stress that it is an iterative process. one that can be updated to coincide with design development.

(Figure 5-66)

This is the sort of thing that you get out of a fault tree analysis that enable you to verify compliance with established safety requirements; it gives you a means of identifying design safety deficiencies which have developed in spite of existing requirements; it allows you to establish preventive measures to limit or control identified design safety deficiencies; you can evaluate the adequacy of established preventive measures and establish safety requirements for the next design phase.

Referring back to Figure 5-61 you start with generating the fault tree. The intent eventually is to put probabilities on each of these branches. You can then take these probabilities and construct a matrix to calculate the degree of risk associated with using the system.

As you can see from the crudeness of this (I drew it quickly yesterday), there's no great thought gone into it. It's just a means to show the process, to demonstrate the methodology associated with fault tree analysis. But you can see that you can throw things in to suit your own viewpoints on these things.

The symbols indented at the bottom imply an "or" event. Any one of the operations, the events underneath, could create the main event. Where there's a flat bottom to it, it's "and," that both the events below have to occur before anything goes wrong. In other words, in reversal, where you've got a cell with low capacity, you'd have to have diode failure as well before you'd get into the situation where your undesired event would take place.

The other formality of this is that you should terminate in all cases with a diamonds and not squares. You pursue the thing logically down until you reach the point which is a source.

Obviously this can be continued a lot further than it is here. When you get to actual production and use of cells, these will go on into individual components, each one of these here, individual methods of fabrication and all factors that contribute to the construction and delivery of the cell for use.

The other points that you get from a fault tree are the degree of interaction of variables; where you have numbers on the chart, it indicates that you have another point on the tree where the same events are of importance.

I notice now that I left out one important thing. The "one" associated with the explosion right at the top—there was to have been another diagram off to the right showing a safe venting process. I'm afraid it got left out altogether.

So the important thing is to first of all get your fault tree right, and this should be done by discussion and interaction with other people. It should not be a unique process. Then there should be a collection of data to establish probabilities, and the probabilities can be filled into the fault tree to come up with some reasonable figures for the degree of risk associated with using the particular system.

The mathematics get quite complicated. The whole process becomes even more complicated when you introduce a time scale to this: when you look at it not just as a single event occurring at any one time; you look at the effect of elapsed time and the requirement for overlap of events to create an explosion.

## DISCUSSION

HOLLECK: You referred to these voltage fluctuations in our measurements. Even so, I think in principle, an explanation that you brought up might be possible, but in these measurements the fluctuations come from contact loss between the lithium and the current collector grid rather than from the making and breaking of the lithium film.

PARRY: Yes, I agree with that.

TAYLOR: In regard again to that graph you showed, do you have any data on temperature measurements ? You seem to be suggesting that the temperature gradually builds up. Is there any indication, in fact, that that does occur resulting finally in a—let's call it a thermal runaway ?

And secondly, I always tend to go to the end and see when the explosion occurred. Was all the thionyl chloride gone at that stage ?

PARRY: It's not my data, Harry: I can't answer that.

TAYLOR: Can Gerhard ?

PARRY: The comments I made there are written comments in a GTE report, and I couldn't find any numbers or curves to go along with the contention that anode limited cells do increase in temperature more than cathode limited cells in reversal.

TAYLOR: Perhaps EIC would like to comment, however, on those data.

HOLLECK: There was no measured temperature increase prior to the explosion in those measurements, and the thionyl chloride was not consumed completely before.

MARINCIC: Regarding the comment of the anode limited cells: anode limited cells are not anode limited until you run out of anode. So if you run out of anode, you are dealing with a common collector against carbon. Therefore, in the process of discharge (depends on at which phase you are studying it) the cell doesn't know and you don't know whether it's anode limited or not.

The second thing: regarding your chemistry, John. Of the two possibilities that you suggested, I would say it's at least controversial if not totally wrong, because if all you need is a bare lithium surface to dip it in thionyl chloride to make an explosion, we will have an explosion every time we assemble a cell, which we don't.

Another thing is, have you ever tried to create fresh lithium inside the cell which you know is bare while you're cathodically depositing it on it and then stop the deposition and see what happens inside? It really is not enough to generate heat to get the explosion going, because the process that in your explanation causes the explosion is actually compensating—it's actually curing itself, because the result of that reaction is passivation, which stops it.

Therefore, you would have a very large surface area of lithium and clean all the way up to the last moment and allow all of it to react at precisely the same moment to create enough heat to do that. Otherwise, if you do it step by step, as you are stopping it, it's getting passivated. So I somehow can't go along with the chemistry, that's all.

PARRY: Well, first of all, the question of there being no anode left in an anode limited cell in reversal: I disagree with that completely. Perhaps you do make the perfect cell where all the lithium disappears when it's supposed to disappear, but I think you get isolation of active material that means that even though the cell is in reversal you still have a large amount of lithium left in that cell.

Now, it's not capable of discharging at any significant rate, but it is an equipotential, so you are dragging that inert mass, as it were, up to the potential of reversal. So that, I think, happens in practice, particularly in big cells.

With regard to having a catastrophic reaction anytime you put lithium into thionyl chloride, well, no, you don't. It passivates immediately. You form lithium chloride on the surface. That's why it doesn't explode. But if you now take that lithium, or if you can take that lithium to a potential where you can destroy the lithium chloride, then you have a clean lithium surface that can react with other species.

MARINCIC: Well, there are very few things that we agreed on last time in Atlantic City, but one thing was, by at least Honeywell, Mallory, and GTE, they all reported all discharge and other charging with no explosion, and those are the situations where you generate new surfaces.

PARRY: One of the most dangerous circumstances you've got is an anode limited cell in reversal. Those are the ones that routinely explode. I think the EIC people could confirm that. Cathode limited cells are very well behaved.

MARINCIC: Another thing is that I don't know where you get the data of anode limited cells generating more heat on discharge. We don't have anything to prove that.

PARRY: Well, it's in one of Carl Schleger's reports.

MARINCIC: I don't remember ever experiencing that. I was just checking here with everybody else, and we don't remember that.

PARRY: I have the report with me; I can show you.

IN REVERSAL THE ANODE OF AN ANODE LIMITED CELL CAN REACH POTENTIALS > 4V ON THE LITHIUM SCALE.

UNDER THE CIRCUMSTANCES THE PROTECTIVE FILM OF LITHIUM CHLORIDE CAN BREAK DOWN AND THE LITHIUM METAL CAN UNDERGO MORE ENERGETIC REACTIONS IN WHICH THE FREE ENERGY CHANGES CAN BE GREATER THAN 300 KCAL/MOLE.

Figure 5-59

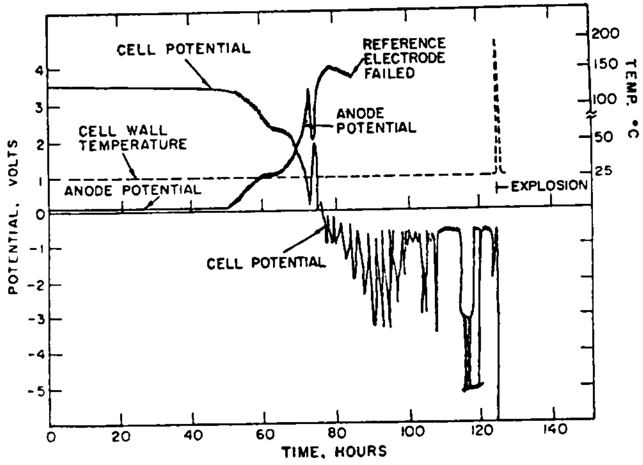


Figure 5-60

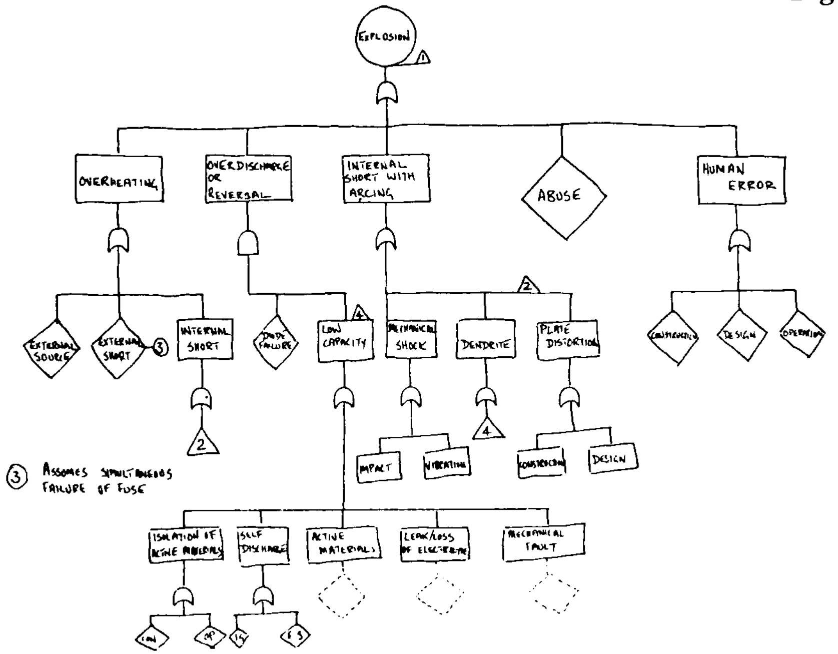


Figure 5-61

FAULT TREE ANALYSIS PROVIDES A LOGICAL AND GRAPHIC REPRESENTATION OF THE VARIOUS COMBINATIONS OF POSSIBLE EVENTS WHICH CAN CAUSE A PREDEFINED, UNDESIRED EVENT.

Figure 5-62

THE GRAPHIC PRESENTATION EXPOSES THE INTERRELATIONSHIPS OF SYSTEM EVENTS AND THEIR INTERDEPENDENCE TO THE POINT OF OCCURRENCE OF THE UNDESIRED EVENT.

Figure 5-63

THE COMPLETED FAULT TREE STRUCTURE CAN BE USED TO DETERMINE THE SIGNIFICANCE OF FAULT EVENTS AND THE PROBABILITY OF THEIR OCCURRENCE GIVEN A SIGNIFICANT DATA BASE.

Figure 5-64

FAULT TREE DEVELOPMENT IS AN ITERATIVE PROCESS WHERE THE INITIAL STRUCTURE IS CONTINUALLY UPDATED TO COINCIDE WITH DESIGN DEVELOPMENT.

Figure 5-65

THE RESULTS OF SYSTEM SAFETY FAULT TREE ANALYSIS ARE:

- VERIFICATION OF DESIGN COMPLIANCE WITH ESTABLISHED SAFETY REQUIREMENTS.
- IDENTIFICATION OF DESIGN SAFETY DEFICIENCIES WHICH HAVE DEVELOPED IN SPITE OF EXISTING REQUIREMENTS.
- ESTABLISHMENT OF PREVENTIVE MEASURES TO ELIMINATE OR CONTROL IDENTIFIED DESIGN SAFETY DEFICIENCIES.
- EVALUATION OF THE ADEQUACY OF THE ESTABLISHED PREVENTIVE MEASURES.
- ESTABLISHMENT OF SAFETY REQUIREMENTS SUITABLE FOR THE NEXT DESIGN PHASE.

Figure 5-66

# SEAL PROBLEMS OF LITHIUM CELLS

S. Gross
Boeing

One of the important problems in most lithium systems is the problem of seals. If you have leakage through a seal, then you have a problem of leakage of electrolyte, leakage of gaseous cathodes and soluble cathodes, which are all reactive and corrosive. You have a problem also of ingress of water vapor and oxygen and nitrogen into the cell, and depending on the particular kind of cell you have, these can cause reactions which are explosive.

In some cases, the reactions are with the active materials in the cells, and in other cases, the reaction is with by-products.

(Figure 5-67)

The experience of most of us is with leakage of alkaline systems, and with alkaline systems, the leakage occurs due to two causes, generally: the mechanical leakage due to tiny holes, tiny crevices, scratches and so forth; and in addition, due to electroosmotic forces which force electrolyte into the space between the negative terminal and the seal.

This figure, incidentally, is just to show that lithium cells do leak at seals, but my purpose is not to really go into that particular problem but to discuss it in general.

In lithium cells, you have some different problems. First, you do have the mechanical problem, loss or transmission of materials through the seals, and in addition you have electrochemical problems. The mechanical problems originally start with the crimp seals, and people have more or less abandoned those because they're really not reliable and you can't get a good mechanical seal.

Ceramic seals are usually considered to be very good, but if you're talking about applications where you must have 100 percent sealing (you must not allow the ingress of any material, such as, for example, in the lithium thionyl chloride cell), there's good reason to believe that you should not allow any water vapor to enter the cell, because it can react with ingredients in the cell and cause explosions.

Now, the ceramic seal has a problem. Those of you who are familiar with the technology on this, you'll note that, for example, the NASA specifications (or at least some of the specs that we've been using at Boeing) have requirements that the area of coverage of the seal has to be on the order of 75 percent. Even though it's very, very good for alkaline cells, when they break these seals apart, they usually find that the 75 percent requirement is met, but it's very seldom that the coverage is in excess of 90 percent. So you do have these tiny hairline cracks or pathways which are possible.

Now, the other category of seals that's commonly used in lithium cells is glass-to-metal seals, and the glass-to-metal seal technology involves first putting an oxide on the metal, and then this oxide is allowed to mate with the glass material.

Typically you have a metal terminal, then the seal, and then the metal can. The problem with that is that either the metal terminal or the metal can is going to be at the lithium potential, and when that happens, the metal oxide on the metal can be reduced by the lithium to metal, and that can allow the destruction of the seal over a long period of time.

So that's the basic problem that we have to contend with.

## DISCUSSION

TAYLOR: In regard to your latter statements about glass-to-metal seals, it is not always essential to put oxides down on metal interfaces to get a good glass-to-metal seal. One can, of course, talk about something like covar-to-covar seals where it is recommended to put oxides on the surface. Those are matched seals.

If you go to compression seals, such as using a cold rolled steel jacket matched to some other metal (say, a valve metal), you do not put an oxide down on the surface. Let's just leave it at that.

GROSS: Thank you.

REED: I'm a little at a loss to know about the circumstance under which you say the ceramic metal seals don't work. I think you have to qualify it a little bit more by discussing the systems. I think perhaps after some of the systems that you've examined have been with lithium, they are inherently not compatible. Are you metallizing or are they active metal systems ?

The second part of my comments would be that ceramic metal seals have been around for an awful long time, and they've been used in many electron tube applications, and I would ascribe the cracks that you talk about more to bad workmanship rather than to an inherent characteristic of ceramic metal seals.

GROSS: I don't deny that it's not possible to make a good ceramic metal seal, and in fact there probably are many that are made very well. But many of those that are currently used (for example, in the alkaline battery industry) are really not what I'm calling the real, full 100 percent quality required to make absolutely sure that you don't get any microcracks.

Because, for example, in the alkaline cells, a tiny, tiny leak is not really causing the problem.

REED: I think we'd like to have the privilege of furnishing you with some of the seals, but I think the main problem in using ceramic-metal seals in your application is cost, isn't it? They just have to cost a couple of cents? What cost could you tolerate?

GROSS: Well, my first concern is that you make it work, and then you make it cheap. That's usually a good rule for engineering. And, of course, with the lithium systems, it first has to be safe and then cheap. I'm only pointing out the historical events that have happened.

Historically, the developments have been to develop the ceramic seals so they're good enough for the alkaline systems (at least those of us who are using alkaline systems), and they are now good enough. But my point is that these may not all be good enough for the lithium systems. So I'm only pointing out this potential problem to make sure that we don't get lulled into thinking that ceramic seals are going to be great and you just use any ceramic seal and you go off and run it and you're going to get a good system. You'll get some serious disappointments if you do that.

METHLIE: I think it's true, and somebody in here correct me if I'm wrong, but all of the insulating materials which can be considered for any kind of a seal here, wet seal, brazed seal, comparison seal or whatever, are all reducible at lithium potential.

So what we're getting involved in primarily is the kinetics of the situation, and for your particular design application, how much stability is good enough. That requires you to do the best you can with design and an awful lot of testing to determine that you really do have the stability which you need to have, which in my opinion, most often you can get.

GROSS: I agree.

MARINCIC: I don't agree.

TAYLOR: I sort of beg to differ with that latter very bald statement. All metal oxides are not reducible at lithium potential.

METHLIE: I think, Harry, I said that theoretically they're thermodynamically reducible.

TAYLOR: They're not all thermodynamically reducible, that's my point.

METHLIE: Okay. Which one do you have in mind that isn't? Okay. Maybe you're aware of something that I'm not, Harry.

TAYLOR: Yes, I think I am, but I'm not going to tell you.

METHLIE: Have we been able to find a new element?

TAYLOR: No, it doesn't require a new element.

HOLCOMB: I suggest that you two talk on your own to determine what that is. Did you have another comment you wanted to make?

TAYLOR: I do have one quick comment about ceramic seals, because Sid Gross was talking about leakage through cracks. One also does have to bear in mind that the ceramic seal uses various braze materials, and the question then remains as to what the stability of those braze materials is, particularly at cathode potential. They might dissolve. It's worthwhile bearing that in mind also.

MARINCIC: Would you tell us something about them?

TAYLOR: You should be so lucky also.

REED: I somehow think we've got a different crew here today than Tuesday, and I gave a paper on Tuesday on ceramic-to-metal seals for advanced battery systems. I didn't talk about the low temperature system because I thought there weren't any problems with it. I just talked about lithium and sodium sulfide systems, but a lot of the remarks I made there would be applicable to the low temperature lithium systems.

For example, the ceramics which we are investigating are not a new element: they're yttrium oxide and high purity beryllium oxide. The brazes that we're investigating are zirconium nickel, palladium cobalt, gold, and other intrinsically electrochemically compatible materials, and the results are regarded as encouraging in the high temperature systems.

So if things will work at 475 degrees, which is required for load level, at these low temperatures (except when things explode), I would think that you'd get very long life indeed.

HOLCOMB: I think his comment is correct. We have pretty much a new crew today compared to what we had the last couple of days, and it would be interesting for somebody to read the other parts of the Proceedings.

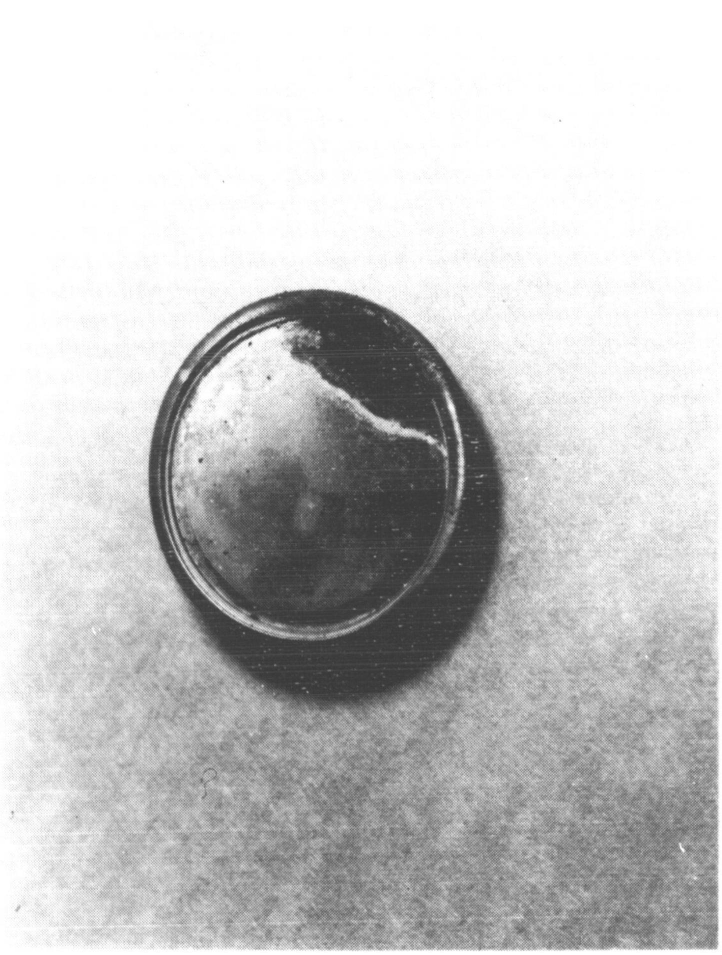


Figure 5-67

# CHARACTERISTICS OF Li-$SOCl_2$ CELLS

D. C. Warburton
Naval Surface Weapons Center

I don't propose to be quite so esoteric, but I do think that the point has been made and needs to be made again, often over and over, that we do not have an adequate data base for any of our lithium systems—principally the thionyl chloride—to give us any kind of reliable assessment. However, we're all trying to go toward that base in various DOD agencies and NASA, and all of these efforts are not to leave out the manufacturers, who perhaps are providing, in their own way, more information than we are in the DOD or NASA.

At the Naval Ordinance Lab or the Naval Surface Weapons Center, as it's now called, we are studying these three types—prismatic, cylindrical, and disc—and you can guess who made what.

(Figure 5-68)

The sizes here are ranging from a few milliampere-hours to 500, and in the case of Joe McCartney at NOSC, 1000 ampere-hours and above.

(Figure 5-69)

Now, here's my fault tree. In a sense, I hope that it will provide the data that we need to do some kind of a fault analysis that Mr. Parry has alluded to, and I think it's a very interesting way of looking at a design and assessing risk. Perhaps we should have used this much earlier in the game, and we would have changed the structure of our test plans perhaps.

These are self-explanatory. The only one that I would like to point out is that in the Navy, we have a very severe water entry shock. It's a two-phase shock. It would be a quibble to make equivalent dropping an object from 30,000 feet into sea water. We have a spike that has 5,000 to 10,000 G that occurs in a tenth of a millisecond; then we follow a drag phase of 500 G for 15 to 45 milliseconds. So that represents quite a shock.

The other is the shock gun launch spin. The spin has not been addressed yet, I don't think, in any of our design considerations in the thionyl chloride or the sulfur dioxide as such, as a very stringent parameter.

The storage tests that we want to conduct and have samples in this program range from half a year up to five years at these various temperatures.

The destructive tests in the Navy applications that we're interested in—we range from an hour, sometimes we may be down to a half-hour if we talk about the torpedo propulsion. Many of our applications are four months and a year, and there we do need seals and there we do need to know what the electrochemical processes are with time.

Cell reversal, short circuit current, incineration, and oven heating all pertain to various modes of failure, various conditions that would be in our stockpile-to-target sequence.

Not to be outdone by some of the people with electrochemical and chemical analysis, we do intend to use these methods in analyzing the guts of the batteries, if you will, at various stages of discharge, after discharge, forced discharge, et cetera.

I'd like to make one more comment. The lithium battery industry has been moving ahead in the last decade very rapidly, exponentially now, in the last few years. And the design changes and the knowledge that's been gained, and I think produced primarily at the battery manufacturers, has led us to the point now where we can have cells that are produced and we can test these and have some reasonable confidence that the test results that we get are valid and can be used for prediction.

We have some 2,000 samples at the lab that I have essentially discarded, because I feel that they're first and second generation, and the data we generate under those things, while it may be of academic interest, I think can lead to sometimes false conclusions.

Now, I want to present just two pieces of information with regard to the thionyl chloride system.

(Figure 5-70)

This is a design that was made in 1975, and we have samples of a 1-1/2 ampere-hour cylindrical size cell. The controls gave us about 2 ampere-hours at a discharge rate of 1800 ohms, which is about 2 milliamps. After vibration and shock, we had 85 percent of that capacity at minus 54, indicating perhaps some degradation at this low temperature, while at vibration and shock at 71, we seem to have improved things a little bit.

With the thermal cycling (the temperature and humidity cycling that I think most of you are familiar with, the standard jam cycle of the DOD), we had a significant degradation. In storage, taking again as our base one month at room temperature as 100, one month at 71°C, we lost essentially no capacity. At 54, 80 percent. As we came down in temperature, we had a few changes.

Then, when we got to room temperature in storing from one and two years, we saw some degradation. I think this is significant. I don't think this is just due to sampling in the cells that we have. But as I said before, this is 1975 vintage. I also might say that these were discharged in the horizontal position, which— you may be aware that there is some position sensitivity with these systems. Again, that depends on design.

At 0°C, after a year, we had 85 percent, and then we also store these things at -54°C for a year. You may feel that that was not realistic, but we always have the carry-over from the Leconche system, and people say, "Hey, do you really gain anything by storing electrochemical systems cold?" So this is a carry-over from that, and in some cases we have an indication that other things may be going on here. We have almost a 40 percent reduction there.

(Figure 5-71)

Now, this same cell size gives you an idea of what one can achieve in current density. Someone was asking a little while ago about what current densities can be obtained, and I realize that this is a nebulous parameter because you never really know what the true apparent area is. But with some judicious choices, you have to make some estimate of what a system can do when you begin to design a battery.

Here we've gone across the board for -54 to + 71°C, and it gives you an idea of the polarization that occurs in this bobbin construction.

Now, this is also made in a wound construction, and these levels are almost moved by a factor of 10, so that this would then be 1 ampere, 100 milliamperes, and 10 milliamperes.

(Figure 5-72)

Oh, I want to just give you an idea that you people are working with a system that has an excellent voltage regulation. This is for a 40-day rate discharge. Many of our applications are relatively low continuous background current, if you will, and we also have requirements for various pulses. By pulsing these at a certain percentage of the time, we try to get an idea not only of the polarization and internal impedance, but also what happens out toward the edge.

This is, I think, pretty indicative of one of the very useful parameters of the lithium system.

(Figure 5-73)

Now, what happens when you want to go for a year's discharge? This is 18,000 ohms now, and hopefully we would have come out to 400 days. We have some bouncing around in here, but again, we are achieving, I think, a very good energy density.

The energy density of these cells is on the order of 10 to 15 watt-hours per cubic inch, and 150 to 200 watt-hours per pound.

People have been talking about the Altus. We're involved in evaluating their product, and I want to emphasize again that, I think, when any company comes out with something new, we tend to grab at it and see what it does and not realize that they aren't making millions of these things; they haven't had a production line that's been running for a year or two years, so the variation is going to be there and there are going to be a lot of things that crop up that we feel should have been there in the first place.

(Figure 5-74)

These are just two of the cells. This is the 401 and the AL-101 that was alluded to earlier. Now, one of the things that we try to do is to get some sense, as I showed before, of the current density of these systems.

Here, if we ran from -54 to, again, 71°C, the polarization here at 10 milliamps per square centimeter, 100 and 1 amp. Now, I've drawn in a line based on some of our data from the lithium sulfur dioxide system at 10 milliamps just to give you an idea what is happening at the lower temperatures.

Now, I'm not sure to what extent one can manipulate the electrolyte and so forth to shift this out, but at the present state of the art, at any rate, the thionyl chloride system for some of our applications would be marginal, because we do have to go down and operate at -54.

It does say that the Altus people have made a significant contribution to the current density, but as I had pointed out before, the wound cells in the cylindrical shape of the $1\frac{1}{2}$ ampere-hour cell had also done the same thing, so it is, I think, debatable whether it has significantly been done on a current density basis. It may be in a design or a battery as you scale up.

There is considerable delay in the voltage. What we did here was just to pulse the cells to get an idea of what kind of voltage time is involved.

These are the temperatures, and this was a 10-ohm load. Again, you have a considerable delay and this has to be accounted for. It can be erased, if you pulse this consecutively or discharge it at a relatively high rate, (we repeated these measurements immediately, and we erased much of this delay portion here), but if we let them sit for another week or two, we had the same shaped curves right back.

(Figure 5-75)

We have discharged the $1\frac{1}{2}$ ampere-hour Altus cell, and we were trying to target for a one-hour rate. We have vibrated and shocked these things at -54 room temperature and +71; there seems to be no significant effect there. The discharge temperature is more significant—0 at room temperature and approximately 37°C.

We had one cell without any treatment that we discharged at room temperature that did give us a reasonable discharge. Again, this is just to give an idea of what the cell is capable of at the one-hour rate. We don't have our four-month rate data yet available.

Now, we can make them explode. I don't know whether this is an explosion or not, but we discharged this on a fixed resistance and then we put it into reversal at approximately 1 amp for five hours and then another four hours. The temperature during discharge rose about 25 degrees Centigrade, then came down toward the end of discharge.

During the reversal, the temperature remained somewhere around 35-40 degrees, and then all of a sudden it rose almost instantaneously to 150°C. But that's quite remarkable, I think, to be able to put this much energy into the cell before something happened.

Now, of course, you'll say, "Well, the energy or the current may be dissipated; it may be just running through a shunt of some means or other." But at any rate, we did have this effect. It blew the cell seal apart and melted some of our plastic material around it. There was nothing left in the vessel by this venting, if you want to call it a very high pressure vent or an explosion.

We did analyze the material that was in the vessel, and we found quite a bit of sulfur. I think that Altus has demonstrated that, under certain conditions, the safety has been increased. This doesn't mean by any means that they're the only company that can do this.

Our data base is extremely limited, and all of these bits and pieces that are being presented have to be correlated, and that's one of the things that bothers me a little bit. In order to get all of the data that people have, so that we can make some semblance out of it and perhaps give us a little better direction in our testing.

## DISCUSSION

GROSS: The reversal test in which the thionyl chloride cell blew up had, as I calculated, about 13 ampere-hours of reverse current in a 1 ampere-hour cell. Normally you wouldn't expect more than 1 ampere-hour of reversal would be possible in an application. What is your belief on how much reversal protection is required in the cell design?

WARBURTON: I don't know. First of all, I think we need to have data that gives us an idea of what the cells can do. I think that sort of a rule of thumb people have used is cell reversal equivalent to the capacity at some rate, if it's equal to the rate of whatever discharge that you may be having in your application.

GROSS: Do you agree that it's never required to be more than the capacity of its maximum capacity plus all the tolerances on capacity? In that case, $1\frac{1}{4}$ or so ampere-hours reversal protection would be quite adequate.

WARBURTON: Again, I think I'd have to qualify it, but I think that's certainly an initial start.

IMAMURA: On your last chart, it wasn't clear to me whether you control the reverse current. One amp constant current?

WARBURTON: One amp constant current, yes.

IMAMURA: Okay. Therefore, the voltage built up through what level?

WARBURTON: The voltage was less than a volt. I think on the curve—no, it wasn't plotted on there.

IMAMURA: Right.

WARBURTON: We were around 0.3 to 0.4 negative.

IMAMURA: Four-tenths?

WARBURTON: Yes.

IMAMURA: How about 2 amp?

WARBURTON: Not much change in potential.

IMAMURA: Thank you.

HOLLECK: I think if you want really to have any confidence in having a safe cell, you have to go beyond phenomenological measurements of whether a cell will explode. You have to try to understand what goes on, because the conditions under which a cell might explode are so different and so variable that if you test some number of cells and you don't find, under certain test regimes, any problems, you cannot be sure that you won't have a problem if you have just a slight difference in your test regime.

WARBURTON: Granted, granted.

BENE: How many cells have you succeeded in exploding of this type?

WARBURTON: We have sample sizes of five in each condition. We have done five of these. This is typical.

BENE: You had five out of five explosions?

WARBURTON: Yes, under the reverse. Yes.

BENE: Thank you.

TAYLOR: Again, not to belabor a point, but I am inclined to agree with Dr. Gross. I'm fed up with hearing about explosions. Let's not be ridiculous. You can't take a cell to that degree into reversal. That's looking for trouble, and it's looking for trouble that you're never going to get into in a real situation. Why do it? Why cry and say, "It's exploded?" Of course it's exploded. Damn it, take a regular cell—alkaline cells—do that to them, and they'll explode.

In any event, as I say, what's the point? It'll never get there. So I don't like to hear this word "explosion" again and again and again, not just with reference to thionyl chloride but also with reference to $SO_2$. I'm prepared to admit that problems can exist and one should therefore test to realistic regions, to realistic degrees, but not 13 ampere-hours for a $1\frac{1}{2}$ amp-hour cell.

If you disagree with that, please tell me how it's going to get there in the first instance.

WARBURTON: No, I don't; I agree with your comment. I do think, however, we have to test these under these conditions to see where the limits are, and I'm not so sure that they might not give us some indications of what happens when we start to scale up into 1000 ampere-hour cells.

If we have the ability to go inside these things and take a look and to couple the performance data with analytical and our chemical analysis of these things I don't think I can emphasize too strongly that the data that I've presented here without the chemical analysis leaves considerable to be desired, and it is our intent to couple the chemical analysis of these things with the experimental data that we generate.

LITHIUM CELLS SELECTED FOR STUDY

| SHAPE | CAPACITIES (AH) |
|---|---|
| PRISMATIC | 200,500 |
| CYLINDRICAL | 0.5, 1.5, 10, 20, 50, 100, 500 |
| DISC | 0.2, 1.5, 20, 50, 100, 200, 500 |

Figure 5-68

TEST PLAN FOR LITHIUM CELLS

- NONDESTRUCTIVE TESTS
  - OPEN CIRCUIT VOLTAGE
  - LOADED VOLTAGE
    - (1000, 100, 10, 1 AND 0.1 Ω LOADS APPLIED AT - -54°C TO 71°C)
  - AC RESISTANCE AT 1000 Hz
  - RUGGEDNESS AT -54, 21 AND 71°C
    - GROUND, SHIP AND AIR TRANSPORTATION
    - THERMAL SHOCK
    - WATER ENTRY SHOCK
    - GUN LAUNCH (SET BACK, SPIN)
    - TEMPERATURE AND HUMIDITY CYCLING
  - STORAGE

| | |
|---|---|
| -54°C | 1,5 YR |
| 0 | 1,5 |
| 21 | 1, 2 AND 5 |
| 32° | 1, 2 AND 5 |
| 54 | 0.5,1 AND 2 |
| 71 | 0.5 AND 1 |

- DESTRUCTIVE TESTS
  - DISCHARGE AT 1 HR AND 4 MO RATES AT -54° TO 71°C
  - CELL REVERSAL (FORCED DISCHARGE)
  - SHORT CIRCUIT
  - INCINERATION
  - OVER HEATING OF UNDISCHARGED AND DISCHARGED CELLS (UP TO 1000°C)

Figure 5-69

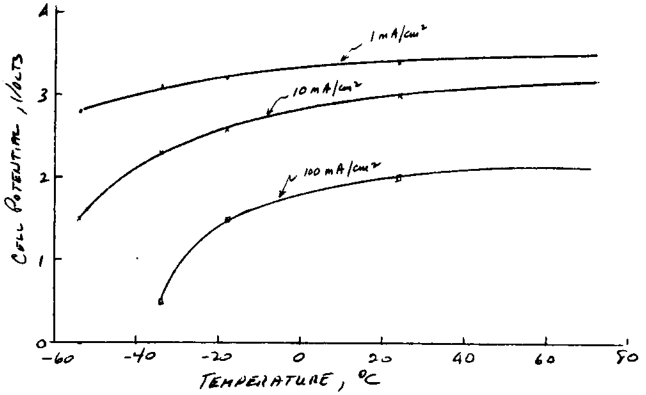
CAPACITY RETENTION
$LiSOCl_2$, 1.5 Ah, BOBBIN DESIGN (1975)
(1800 Ω Discharge at 21°C)

| TREATMENT | | CAPACITY RETAINED AS PERCENT OF CONTROLS |
|---|---|---|
| Controls | | 100 = 2.0 Ah |
| V&S -54°C | | 85 |
| V&S 71°C | | 110 |
| T&H (28d) | | 75 |
| STORAGE | | |
| 71°C | 1 mo | 100 |
| 54 | 3 | 80 |
| 32 | 6 | 110 |
| | 12 | 105 |
| 21 | 1 | (100) |
| | 12 | 90 |
| | 24 | 70 |
| 0 | 12 | 95 |
| -54 | 12 | 60 |

NSWC : R33 : DLW : 11-78

Figure 5-70

TYPICAL POLARIZATION
$LiSOCl_2$, 1.5 Ah SIZE, BOBBIN DESIGN (1975)
CURRENT DENSITY VS TEMPERATURE



NSWC : R33 : DLW : 11-78

Figure 5-71

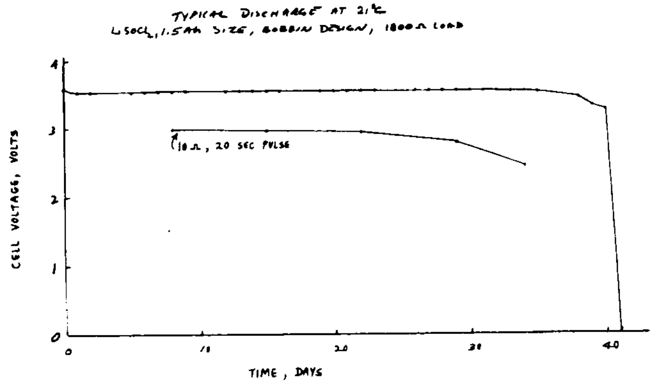


Figure 5-72

NSWC : R33 : DLW : 11-78

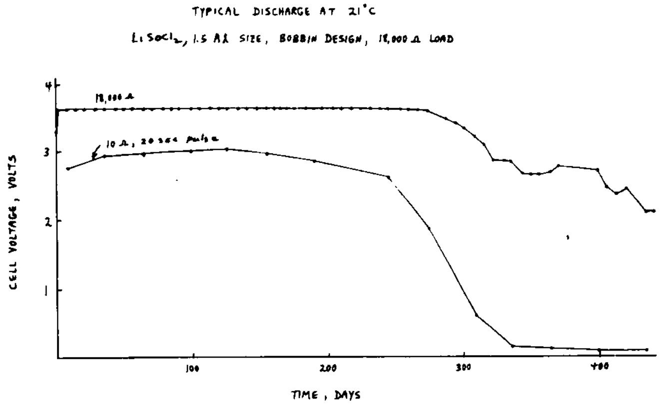


Figure 5-73

NSWC : R33 DLW : 11-78

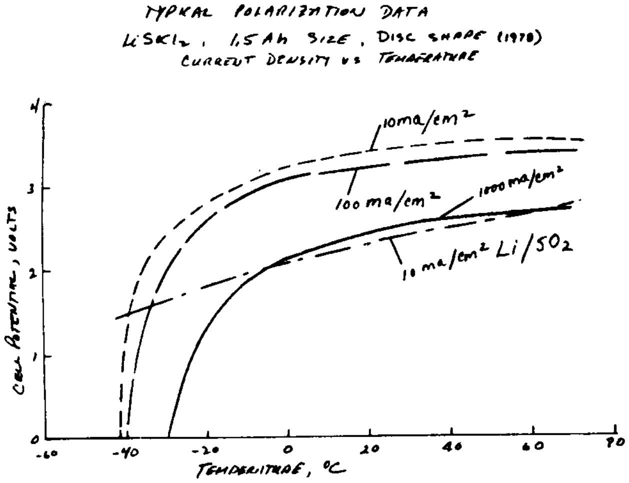
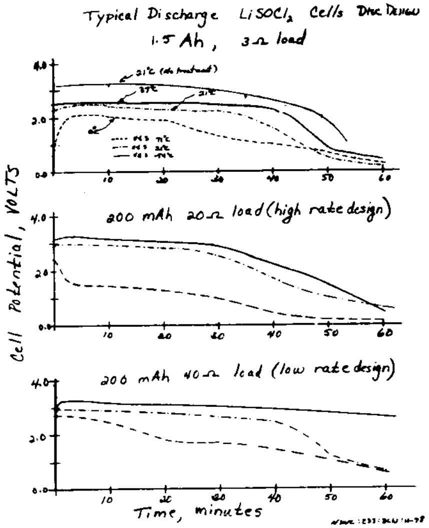


Figure 5-74

NSWC : R33 : DLW : 11-78



NSWC : R33 : DLW : 11-78

Figure 5-75

# TRADEOFF ANALYSIS WITH LITHIUM CELLS

C. Bennett
General Electric

(Figure 5-76)

First of all, this is primarily going to be a presentation of characteristic data primarily on high rate lithium sulfur dioxide designs, basically in the "D" cell and "DD" cell configurations, both before and after much exposure to environmental conditions which I'll talk about later. The cells were all hermetically sealed, glass-to-metal type configuration. Some were stainless steel; some were cold rolled steel, and they were, again, as I mentioned, the standard sizes of both "D" size and "DD" size. This was aimed at looking at the feasibility of using these systems for the Galileo probe conditions.

(Figure 5-77)

The environmental test data that we ran was run not on cells per se, but on batteries in 6 and 12 cell configurations. Most people have been showing cell data, but primarily you get into troubles when you scale up and put these things into series and parallel.

I'll start up at the top. The "DD" high rate cell that we used was a 1500 square centimeter effective cathode surface area. Again, it's difficult to decide exactly what you want to use for a calculation on that. The cells were both new and aged. The aged cells were 14 months, ambient. They were subjected to various vibration regimes, both sinusoidal and random, and various acceleration tests.

The vibration was in the upright, inverted, and cross axis positions. The accelerations were again in those same three positions. The units were also put through a cobalt whole-body irradiator radiation test. This was done on the 6 cell configurations, as far as batteries were concerned. They were tested to four total doses, from $2.5 \times 10^4$ rads, to $1 \times 10^6$ rads. The dose rate was fairly low at 115 kilorads per hour, which was the limitation of the facility.

The units were discharged both during and after exposure to all of these environments, and we have found that there has been no degradation caused from any of these exposures, either the radiation, the vibration, or the acceleration.

(Figure 5-78)

Electrically, the V-1 characteristics of that "DD" cell—these had a 1.25 to 1 lithium-to-$SO_2$ ratio for those that are more concerned about the more recent designs which are going to a balanced electrochemical system.

This is new data at 20°C, and this is on 14 month aged cells, ambient, also at 20°C. As you can see, it's from a current density to 16 milliamps per square centimeter, which is equivalent to somewhere around 24 amperes. These 12 cell batteries were built using both new cells and old cells through the same environment, so that we could minimize the total number of tests that we ran.

The new cells, under a low temperature condition, performed under that type of a curve. This data was found to hold from about 5 percent into the discharge to about the 85 to 90 percent point depth of discharge. Early, the internal impedance on a dc basis is a little higher, and at the end, when you start getting at the end of the capacity curve, the internal impedance again starts going up, so this type of data doesn't hold.

But using this data to size predicted voltage levels on an electrical system in a vehicle at different current loading and temperature loading conditions showed to be fairly accurate within about plus or minus 8 percent on subsequent units that we tested.

(Figure 5-79)

The rest of the data is all going to be on high rate "D" cell designs of two manufacturing techniques. This is LO 26 SH. Those that know will know which ones are made by whom. It's got effectively 660 square centimeters. It's 1.25 approximately to 1, lithium to $SO_2$, and it gave the following V-1 characteristics at these temperatures. This is based on approximately 15 to 20 cells. These were not tested as batteries; these were tested as cells. I might mention that this is a double cathode, double anode construction in that particular cell.

(Figure 5-80)

Similarly, here is corresponding data for another system, which is a G3091B, which had 580 square centimeters. This is of a new balance design, which is 1 to 1 lithium to $SO_2$. Its performance is a little bit lower, probably due to the change in lithium ratios, although the performance as far as expected voltage response as a function of current density is still fairly flat, and the curves are good curves. Again, this data holds over the majority of the depth of discharge range.

(Figure 5-81)

Taking both of these sets of data and cross-plotting them as a function of temperature, you can come up with a curve that looks something like that, showing that the difference in manufacturer doesn't really have that much effect on the overall performance. These two sets of high rate "D" cells pretty much perform similarly.

At the high temperature condition, the 1.25 to 1 lithium to $SO_2$ cell did perform a bit better, but I think, again, that's primarily due to the difference in the ratios.

What it is intended to show here is that over the temperature range that we're concerned about, the performance, as far as voltage fluctuation is concerned, is fairly good, and in scaling these up to battery configurations, you can get very efficient battery systems for use in electrical systems, maintaining fairly tight voltage response over fairly wide temperature ranges.

The one thing that is affected is the cell capacity to 2 volts as a function of discharge rate. This is for both configurations, the 1 to 1 and the 1.25 to 1 designs.

I want to make one mention here. One reason why the low temperature data on these cells shows considerable electrochemical capacity is that these cells were discharged in the battery configuration and they were wrapped in insulator (in this case it was fiberglass and tape) so that it would more or less simulate the condition of the cells being potted in a battery configuration. So they did have the advantage, even though they were stabilized at those low temperatures, of their internal heat actually bringing them to ambient and above conditions for the bulk of the discharge.

These were more or less adiabatic with the low temperature condition and were not insulated, so this isn't to show that there is a significant difference between the two different manufacturing techniques. This is merely a matter of difference in test technique.

There has been some question earlier about what these cells do under high rate conditions. As a function of discharge rate, you can see these are significant rates for a "D" cell, and we consistently get this kind of performance. This is based on better than several hundred cells' worth of data.

(Figure 5-82)

Again, taking this same data and plotting it as a function of current density, so that you can get a more accurate comparison, since the two cells did have different surface areas, and putting them on a common denominator, you do see that in the 20 degree range and in the range where we had consistent data or coincident data, there is very little difference between performance in high rate cells from manufacturer to manufacturer.

Again, these cells are the ones that were insulated, so you can't directly compare this data with these. One reason why there is a minimum amount of data beyond this point, for the Galileo application, we have a maximum discharge rate of approximately 3 to 4 amperes, and these cells which have been run more recently, being of the 1 to 1 design, have only been run to that maximum profile, where these were run at an earlier time and were covering a much wider range of data.

(Figure 5-83)

Also, about three years ago, when hermetically sealed cells were first available, as an early part of a feasibility study for NASA/Ames, we put some heretically sealed cells on storage at three conditions: -15°C, +22°C, and 60°C. In 32 months, we pulled them off and got these capacities as a percent of fresh cell capacity.

There were 50 cells at each temperature. They have not all been discharged yet, but this is based on about 10 of them. So you can see that even at high temperature conditions, there is significantly good capacity retention on this type of a system. At low temperature conditions, the capacity retention is even better.

(Figure 5-84)

I realize that this doesn't adhere to very many of Arrhenius' laws and various other things, but cross-plotting this data, just to change the parametric impetus as far as where your digital or analog parameter is, you can see the effect of temperature and time on the percent of capacity retained.

In the spirit of this being an electrochemical workshop, I'd like to point out one item that hasn't really been mentioned today but I know is commonly known of in the electrochemistry industry as far as the manufacturers are concerned, and that's that I autopsied these cells after these 32 months and found some very startling things.

(Figure 5-85)

At low temperature conditions, the 15°C cells, the internals, looked exactly like they did when they started. There was no difference whatsoever. The 22 degree cells, however, if you looked at the inside of the header after the 32 months, you found that along the outside of it the glass was etched away. Or if you looked at it initially, it had a flocculated substance deposited on it.

If you looked at the cells from 60°C, which is not an unrealistic environment being only 140°F, you find that the entire glass-to-metal seal on the inside is totally covered with a flocculated substance. You take these headers, put them into water, and collect the generated gas that is violently given off, and you find it's hydrogen, which kind of implies that there's a lithium replacement reaction taking place, and you look at what's left of this glass-to-metal seal and you find that it's 60 percent gone.

I'd like to throw this out to the manufacturers: either this afternoon or now, maybe they could give us some idea so to what they're doing to correct this problem, because everybody seems to have said glass-to-metal seals are great, but there is a definite corrosion problem with them.

One other thing that's happened in this: some of these cells were inadvertently laying on their sides. These cells were all upright. I notice that in the cells that were on their sides, the glass-to-metal seal was totally gone. So it seems to be orientation sensitive, and if it does occur (which has been shown to occur) at 22°C in an upright position where the electrolyte is not in contact with the glass surface, what happens when it is, say, in a free space environment for a long period of time? Does the reaction take place much faster, and say that there is some catastrophic failure mode that happens at some life, when that glass gets thin enough that it can no longer support the pressure of the cell.

Now, if anybody would like to look at them, I have those headers with me. I can show them to you later if you're interested.

## DISCUSSION

TAYLOR: Could we go back a couple of figures to your capacity versus rate? Between—temperature, I think it is.

BENNETT: Which one?

TAYLOR: Well, the one which shows capacity versus discharge rate in amps, not milliamps per square centimeter, as a function of temperature, discharge temperature.

BENNETT: Okay, that's this one.

TAYLOR: As you were going through the paper, I just wanted to make a couple of comments, and one of them here is not relevant to your latter statements but relevant to people who are interested in what the system can do, and it is that if you take the lower curve at -28°C, you can see that there's pretty much an independence of capacity on discharge rate.

People might assume, then, from that that if you go left to lower rates, you don't really climb up much in capacity.

BENNETT: That's not true.

TAYLOR: But in fact, that's not true, and I wanted to make that point. You're at the bottom of the curve.

BENNETT: Yes. For my application, I was interested primarily in rates from here out. This curve does, in fact, taper up like this, and you will find that the low temperature performance at low current densities is quite good on these systems.

TAYLOR: I wanted to make that point. Thank you very much.

BENNETT: Yes. I'm sorry, I should have made that point at that time. Thank you, Harry.

TAYLOR: Any other points you'd like to make?

BENNETT: Any other points you'd like to make?

TAYLOR: Go on to the next—I think the storage at minus 15, 22, and plus 60.

BENNETT: Okay.

TAYLOR: I did want to make a point about this, in that you've extrapolated on those dotted lines.

BENNETT: Primarily what I wanted to show is that the data to this point is real time data, and as far as what I've seen, this is the longest data that's available on hermetically sealed $SO_2$ systems as a function of temperature.

TAYLOR: Okay.

BENNETT: And it does show very, very good electrochemical independence, shall we say, on life compared to other electrochemical systems. It shows that these cells have the potential of storing extreme periods of time.

However, the other problem that I brought up was that there seem to be some potential failure modes that could crop up, and that is the one of the glass-to-metal seal problem.

TAYLOR: Okay. We'll come to that. You are saying what I hoped you would say in terms of capacity of retention. In fact, if I were to draw those curves, I'd be inclined to draw them more sharply at the start and then leveling out.

BENNETT: Yes.

TAYLOR: Because, for an example, if you take a couple of months' storage at high temperatures, say, 160°F, you would think that you're going to have about 20 percent of your cell capacity after a year.

BENNETT: You actually get an increase.

TAYLOR: In fact, you've got far, far more than that.

BENNETT: Yes.

TAYLOR: So the maximum decaying capacity is seen in the initial periods of storage.

BENNETT: Actually, not on these cells but other cells that were in this program, which were crimp sealed cells which were not hermetically sealed, that were stored at the high temperature conditions, I started pulling them very, very early (like at one, two, and three week periods), and up to that point, I found increases in capacity at 60 degrees, up as high as 20 percent.

TAYLOR: You've got me there. I'm not going to argue with it. Sounds good.

BENNETT: But then the rate of degradation increased very rapidly compared to the other temperatures, so maybe there is some high temperature stabilization period that does something electrochemically as far as balancing out what the equilibrium that is reached is concerned. Maybe it gets it there a lot faster.

TAYLOR: Okay, I don't know. You're talking about your particular data.

The last question, the question of glass-to-metal seals: I think I have come across those saying that perhaps everything is not rosy in the garden, but if you're doing those seals, you can get glass-to-metal seals for, I think, at least the $SO_2$ system which will stand up very well. There are a couple of points I want to make.

BENNETT: Do you have data on that in inverted positions at high temperatures?

TAYLOR: Yes.

BENNETT: I'd like to see it.

TAYLOR: Okay.

BENNETT: Because I have an application for the Galileo mission that's directly impacted by that.

TAYLOR: Okay. Let me make a couple of points, however, with regard to your graphs first of all, and that is that 32 months at 140°F was a hell of a storage period.

BENNETT: Sure is.

TAYLOR: Perhaps not something that one would realistically expect, however.

BENNETT: However, I might say that the attack on the glass is apparent after as little as one month at that temperature.

TAYLOR: Agreed.

BENNETT: And my question in bringing it up here is: what happens between ambient and 140°F, since it obviously happens at ambient? And a lot of our environmental conditions for a lot of the applications involve periods of storage (like tropical storage for Army cells) which could be in the 100 to 120 degree range for fairly long periods of time.

TAYLOR: You mean three years, for example?

BENNETT: In uncontrolled conditions, sure.

TAYLOR: Three years at 140, I mean.

BENNETT: No.

TAYLOR: Thank you.

BENNETT: But I'm saying, what's the interpretive process between those two temperatures? Obviously, it's a tough—

TAYLOR: Well, I don't have full data on it; I think you would understand that. I would say that obviously the higher temperatures will give you more of a problem. You can quote your three years at 140; the best I can quote, frankly is one year at 160°F, and we do have to see the attack. We don't have attacks such as you run into a problem in terms of very large capacity losses, and no place was there any leakage.

Now, I think everybody would accept that we're not damned fools: we have cut the cells apart; we have seen the seal corrosion problem. The impression I'd like to convey here is that you do have a baseline, and that baseline has a very good storage capability, as you have shown from your data.

BENNETT: Yes.

TAYLOR: Recognizing, then, that we still have seen the problem and worry about even longer terms, even if they are unrealistic, you'll just have to take my word for it when I say that there are solutions to that problem, not just one, but several solutions to the problem. I don't know whether I should quote our manufacturing people or not, but these will be coming along the line in the not-too-distant future.

BENNETT: Good.

TAYLOR: So again, I was harping back to what George Methlie said about there being no oxides, for example, which will be stable thermodynamically against lithium. I would dispute that point. What I am definitely saying to you is that there are seals, in my opinion, which will stand up much better than you see there.

The final point is that what you see there is pretty damned good already.

BENNETT: Yes, I agree with that.

TAYLOR: Okay.

BENNETT: I agree with that. However, when you've got a seven-year mission, as in our particular case, we're not that concerned about it, in that the bulk of our storage time is at free space environment, which is very low temperature (0 to -20°C). We can make a story that we don't have that kind of a problem.

But I was thinking more about the terrestrial applications, primarily in the Army and Air Force and some of the other utilizers, where they do have uncontrolled orientation and they do have uncontrolled storage, in silos and in hangars and on air strips. If you look at the spec requirements on things for buoys and sonobuoys, some of the temperature times and durations get pretty out landish when they talk about storing these things on air strips in the Sahara Desert for three years. It's ridiculous. But there are no temperature controls yet specified, and I think there should be, and possibly orientation controls.

TAYLOR: Well, again, let me finish up by saying we have seen the problem; we have done something about it, and you can, in the not-to-distant future, get cells that are even better than what you see there. Trust me, Chuck, trust me.

BENNETT: Okay.

LEUPOLD: The specification for the sonobuoy is five years at 70°C.

## CHARACTERISTIC DATA

## FOR

## LITHIUM-SULFUR DIOXIDE CELLS

- HIGH RATE DESIGNS
- HERMETICALLY SEALED
- ENVIRONMENTALLY TESTED
- STANDARD SIZES
    - "D"
    - "DD"

Figure 5-76

- TESTED AS CELLS AND BATTERIES
    - SIX AND TWELVE CELL CONFIGURATIONS
- "DD" - HIGH RATE (1500 $CM^2$)
    - NEW
    - AGED (14 MONTHS AT AMBIENT)
- VIBRATION
    - SINUSOIDAL
        - 15 g PEAK AT 2 OCTAVES PER MINUTE
    - RANDOM
        - 12.3 g RMS
        - 0.6 $g^2$/Hz (35-100 Hz)
        - 0.05 $g^2$/Hz (185-2000 Hz)
        - FOUR (4) MINUTES PER AXIS
    - ACCELERATION
        - 500 TO 800 g's (GRADIENT ACROSS UNIT)
        - TWO AXIS
        - SIX (6) SECONDS PER LEVEL
    - RADIATION EXPOSURE TESTS
        - APRF COBALT WHOLE-BODY IRRADIATOR
        - FOUR LEVELS OF TOTAL DOSE
            - $2.5 \times 10^4$ RADS
            - $5.0 \times 10^4$ RADS
            - $1.0 \times 10^5$ RADS
            - $1.0 \times 10^6$ RADS
        - DOSE RATE OF 115 KRADS (Si) PER HOUR
        - DISCHARGE DURING AND AFTER EXPOSURE

Figure 5-77

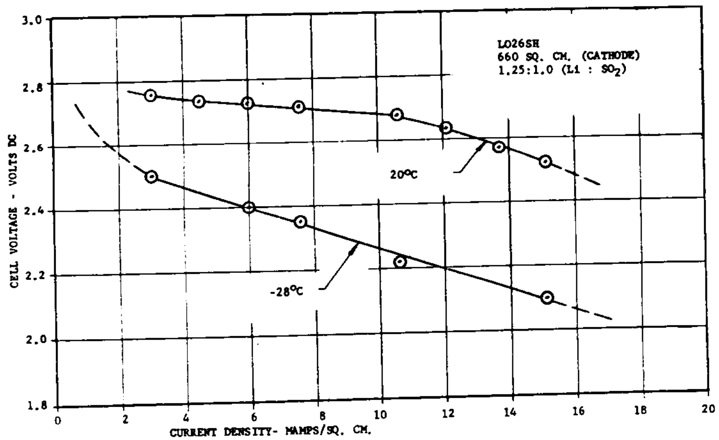


Figure 5-78

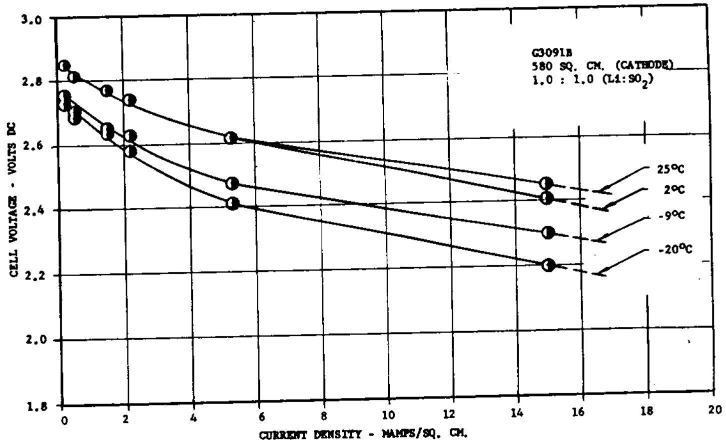


Figure 5-79

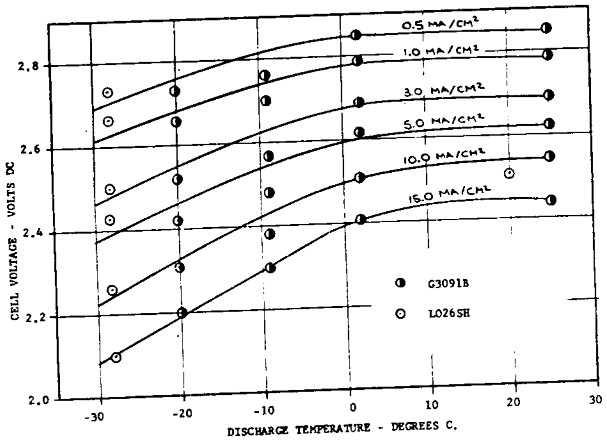


Figure 5-80

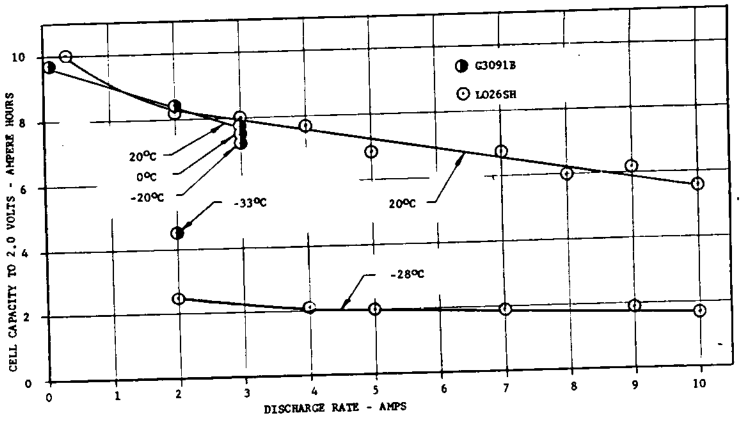


Figure 5-81

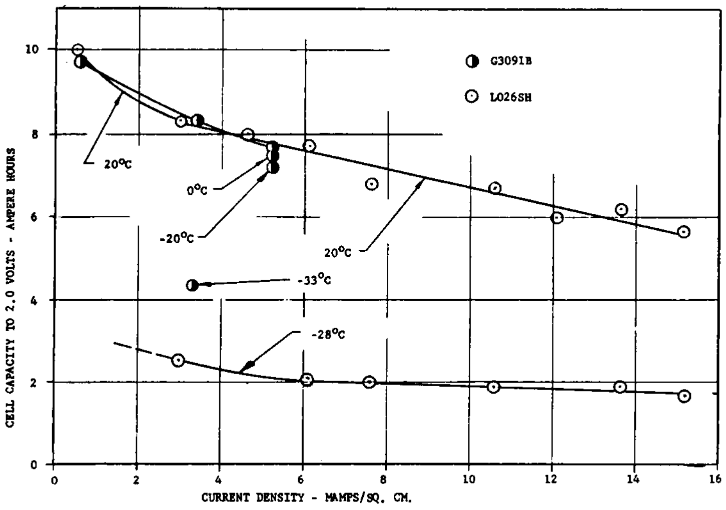


Figure 5-82

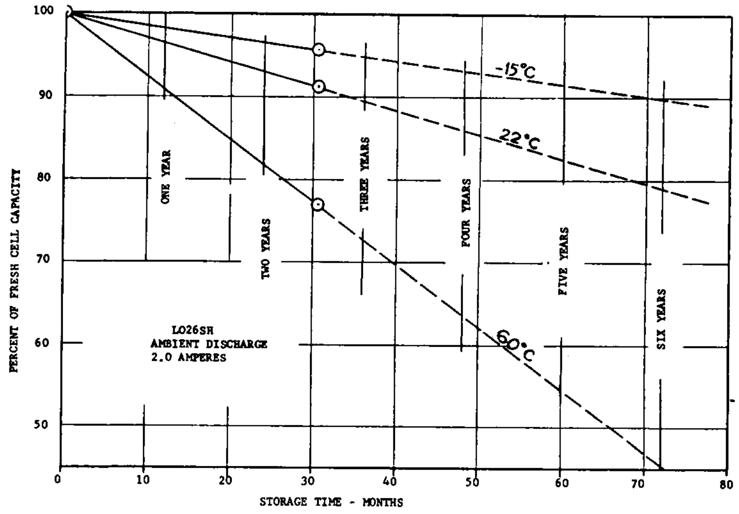


Figure 5-83

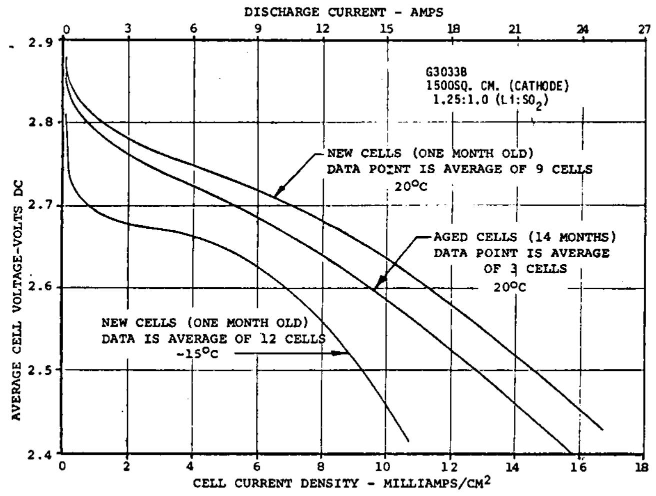


Figure 5-84

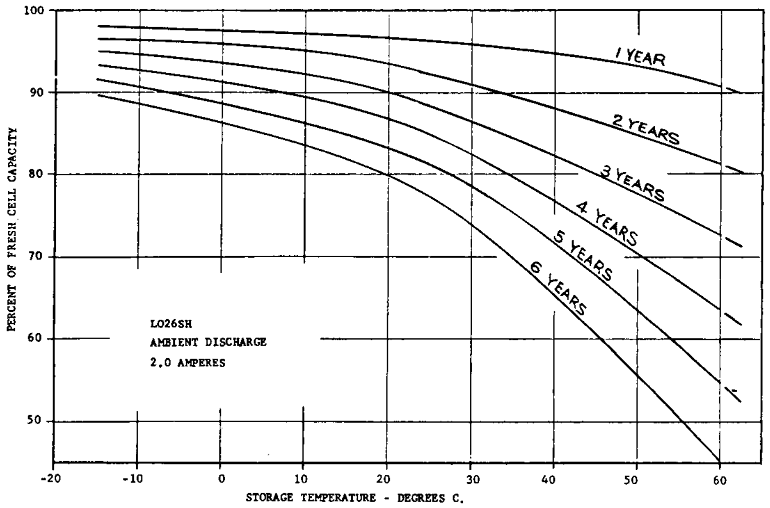


Figure 5-85

# LIFE TESTING OF MALLORY CELLS

D. Dugan
NASA/Ames

(Figure 5-86)

The purpose of this test was to assess the effects of storage time, storage temperature, vibration, discharge rate and temperature, and capacity of high-rate "D" size lithium sulfur dioxide cells. The range of those temperatures was more or less dictated by the Galileo probe environment during transit from Earth to Jupiter and then during the coast phase from after separation (150 days plus or minus 50 days) at about 0 degrees or a little less, and then for the first part of the environment it would go down to about 0 degrees ambient temperature outside with the water clouds, and then on down where the temperatures will start rising.

But it's only a thirty-minute trip down to 10 bars (thirty minutes or a little over), and the mission is essentially over there, except we hope to get down to 20 bars by 45 minutes, barring unforseen accidents.

The procedure was to screen, first of all, at a 1 amp rate to a plateau voltage in order to eliminate the nonaverage cells. We struck for a 5 percent variation at the maximum. We wanted to throw out cells that would be more than that.

We subjected one-half the number of cells to sinusoidal and random vibrations expected during launch by the space transportation system. That's very similar to the one Chuck Bennett presented.

Store cells at room temperature, 0°C, and -18°C up to seven years to get a spread of the variation in temperature. Test cells at the same temperature at which they are stored and at discharge rates of 2, 4, and 6 amps. That is perhaps different from the previous examples, where they were stored at various temperatures but then brought up to room temperature and tested at a given rate, so if you see some differences here, I think they might be due to that.

(Figure 5-87)

Here are the historical data. We obtained 800 of the $LO_2S_6$ sealed and high rate cells, purchased December 1976. We had two different shipments: one about 330 cells, and the remainder later. The cells were screened between June 3 and 14, 1977. There should be 387 of the cells that were stored; that would be half of the cells that we selected. They were vibrated June 21st to June 28th, 1977.

Three boxes, 54 cells altogether (there's 18 cells to a box) tested October 14th, 21st, 1977. That was our basis. We called that zero time, although the cells were about eight months old at that time, plus whatever the data of manufacture was. I'm not sure.

DUGAN: Three boxes were tested six months later and three boxes just recently, October 31st to November 8th. Finished up on Thursday, Friday was a holiday for everybody but me.

(Figure 5-88)

To give you an idea of what the arrangement of the test was, we selected the boxes which would hold the 18 cells. Three of them (one, two, and three) were all at 1 amp, and the same arrangement was used for screening. But for the tests that we ran (2, 4, and 6 amps), one, two, and three were at 2 amps; four, five, and six at 4; seven, eight, and nine were at 6, and those were called the control cells which were nonvibrated. They were just received as received and not changed in any other way.

On the right-hand side, ten, eleven, and twelve are the 2 amp; thirteen, fourteen, and fifteen were the 4 amp; and sixteen, seventeen, and eighteen were individually tested at 6 amps. Those constituted what we called the test group that had received the vibrations.

(Figure 5-89)

The results of the screening test: all the 800 cells that we ran were acceptable. The plateau voltage at 1 amp was 2.800 volts, plus or minus 0.008—8 millivolts. The maximum difference from the average voltage was minus 0.039 volts, or that constituted about 1.39 based on the average. 774 cells, 43 boxes of 18 cells each, were selected for further tests.

(Figure 5-90)

This gives you an idea of the data that we received from the tests, just an example. The first three cells at the top are the 2 amp, and you can see how they fall off eventually out here. The time scale is ten minutes for every major division from the start.

The 4 amp cells on the control group were next, and then the 6 amp have this peculiar little saddle in their voltage characteristics. That's voltage on the on the left-hand ordinate and time on the bottom, by the way. So you can see how the cells went.

The curves down here are the thermistors that we had on the 4 amp middle groups (that would be number five), and p. 132 also, similarly, on the test group. We had only four thermistors available for the number of channels we had. So you can see how the temperature goes up as we approach the 2 volts limitation at which we made a cut-off, and the temperature immediately drops then from that point on. This was at minus 18 degrees, by the way.

(Figure 5-91)

First of all, here are the data that we have based upon the time that we stored them (up to one year, 1.05 years). On the left-hand vertical scale, we have the average capacity of the three cells at each of the temperatures. The first one is the 2 ampere one, and the top ones will be the room temperature (the circles); the next group down will be the 0°C (squares); and the minus 18 degrees are shown with the diamonds. I'd better show the top there a little bit.

(Figure 5-92)

You see, there, I also put on the aerobars. The top one represents the maximum reading of that particular cell in capacity, and the lower bar represents the minimum, whereas the symbol includes the average. Not much difference at 0 degrees or at room temperature, for example, but at 0 degrees we had an anomaly, and I have more or less eventually thrown out that particular group as being nonrepresentative. Something happened there. I don't know if it was the test procedure or if it's a supercell that Mallory makes that responded that way at six months. So this is not particularly typical at either 2, 4, or 6 amps, as we'll see.

Now, there's one peculiarity here that seems to persist, and that is this one at minus 18 degrees, where we get a definite drop-off much greater than at 0 degrees, which is anomalous. No one seems to agree with that, although as I say, we're not testing at room temperature after the cells have been cooled and stored. We're testing at the same temperature at which they were stored, and at 0 degrees you can notice that there's a drop-off in capacity, as you would expect, but the capacity drop-off seems to be more as you go on in time, which is anomalous, and I'd like some comments on that.

(Figure 5-93)

You see much of the same thing at this level. This is the test group at 2 amps, and I think we'll see that later on when I compare the two. It shows much the same thing. This high spot, again, occurs even though we are with the test cells. It should be the same.

(Figure 5-94 and 5-95)

At 4 amps, we get a little falling off at the low temperature. That's a little surprising, but the aerobars are quite wide and one could probably fair a curve down, or it might be a tapering off. You notice I didn't draw any lines on these symbols. I have to get more data to verify how the thing is behaving with time.

The aerobars are quite wide on this, and I noted that at the lithium workshop meeting in August here. They're about the same, perhaps not quite as bad as they were in the first. They seem to improve with age.

The same is true for 4 amps with the test group. Again, we don't get that falling off, that little difference there. We do get a straight line relationship of the averages, at least. The 0 degree one could fair probably out to a straight line and not represent too much of a loss.

Did I leave out that one for 0 degrees in this one? I don't see it.

(Figure 5-96)

To make a long story short or a short story shorter, I'll go to the final chart here, which compares the loss in capacity or the remaining capacity, I should say, after one year, just taking the zero baseline and the one-year data.

At the bottom, we have the change in capacity or the remaining capacity in percent. Notice at the room temperature at the top and the 2 amps, there's practically no change either in the test cells, and the control cells look much the same; no viable difference. The same for the control and test cells at 4 amps. There's a little loss in capacity indicated; whether it's true or not, I'm not sure. At 6 amps, we have even more loss indicated, and the test and control cells look essentially the same.

But as we get down to 0 degrees, we have an anomaly there, which does not include the anomaly I spoke of before at 0 degrees. We get over 100 percent on the control cells, but the test cells indicate a little loss, and at 4 amps it's more of a loss on the control and not so much on the test. There again, at 6 amps we get another anomaly.

It seems that, as these cells were stored in the boxes with no insulation except for that little sleeve that they put around them, they responded to the temperature by heating a little bit at 6 amps more than they did at the 4 amps, and of course much more than they did at the 2 amps. So there may be some gain in performance from that self-heating.

At 18 degrees, we had, as we saw on the other charts, considerable loss at 2 amps and not so much at 4 amps, and again, not so much at 6 amps, which may be due to that self-heating.

Another thing to note on this is that, at the lower temperatures, we are getting more of a loss apparently on the test group of cells than we are on the control group, which may or may not be indicative. We noticed that soon after the baseline, there was practically no difference between the test group and the control group, but as time goes by, it may become more significant.

(Figure 5-97)

So we can make the following tentative conclusions. The capacity appears to decrease with storage time more with high than with low discharge rates, and the results so far indicate that cells stored and discharged at low temperatures lose larger percentages of their capacities with storage time than those at higher temperatures. There appears to be more loss of capacity with time in cells subjected to vibration at time zero than in cells not vibrated, especially at lower discharge temperatures.

More data at longer storage times may prove or disprove the above conclusions.

## PURPOSE

TO ASSESS EFFECTS OF STORAGE TIME, STORAGE TEMPERATURE, VIBRATION, AND DISCHARGE RATE AND TEMPERATURE ON CAPACITY OF HIGH-RATE "D" - SIZE LITHIUM SULFUR-DIOXIDE CELLS

## PROCEDURE

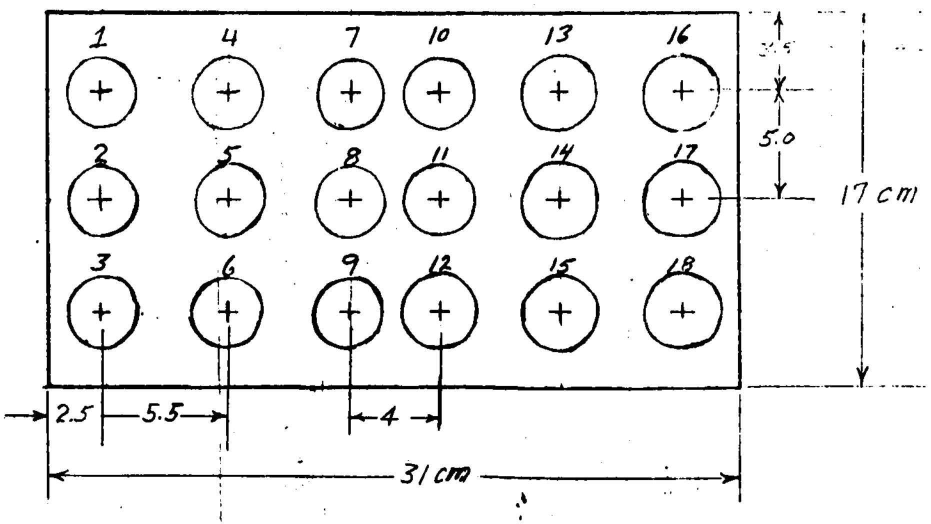
1. SCREEN CELLS AT ONE-AMP RATE TO PLATEAU VOLTAGE IN EFFORT TO ELIMINATE NON-AVERAGE CELLS.
2. SUBJECT ONE-HALF OF THE NUMBER OF CELLS ACCEPTED TO SINUSOIDAL AND RANDOM VIBRATIONS EXPECTED DURING LAUNCH BY STS.
3. STORE CELLS AT ROOM TEMPERATURE, 0°C AND -18°C UP TO SEVEN YEARS.
4. TEST CELLS AT SAME TEMPERATURE AT WHICH THEY ARE STORED AND AT DISCHARGE RATES OF 2, 4, AND 6 AMPS.

**Figure 5-86**

## HISTORICAL

- 800 L026SH D CELLS PURCHASED DECEMBER, 1976
- CELLS SCREENED JUNE 3 - 14, 1977
- 380 CELLS VIBRATED JUNE 21 - 28, 1977
- 3 BOXES (54 CELLS) TESTED OCT. 14 - 21, 1977 AT RT, 0°C, AND -18°C, 3 CELLS OF EACH GROUP AT 2, 4, OR 6 AMPS.
- 3 BOXES TESTED APRIL 13 - 18, 1978
- 3 BOXES TESTED OCT. 31 - NOV. 8, 1978

**Figure 5-87**



*Arrangement of cells in box*

**Figure 5-88**

## RESULTS OF SCREEN TEST

- ALL 800 CELLS WERE ACCEPTABLE.
- PLATEAU VOLTAGE AT 1 AMP WAS 2.800 ± 0.008 V.
- MAXIMUM DIFFERENCE FROM AVERAGE VOLTAGE WAS -0.039 V., OR -1.39%
- 774 CELLS (43 BOXES OF 18 CELLS EACH) WERE SELECTED FOR FURTHER TESTS.

Figure 5-89

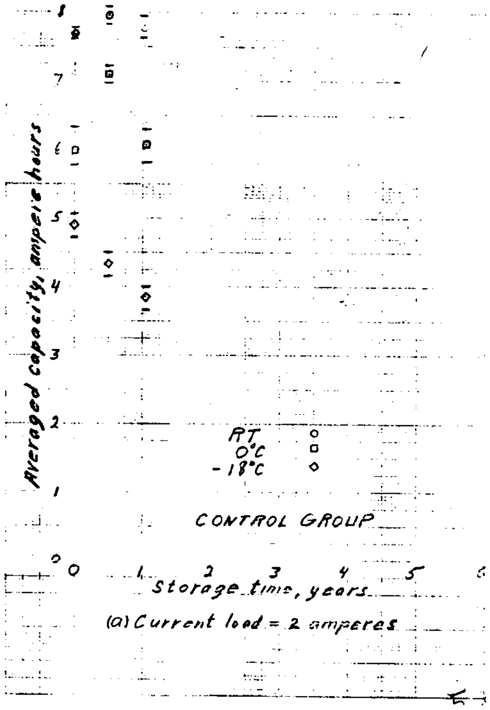
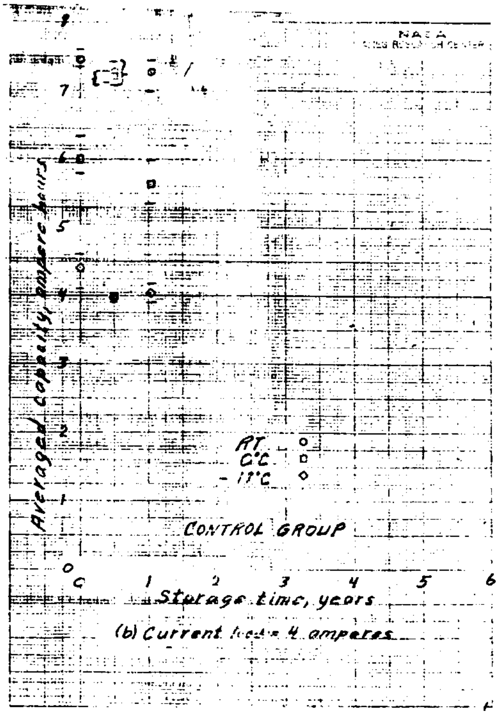


Figure 5-90



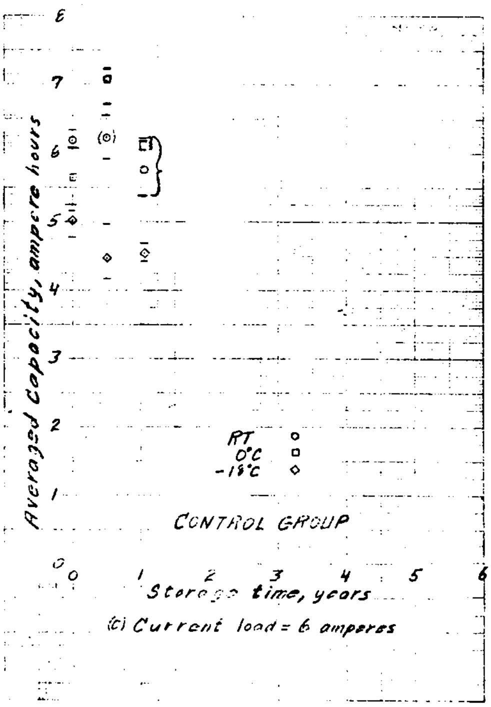


Figure 5-91

Figure 5-92

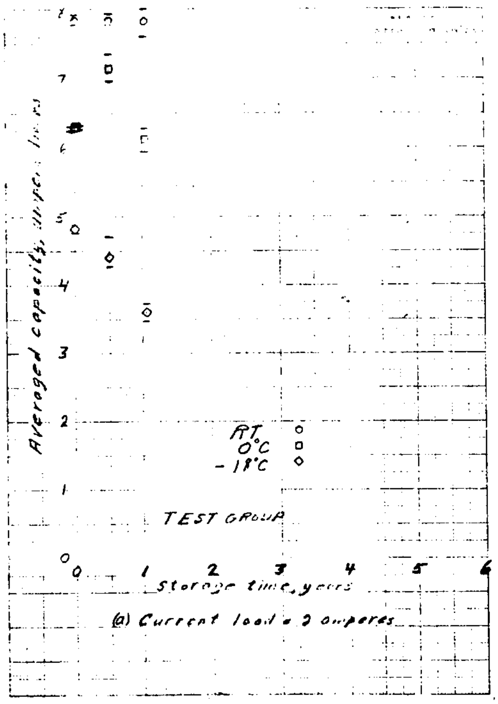


Figure 5-93

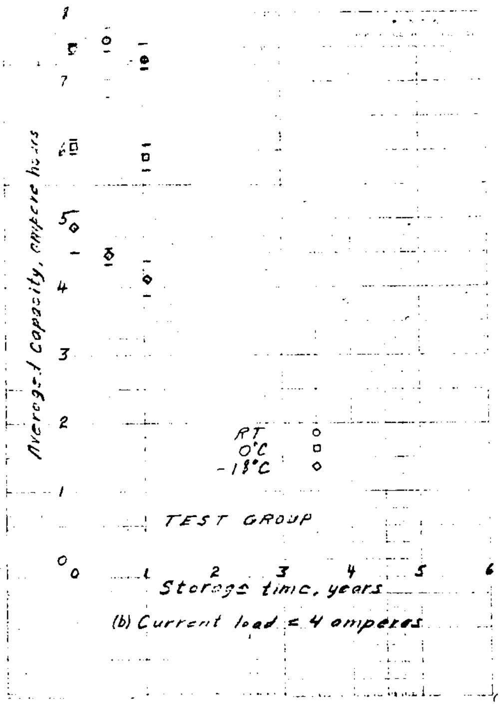


Figure 5-94

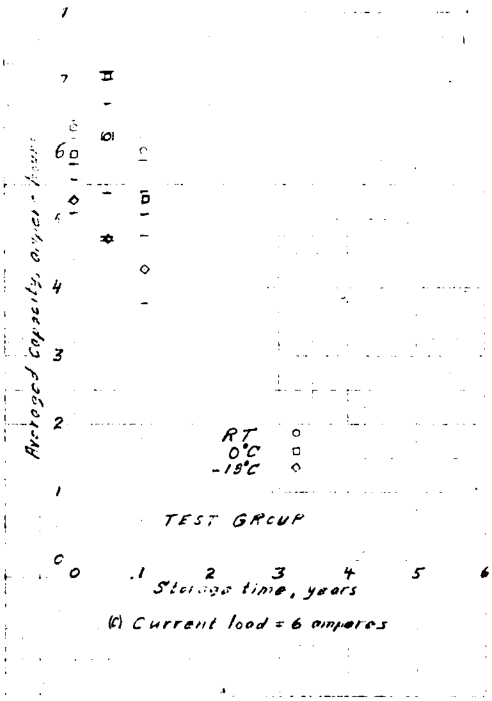


Figure 5-95

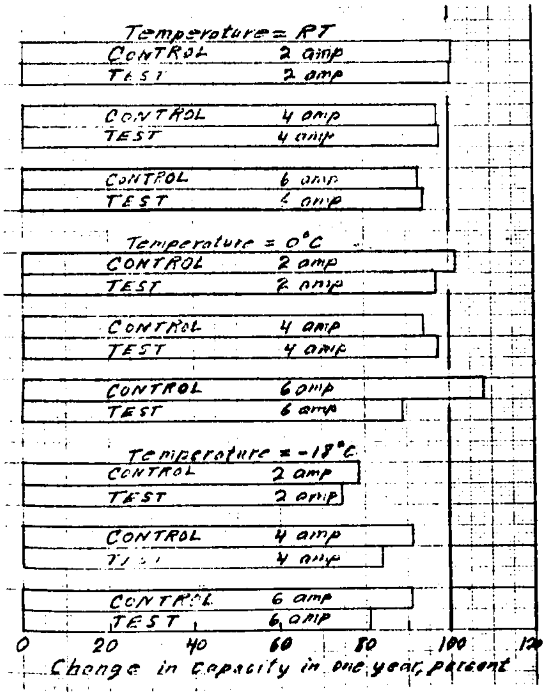


Figure 5-96

## CONCLUSIONS

## (TENTATIVE)

- CAPACITY APPEARS TO DECREASE WITH STORAGE TIME MORE WITH HIGH THAN WITH LOW DISCHARGE RATES.

- RESULTS SO FAR INDICATE THAT CELLS STORED AND DISCHARGED AT LOW TEMPERATURES LOSE LARGER PERCENTAGES OF THEIR CAPACITIES WITH STORAGE TIME THAN THOSE AT HIGHER TEMPERATURES.

- THERE APPEARS TO BE MORE LOSS OF CAPACITY WITH TIME IN CELLS SUBJECTED TO VIBRATION AT TIME ZERO THAN IN CELLS NOT VIBRATED, ESPECIALLY AT LOWER DISCHARGE TEMPERATURES.

- MORE DATA AT LONGER STORAGE TIMES MAY PROVE OR DISPROVE THE ABOVE CONCLUSIONS.

Figure 5-97

# LARGE CELLS AND THEIR PERFORMANCE

F. Goebel
GTE Sylvania

I want to introduce to you some of the large primary cells presently made at GTE Sylvania, ranging in capacity from 2000 to 10,000 ampere-hours. I think that is presently one of the largest primary cells ever built.

(Figure 6-1)

This figure shows you a schematic design of an earlier design of a 10,000 ampere-hour cell, hermetically sealed, stainless steel container, with a vertical orientation of rectangular plates. The dimensions were 13-1/3 by 6 by 27 inches. One of the newer versions (I'm sorry that they don't come out here in the projection too good) is 12.3 times 9 times 11.6 inches, which adds up pretty much to the same volume.

You see on top of the cell a fairly large space that is provided for the excess of electrolyte since, during discharge, you run into a volume shrinkage due to density changes of the products.

(Figure 6-2)

The weight is approximately 140 to 150 pounds. This is the actual size of a two-case cell, a demountable unit which we test presently in our laboratories. For economical reasons, we make it a demountable unit, to be able to take it apart and do some autopsy on it at the end of the test. As a reference, we have here a keychain on it to show you how big the cell actually is. That is a 2000 ampere-hour cell.

Comparing the 2000 and the 10,000 ampere-hour cells, the height is identical in both; they are just scaled up or scaled down by the factor of 5.

(Figure 6-3)

This is an actual stack as we tested it in a 2000 or 10,000 ampere-hour cell arrangement, anode plates with their terminals on them. And you see the arrangement of the lithium on the substrate. We obtain our lithium in strips, and you still see how the strips run down the plate. In the back, the dark ones are the cathode, separated from the anode by glass mat insulators. That is an actual stack as it was tested in one of the cases, the cell arrangement I showed you before.

(Figure 6-4)

This is a group of hermetically sealed 10,000 ampere-hour cells as we have tested them about three years ago at the Hill Air Force Base. They provide you an energy package of about, I think, 300 kilowatt-hours, and we have tested these cells in the form of batteries, putting 5 bells in series.

(Figure 6-5)

The package in the form of a battery looked like this. These are the five individual cells connected with heavy copper bars in series. They were contained in one of these heavy steel boxes and then discharged at the rate of approximately 27 amperes. That is a nominal rate of this cell.

(Figure 6-6)

The new versiono f a 10,000 ampere-hour cell will be arranged in such a module for the Minuteman program. A module consists of three submodules. Each submodule will contain three 10,000 ampere-hour cells. All the nine cells (three times three is nine cells) will be connected in series to provide you with battery voltage of about 30 volts. The energy density of such a package is between 250 and 280 watt-hours per pound, or about 550 watt-hours per kilogram.

On the side of this module you see a little box, an attachment. A tube comes out of the box and goes back to the cells. That box incorporates a chemical scrubber in case of pressure build-up in the cell in the form of $SO_2$ or vapors caused by high temperatures in the cell. The cell will vent into this scrubber and all the gases will be chemically absorbed there.

(Figure 6-7)

To give you an idea what these cells can do on tests, here is a performance sheet obtained on a 2000 ampere-hour cell. Voltage, cell pressure, temperature, and room temperature are plotted as a function of time while the cell was on discharge.

To go to the first curve, which represents the voltage characteristic during the total discharge cycle, it is a very flat one, and a sudden drop, a very short run-out, since it is a lithium limited design. The cell temperature was in the reasonable vicinity of the room temperature, maybe 2 degrees or

2 1/2 degrees higher than the room temperature, and cell pressure was almost at an equilibrium with the outside. Initially we had a slight dip into a vacuum, but then a pressure recovery to the equilibrium. At the end, where the voltage is dropping to about 1 volt, we see a slight increase in temperature, and this results in a slight increase in pressure as well, but it is not critical at all. It is still in the range between 1 and 2 psi.

(Figure 6-8)

The same characteristic we obtained on one of the newer versions of the 10,000 ampere-hour cell. The voltage characteristic is again very flat at a nominal discharge rate of 40 amperes, very flat characteristic until the end and a sudden run-out. Between 3 watts and 0 volts, we obtained the capacity of less than 25 ampere-hours, which means a high utilization of usable ampere-hours above 3 volts. That's what the customer asked for.

Cell temperature is very reasonable; cell pressure was not plotted, since the cell pressure is immediately related to the cell temperature and was in a very reasonable range.

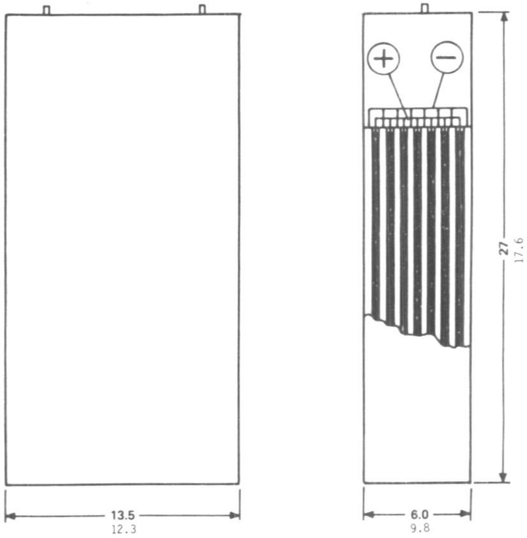


Figure 6-1

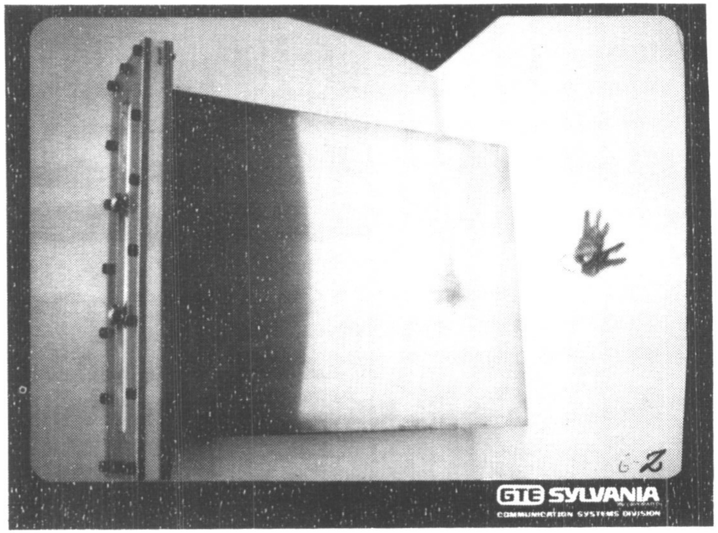


Figure 6-2

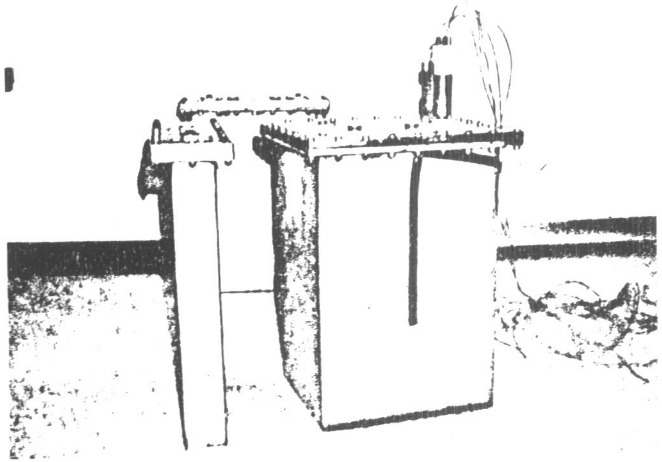


Figure 6-3

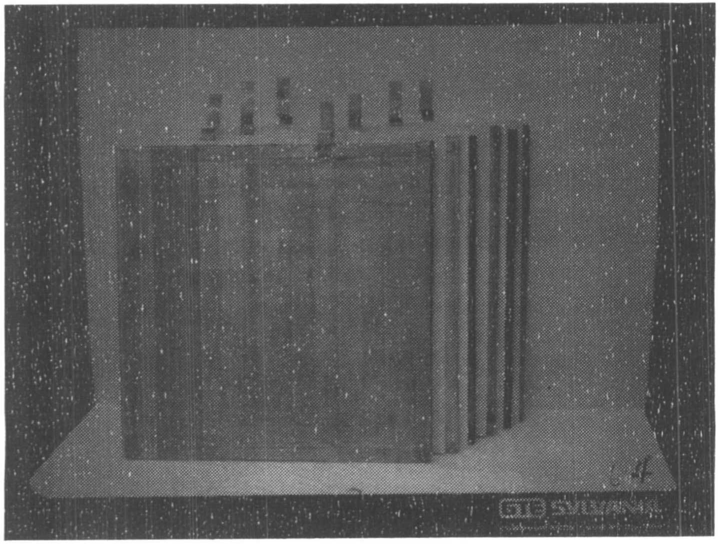


Figure 6-4

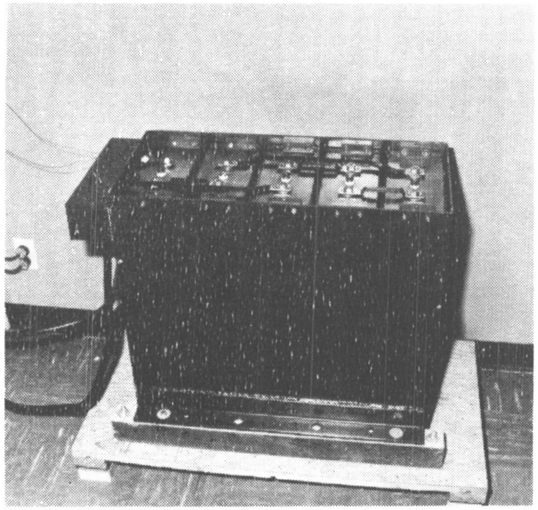


Figure 6-5

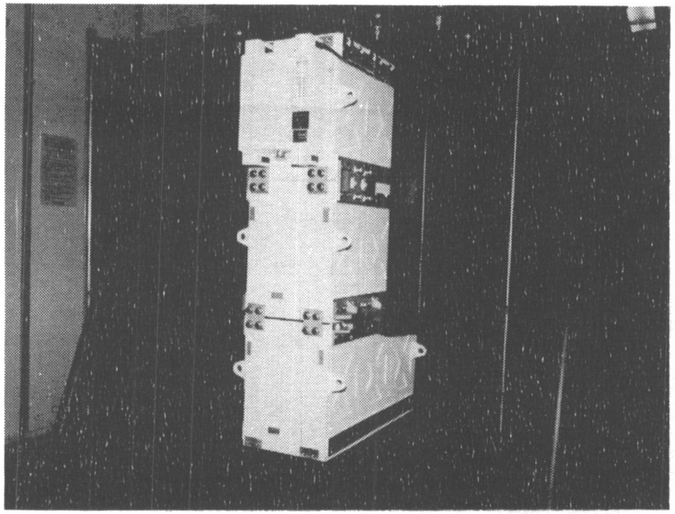


Figure 6-6

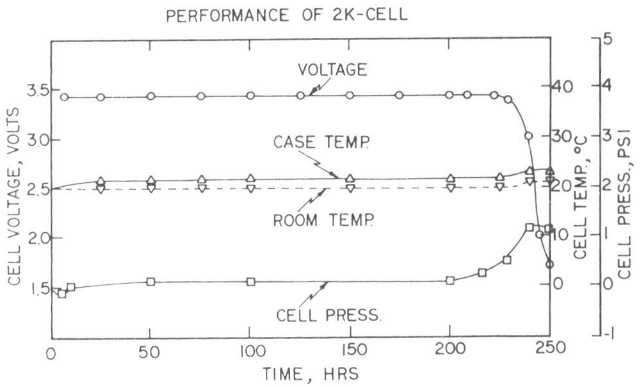


Figure 6-7

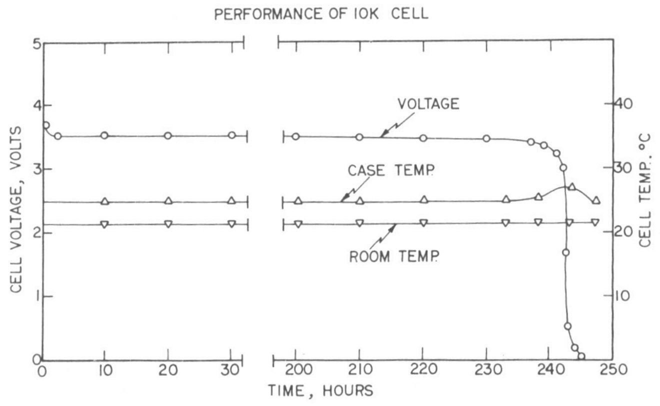


Figure 6-8

# SAFETY AND ABUSE TESTING

G. Younger
GTE Sylvania

GTE Sylvania has initiated, as part of its engineering test program, a series of abuse tests on large lithium thionyl chloride cells. My presentation will concentrate on the performance data obtained in testing rectangular 2000 and 10,000 ampere-hour cells.

The purpose of these tests was to demonstrate the cells' capabilities to safely withstand conditions of abuse that may be encountered during storage, handling, and transportation environments.

(Figure 6-9)

Figure 6-9 graphically illustrates the test results obtained on an early design 2000 ampere-hour cell that was discharged at an excessive rate. A 12 milliohm resistive load was extremely applied across the cell terminals and it was maintained while continuously monitoring the voltage, current, internal pressure, and case temperature.

As shown by the curve, the cell delivered a current slightly below 200 amps for a period of 40 minutes before dropping to its 3 volt cut-off level. Now, at this point, the voltage and current dropped rapidly for approximately 10 minutes, and then continued to decrease at a slower rate. After 90 minutes of testing, a brief interruption in current flow and voltage occurred. Now, this was analyzed to have been caused by a temporary internal short with a corresponding voltage drop. During this period, most of the discharge current bypassed the monitoring circuit.

With the resumption of current flow and voltage, it indicated a disappearance of that internal short. It was burned off. Cell case temperature showed a steady rise throughout most of the testing, with a slight acceleration while experiencing the internal short. Cell pressure was not affected during the initial period of steady discharge. After 50 minutes, pressure began to rise, reaching a peak pressure of 19 psi, at which point testing was terminated.

The cell, being sensitive to pressure because of its shape and the absence of a pressure relief valve, doubled in thickness during the test, but it showed no signs of rupture or leakage. A post-test inspection verified the cell's ability to safely withstand the temperature and pressure it generated during an excessive discharge rate.

(Figure 6-10)

Figure 6-10 summarizes the various tests performed on 2000 and 10,000 amp-hour cells, which incorporated updated design changes.

For the purpose of this presentation, I have chosen to discuss a few of the tests that demonstrate extreme conditions of abuse.

(Figure 6-11)

A 2000 ampere-hour cell in a nonoperating configuration was subjected to a vibration test in three axes. Prior to the vibration test, a one-hour 8-amp discharge was performed to confirm proper operation of the cell. The cell was then subjected to vibration in each of its three mutually perpendicular axes. Cell voltage, temperature, and pressure were monitored during the course of this test. The frequency of vibrations ranged from 5 to 2000 to 5 hertz, traversed at a rate of one octave per minute. The vibration level applied was 5 G's peak from 5 to 50 hertz, and 2 G's peak from 50 to 2000 hertz.

After each axis of vibration, the cell was discharged for one hour. This was to verify cell performance. There was no change that was observed in voltage, case temperature, or pressure during the performance of the vibration test, and a post-test inspection revealed no evidence of electrolyte leakage or cell case deformation.

(Figure 6-12)

Figure 6-12 represents the data obtained on a 2000 ampere-hour cell that was subjected to a full discharge at a constant current of 8 amps, following an overdischarge equivalent to 50 percent of the capacity obtained on discharge.

The cell voltage, discharged current, internal pressure, and case temperature were monitored for the duration of discharge and overdischarge. The test actually lasted for a total of 380 hours, of which the cell voltage remained positive for 252 hours. During overdischarge, the voltage remained at a constant value of -1.7 volts for almost the entire period.

Cell case temperature and internal pressure remained constant during the normal period of discharge. A steep increase in temperature and pressure, peaking at 35°C and 4.5 psi, coincided with the onset of overdischarge, then continued to decrease for the remaining portion of the test. No leakage, venting, or adverse condition was noted during or after the overdischarge test.

With reference to the tests shown on Figure 6-11, a 10,000 ampere-hour cell was subjected to a transportation shock test. Prior to the shock test, as in vibration, a one-hour 36-ampere discharge was performed to confirm proper operation of the cell. The cell, in its normal upright position, was subjected to six 100-G shock pulses, two in each of its three mutually perpendicular axes. The shape of the shock pulse was terminal peak sawtooth and was 6 milliseconds in duration.

Here again, after each axis is shocked, the cell was discharged for one hour, verifying operational performance. No change was observed in voltage, case temperature, or pressure during performance of the shock test, and here again, post-test inspection revealed no evidence of electrolyte leakage or cell case deformation.

Finally, a 10,000 ampere-hour cell in a nonoperation configuration was subjected to a puncture test. The purpose of this test was to confirm that no explosion would occur when the cell was subjected to case penetrations, thereby causing an internal short circuit.

This cell was penetrated perpendicular to the center of its larger side with a remotely operated, quarter-inch diameter drill bit. The depth of penetration was 4 inches, resulting in a metal-to-metal internal short. The open circuit voltage immediately dropped from 3.65 volts to 3.45 volts and continued to decrease gradually over the next 60 minutes until the cell reached its 3 volt cut-off level. At this point, the quarter-inch diameter drill was removed and the test was considered terminated.

The maximum cell temperature recorded during the test was 32°C, indicating a 3°C rise and a maximum pressure of 4.2 psi. There were no adverse or hazardous conditions resulting from the performance of this test.

Finally, post-test discharging and deactivations of cells were performed after concluding each test. This was accomplished by discharging the cell at a normal drain rate until reaching its 3 volt cut-off level. Discharging was then continued at half the normal drain rate until the cell output voltage indicated 10 millivolts. After removing the discharge load, open circuit voltage was monitored for 30 minutes, recovering to a level no greater than a half of a volt.

The cell at this point was considered electrochemically discharged and was then submerged in a deactivation well containing a neutralizing solution of water and soda ash. This was for a period of two weeks. As a final disposal step, following the neutralization period, the deactivation well was covered with earth.

Throughout this process of disposal, there were no resulting indications that could be considered as adverse or hazardous.

## DISCUSSION

BENNETT: Why did you terminate the puncture test when it reached 3 volts? It seems to me that if you had an in-field puncture test, it's not going to automatically terminate itself when the cell gets to 3 volts. And is there something that could possibly happen as the cell goes further down?

YOUNGER: I think what I failed to identify is that that particular cell was discharged already to cut-off.

BENNETT: Oh. In other words, it was not a fresh cell?

YOUNGER: That's right. It was discharged to cut-off, and the flow chart indicated it.

BENNETT: Have you done puncture tests on fresh cells?

YOUNGER: It hasn't been done as yet, but we have it scheduled for our next series of tests which will be performed very shortly. But we do have that scheduled.

BENNETT: Thank you.

BOWERS: Your deep discharge tests were all at low rates. Have you done anything at higher rates, say, on the order of several hours' discharge?

YOUNGER: Well, I think the test that I described at the beginning was the external short circuit; it's shorting the terminals out.

BOWERS: The graph that I'm talking about had, on the X axis, time in terms of days, and you showed a break at about 10 days, I believe.

YOUNGER: Maybe I'd better refer that question to Franz. Can you answer that, Franz?

BOWERS: This is the overdischarge test, sir.

GOEBEL: The overdischarge test was performed at the nominal rate, which is 8 amperes for the two-case cell and 36 amperes for the ten-case cell, and it was continued to 50 percent of the total capacity into overdischarge at that nominal rate of 36 amperes. We haven't done anything at any higher rate yet.

GROSS: Would you please discuss the problems associated with leakage of electrolyte and dissolved catholyte due to a puncture and subsequent removal of the puncturing device?

YOUNGER: Well, the only experience that I've had with the handling of electrolyte in the puncture is that we do have electrolyte coming from the cell, from the puncture wound there, and that's handled stricly in a manner of putting baking soda and handling it in the manner specified through our disposal procedures. But we have not run into any problem where we have hermetic seals letting loose and electrolyte emitting from the cell.

PALANDATI: During your vibration test, did you make any attempt whatsoever to monitor the open circuit voltage of the cells during vibration?

YOUNGER: During vibration, the open circuit voltage was monitored continuously, and there was no change whatsoever during any of the vibration nor shock criteria.

MISERENDINO: Let me make one comment. These tests were not performed by GTE. These tests were performed by an independent test laboratory, Wylie Labs, under contract to the Air Force.

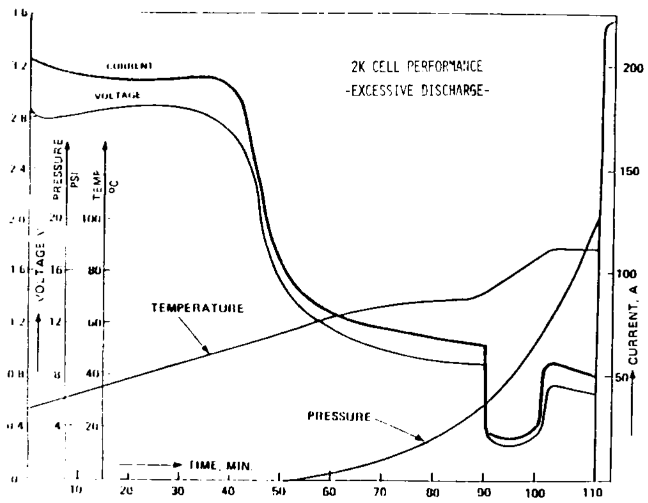


Figure 6-9

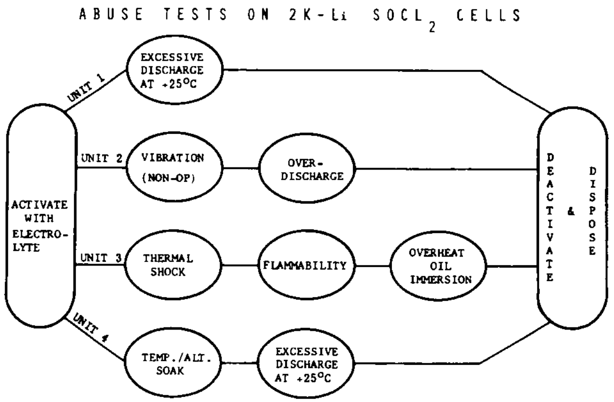


Figure 6-10

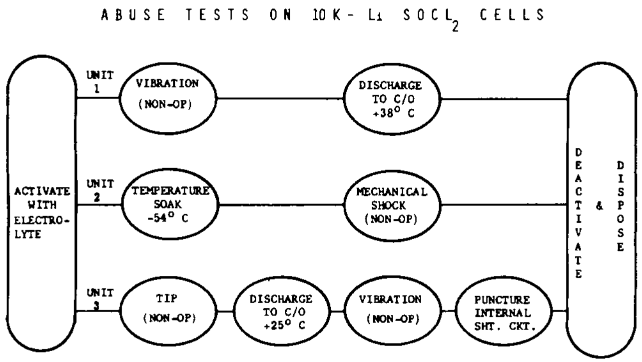


Figure 6-11

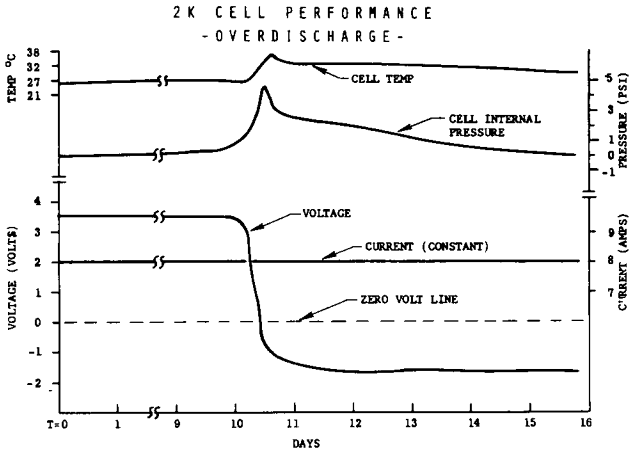


Figure 6-12

# APPLICATIONS AND SAFETY DATA

N. Berlangieri
Honeywell

There are numerous applications and safety data that have been generated by Honeywell Power Sources Center. In order to give you a general overview of everything that we've been doing, our presentation outline will consist of a very brief introduction, a history of Honeywell lithium batteries, where it will show the various applications and data that we've been performing for numerous industry and governmental sponsors. Also, we're going to touch on electrochemical criteria selection on the three systems that we're now developing at Honeywell Power Sources Center, and also typical storage and data that we've been achieving from all these systems, and also the current safety work that we're doing on a high rate "D" $SO_2$ cell.

(Figure 6-13)

As you'll note, we've been actively involved in lithium and ammonia batteries. The whole purpose of this talk will be the lithium section, but we're developing three chemistries: lithium vanadium pentoxide, lithium sulfur dioxide, and lithium thionyl chloride in both active and reserve configurations. Now, all the chemistries that we're developing are slightly different from many of the other manufacturers', and this is something that I think we should note. Performance, safety, and all this type of data differs from various manufacturer to manufacturer, and I think that's one thing that should be brought out.

The cells that we're developing range from a capacity of a 90 milliamp-hour reserve cell to a theoretical capacity of 17,000 ampere-hours for an MX application. This is a next-generation Minuteman battery, of which we originally built a few smaller size cells, around 12,000 ampere-hours.

We also have production, development, and facilities that are part of the Defense Systems Division within Honeywell. I think they're probably some of the finest in the industry, and we're presently now doubling our manufacturing facilities in Horsham, Pennsylvania, to go along with the increasing demands that we're seeing that governmental users would now demand or put upon us.

(Figure 6-14)

If you'll note, back in the early 60's, NASA was one of the primary sponsors of Livingston Electronics, which Honeywell procured, and they led the way in some of the work that has now been developed by Honeywell. If you'll note, that the end of the '60s, we received two patents for the $V_2O_5$ and $SO_2$ chemistries—$SO_2$ along with American Cyanimid. It wasn't too long that we realized, in the beginning of the '70s, that lithium had a tremendous advantage, and from the '70s on, we developed it for various agencies.

Looking at 1974, we've been developing $SO_2$ reserve batteries for the Navy; we've been developing thionyl chloride acid batteries for the Air Force; thionyl chloride reserve and also vanadium pentoxide reserve for the Army; the range of applications and the number of cells and the different sizes are in the hundreds. Only a few of them have made it to production so far. In our $V_2O_5$ chemistry, which has been over ten years in development, we're now producing one cell that's a 90 milliamp-hour glass ampule reserve cell, and we now can produce up to 15,000 cells per month.

Of all the cells to facilitize first, the small reserve glass ampule cell is probably one of the worst that we could probably have picked, but I think it's led the way, and some of the data that we've noted on this particular cell will be very beneficial for our $SO_2$ facilitization, which is underway, and also for our thionyl chloride large battery facilitization for our MX contract.

At the end of the '70s, two production contracts were let to Honeywell: one for the Adam, which is a scatterable mine, and also for the MX program; SAMSO is sponsoring us. And as I mentioned, we are presently doubling our manufacturing facilities.

(Figure 6-15)

If you look at some of the application data, why we selected the three systems that we're in, this truly is applicable to any user. If you're interested in trying to figure out what is the best chemistry, you must look at the things in terms of energy density, costs. And costs, you have to realize, are going to be dependent upon production. Initially all of these cells in development are much, much more expensive, and all the manufacturers are producing lower costs for production-type items.

Voltage regulation is another important criterion, and some of the systems differ. The $V_2O_5$ system is peculiar in that it starts at a 3.4 voltage open circuit and it drops down to around 3.2 volts and then it drops down to about 2.4 volts on the second electron change. This is not the case for thionyl chloride or $SO_2$ systems.

We evaluated the other systems that I've shown (carbonofluoride, silver chromate, to name a few), and our conclusions are (and I think this is very important): there's no single lithium power source that's capable of satisfying everyone's needs. There are distinct differences between our cells and everyone else's cells, and I think that must be taken into consideration.

When we discuss safety, people kind of lump safety in terms of lithium, but it's not necessarily lithium $SO_2$ nor is it lithium $V_2O_5$. There are all different incidences, and I think we fail as a group not specifying which of the chemistries and what the problems are that surround each of these.

(Figure 6-16)

This shows you our general lithium systems characteristics for the three systems that we're developing. If you'll note, I'm showing energy densities for a $V_2O_5$ of 120 watt-hours per pound. This is a 2 electron change down to 2 volt cut-off. I'm also showing 140 watt-hours per pound for the $SO_2$ system, and 300 watt-hours per pound for the thionyl chloride system.

This changes dramatically with design, and this is something that you have to take into consideration. For the purposes of today's talk, I've decided to pick the best that we've been able to do, but we could also do a lot worse than this, and it depends again on design and what you put in the cells.

(Figure 6-17)

All of the cells that we're building are stainless steel. They must be stainless steel in the $V_2O_5$ and thionyl chloride systems, and we are also developing stainless steel for the $SO_2$ system. We're doing this in conjunction with a mantech program for the Air Force for most of their life support equipment.

Again, the capacities range in the 100 milliamp-hour to 30 ampere-hour size for $V_2 O_5$, and 700 milliampere-hours to 160 ampere-hours size in $SO_2$ cells. All the $SO_2$ cells must be hermetically sealed and also must have safety vents. At present, this is not the case for $SO_2$, for thionyl chloride cells. The cells that we're building which are 17,000 ampere-hours are not vented cells, and I'll discuss some of these short circuit tests that we did a little later.

The vanadium pentoxide, as I mentioned before, is available in both active and reserve configurations. Of all the systems, we have the most history on this. We've developed Arrhenius plots that we feel can predict storage at various temperatures, and we're also trying to do this for thionyl chloride. However, this has not been done yet, and we have real time data that we're using as comparison.

(Figure 6-18)

If you'll look at this particular graph, this is showing a $V_2O_5$ active cell, and the top line indicates cells that have no storage and their discharge performance. The second line shows you cells that have been stored at room temperature and discharged up to four years and shows you the degradation that you've seen with time. This is approximately 8 percent of total capacity degradation with time. Now, this is room temperature storage. This particular system is not really beneficial for high temperature storage. We have not stored these at +160 F because this system will lose $\frac{1}{2}$ percent of its theoretical capacity for each day at plus 160. So we know that within less than a year this system would not be one for high temperature storage.

But I think it is indicative that the lithium cells do have tremendous storage potential.

(Figure 6-19)

This particular figure is of our lithium $V_2O_5$ reserve cell. Now, what we've done here is: we initiated five years ago a room temperature storage of these cells in reserve configuration, and rather than try to pick out which did what, if you'll notice, there's not much difference in the reserve configuration between cells which were baseline and cells that have been stored for five years.

Now, I just showed you single cells. There were three cells at each data point, and the data doesn't change much at all. We also discharged these at low cycle, which truly is an indication of any self-discharge mechanisms. You store cells, discharge them cold, and then you'll really see what cells can hold up.

(Figure 6-20)

We've also done this with outside ambient temperature conditions. Now, this is a temperate climate, and these were stored outside the Honeywell Power Sources Center in Horsham, Pennsylvania. Again, we only have four years' worth of data on this. The fifth year will be coming up. There are 10-year plans that are on test for this particular system.

This would simulate bunker-type conditions for the mines. These cells were developed for Army scatterable mines, and again, very, very little depletion with storage.

(Figure 6-21)

Our sulfur dioxide system is the next one that we're going to discuss, and here we've been developing active and reserve cells. The active storage is something that I'm going to be showing first.

(Figure 6-22)

This is kind of an unusual figure. You'll allow me a little bit of license. The dotted graph is not real accurate, but it's just showing some passivation that has occurred with time. The top line is typical discharge performance of cells. Now, there were eight cells tested. These were nonhermetic. The original lithium sulfur dioxide cells were all nonhermetic, and of the eight cells tested, you see this spread. They dropped out anywhere from 17 to 23 hours.

After this point in time, we tested cells again, and the next test is 9-1/2 months, which you see here.

You'll notice eight cells were tested again, but the spread became much closer and tighter. It kind of, with age, got a little bit better. At 17 months, they still fell within the same spread, and again after 30 months, which we just concluded in February of this year, they still fell within this range. So there has been tremendous room temperature storage data in, again, nonhermetic configurations, but I think it does prove that the electrochemical systems are stable.

(Figure 6-23)

This, I think, is one of the most impressive bits of data that we have on $SO_2$ cells. It's showing cells that have been stored upside-down at +165°F for over 30 months, and it's also comparing it to a six-month storage that we've had.

Now, these are not typically the cells that we're producing today. These cells had ceramic seals of a special nature that I'd rather not go into, and as you can see, after 32 months at plus 160, there is a tremendous amount of capacity left, greater than 50 percent of theoretical.

This environment is just tremendous for any battery, be it lithium or whatever, and I think that, again, it's showing the electrochemical systems. There is a problem that exists today with the glass-to-metal seals. They're not performing as well, but you have to remember that if you get a year's storage as plus 160, it's equivalent in chemical terms to close to ten years, but we must develop an Arrhenius relationship to see if this is true, and make sure that high temperature doesn't change some of the reactions.

(Figure 6-24)

We probably have the least amount of data on thionyl chloride, and the reason for that is that it's the youngest of all the systems. It potentially has the best, in terms of opportunity for many applications, but it's not as good as $SO_2$ at cold temperature applications, so you have to take into consideration what your true end use is going to be and select the system that best meets your needs.

(Figure 6-25)

The top line indicates a typically discharged cell, 1.6 ampere-hour, and again, it's just exaggerated for purposes. We've stored these cells at +140°F for one year and then discharged them, and you'll notice here the passivation effect. That's an error. It did really get a little higher in voltage than the other cell, but you'll see, with time, the cells were stored, and there was some degradation with voltage. This particular cell had an $SO_2$ dopent that we've developed at Honeywell Power Sources Center, and it has probably minimized the amount of passivation that you can see with the thionyl chloride system better than cells that have been stored without it.

Now, again, this is very rate-dependent, so you have to look at a cell and know what the internal surface areas are. We're talking about 1.4 milliamps per square centimeter. That's our typical discharge current density. If you would probably test this at 7 milliamps or 10, you would see a much more dramatic representation of passivation.

(Figure 6-26)

This particular cell was one of the first cells that we had also built for the Minuteman to at least test feasibility of large cells. It was a 13,000 ampere-hour theoretical capacity. We discharged it at 150 amps at ambient temperature, and we obtained 11,000 ampere-hours from this particular cell.

The design of our 17,000 ampere-hour cell has changed somewhat from this, and there are a few differences that are now existing, but what it's proving is that the systems are very stable and it has a very good voltage level. The 17,000 ampere-hour theoretical cells that we're now building—we've just completed short circuit testing of two cells.

Now, these cells are a 15-inch cube, and under short circuit conditions, we were generating over 1000 amps short circuit current. We generated up to 800 amps for over two hours, and we still have case temperatures as high as 250 to 300 degrees, with absolutely nothing occurring with these cells. They just sat there, and I think it's been at least three hours that they were on. Is that right, Lou (Levy)?

LEVY: I believe one was on for about two months under short circuit conditions.

BERLANGIERI: Two months under short circuit conditions. So I think, if anything, we're very, very proud of and pleased with this. I think there's a lot more work that needs to be done in terms of safety with $SO_2$ and also thionyl chloride, but when you start short circuiting cells and generate 1000 amps and have nothing occur, I think that's something to really hang your hat on.

(Figure 6-27)

This shows you thionyl chloride cells in a reserve configuration. Again, most of the work that we've done is program-related, and the specific loads here are program-related. This particular curve is something around a six-month rate for, again, an Army scatterable mine application. What we're showing here are cells stored for one year at plus 160 (these were reserve thionyl chloride cells), then discharged after three, six, and twelve months.

You'll see, at that particular rate, there's very little self-degradation. We did not discharge any of the other cells at the other rates that are shown, because it wasn't part of our contract.

(Figure 6-28)

This is probably the newest piece of data that we've shown to date. I'm not showing a whole lot because we haven't even given it to our sponsor yet, which is out of Ft. Monmouth, but it's our high rate "D" $SO_2$ cell. The objective of this was to develop a "D" size cell which is safe when force-discharged at 2 amps to 200 percent of theoretical capacity.

Now, we're force-discharging these cells at 2 amps constant current, and I'm going to be showing you the data that we obtained with this and also give you some reliability numbers. One of the questions that I guess is put to me almost every day is: what kind of reliability figures can we give? This is something that you have to understand is very limited, because we have still not finalized on cell designs, and you can't truly give reliability data on hardware that hasn't been fabricated and the final engineering bugs worked out of it.

We can give you, I think, systems reliability data, but not on actual hardware, because the hardware hasn't changed—or it's still changing.

Our eventual goals were to develop a four-hour discharge rate at 2 amps at room temperature and at -20°F discharged for two hours. Now, these are five different production builds, and we've been varying a lot of things there. We've been varying cathodes, anodes, double anodes, et cetera, to come up with the safest cell that we could, cells that would not vent with flame. This was the problem when you would force-discharge an $SO_2$ cell.

(Figure 6-29)

The contract is not completed yet, but our final design, which is shown here in Design 6, which has met goal, is not discharging or is not venting with flame after it's being discharged at 2 amps constant current.

(Figure 6-30)

This particular graph shows you a typical cell prior to what we would call our final cell design. The cells would discharge for some time, and then they would go down very low. Now, this is at 2 amps forced constant testing, and we saw peaks of -28 volts under a 2 amp discharge. You'll note there was a temperature rise here until this particular point, and then they would vent with flame. You may want to call that an explosion if you want, but the cases did not fall apart. They did vent, but there was flame. You'll see the temperature rise of about 266°F peak.

(Figure 6-31)

After our final design, this is the discharge of a typical cell, again at 2 amps constant current, and it ran for over four hours. This is room temperature. The same is true for -20, but it was a two-hour run. The cells would then go negative for about 1 volt, and we had them on for at least ten hours.

You'll see some increase in temperature as the cell dropped to the negative point, but then a decrease in temperature, and the cells would not vent. The sample size on the $SO_2$ cells was fifteen cells at each temperature.

(Figure 6-32)

This figure shows you the performance on what we would call Lot 6. It's still not our final design cell, tying to a 2 volt cut-off, 4.2 hours and 2.2 hours at -20. Safety venting, no venting, no venting with flame. After being force-discharged at 2 amps up to ten hours, the cells just sat there.

And now we give you some reliability numbers. I'm not a QC type, but 95 percent should discharge greater than 4 volts at two hours at room temperature, and it's the same for -20°F to a 2-volt cut-off, 1.8 hours. The safety: 85 percent or greater should withstand ten hours of discharge at 2 amps without venting. The only reason why we say 85 percent is because of the sample size. It's limited. There are only fifteen cells.

(Figure 6-33)

In summary, I guess we have an expertise in three major lithium electrochemistries that's probably unequalled by anyone here. I know that there are many companies involved in at least two, but we are developing three. The storage predictions of the past are now becoming reality, and that's true if you're looking at the systems. There are still some hardware problems that must be resolved, but I think, on the whole, all these predictions are coming true.

In regard to safety, 75 percent of Honeywell's 1979 research and development is directed at safety of all the systems ($V_2O_5$, $SO_2$, and thionyl chloride). The bulk of it is with thionyl chloride and $SO_2$ cells. Maybe we're a little conservative, but you just can't build them too safe, and I think that would give the users a better feel for it if we have a high degree of confidence in them.

We have to continue storage programs. We're doing some accelerated temperature testing. We must improve designs in cathodes, because we find this is an area that needs improvement. We're also continuing in trying to improve on our anodes, and our glass-to-metal seals need improvement also.

Disposal is something that we have to look at. We have to come up with an environmentally safe way of disposing of any of these cells. To this point in time, we always throw up the criticisms of lithium, but you look at mercury cells or you look at alkaline cells that you're not supposed to incinerate, but all users throw them probably in their trash, which eventually becomes incinerated.

So I don't really see where the horrors of lithium are any worse than any of the other systems of either mercury or alkaline. There's a lot more energy in a package, but I think that, with time, we can probably solve all these problems.

## DISCUSSION

LEAR: On your battery discharge curve there for the MX program, your 13 ampere-hour cell, I notice that the load was removed at 35, 55, 62, and 72 hours. Was there a specific reason for this?

BERLANGIERI: Yes. They were doing various tests. It was supposed to have been removed when they were checking out the batteries, et cetera.

LEAR: It was not temperature-related or anything to do with temperature?

BERLANGIERI: Nothing to do with temperature, no.

MARINCIC: You have shown us some data not long ago where you had a problem either on storage or on excessive discharge with the pressure inside the cell. In your short circuit tests, did you monitor the pressure during the discharge?

BERLANGIERI: Yes, pressure and temperature. It was about 120 psig on the pressure.

MARINCIC: 120 psig on pressure?

BERLANGIERI: Yes, maximum.

MARINCIC: What kind of container are you talking about, rectangular?

BERLANGIERI: Yes.

MARINCIC: That must be a very strong container.

BERLANGIERI: It is.

MARINCIC: Okay. Do you still see any pressure on storage of your cells?

BERLANGIERI: On large cells?

MARINCIC: On large cells.

BERLANGIERI: We don't really have large cells on storage.

MARINCIC: You had some in Atlantic City. You showed us—

BERLANGIERI: Those are smaller ones. They're the only 500 ampere-hour size cells. There's no problem with those.

KROUSE: You said at one time some of your cells had ceramic-to-metal seals, and it appears that most recently you've been using glass-to-metal almost exclusively. There have been noted to be some problems or potential problems with corrosion of the glass-to-metal seals. It seems like everybody spent a lot of time showing the excellent storage capability of the various lithium systems, and certainly NASA is considering some very, very long-term planetary missions in which it appears now the weak link might be the sealing of the lithium systems rather than the electrochemistry of it.

Why did you abandon the ceramic-to-metal seals? Have you looked at polymer compression seals? In your glass-to-metal seals now, what are you doing to solve some of the potential problems with corrosion?

BERLANGIERI: Number one, we "abandoned" ceramic seals because of cost. The glass-to-metal seals that we developed we felt were good enough. The ceramic seals have problems of their own, so you have to watch here what your trade-offs are. You could have other problems with ceramic seals that you wouldn't have with the glass-to-metal seal in terms of leakage or cracking, et cetera, so we wanted to be careful about that.

The ceramic seals are good; the glass-to-metal seals are good, but they both have some problems. Now, these are mechanically related problems that stem from an electrochemical problem.

Let me get to your third question about what we're doing. We're presently developing an Arrhenius relationship on our $SO_2$ cells with our present glass. Now, we've built cells in various hardware configurations where we've used different glasses from different vendors. Most of these vendors hold everything in proprietary, and it's their word that they've supplied the same thing five years ago as they're supplying now, and we have to develop better QC with the glass-to-metal seal manufacturers. I'm pretty sure we'd find out the same thing with some of our ceramic seal vendors.

The problem that we're seeing with $SO_2$ cells is temperature-dependent, and high temperatures. We can have cells that could have a problem anywhere from nine to twelve months at plus 160, but if you're looking at real time data (and again, we don't have an Arrhenius relationship) that is, I guess, equivalent to at least six or seven years at room temperature. If you store them at room temperature or colder, we don't see the problem.

KROUSE: How about the polymer compression seals of various types?

BERLANGIERI: Well, we've built cells with, say, Seigler seals, and we also are developing one for the Naval Surface Weapons Center, which is a PPS (polyphenylene sulfide seal) that's a compression seal that we've had on storage for I guess three years at plus 160 with absolutely no degradation.

But the problem here is what you really call hermetic. The normal leak rate that we have to produce cells to ($2 \times 10^{-8}$ $cm^3$ of helium per second with reference to air), and when you start talking about compression seals, everybody says they're nonhermetic. Now, I guess it's in the way you define hermeticity.

As I know it, when you start talking crimp seal or Seigler, people say they're not hermetic.

KROUSE: Does your PPS seal meet the $2 \times 10^{-8}$?

BERLANGIERI: Yes.

KROUSE: Then it's hermetic.

BERLANGIERI: I agree with you.

LEVY: In reference to the question that was asked previously about pressures seen on the very large cells that are in storage: yes, we do see pressure; it is temperature-related and they're consistent with the data we indicated in Atlantic City, running anywhere from, oh, 15 to 30 psi.

HALPERT: You made a comment at the end about dealing with disposal of these lithium cells, and disposal is one of the concerns that we have. Your comment was that we're going to have to find some way of disposing of them or words to that effect.

BERLANGIERI: Environmentally safe, yes.

HALPERT: What do you tell your customers when you sell them? Do you have some responsibility of informing them on what to do with them when they're finished with them?

BERLANGIERI: Our present methods of disposing of cells are, I guess, typical of what any of the other manufacturers are doing. There are two programs out now that I think the Army is sponsoring on trying to come up with disposal techniques. You can put them in landfill, et cetera. You shouldn't throw them away or incinerate them, that's number one.

You could discharge them down to a very low level and take all the capacity out of the cell. That would be another way you could safely dispose of the cells. But I don't have all the answers on that. It is a little difficult, but it's something that we should address, and again, I'd just like to emphasize: I don't know what people do with mercury cells and also some of the alkaline cells in their disposal techniques. All I can say is, whatever problems we've caused, everybody else is also causing with some of their other batteries.

TAYLOR: May I just comment on that last question? The Versar Report, the second version of it, does address the question of cell disposal for lithium $SO_2$ cells, and I think as far as the users here are concerned, it's probably best that they refer to that, an unbiased report.

BERLANGIERI: Good.

TAYLOR: The final report by Versar on, at that time, ECOM, U.S. Army ECOM contract, Ft. Monmouth, came out in the spring of this year, '78.

## INTRODUCTION

- ACTIVELY INVOLVED IN PRIMARY BATTERIES - LITHIUM/AMMONIA
- TRACKING THE EVOLUTION OF LITHIUM SECONDARY
- 3 LITHIUM COUPLED CHEMISTRIES AVAILABLE - ACTIVE/RESERVE EACH WITH A SEPARATE DRY ROOM AT PSC
- CELLS RANGE FROM 90 MILLIAMPERE HOUR RESERVE TO 17,000 AMPERE HOUR ACTIVE
- PRODUCTION - CUSTOM BUILD TO HIGH VOLUME, ALL WITH THE HIGHEST QUALITY AND RELIABILITY
- DEVELOPMENT - CONCEPT FORMULATION TO SYSTEM INTEGRATION WITH FULL QUALITY AND DOCUMENTATION CONTROL
- FACILITIES - HONEYWELL PROVING GROUNDS, DEFENSE SYSTEMS DIVISION, MINNEAPOLIS, MINNESOTA AND POWER SOURCES CENTER
- ENGINEERING - CORPORATE TECHNOLOGY CENTER, SYSTEMS & RESEARCH CENTER, DEFENSE SYSTEMS DIVISION AND POWER SOURCES CENTER

Figure 6-13

## HONEYWELL POWER SOURCES PRODUCT AREA HISTORY

| | |
|---|---|
| 1963 | NASA Contract to develop high energy primary batteries issued to Livingston Electronics/Honeywell |
| 1968-1969 | Li Battery patents issued for $V_2O_5$ and $SO_2$ chemistries |
| 1971 | Concentrated all IR&D on Lithium systems |
| 1972 | Development of Li/$SO_2$ cell and battery product line |
| 1974 | Moved to new facility in Horsham<br>Won NSWC Li/$SO_2$ Reserve battery contract<br>Won WPAFB Li/$SOCl_2$ Active battery contract<br>Won Army Li/$SOCl_2$ Reserve Cell Development program |
| 1975 | Developed Li/$SO_2$ vent, hermetic seal<br>Initiated build of large Li/$SOCl_2$ hardware |
| 1976 | Army contract for Li/$V_2O_5$ Reserve cell production facility and ADAM Ammonia battery production<br>Initiate MM-MX Li/$SOCl_2$ Active battery work<br>Li/$SO_2$ MANTECH production contract |
| 1977 | SAMSO contract for MX battery |
| 1978 | Expansion of facilities for Li/$SO_2$ and Li/$SOCl_2$ battery development & production facilitization<br>Initiated low rate initial production of Li/$V_2O_5$ Reserve cells |

Figure 6-14

## WHY $SO_2$, $V_2O_5$, AND $SOCl_2$ ?

- 13* Lithium chemical couples were evaluated by Engineering and each given a performance rating.
- Characteristics evaluated were:
  - Watt Hours/lb
  - Watt Hours/in$^3$
  - Cost
  - Safety
  - Power
  - Stability
  - Operating Voltage
  - Voltage Regulation
  - Low Temperature Performance
  - Ease of Electrode Fabrication
- $SOCl_2$ scored higher, followed by $V_2O_5$ and $SO_2$

*Other candidates were CF, $MnO_2$, $Ag_2CrO_4$, $MoO_3$, $CuCl_3$, CuS, $CuF_2$, AgCl, $I_2$

CONCLUSION

- NO SINGLE LITHIUM POWER SOURCE IS CAPABLE OF SATISFYING ALL REQUIREMENTS
- There are distinct electrochemical and hardware differences that impact each application
- $V_2O_5$, $SO_2$ and $SOCl_2$ will enable Honeywell to objectively offer the broadest base Lithium capability

Figure 6-15

## GENERAL LITHIUM SYSTEM CHARACTERISTICS

Lithium Vanadium Pentoxide ($V_2O_5$)

| Nom. OCV | Nom. CCV | Energy Density Whr/lb | Energy Density Whr/in$^3$ |
|---|---|---|---|
| 3.42 | 3.00 | 120 | 11 |

- Primary active or reserve in varying cell configurations
- Crimp seal or hermetic safety vent not required
- Stainless steel cases and headers
- 100 mAhr to 30 Ahr cell capacities

Lithium Sulfur Dioxide ($SO_2$)

| Nom. OCV | Nom. CCV | Energy Density Whrs/lb | Energy Density Whr/in$^3$ |
|---|---|---|---|
| 2.90 | 2.75 | 140 | 8 |

- Primary active or reserve only in cylindrical configuration
- Hermetically sealed safety vent required
- Stainless steel cases and headers
- 700 mAhr to 160 Ahr cell capacities

Lithium Thionyl Chloride ($SOCl_2$)

| Nom. OCV | Nom. CCV | Energy Density Whrs/lb | Energy Density Whr/in$^3$ |
|---|---|---|---|
| 3.60 | 3.30 | 300 | 18 |

- Primary active or reserve in varying cell configurations
- Hermetically sealed
- Stainless steel cases and headers
- 360 mAhr to 17,000 Ahr cell capacities

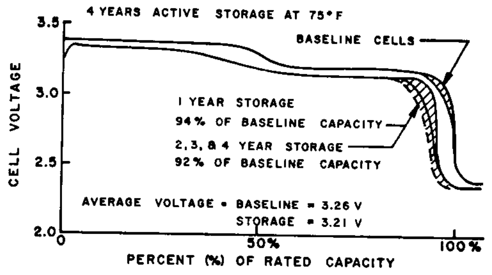
Figure 6-16

# VANADIUM PENTOXIDE

## $V_2O_5$

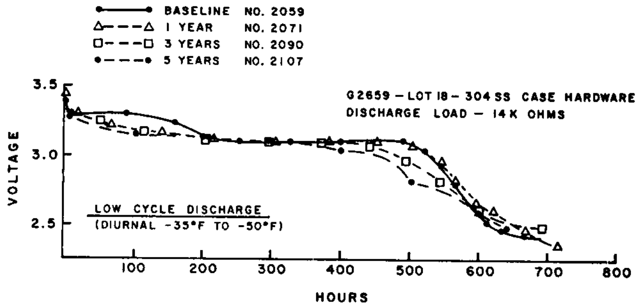
## STORAGE AND PERFORMANCE DATA

Figure 6-17



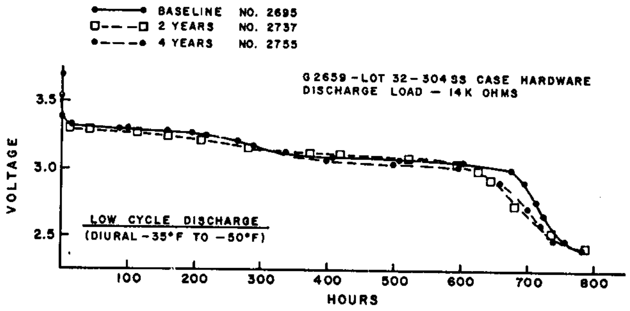
STORAGE CHARACTERISTICS OF G2659 $Li/V_2O_5$ ACTIVE CELL

Figure 6-18



DISCHARGE PROFILES AFTER INACTIVE STORAGE AT ROOM TEMPERATURE ENVIRONMENT

Figure 6-19



DISCHARGE PROFILES AFTER INACTIVE STORAGE AT OUTSIDE AMBIENT CONDITIONS

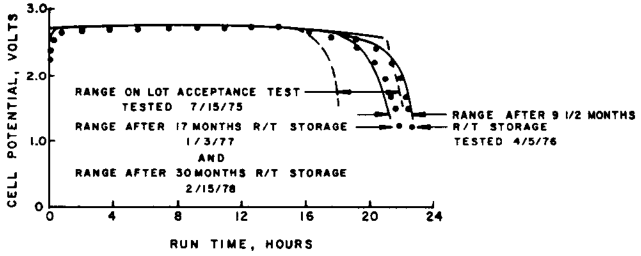
Figure 6-20

## SULFUR DIOXIDE

## $SO_2$

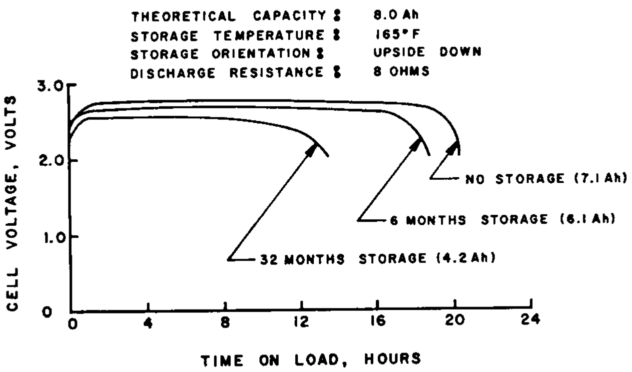
## STORAGE AND PERFORMANCE DATA

Figure 6-21



G2686E CELLS ON 8 OHMS LOAD — NONHERMETIC CELLS

Figure 6-22



G2686 HERMETIC "CC" CELL STORAGE

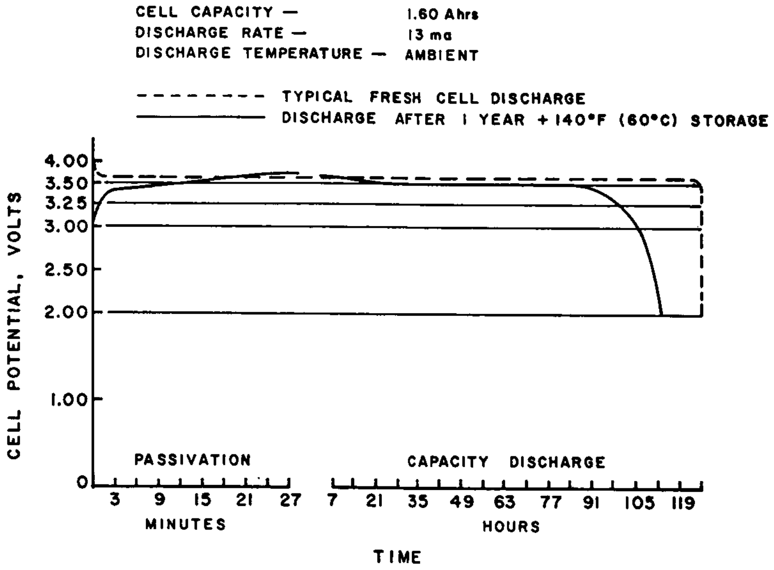
Figure 6-23

## THIONYL CHLORIDE

## $SOCl_2$

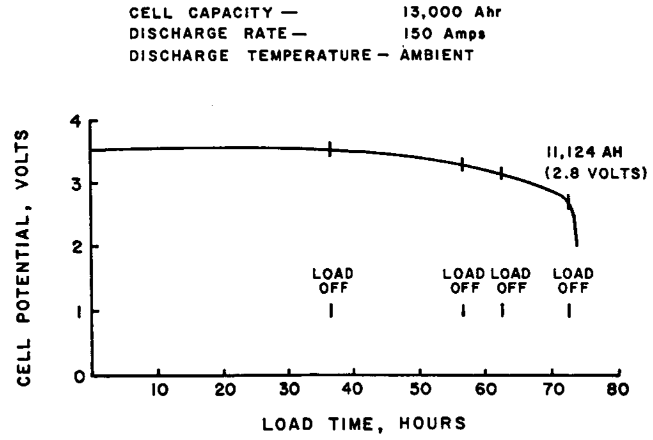
## STORAGE AND PERFORMANCE DATA

Figure 6-24



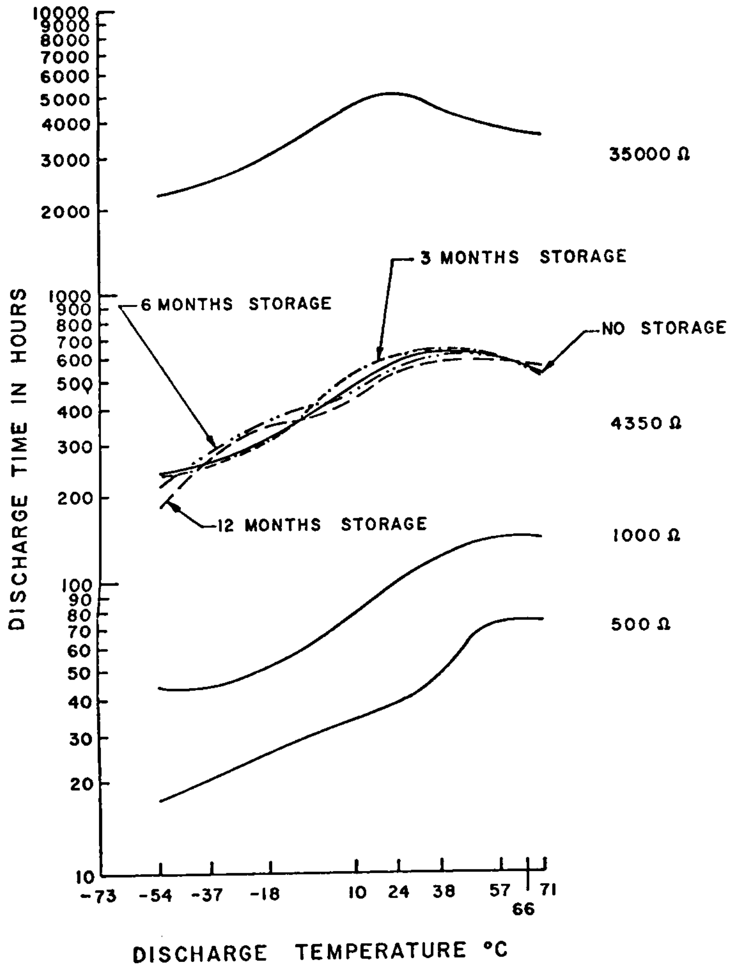
STORAGE CHARACTERISTICS OF G3013C Li/SOCl$_2$ CELL

Figure 6-25



TYPICAL DISCHARGE PERFORMANCE OF 13,000Ahr Li/SOCl$_2$ CELL

Figure 6-26



Active Life & Storage Characteristics of the Model G2659B1 Cell

Figure 6-27

## ERADCOM SAFETY STUDY

OBJECTIVE

Develop a "D" size Li/ $SO_2$ cell which is safe when forced discharge at 2 amps to 200% of theoretical capacity.

SCOPE

Two 6 month programs testing numerous design iterations which have culminated in a demonstration of a safe high rate "D" cell design.

STATUS

Program complete November 1978

Figure 6-28

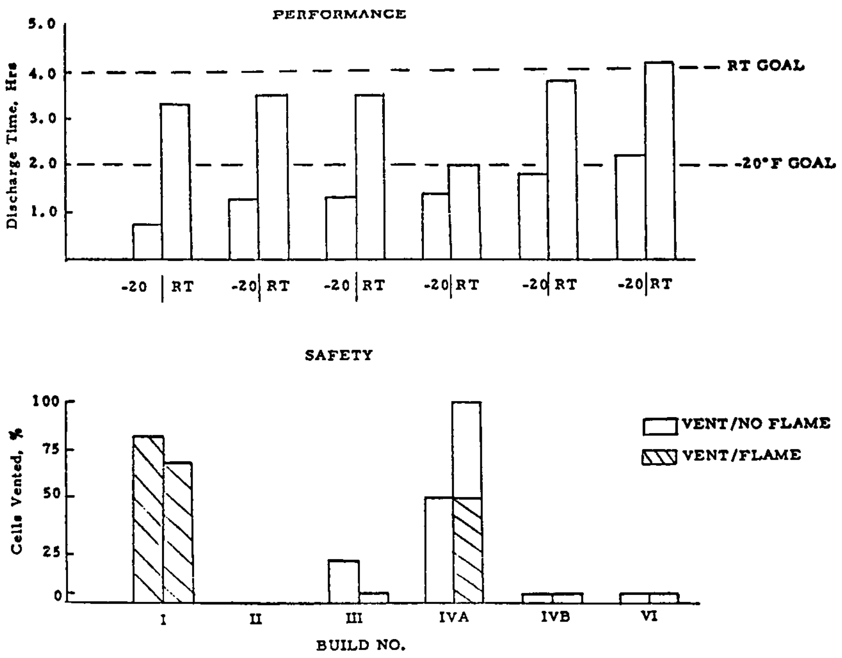
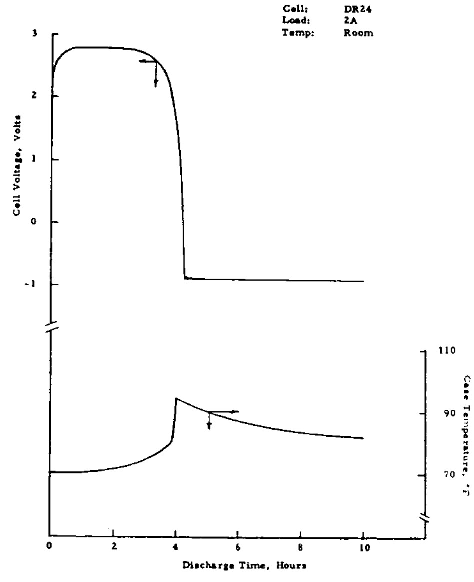
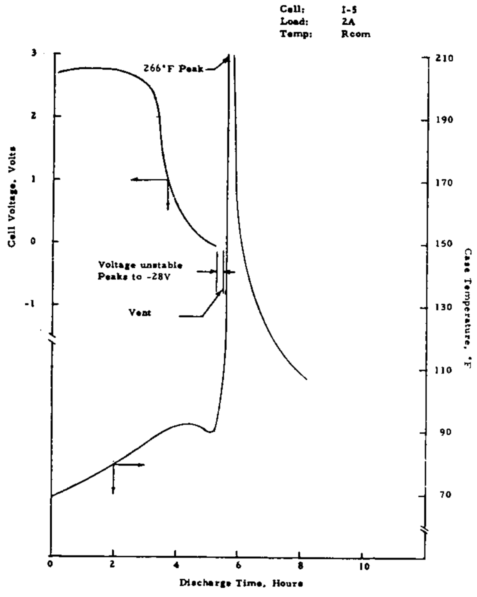


Figure 6-29



FINAL PERFORMANCE/SAFETY TEST - HIGH RATE "D" CELL

Figure 6-30



INITIAL PERFORMANCE/SAFETY TEST - HIGH RATE "D" CELL

Figure 6-31

ACTIVE Li/ $SO_2$ CELL CHARACTERISTICS
STATISTICAL RESULTS OF HIGH RATE "D" CELL SAFETY TESTS

RESULTS

| | ROOM TEMPERATURE | -20°F |
|---|---|---|
| Number Cells | 15 | 15 |
| Avg. Time to 2.0V (hrs) | 4.2 | 2.2 |
| Range (hrs) | 4.1-4.3 | 1.9-2.4 |
| Standard Deviation (hrs) | .07 | .16 |
| Safety (venting) | None | None |

RELIABILITY PROJECTIONS BASED ON BASELINE CELLS AT 90% CONFIDENCE

- Performance

  Room Temp:

  95% should discharge greater than 4.0 hrs to 2.0V

  -20°F

  95% should discharge greater than 1.8 hrs to 2.0V
  75% should discharge greater than 2.0 hrs to 2.0V

- Safety

  Room Temp & -20°F

  85% or greater should withstand 10 hrs of discharge at 2A without venting

Figure 6-32

## SUMMARY

- We have expertise in three major Lithium electrochemistries in both active and reserve configurations.

- The storage predictions of the past are now becoming real.

SAFETY - Continued efforts are needed in all Lithium chemistries. 75% of Honeywell 1979 IR&D addresses this area.

HARDWARE - Continuing storage programs, microcalorimetry, and improved designs in cathodes, anodes and glass to metal seals are planned.

DISPOSAL - Similar to other battery chemistries, environmentally safe disposal methods of cells must be addressed.

Figure 6-33

# TADIRAN-PLAINVIEW ELECTRONICS PRESENTATION

B. Erde
Plainview Electronics

First I'd like to explain one minor complication. I'm representing Plainview Electronics, which imports and distributes cells made by Tadiran Israel Electronics in Israel, and so I am not directly with Tadiran and the presentation I have is based on material they furnished me, and regrettably, beyond the material, I am relatively stuck.

One of the major emphases, I think, that Tadiran places in their cells for safety is very simply that if the cell is built properly, if you cannot pass too much current through the lithium, then the cell will remain safe. So they've built their cell with a very high heat dissipating medium, where they have the lithium foil suaged to the outer container, which is could rolled nickel steel.

They also limit the reactive area of the cell, and they greatly limit the short circuit current.

(Figure 6-34)

The cell basically is constructed very much like a carbon/zinc cell, with the can, anode, et cetera, and with a glass-to-metal seal at the top, but beyond the glass-to-metal seal is an epoxy filling, so it's an additional seal on the cell.

(Figure 6-35)

I'm including this mainly so that you can look at it in more detail in the book. The topic is safety. The cells that Tadiran makes, first of all, are production cells. They're offering them in four sizes at present: half "AA," "AA," "C," and "D." These are in production, they've available, they're stock and off the shelf.

They have run them under various environmental tests, and I had slides on those, but I wanted to keep it a little bit brief. We do have information on the various mechanical, vibration, shock, et cetera, tests, and all of these cells have been tested to these mil specs. They are hermetic, I believe to $1 \times 10^{-8}$ $cm^3$.

Going on, under safety, they've submitted the cells to various tests which they think would be more stringent than one would normally encounter. We've punctured them with a penetrating nail. Regrettably, I do not have statistical data. The conclusions in each case are that no explosion took place, that the cells are safe.

(Figure 6-36)

As you can see, we punctured the cells with a 3.2 millimeter nail, and the observations are: of course you get some electrolyte leakage, but there is no pressure build-up in the cell. By the way, these cells are not vented; these are hermetic. The contention is that the way the cells are constructed, there is no necessity whatsoever for venting. I'll get to that in a moment.

(Figure 6-37)

I'm going to run rapidly through these. The cells have been compressed to the point that they short circuited. There is no explosion or release of electrolyte or any other deleterious effects.

(Figure 6-38)

We have short circuited these at 25°C. This is a "D" size cell. As you can see, the voltage dropped; however, maximum short circuit current was 6-$\frac{1}{2}$ amps, but there was no explosion, no release of electrolyte. Cell diameter remained unchanged, but there was a slight swelling at the bottom and the cover of the cell. As you can see, the length did increase by 1 millimeter, but that is under full short circuit, no venting.

(Figure 6-39)

Short circuiting at 72°C: same conclusions, except the swelling was another millimeter. It swelled to 2 millimeters.

(Figure 6-40)

Decreasing load test: again, no swelling, no electrolyte leakage. The initial voltage on the Tadiran cell, open circuit voltage, I didn't mention before; it's 3.7 volts, with an operating voltage of 3.4 volts.

(Figure 6-41)

High temperature at 150°C to three hours, and again no explosions. Again, some minor swelling at that temperature. But the swelling, interestingly enough, is not in the diameter, and if they were placed in a tube, they would not get hung up.

(Figure 6-42)

Under forced discharge, again, the cells were discharged, as you can see, and force-charged with half an amp, and again they have remained safe. As you can see, the temperature did rise during forced discharge. I have another curve.

(Figure 6-43)

The cells were heated on a hotplate to 250°C on this side, and they were heated on the bottom.

(Figure 6-44)

The temperature rose. We seem to get a reverse portion of the temperature curve of the cell after about twenty or thirty minutes; however, at 250°C on a hotplate, the cell again was safe.

I think the key, again, as I said in my opening remarks, is that basically we have a limited amount of lithium per cell. The way it's contructed.

(Figure 6-45)

This is the hotplate on the bottom. Basically, you don't have enough material to cause a severe reaction.

(Figure 6-46)

Figure 6-46 shows the conclusion of that. Again, you get that reverse.

(Figure 6-47)

Charging of discharged cells: these have been force-charged again. These tests were, of course, only charged with a half amp, but again, for a period of time for twelve hours and with no dangerous effects to the cell.

(Figure 6-48)

We've also fully recharged fully charged cells with a half amp, and again, no problem encountered. Again, the cells are not spiral wound. There's a limited amount of lithium. The one negative to the cells, as far as I can determine, is they are self current limiting, and they're not usable under very high current applications. Generally, I would say the largest amount of current that you can operate them at normally would be possibly several hundred milliamps, but beyond that, the cell life is shortened.

To counteract that, one of the things that Tadiran is working on at the present time is remote-activated cells, and they have just completed development on a remote-activated cell about the size of an "AA" cell. At present they're getting about 250 milliampere-hours out of the cell with currents up to an amp, but they do not intend to go into the spiral cells.

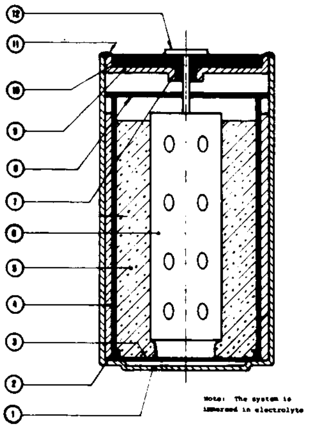
## DISCUSSION

TAYLOR: Concerning the data you showed on the hotplate test, I would hate to leave the audience with the impression that you can stick cells on a hotplate at 250°C and not run into a problem. Let's just simply say that you can do that with fresh cells. I believe that. I'm inclined to disbelieve it, because the lithium would be molten long since.

If you discharge a thionyl chloride cell, you generate sulfur, and the data which have been presented in previous publications at previous meetings would suggest there's a very strong exothermic reaction between lithium and sulfur. Would you care to comment on what would happen, then, on your hotplate test on a discharged cell, or should we leave it that, in fact, the cells shouldn't be subjected to that sort of test and would blow up?

ERDE: I really can't comment. Regrettably, I don't have the data. I'll even grant you it's possible that this was done with a new fully charged cell. I don't know what would happen with a partially discharged or fully discharged cell.

I would only imagine that the way the cell is constructed, with the lithium attached to the steel, that it would dissipate the heat sufficiently not to raise the lithium to the wrong temperature. But I really can't comment about a partially discharged cell.



KEY:

| | |
|---|---|
| 1 - CAN | 7 - GLASS-TO-METAL SEAL |
| 2 - ANODE | 8 - TOP INSULATOR |
| 3 - BOTTOM INSULATOR | 9 - COVER |
| 4 - SEPARATOR | 10 - EPOXY FILLING |
| 5 - CATHODE | 11 - HERMETICALLY WELDED SEAM |
| 6 - COLLECTOR | 12 - POSITIVE TERMINAL |

Figure 6-34

3.2 <u>ENVIRONMENTAL TESTS</u>

TADIRAN High Energy lithium inorganic cells have undergone intensive environmental tests to withstand rigorous military standards and specifications as follows:

| | |
|---|---|
| U.S. Army Electronics Command | - SCS-459 |
| Military Specification for Dry Batteries | - MIL-B-18D |
| Military Standard for Environmental Test Methods | - MIL-STD-810C |

Various groups of cells were used for each of the following tests.

The cells in each group were selected at random from production batches following final inspection:

| | |
|---|---|
| - Mechanical Vibration | - (3.2.1) |
| - Mechanical Shock | - (3.2.2) |
| - Combined Mechanical Shock and Vibration | - (3.2.3) |
| - Thermal Shock | - (3.2.4) |
| - Pressure Test | - (3.2.5) |
| - Altitude Test | - (3.2.6) |
| - Impact Test | - (3.2.7) |

The following test reports and their results prove that the TADIRAN High Energy lithium cells pass the environmental tests as specified.

Figure 6-35

5.2.1 <u>PUNCTURE TEST</u>

I. <u>Cells Tested</u>: Full capacity and discharged D size.

II. <u>Test Conditions</u>:

Ambient temperature : +25°C
Relative humidity : 70%

III. <u>Description of Test</u>:

1. A 3.2 mm diameter nail thrust through the cell, perpendicular to its longitudinal axis, with the aid of a press (Figure 5-1).
2. The cell remained under observation for an additional 24 hours.

IV. <u>Observations</u>:

1. Slight leakage of electrolyte at point of puncture - no spray or hissing substantiating lack of internal pressure.
2. No swelling.
3. Cells short circuited and temperature rise recorded.

V. <u>Conclusions</u>:

TADIRAN High Energy lithium cells are safe (do not explode) when penetrated by a nail.

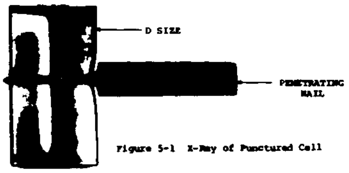


Figure 5-1 X-Ray of Punctured Cell

Figure 6-36

5.2.2 <u>COMPRESSION TEST</u>

I. <u>Cells Tested</u>: Full capacity and discharged D size.

II. <u>Test Conditions</u>:

Ambient Temperature : +25°C.
Relative humidity : 70%

III. <u>Description of Test</u>:

1. Each cell was compressed in a suitable rig.
   (a) Compression area : 32 x 32 mm.
   (b) Direction of compression perpendicular to the cell's longitudinal axis.
2. Observations were made at two stages.
   (a) At a compression depth of 30% normal cell diameter.
   (b) Completely crushed.

IV. <u>Observations</u>:

1. 30% diameter compression : cells short circuited, no explosion or release of electrolyte.
2. Completely crushed : cells short circuited, electrolyte leakage, no explosion.

Figure 6-37

### 5.2.3 SHORT CIRCUIT TEST AT +25°C.

I. **Cells Tested:** D size.

II. **Description of Test:**

1. Nickel tabs were spot-welded to cell terminals.
2. Cells were short circuited at an effective resistance of approximately 0.005 ohm.
3. Cells were short circuited for 24 hours.
4. Observations were made during the 24 hour period.

III. **Observations:**

1. After being shorted for 30 seconds the voltage dropped to 0.007 V.
2. Maximum short circuit current obtained : 6.5 A.
3. Slight swelling observed at the bottom and the cover (increase in length : 1 mm).
4. Cell diameter remained unchanged.
5. Cell weight remained unchanged.
6. No leakage of electrolyte.

IV. **Conclusions:**

When short circuited, TADIRAN High Energy lithium cells do not explode or release electrolyte.

Figure 6-38

### 5.2.4 SHORT CIRCUIT TEST AT +72°C

I. **Cells Tested:** D size.

II. **Description of Test:**

1. Nickel tabs were spot-welded to the cell terminals.
2. Cells were stored for 16 hours at a temperature of +72°C (± 2°C).
3. Cells were short circuited at an effective resistance of approximately 0.005 ohm.
4. The shorted cells were stored for a further 24 hours at +72°C (± 2°C).
5. Observations were made during the 24 hour period.

III. **Observations:**

1. After being shorted for 30 seconds the voltage dropped to 0.008 V.
2. Maximum short-circuit obtained : 6 A.
3. Maximum swelling of 2 mm. at the bottom of the cells.
4. No leakage of electrolyte.
5. No change in cell weight.

IV. **Conclusions:**

TADIRAN High Energy lithium cells short circuited at high temperatures (+72°C) do not explode or release electrolyte.

Figure 6-39

### 5.2.5 DECREASING LOAD TEST

I. **Cells Tested:** D size.

II. **Test Temperature:** +25°C.

III. **Description of Test:**

1. Cell loaded initially at c/200 A (50 mA for D size).
2. Load was decreased at a rate of c/200 A per minute until short circuited.
3. Cell voltage was recorded as a function of load current, and other observations made.

IV. **Observations:**

1. Voltage recorded as a function of the current.

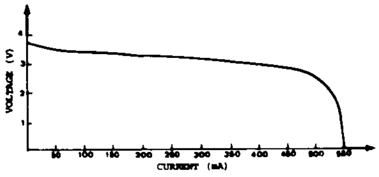


Figure 5-2 Decreasing Load Curve

2. No swelling.
3. No electrolyte leakage.

V. **Conclusions:**

TADIRAN High Energy lithium cells withstand a varying load without exploding or leakage of electrolyte.

Figure 6-40

### 5.2.6 HIGH TEMPERATURE TEST (+150°C)

I. **Cells Tested:** D size.

II. **Test Conditions:** Cells kept in an oven at +150°C (± 5°C) for 3 hours.

III. **Test Description:**

1. Dimensions and weights of the cells recorded before and after test.
2. Cells open circuit voltage recorded every 10 minutes while in the oven.

IV. **Observations:**

1. Swelling at top and bottom of cells (2.5 mm maximum increase in overall height).
2. No change in cell diameter.
3. No leakage of electrolyte.
4. Open circuit voltage change while in the oven, recorded as follows:

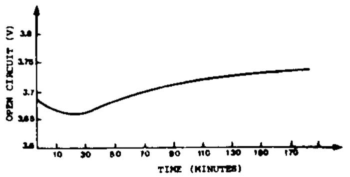


Figure 5-3 Open Circuit Voltage Curve at High Temperature

V. **Conclusions:**

TADIRAN High Energy lithium cells do not explode or release electrolyte when heated to a temperature of +150°C in an oven.

Figure 6-41

## 5.2.7 FORCED DISCHARGE TEST

I. **Cells Tested:** D size.

II. **Test Temperature:** +25°C.

III. **Description of Test:**

1. Cells discharged at 60 mA to an end voltage of 2.0 V.
2. A forced current of 500 mA was then passed through the cells for 12 hours.

IV. **Observations:**

1. On application of the forced current, the cell voltages reversed immediately reaching a peak negative value after 3 hours. The peak inverse voltage reached was -8.0 V and the cells subsequently stabilized at -6.0 V for the remainder of the test, recorded as follows:

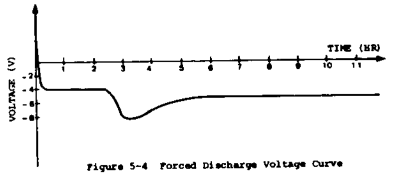


Figure 5-4 Forced Discharge Voltage Curve

2. Cell temperatures were approximately +70°C at the end of the test period.
3. No electrolyte leakage detected.
4. No change in cell dimensions and weights.

V. **Conclusions:**

TADIRAN High Energy lithium cells do not explode or release electrolyte when force discharged.

Figure 6-42

## 5.2.8 (a) HOT PLATE TEST - CELL ON SIDE

I. **Cells Tested:** D size.

II. **Test Procedure:**

Heating on an electric hot plate in an open environment to +250°C.

III. **Description of Test:**

1. The cell was laid on its side on a hot plate.
2. The testing circuit set up was as follows:

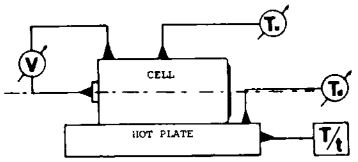


Figure 5-5 Hot Plate Test - Circuit Set-up Cell on Side

3. The temperature of the hot plate (Td) was increased at a rate shown on the curve in Figure 5-6.
4. The hot plate surface temperature and cell upper surface temperature (Tu) were recorded (Figure 5-6).
5. Open circuit voltages were measured during the heating period.

Figure 6-43

IV. **Observations:**

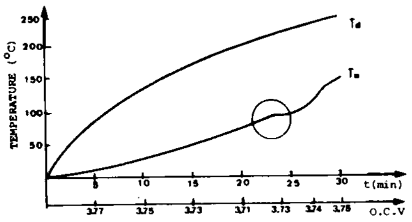


Figure 5-6 Hot Plate Test - Cell Temperature and OCV Curve

1. The Tu curve becomes flat in the area 20-30 minutes. During the same period, the cell open circuit voltage changes from a falling to a rising characteristic. This phenomenon, which indicates an endothermic reaction within the cell, could be the result of a phase transformation occuring at this particular stage.
2. Swelling was noted at the top and bottom of the cells.
3. No electrolyte leakage.

V. **Conclusions:**

TADIRAN High Energy lithium cells do not explode or release electrolyte when heated on a hot plate (on their side) up to +250°C.

Figure 6-44

## 5.2.8 (b) HOT PLATE TEST - CELL STANDING

I. **Cells Tested:** D size.

II. **Test Procedure:**

Heating on an electric hot plate, in an open environment to +250°C.

III. **Description of Test:**

1. The cell placed standing on its bottom on the hot plate.
2. The testing circuit set up was as follows:

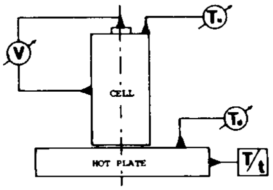


Figure 5-7 Hot Plate Test - Circuit Set-up of Standing Cell

3. The temperature of the hot plate (Td) was increased at a rate shown on the curve in Figure 5-8.
4. The hot plate surface temperature and cell upper surface temperature (Tu) were recorded (Figure 5-7).
5. Open circuit voltages were measured during the heating period.

Figure 6-45

IV. <u>Observations</u>:

1.

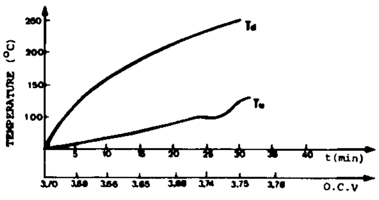


Figure 5-8 Hot Plate Test - Cell Temperature and OCV Curve

1. The Tu curve becomes flat in the area 20-30 minutes. During the same period, the cell open circuit voltage changes from a falling to a rising characteristic. This phenomenon, which indicates an endothermic reaction within the cell, could be the result of a phase transformation occuring at this particular stage.
2. Swelling was noted at the top and bottom of the cells.
3. No electrolyte leakage.

V. <u>Conclusions</u>:

TADIRAN High Energy lithium cells do not explode or release electrolyte when heated (standing on their bottom) on a hot plate to +250°C.

## Figure 6-46

5.2.9 (a) <u>CHARGING OF DISCHARGED CELLS</u>

I. <u>Cells Tested</u>: D size.

II. <u>Test Temperature</u>: +25°C.

III. <u>Description of Test</u>:

1. The cells were completely discharged at 60 mA.
2. A current of 500 mA was forced through the cells for 12 hours.
3. Cell voltages were recorded during the test.
4. Cell temperatures were measured at the end of the charging period.
5. Cell dimensions and weights were measured before and after the test.

IV. <u>Observations</u>:

1. At the start of the "charging" period, the cell voltage rose to 5.0 V then fell gradually and stabilised at 3.7 V for the remainder of the 12 hours.
2. Cell temperatures after 12 hours of "charging" reached a maximum of +53°C.
3. At the end of the test, no change was noted in dimensions and weight of cells.
4. No electrolyte leakage.

V. <u>Conclusions</u>:

Discharged TADIRAN High Energy lithium cells do not explode or release electrolyte when charged with a current of 500 mA.

## Figure 6-47

5.2.9 (b) <u>CHARGING OF FULL CAPACITY CELLS</u>

I. <u>Cells Tested</u>: D size.

II. <u>Test Temperature</u>: +25°C.

III. <u>Description of Test</u>:

1. A current of 500 mA was forced through the cells for 12 hours.
2. Cell voltage was recorded during the test.
3. Cell temperature was measured before and after the test.
4. Cell dimensions and weight were measured before and after the test.

IV. <u>Observations</u>:

1. At the start of the "charging" period the cell voltage rose to about 4.0 V and remained at this value throughout the test.
2. At the end of the charging period, cell temperatures recorded reached a maximum of +62°C.
3. No changes in dimensions and weight were observed at the end of the test.
4. No electrolyte leakage.

V. <u>Conclusions</u>:

Full capacity TADIRAN High Energy lithium cells do not explode or release electrolyte when charged with a current of 500 mA.

## Figure 6-48

# SAFETY CHARACTERISTICS OF THE LITHIUM $SO_2$ SYSTEM

T. Watson
PCI

Before I start my presentation, I'd just like to make one quick comment with respect to the glass seal corrosion that Chuck Bennett had referred to earlier this morning, and that is: first of all, several glass seal manufacturers have analyzed several of the corroded glass-to-metal seals, and they have verified that lithium is present in the seal. It is their contention that the lithium has displaced some of the metallic filler materials in the glass-to-metal seal.

Now, the metallic filler materials are presently in the glass for a specific purpose. Number one, they give the glass its characteristic color, and number two, they also contribute to the flowability characteristics in the molten state.

The corrective action which is presently being implemented with respect to this problem is that several glass-to-metal seals have now been developed with inorganic metallic fillers, and also a glass formulation has been developed with a high lithium content glass, the purpose of which is to hopefully retard or prevent electrochemical corrosion from occuring in the glass-to-metal seal.

Now, I don't have a lot of data which I'd be able to present to you. I have some qualitative data which I can comment on at this time, and that simply is: after about two months, 160°F storage, qualitatively speaking, the new seals with the inorganic fillers appear to be considerably better than the present lithium $SO_2$ seal.

So in answer to the question earlier, yes, we are aware of the problem, and yes, we are working towards solving the problem. And based on the preliminary results that I have seen to date, I think that a new glass-to-metal seal will be forthcoming fairly shortly.

Now, the subject of my discussion today is going to center around the safety characteristics of the lithium $SO_2$ system. Extensive tests have recently been conducted by PCI to quantitatively define the safety characteristics of high rate lithium $SO_2$ multicell batteries under various discharge and temperature profiles, which closely simulate actual field-use conditions.

My presentation this afternoon will briefly summarize the resulting behavior patterns of these multicell batteries and the corrective action which can be implemented to minimize or prevent hazardous battery performance.

These studies were conducted on various size high rate cells and batteries, ranging from 8 to 30 ampere-hours. The hermetic cell structure, which is the basis for these studies, is shown in Figure 6-49.

(Figure 6-49)

It essentially consists of three primary components: a lithium anode, a porous carbon cathode, and a porous insulator barrier, which are assembled into a laminate, spirally wound, and inserted into a steel casing. After appropriate electrical connections are made, the cell periphery is hermetically sealed, and electrolyte introduced into the cell.

(Figure 6-50)

Several battery design approaches and techniques, as shown here in Figure 6-50, have been developed to ensure safe operation of multicell batteries under field use conditions. They include the following: First, an electrical slow blow fuse, normally installed within the positive leg of the battery, can be used to electrically deactivate the battery and prevent possible cell venting in the event of inadvertent shorting of the oupput perminals.

Second, an electrical diode, normally installed within the psoitive leg of parallel-wired cell stacks, can be used to ensure proper directional flow of current and prevent possible forced cell reversal, a condition whereby active cells within a multicell battery force a weak or dead cell into reverse voltage.

Third is an insulative jacket, which normally is installed on the cell exterior to prevent inadvertent short circuits during battery assembly, and operation. Shrinkable Mylar insulative jackets have been observed to be far superior to conventional polyvinyl chloride jackets, especially during exposure during various shock and vibration environments.

In addition, Mylar has excellent dielectric and mechanical strength characteristics and exceptional resistance to thermal shock. Mylar has been found to significantly reduce the incidence of external short circuits due to surface abrasion of the jacket by inner-cell connection tabs and also due to splitting or cracking of the jacket during exposure to thermal shock environments.

Fourth is battery encapsulation. Now, encapsulation of the battery is sometimes required to prevent movement within the battery structure, especially during vibration, shock, and normal handling. Such encapsulation must be carefully controlled to prevent reinforcement of the cell vent structure, which may compromise its normal activation pressure.

Extensive test have shown that the preferred technique is utilization of a suitable, nonflammable elastomeric or foamed encapsulant, which will not affect operation of the safety vent.

The final consideration here is the thermal switch. Limited thermal control of the battery can be accomplished to prevent overheating and possible venting of cells within the battery structure, especially during prolonged electrical discharge at elevated temperatures.

(Figure 6-51)

The selected approach, as shown in Figure 6-51, utilizes an automatic, normally closed, temperature-sensitive thermostat. The thermal response and sensitivity of the thermostat primarily results from proper selection of the temperature limits and its location relative to the internal cell stack structure.

In order to minimize thermal lag, the thermostat can be mounted on a copper heat sink contoured to the shape of adjacent cells, as shown here in the lower illustration. Electrically insulated, thermally conductive epoxy can be used to secure the heat sink to the thermal switch and to adjacent cell surfaces to allow rapid heat transfer from the cell casings.

Other alternative methods of mounting are possible, depending upon thermostat selection and the desired degree of thermal response.

Thermal switches have been successfully utilized in such high-rate multicell batteries as the BA-5599, which consists of three series-connected 8 ampere-hour cells discharged at 2 amperes constant current, and the BA-5840 battery, which consists of ten series-connected 25 ampere-hour cells which are discharged primarily at 3 amperes constant current.

The thermostat used for both these applications has an open temperature of +185 F and a closed temperature of +140 F.

(Figure 6-52)

This figure shows a typical performance versus a temperature curve of a BA-5840 battery during a 3 ampere constant current discharge at plus 130 degrees within a temperature-controlled chamber.

You'll note that the thermal switch does not activate under this environmental profile, since thermostat temperature does not rise above +175°F, a value reached near end of service life, as shown on the graph.

Also note that the external battery case temperature follows the thermal switch temperature profile, but at a significantly lower level.

(Figure 6-53)

This figure illustrates the behavior of a second BA-5840 battery identically discharged under the same thermal environment. But in this case, the battery was enclosed in a thermally insulated container to prevent heat dissipation, as might occur under certain field use conditions.

Note here that the thermal switch has now safely deactivated the battery at the desired temperature and has permitted resumption of the discharge at a safe thermal level. Performance of this test on similar batteries containing no thermal switch consistently resulted in the venting of one or more cells.

There are, however, several abusive test environments under which a thermal switch cannot acceptably deactivate the battery, the most important of which are forced cell reversal and internal cell short circuit conditions, which must be corrected by appropriate design changes within the cell.

(Figure 6-54)

Several cell design approaches, as shown here in the next figure, have also been developed to ensure safe operation of high-rate multicell batteries. They include the following: first, the safety vent. Since the lithium $SO_2$ electrochemical system utilizes a pressurized electrolyte, a pressure-activated safety vent mechanism was developed to exhaust overpressurized electrolyte at a predetermined temperature to effect cell deactivation and preclude a hazardous explosion.

(Figure 6-55)

The safety vent, as shown here, essentially consists of a coined cross section located in the can wall and parallel to the center line, a configuration which occupies minimal internal volume.

Extensive abuse tests conducted on this particular vent design have shown reproducible cell venting at a pressure of approximately 450 psi during exposure to such tests as short circuit, high current discharge, hotplate tests, elevated thermal storage tests, hydraulic pressurization, incineration, and many conditions of cell reverse discharge.

Going back to the previous figure, additional cell design considerations include the electrode design, specifically the power limited and the balanced electrode configuration. The power limited cell design structure essentially consists of an electrode which is structured in such a manner as to minimize the exposed electrode surface area and the resulting short circuit current.

The cell encasement is designed to withstand the pressure developed during short circuit conditions, thus precluding vent activation. Such a configuration is often desirable in low rate applications, where adjacent electronic equipment or components or personnel could be severely damaged by vented electrolyte.

The balanced electrode configuration essentially utilizes an electrochemically balanced proportion of the active materials, a very important consideration in minimizing or preventing hazardous multicell battery performance.

Several design considerations must be addressed, however, to fully understand this design concept. First, it is necessary that a stoichiometrically balanced proportion of the active components be maintained, specifically the quantitative amount of lithium to available sulfur dioxide. Numerous tests have verified that failure to maintain a lithium-to-$SO_2$ ratio reasonably close to 1 may result in violent cell rupture, especially in the event of forced cell reversal at high discharge current rates.

However, equally important to limiting the amount of lithium within the cell is ensuring that a sufficient amount of active carbon is available to permit complete utilization of the active components, especially under high current discharge profiles. Cathode efficiency is primarily a function of the quantitative amount of carbon present, the cathode porosity and its corresponding electrical conductivity and the level of residual contaminants within the cathode pores.

Extensive tests have verified that failure to provide a sufficient number of active carbon sites can result in hazardous cell rupture, independent of the lithium-to-$SO_2$ ratio.

In the process of designing a lithium limited cell, one must make provisions to ensure that the lithium anode does not become electrically isolated during discharge, especially near the end of cell service life. This condidion, which is characteristic of high-rate electrochemically balanced designs, is primarily the result of localized fracturing or severing of the anode near its conductor tab due to nonuniform utilization of the anode.

Such anode fracturing typically results in immediate loss of cell output voltage which, within multicell batteries, will often result in forced cell reversal. Continued discharge of the battery under these conditons has been observed to result in hazardous cell rupture or venting, dependent upon the discharge profile, battery temperature, and the quantitative amount of isolated lithium within the cell.

In addition, anode fracturing results in premature cell service life, which compromises the performance and the efficiency of the battery.

Several corrective measures have recently been developed to minimize or prevent this condition, as shown in the next figure.

(Figure 6-56)

The top part of the illustration shows a conventional anode with a current collector tab at one end, a configuration which has shown to be more prone to anode fracturing. The lower part illustrates a multiple tab configuration with a current collector located at each extreme end of the anode. This construction technique has been shown to minimize or prevent localized fracturing of the lithium and substantially increases electrode utilization efficiency. However, use of this technique is quite cumbersome and does not readily lend itself to eventual automation.

(Figure 6-57)

The preferred approach as shown in this figure, essentially consists of a continuous anode current collector, approximately 1/8 inch in width, which is laminated along the length of the lithium during fabrication of the anode. This configuration permits efficient utilization of the anode without the risk of lithium isolation and its associated hazards. In addition, this technique is quite amenable to automatic electrode fabrication.

An alternate approach, as shown here in the lower illustration, often used in very high rate applications, consists of a parallel electrode configuration, whereby two independent anodes are wound in parallel with two independent cathodes. This method of high rate construction allows the use of large surface area electrodes without the need for very long electrode structures and their related shortcomings.

Based upon years of extensive test history and field experience on hermetically sealed lithium cells and batteries, it can be reasonably concluded that the lithium $SO_2$ system is safe and reliable for most military and commercial applications. Furthermore, it should be mentioned that PCI has not had a single hazardous incident reported in the transportation or shipment of over one million cells over the past several years.

However, like other high-energy electrochemical battery systems, lithium $SO_2$ has certain limitations and restrictions which may, at times, present potentially hazardous conditions, as may be encountered within multicell batteries, under very high current discharge profiles, and thermal extremes.

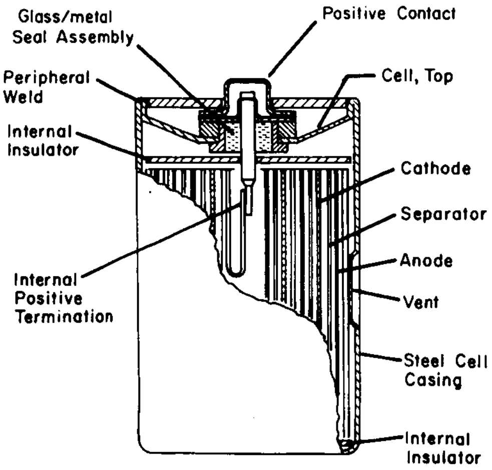
Significant effort has been directed towards defining and characterizing these conditions and implementing corrective designs where necessary, in an effort to minimize these limitations.

It is important that these atypical battery applications and high-rate discharge profiles be carefully assessed to determine practical trade-offs between battery performance, safety, and economics in an effort to achieve an optimal safe design.

Judicious use of the techniques and design improvements which I have presented today will enable the lithium $SO_2$ system to be safely used in applications previously considered marginal or hazardous. A partial list of some of the areas in which the lithium $SO_2$ system has been successfully deployed is shown in the next figure.

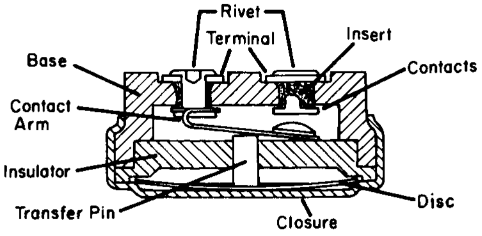
(Figure 6-58)

Some of these have been discussed already this morning. They include atmospheric balloons, oceanographic applications, communications, CMOS memory, emergency beacons, lasers, medical instrumentation, aerospace, telemetering, and test equipment.

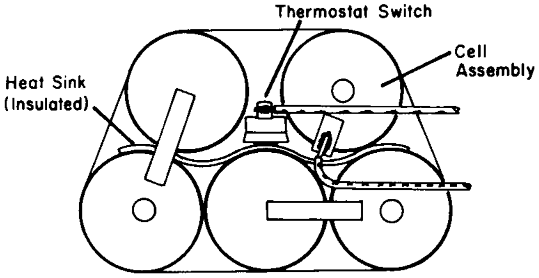


CELL CROSS SECTION

Figure 6-49



THERMOSTAT



BATTERY STACK STRUCTURE

Figure 6-50

## BATTERY DESIGN CONSIDERATIONS

- Electrical fuse
- Diode
- Insulative jacket
- Battery encapsulation
  - non-flammable
  - safety vent activation
- Thermal switch
  - temperature control
  - limitations
    - internal short circuit
    - forced cell reversal

Figure 6-51

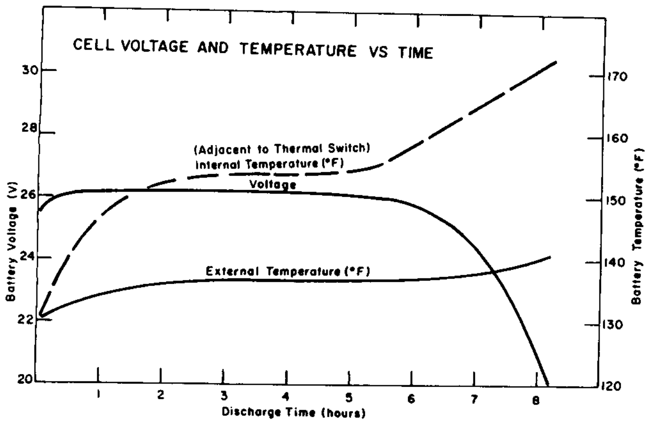


Figure 6-52

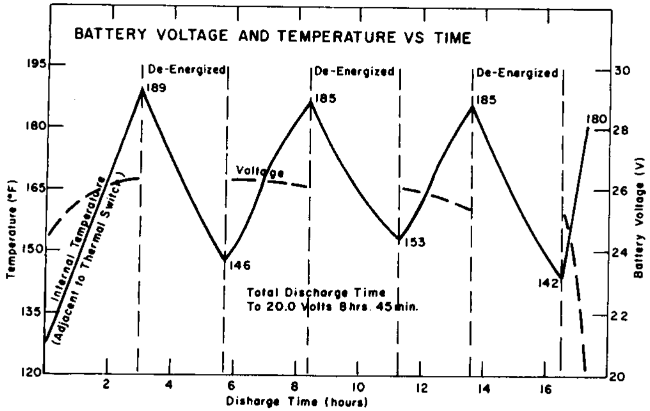


Figure 6-54

## CELL DESIGN CONSIDERATIONS

- Safety vent mechanism
- Electrode design
  - Power limited configuration
  - Balanced electrode configuration
    - Lithium limited
    - Cathode efficiency
    - Anode current collector
      - Multiple tabs
      - Parallel electrodes
- Performance/safety tradeoffs

Figure 6-53

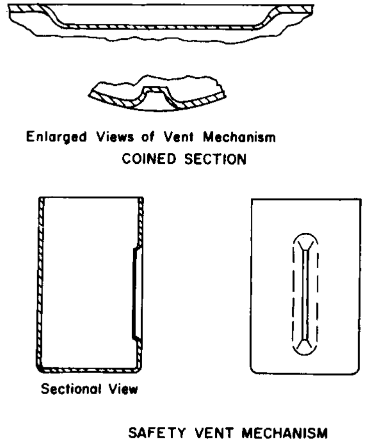


Figure 6-55

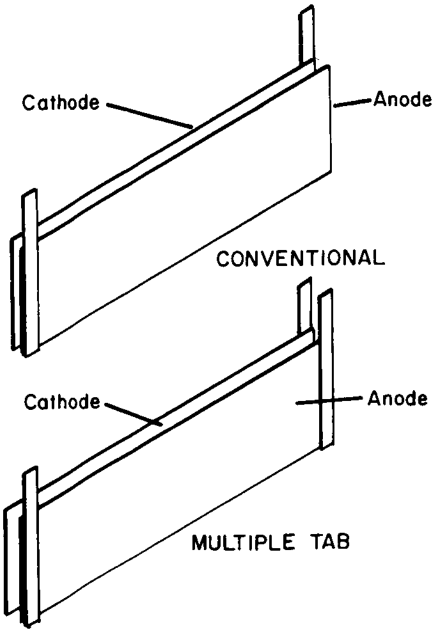


Figure 6-56

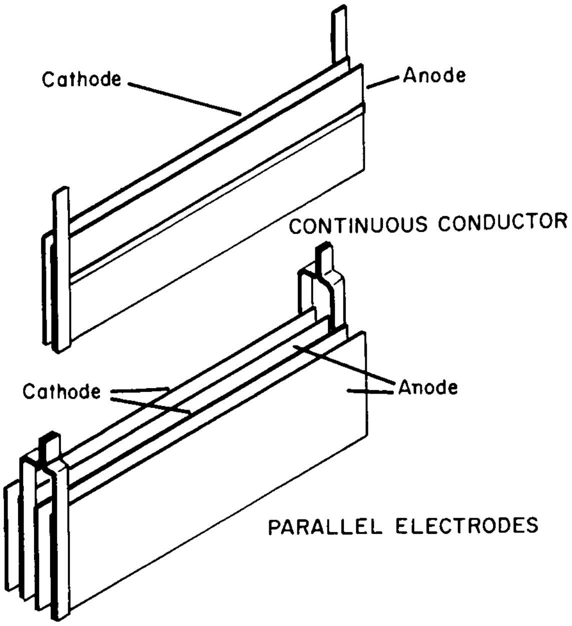


Figure 6-57

GOVERNMENT/MILITARY APPLICATIONS

Atmospheric balloons
Oceanographic applications
Communications
Cmos memory
Emergency beacons
Lasers
Medical instrumentation
Aerospace
Telemetering
Test equipment

Figure 6-58

# 1978 GSFC BATTERY WORKSHOP
November 14 - 16, 1978

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