NASA Conference Publication 2177

The 1980 Goddard Space Flight Center Battery Workshop

A workshop held at
Goddard Space Flight Center
Greenbelt, Maryland
November 18-20, 1980

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PREFACE

This, the 13th Annual Battery Workshop was attended by manufacturers, users, and government representatives interested in the latest results of testing, analysis, and development. The purpose of the Workshop was to share flight and test experience, stimulate discussion on problem areas, and to review the latest technology improvements.

The papers presented in this document have been derived from transcripts taken at the Workshop held at the Goddard Space Flight Center on November 18-20, 1980. The transcripts were lightly edited with the speaker's vugraphs assembled at the end of each presentation for uniformity.

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INTRODUCTION

G. Halpert

Goddard Space Flight Center

On behalf of NASA and Goddard Space Flight Center, I should like to welcome you to the 1980 NASA Battery Workshop.

After an opening paper by Judy Ambrus, and the rest of the morning will be devoted to a session on lithium primary cell technology. This session will continue in the afternoon, and will be concerned mainly with the subject of lithium primary cells and safety in operations. It will be followed by a panel discussion, which I hope you will all find interesting. The panel has been set up by Charles Scuilla of CIA, and its members will discuss safety aspects of lithium and other cells.

Tomorrow we shall start with some discussion of future needs in the aerospace business, and continue with a discussion of electrode material technology. Tomorrow afternoon we shall continue with the subject that has been dear to us for the last few years: statistical analysis of battery data and accelerated testing. This will be followed by a panel discussion on the subject of synchronous orbit accelerated testing. On Thursday, morning we shall discuss the results of space flight testing, and actual on-board experience of nickel cadmium cells. Then, Finally, on Thursday afternoon, we shall discuss the nickel hydrogen area, which is of significant interest here for the future in aerospace.

For your information, we have included a list of the acquisition numbers for all workshop proceedings dating back to 1970.

BATTERY WORKSHOP PROCEEDINGS

		Doc. No.
1979	Workshop	80N20820
1978	Workshop	79N28669
1977	Workshop	79N21565
1976	Workshop	77N21550
1975	Workshop	76N24704
1974	Workshop	75N16976
1973	Workshop (1st Day)	75N15152
	Workshop (2nd Day)	75N17808
1972	Workshop (1st Day)	73N21956
	Workshop (2nd Day)	73N21957
1971	Workshop (Vol. 1)	72N27061
	Workshop (Vol. 2)	72N27062
1970	Workshop (1st Day)	71N28659
	Workshop (2nd Day)	71N28672

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CONTENTS

SESSION I
OPENING REMARKS

SESSION II
LITHIUM PRIMARY CELL TECHNOLOGY

SESSION III
FUTURE NEEDS

SESSION IV
ELECTRODE/MATERIAL TECHNOLOGY

SESSION V
STATISTICAL ANALYSIS AND ACCELERATED TESTING

SESSION VI
NICKEL CADMIUM PERFORMANCE AND TESTING

SESSION VII
NICKEL HYDROGEN CELLS/BATTERIES

SESSION I

OPENING REMARKS

G. Halpert Chairman
Goddard Space Flight Center

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OVERVIEW OF NASA BATTERY TECHNOLOGY PROGRAMS

J. AMBRUS
NASA HEADQUARTERS

I am honored to be here as a representative of the Office of Aeronautics and Space Administration to open the 1980 NASA Battery Workshop. This workshop has traditionally brought together technical experts in the field of batteries from NASA, sister agencies, and government and industry. As such, it has always been observed by NASA Headquarters as one of the most authoritative sources of technical information on the planning and testing of future programs.

In NASA, as in other agencies, batteries are part of almost every mission, and so NASA has many battery programs.

The purpose of the space research and technology program in NASA is to provide a technology base that will adequately support and enhance, current and future activities in the exploration and exploitation of space. Therefore, our programs, the OAST programs, are structured such that they support present battery programs with fundamental understanding and also enhance future missions. Part of our program is to push forward the frontier of technology, as NASA has always done, so that, in future, missions will be possible that we cannot even comtemplate today.

I should like to tell you about the NASA organization, so that you see where this program fits in.

(Figure 1-1)

NASA is organized under an Administrator, at present Dr. Frosch, and there are six associate administrators who run the technical programs. One of these is the Associate Administrator for Aeronautics and Space Technology, who is responsible for our program.

There are also many technical centers, on which we depend to carry out the technical programs. Headquarters makes plans with the aid of the technical centers, and leaves the execution of the programs to the technical centers.

At present most of our interactions are with Lewis Research Center in Cleveland, JPL in Pasadena, Johnson Space Flight Center in Houston, and some here at Goddard. However, there are many other battery programs that I know of, such as at Langley and at Marshall, and I am sure that there are some that I do not know of yet.

Within the Office of Aeronautics and Space Technology we have an organization as such, and here we come down to the technology areas that we support.

(Figure 1-2)

There is a division, the Research and Technology Division which supports fluid physics, propulsion materials and structures, electronics and human factors, and space power and propulsion. Chemical energy storage and conversion falls within the category 'space power and propulsion.'

In other words, our purpose is to provide the technology base in the areas of photovoltaic energy conversion, chemical energy conversion and storage, thermal-to-electric conversion, power systems management and distribution, and to explore revolutionary concepts in energy storage and conversion.

So if you have an excellent idea that would replace batteries forever, please come to us. We support it. However, in the meantime, we still have battery programs.

The missions in general that are envisioned are high-orbit spacecraft, low-orbit earth stations, planetary orbiters and planetary probes. When this is translated into what we want the batteries to do, it comes down to what we always want to do: we want high energy density, high capacity, long cycle life, long storage life, and, of course low cost. Now these sound like "Motherhood" statements, but this is what really drives battery technology in every agency, including NASA.

With this in mind how do we plan the program?

It is very much a team approach. Major meetings are held under Headquarters' sponsorship. One is the Center Managers' Meeting where we discuss with the center managers (the technical experts) what they expect to do.

Program reviews, of course, take place every year. Technology workshops such as this one are authoritative sources, The SSTAC (Space, Science and Technology Advisory Committee) meeting. This committee comprises a group of people from government, industry and universities, who help advise us on the directions in which the technology should go.

We also have informal meetings, we sponsor the Inter-agency Advance Power Group (IAPG), we talk to industrial contractors, and of course attend professional society meetings. From this comes the following documents.

The first is the discipline long-range plan, which gives the 25-year outlook. The next is the space research and technology program and specific objectives. Those of you in NASA refer to this as the famous "Pacer" document, which gives the five-year objectives. And then came the research and technology objectives and plans, where the centers spell out the technical milestones for the next year or two to help them meet those five-year plans.

Figure 1-3 shows the 25-year outlook.

(Figure 1-3)

In chemical energy storage and conversion in the year 2000 we are looking for something bigger than 3MJ/kg -- a very high energy density.

The five-year plan looks more down to earth.

(Figure 1-4)

There are three major areas of concentration: high-energy density batteries, high-capacity energy conversion and storage (primarily fuel cells), and fundamental understanding of alkaline and metal gas battery. The milestones are being met by the different centers: JPL, Lewis, Johnson and Goddard.

The five-year outlook also depends a great deal on the budget.

Let me give you a very brief overview of the actual technical programs that we are engaged in. I shall not give you many details, because the technical experts from NASA here will do that.

About 25% of our program is directed toward understanding the fundamentals of batteries now in existence. That is, of course, nickel cadmium, the good old workhorse of the space program. We have used nickel cadmium batteries, we are continuing to use nickel cadmium batteries, and we probably shall be using nickel cadmium batteries in days to come.

However, complete fundamental understanding still eludes us, and this is where we are trying to help. One of the programs we are supporting is that of understanding the failure mechanism. This has been carried on for a number of years here at Goddard, with some testing at Crane. The data are being evaluated now in view of different helium models. Pat McDermott, who is working under NASA sponsorship will talk about his approach. We shall also hear a talk on the JPL approach, which is sponsored by NASA.

Another approach is to advance the design, and Lewis Research Center has been engaged in that. They want to demonstrate likely components, fabrication and life. EIC has been involved as a contractor in that program.

(Figure 1-5)

The next generation of batteries -- and we shall talk about it during the next three days -- is nickel hydrogen. This will probably be the mid-term outlook for new power sources in space.

We have a program that is carried out by the Lewis Research Center and, to some extent, here at Goddard. The present technology has been carried forward primarily by the Air Force until now, and we are going to pick up at NASA and adapt it to NASA requirements. We have to scale it up to bigger capacity, and shall be engaged somewhat in component technology. This is the kind of application that we are looking for both in geosynchronous orbit and in low-earth orbit.

(Figure 1-6)

Although fuel cells are not really part of battery programs, I shall mention them because they are also a traditional NASA way of converting chemicals to electrical energy. A new concept, at least in the practical sense, is the regenerative fuel cell program. We are engaged in two different fuel cell programs; one is the hydrogen-oxygen-alkaline; the other one the hydrogen-oxygen-acid solid polymer electrolyte.

The solid polymer electrolyte is a General Electric invention: it uses a sulfonated teflon fluorocarbon as the electrolyte. It is an excellent idea to use a fuel cell as a rechargeable system, since water can be electrolyzed; the idea has been to use the fuel cell to provide electricity and then, during the time when the cell is on the sunny side, to recharge it by electrolyzing water. This program has been carried on for some years at Johnson Space flight Center and Lewis Research Center in Cleveland.

So far, we are aiming at multikilowatt large systems for low-earth applications. It is possible under given conditions -- we can see that already -- to get 100 w/kg. Geosynchronous missions seem to be better than low-earth orbit missions.

We have found out so far that Dedicated components are better than using the same cell for both fuel cell and electrolyte. In other words, you have a fuel cell part and an electrolyte part and you switch back and forth.

System design is a very, very important part. Breadboard designs are within the five-year plan. They are going to come down about three years from now. Tradeoff studies are being carried on and lightweight components are being developed.

Also, somewhere along the line we shall have to decide which is the better system, the alkaline or the SPE system. As of this date they are being developed simultaneously.

(Figure 1-7)

Now let us move to the far future. Like everybody else, we are looking at the alkaline systems. In 20 or 30 years, we are hoping to have lithium or sodium-based systems. At present there are two under development at JPL. One is the lithium ambient temperature metal sulfide. We are currently looking at titanium disulfide, but there are others that are still in the running. This system is by no means cast in bronze. The other one is a low temperature (150) molten salt system. Again, the cathode is a sulfide, but this is not cast in bronze either. This is being investigated at Lewis Research Center in Cleveland in conjunction with EIC.

At present we are simply looking for feasibility and fundamental understanding. It is a truly long-range technology based program, and of course this is what we are looking for in the far future.

(Figure 1-8)

For certain missions, such as planetary probes, NASA is also interested in primary batteries for the first time in years. We are of course looking for primary batteries with very high energy density. Like everybody else, we are looking at the thionyl chloride system, and also the sulfuric chloride, the oxychloride systems in general.

Again, because of the very stringent requirements on NASA batteries, we are currently looking for basic understanding: feasibility, safety, rate capability and obtaining relations between component physical characteristics and performance should enable us to rely on very high density energy batteries.

This program is also carried out at JPL, and some of the people who are engaged in it will talk about it talk during the next few days.

So this is, in essence, an overview of the battery programs sponsored by the Space Research and Technology Program.

(Figure 1-9)

To leave you with this though, our program is structured in three different levels: High energy density (200W h/kg), high capacity (100 kw for LEO, 25 kw for 9E0) fundamentals, the life and the understanding of these programs.

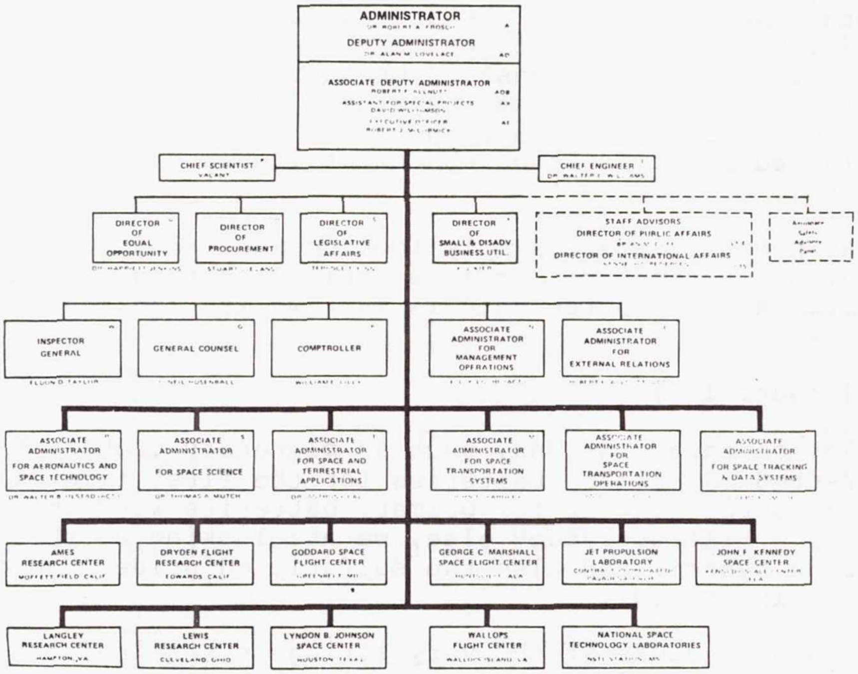

Figure 1-1

OFFICE OF AERONAUTICS AND SPACE TECHNOLOGY

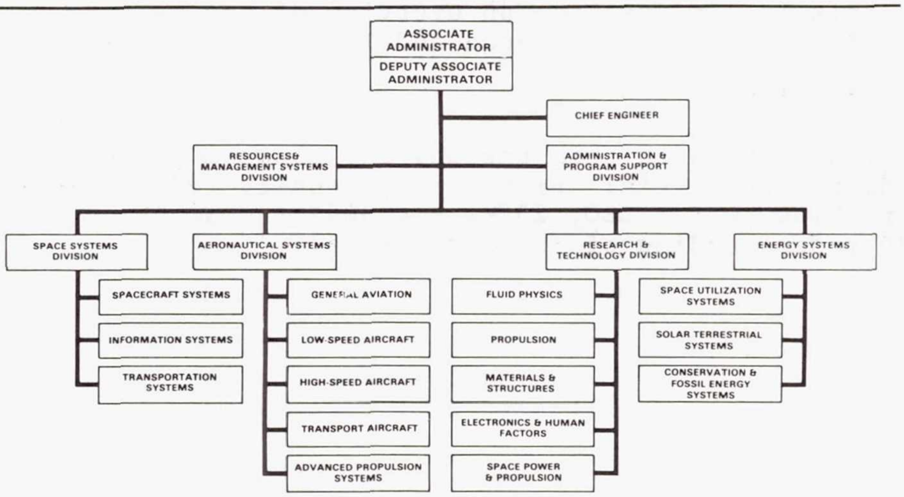

Figure 1-2

SPACE POWER AND ELECTRIC PROPULSION 25 YEAR OUTLOOK

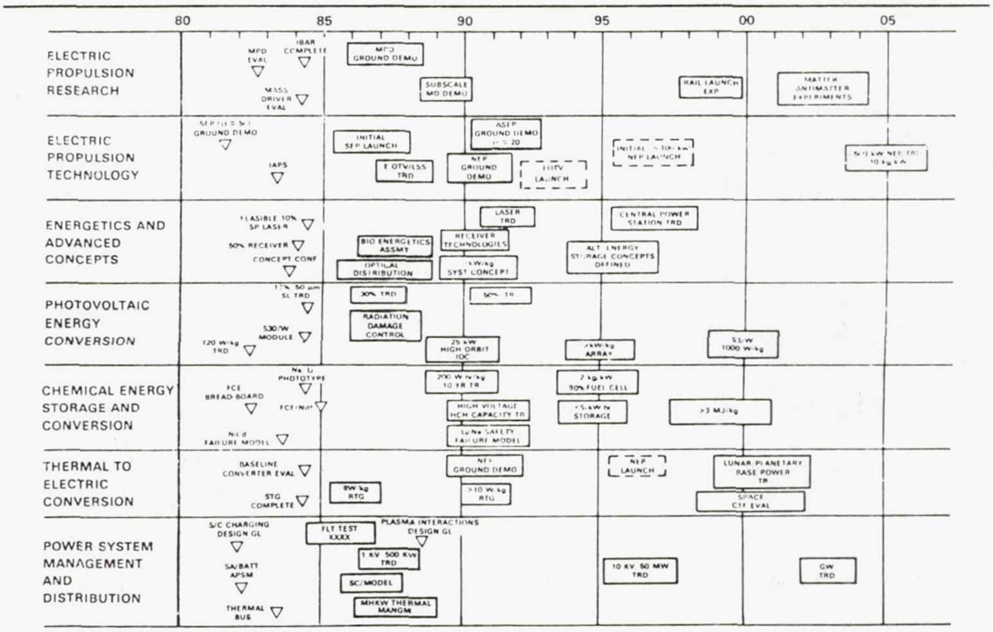

Figure 1-3

CHEMICAL ENERGY CONVERSION AND STORAGE

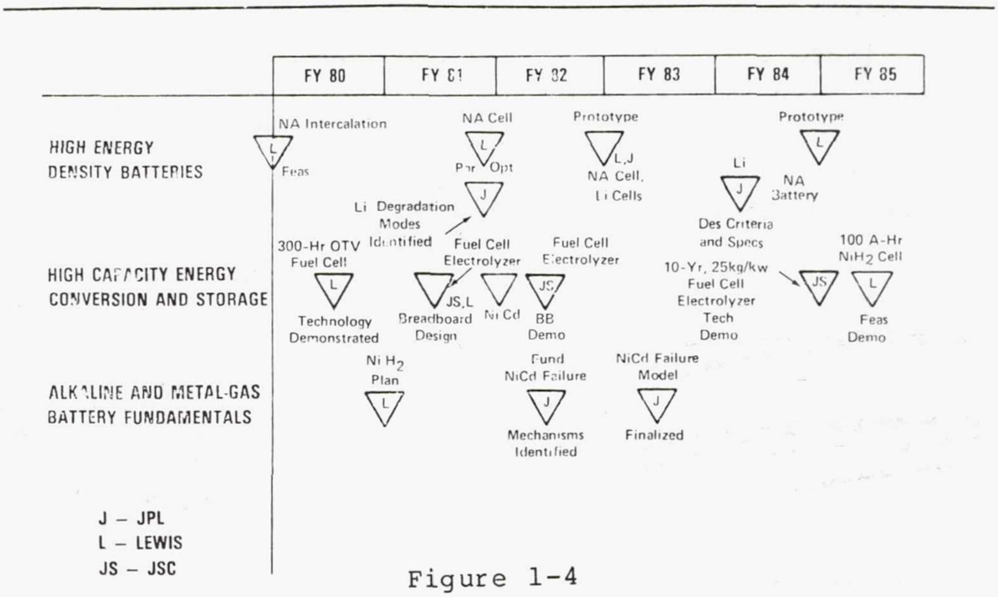

Figure 1-4

ELECTROCHEMICAL SYSTEMS UNDER INVESTIGATION

NICKEL-HYDROGEN

- PRESENT TECHNOLOGY TO BE EVALUATED
- ADAPTATION TO NASA REQUIREMENTS

⟹ 20-25 WHR/KG
SCALE-UP
COMPONENT TECHNOLOGY

900 CYCLES (GEO) 10 YR	6000 CYCLES 1 YR	30,000 (LEO) 5 YR

Figure 1-5

ELECTROCHEMICAL SYSTEMS UNDER INVESTIGATION

FUEL CELL/ELECTROLYSIS

REGENERATIVE

100 WHR/KG
MULTIKILOWATT

H_2-O_2 ALKALINE
H_2-O_2 SPE

DEDICATED COMPONENTS
SYSTEM DESIGN
BREADBOARD
TRADE-OFF STUDIES
LIGHTWEIGHT COMPONENTS

Figure 1-6

ELECTROCHEMICAL SYSTEMS UNDER INVESTIGATION

HIGH ENERGY DENSITY SECONDARY

- LI/2METHF, $LIAsF_6/TIS_2$
- NA/BETA ALUMINA, $NAALCL_4/VS_2$, MoS_3

200 WHR/KG
500 CYCLES
5 YRS
C/2 RATE

FEASIBILITY
FUNDAMENTAL UNDERSTANDING

Figure 1-7

ELECTROCHEMICAL SYTSTEMS UNDER INVESTIGATION

LITHIUM PRIMARY

$LI/SOCL_2$ LI/SO_2CL_2

400 WHR/KG

- FEASIBILITY
- SAFETY
- RATE CAPABILITY
- STORAGE LIFE

FUNDAMENTAL UNDERSTANDING
OBTAIN RELATIONSHIPS BETWEEN
COMPONENT PHYSICAL CHARACTERISTICS
AND PERFORMANCE

Figure 1-8

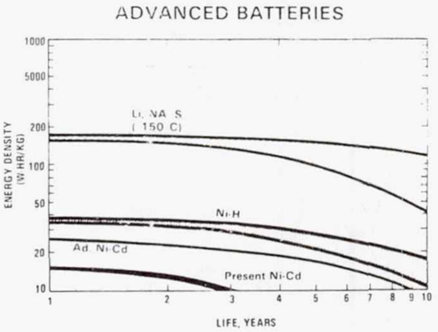

Figure 1-9

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SESSION II

LITHIUM PRIMARY CELL TECHNOLOGY

C. Mueller, Chairman
Naval Surface Weapons Center

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Li/SO$_2$ CELL FOR GALILEO

L. Blagdon, Honeywell
L. Marcoux, Hughes Aircraft

I should like to present some information on special process controls for lithium sulfur dioxide (Li/SO$_2$) batteries, and how those controls have affected two specific programs that we are currently working on.

One of those is the Galileo Probe program, the prime contractor being Hughes Aircraft Corporation, Space and Communications Group; this program is a NASA Ames program.

The other program for which I should also like to present some data is the instrumented test vehicle program out of U.S. Air Force Space Division, contracted through the Systems Division of AVCO Corporation.

The last time we were here at this presentation we said that high tolerances of cells is important. I think there are enough data now to show that that really is true.

I should like to talk a little about the general design considerations that go into any application for basically any type of battery system. However, there are some unique tradeoffs because of the safety characteristics of the Li/SO$_2$ system.

I shall review some of the special process controls that we used on these two programs. There are also differences caused primarily by the environments of the two programs. I shall then disucss some particulars of design and how the need for process controls plays in, and follow that with some data that show the actual impact o those process controls.

(Table 2-1)

First, one of the initial things to be done is the selection of the cell size; this is determined by the requirements of the application. This is nothing new, of course, but we do have some unique characteristics and must talk about the coulombic ratio of our components in terms of safety and also sizing of the cells appears to be reduced to the smallest equivalent package that we can put together.

At that point, the component tolerances built into the cell become more important, and standard manufacturing tolerances for use in communications devices may not have the required reliability or repeatability for a Galileo-type program.

(Table 2-2)

So, I shall spend some time now talking about the actual process controls or variations from standard that we used on these two particular programs.

First, the two programs use different cell sizes. The Galileo program uses a high-rated D cell; early development on that cell and the Galileo battery module was done with a great deal of assistance from the General Electric Corporation, the RESD in Philadelphia. The ITV program uses a high-rated DD cell.

Both programs basically use a polemically balanced cell by design. The Galileo program required serialization of cells, and so we have individual records on all the cells in the program. This is not required by the ITV program.

Carbon collector weights are sorted to a tolerance that is tighter than normal, and recorded on the Galileo program. They are only sorted to a tolerance on the ITV program.

Anode weights seem to be critical for sulfor dioxide or coloumbically balanced cell hardware -- both programs have a tighter than normal weight sort. Both programs use anode current collectors because they are coulometrically balanced. Figure 2-1 some of the others.

(Figure 2-1)

If we first consider the theoretical capacities built into a given cell size, whether it is essentially sulfur dioxide limited or lithium limited, we get a curve with this general theoretical shape. Then, by projecting a nominal from that from data collected in designs on all extremes, we find there is less utilization efficiency on the sulfur dioxide, primarily caused by the fact that both materials are depleting at the same time. This is not really significant.

(Figure 2-2)

However, problems arise when manufacturing tolerances are applied. If sulfur dioxide limited cell hardware is used, typical fill weight tolerances can be controlled very tightly, and normally give a very nice theoretical capacity variation in the cells.

On the other hand, the theoretical capacity variation for the lithium limited configurations begins to broaden out because of manufacturing tolerances and variations. In fact it can reach 10%, which is really not acceptable for the Galileo program.

Therefore weight sorting is a requirement.

(Figure 2-3)

As an example of how that kind of information manifests itself in the ITV program, the lower line in this graph represents a group of high-rate DD cells that were coulombically balanced (Li: 50_2 = 1.0:1). The upper line represents a group of cells that were essentially a sulfur dioxide limited design (Li: SO_2 = 1.2:1). The difference in performance on a nominal basis is obvious, as is the difference in the associated standard deviations. There lower cells had standard tolerance parts in them.

For the ITV program, we retained the coulombically balanced configuration, primarily because the discharge current is about 3A at a lower discharge current rate. However, we applied a tighter weight sort tolerance on the lithium anode and have achieved results similar to the upper dot at the 3-A level.

For a program with a very low rate application, the coulombic balance effects are not as great. On the other hand, for a program with very high rates, the problem seems to expand itself.

By the way, I might mention that this group of cells, when driven into reverse, did vent. It was therefore an unacceptable combination for a multicell series string battery, and we did retain the coulombically-balanced cell.

(Figure 2-4)

I have one graph here that does not necessarily address this specific area. However, last year a great deal was talked about storage capability and glass-to-metal seals, on an industrial basis. I think you will hear more information on the reliability point of view; there has been some work done with the processing of glass-to-metal seals, and some very good positive data have been generated. High-rate D cells were stored in the inverted position at 160 F. Fifteen cells were pulled at each of the different time periods and tested; you can see the overall result during a 16-week period. Glass-to-metal seals had not corroded through, although there was some indication of a reaction taking place on the glass at that point. However, it was not a major, catastrophic characteristic.

(Table 2-3)

Table 2-3 compares some standards with representative lots of high-rate D cells, and shows their mean capacity and standard deviations through a Galileo high-rate cell, which is essentially the only one with tighter tolerances on the manufacturing. There is an effective difference in the shift of the mean and the smaller standard deviation.

The Galileo battery comprises three 13-cell modules that essentially do nothing for three and a half years. At the point of separation, 100 days before the mission, coast time kicks on and also a backup G switch operates.

(Table 2-4)

About five or six hours before the mission, several things start to happen. We simulate a failure mode to the possibility that the timer failed and that the G switch was called upon to operate. You can see the instrument switch on, then after the full transmitter, full instrument package comes on, there is a series of fairly rigorous pyro pulses. Those currents are on top of that baseline 9-A current.

We have three parallel modules putting out a fairly large current, starting around -5 to 0 C; it is a non-trivial test to simulate all these things. Therefore, we were extremely pleased with the ability demonstrated by our subcontractor in being able to perform this very complicated test.

During the mission the three modules are essentially, but not entirely, identical, because early in the game we pulled one module out and coast timer.

(Table 2-5)

So during that 100 days the coast timer module is undergoing a rather bizarre duty cycle of 1.2 mA baseload with a 27.5 mA pulse every and dedicated it to the coast timer was because our discovery was in agreement with that of several other people: that the ability of lithium sulfur dioxide cells to produce high rates was impaired by prior performance at low rates. I think the two test results are interesting.

(Figure 2-5)

The first test is a control, involving the three 13-cell modules. Figure 2-5 shows only the actual seven hours of mission, with a scale that emphasizes the important 48 minutes of actual descent where the transmitter and science packages are operating. In addition to those 48 minutes the test continued for another full 31 minutes above the 28 V required to operate the various science packages. Thus we have about 1.75 mission in the ideal case.

(Figure 2-6)

Another thing we are interested in is the redundancy, in that each module carries an extra cell. We were curious about the effect on load sharing etc. of removing one cell from one of the dedicated descent modules. We still met the mission handsomely, and, in fact, carried on for 18 more minutes.

The real way that failure manifests itself is that rather than sharing equally, one steps in after the other because of a voltage difference. You can see modules 1 and 2 carrying their share of the load. Then, as their voltage drops, the module that has the failed cell kicks in.

This really means that in the failure mode, one module carries enormous currents, up to 7 or 8 A, which is a great deal to ask. However, these did so quite successfully and continued 18 minutes beyoned the mission.

To emphasize quality control and manufacturing tolerances:

(Table 2-6)

These capacities are not really critical. The two curves I showed are critical because we are interested in the amount of time above 28 V at load. However, I think the fascinating data here are the Module 1 and Module 2 capacities and the control, where you see there are two different modules separated by only 0.06 Ah which is a remarkable control. These cells are essentially identical, and play as a battery rather well.

I think, in closing, I should say that we have three years to launch, and undoubtedly we shall have some crises and catastrophes. However, at present we are quite pleased with the way things stand.

DISCUSSION

How tightly are you controlling the carbon loading of the cathode reactors' matrix? In addition to that, how important is this loading to safety, and how does efficiency vary with that loading?

BLAGDON: On the Galileo program, we had a carbon weight control, 13.2 -14.5 g total weight tolerance that we allow.

The efficiency depends on the application. The Galileo application is essentially at 0 or -10 C, and so it is not an extremely cold application.

If you look at the ampere hour capacities, we have not found them to play a significant role at those temperatures. At lower temperatures, such as -20 C, it begins to be more significant.

We have not found a real positive correlation to cathode weight, or carbon collector weight, and discharge performance at the zero.

SCUILLA: Did you find any relation as far as the safety of the cell with the carbon loading?

BLAGDON: No.

CLOYD: Could you give us an idea of the current density on that 6 A on a DD?

BLAGDON: No, I do not know it right off the top of my head.

That cell in the latest design configuration is getting just a little over 19 Ah at a 3 A discharge rate, which is about 2 mA/cm^2, 3 A.

GENERAL CELL DESIGN CONSIDERATIONS

CELL DESIGN ELEMENT	BATTERY DESIGN REQUIREMENTS
CELL SIZE	RUN TIME DISCHARGE RATE RELIABILITY (MARGIN) WEIGHT & VOLUME ENVIRONMENTS
LITHIUM TO SO_2 DESIGN RATIO	SAFETY DISCHARGE RATE
COMPONENT TOLERANCES	RELIABILITY (MARGIN) REPEATABILITY ENVIRONMENTS DISCHARGE RATE LOAD SHARING

Table 2-1

SPECIAL CELL PROCESS CONTROLS

DESIGN ELEMENT	PROGRAMS	
	GALILEO	ITV
CELL SIZE	G3109 HR "D"	G3033 HR "DD"
LITHIUM TO SO_2 DESIGN RATIO	1:1	1:1
SERIALIZED CELLS	YES	NO
CARBON COLLECTOR WT:		
SORT	TIGHT TOLERANCE	STD. TOLERANCE
RECORD	YES	NO
ANODE WEIGHT:		
SORT	TIGHT TOLERANCE	TIGHT TOLERANCE
RECORD	YES	NO
ANODE CURRENT COLLECTOR	DIAG. LEAD	GRID
ELECTROLYTE WEIGHT:		
SORT	STD. TOLERANCE	STD. TOLERANCE
RECORD	YES	NO
SINGLE LOT RAW MATERIALS	CARBON BLACK	NONE
DOCUMENTATION CONTROL	CELL MCD (PRINTS & PROCESSES)	CELL PROD SPEC.
GTM SEAL LEAK RATE	STD. TOLERANCE (100% SORT)	STD. TOLERANCE SAMPLE
VENT BURST PRESSURE	TIGHT TOLERANCE (100% SORT)	STD. TOLERANCE SAMPLE
PROCESS TRAVELERS	SPECIAL	STANDARD

Table 2-2

IMPACT OF SPECIAL PROCESS CONTROLS ON CAPACITY

	TYPICAL STD. HR "D" (1) (AMP-HRS)		GALILEO HR "D" (1) (AMP-HRS)
	LOT A	LOT B	LOT 2
MEAN	7.66	7.63	8.00
STD. DEVIATION	.25	.29	.17

(1) 2 AMP DISCHARGE AT ROOM TEMPERATURE

Table 2-3

GALILEO PROBE DESCENT LOAD PROFILE

START TIME	EVENT	DURATION	BATTERY CURRENT, A
T-100 DAYS	COAST	100 DAYS	
T-10 SEC	VARIOUS CONDITIONING LOADS	10 SEC	
T = 0.0	COAST TIMER FAILURE LOAD	10 SEC	1.44
T +10.0 SEC	PRE-ENTRY LOAD	5.52 HR	0.35
T + 5.53 HR	ATMOSPHERIC STRUCTURE INSTRUMENT LOAD	0.72 HR	1.52
T + 6.24 HR	PYRO PULSE 1	30 MS	7.35
T + 6.25 HR	TRANSMITTER AND SCIENCE PACKAGE LOAD	0.82 HR	9.63
T + 6.32 HR	PYRO PULSE 2	30 MS	7.35
T + 6.40 HR	PYRO PULSE 3	30 MS	7.35
T + 6.48 HR	PYRO PULSE 4	30 MS	7.35
T + 6.56 HR	PYRO PULSE 5	30 MS	4.20
T + 6.64 HR	PYRO PULSE 6	30 MS	4.20
T + 6.72 HR	PYRO PULSE 7	30 MS	4.20
T + 6.80 HR	PYRO PULSE 8	30 MS	4.20
T + 6.88 HR	PYRO PULSE 9	30 MS	4.20
T + 6.96 HR	PYRO PULSE 10	30 MS	4.20
T + 7.04 HR	PYRO PULSE 11	30 MS	4.20
T + 7.07 HR	END OF MISSION (0.1 BAR + 48 MIN)	–	

Table 2-4

GALILEO PROBE 100 DAY COAST LOAD

MODULE NUMBER	NUMBER OF CELLS	COAST LOAD
1	12*	1 μA
2	13	1 μA
3	13	1.2 mA CONSTANT DRAIN WITH 27.5 mA PULSE FOR 20 MSEC EVERY 256 SEC

*FAILURE MODE

Table 2-5

GALILEO PROBE SIMULATED BATTERY TEST CAPACITY

UNIT	TEST 2 – FAILURE MODE CAPACITY, A-HR	TEST 3 CAPACITY, A-HR	MISSION REQUIREMENT CAPACITY, A-HR
BATTERY	21.08	22.48	21.6
MODULE 1	5.13	7.51	7.2
MODULE 2	8.00	7.45	7.2
MODULE 3	8.20	7.87	7.2

Table 2-6

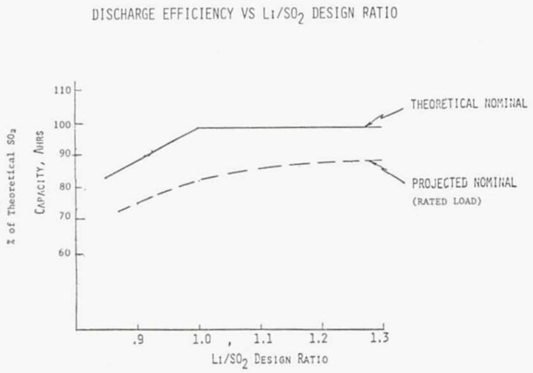

DISCHARGE EFFICIENCY VS Li/SO$_2$ DESIGN RATIO

Figure 2-1

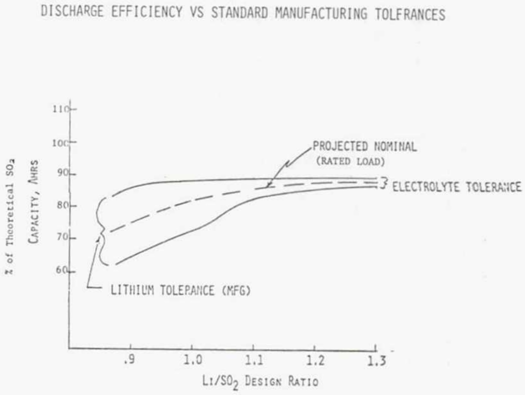

DISCHARGE EFFICIENCY VS STANDARD MANUFACTURING TOLFRANCES

Figure 2-2

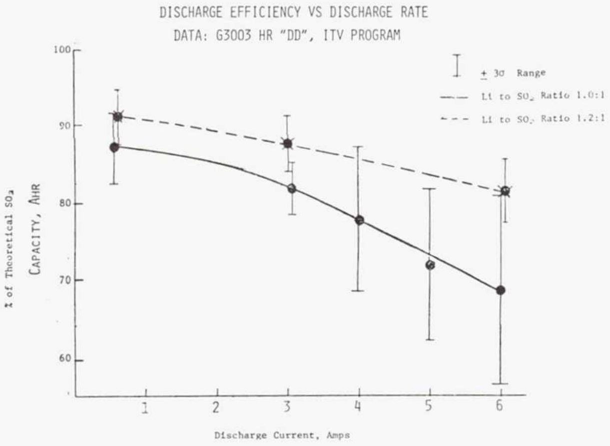

DISCHARGE EFFICIENCY VS DISCHARGE RATE
DATA: G3003 HR "DD", ITV PROGRAM

Figure 2-3

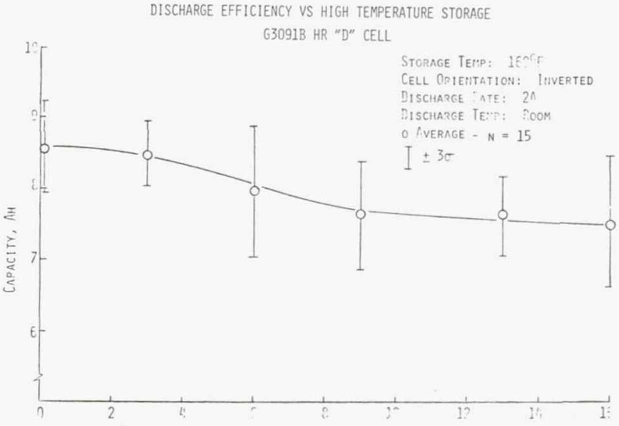

DISCHARGE EFFICIENCY VS HIGH TEMPERATURE STORAGE
G3091B HR "D" CELL

Figure 2-4

GALILEO PROBE SIMULATED
BATTERY TEST 3 (CONTROL)

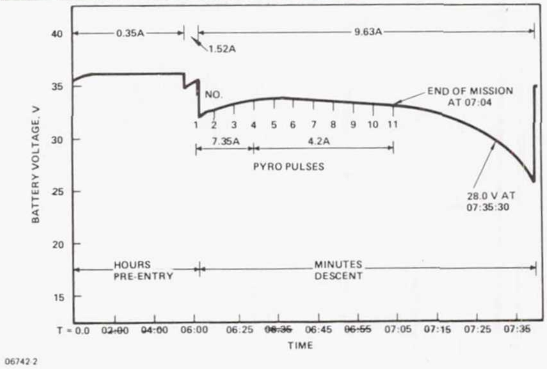


Figure 2-5

GALILEO PROBE SIMULATED
BATTERY TEST 2 (FAILURE MODE)

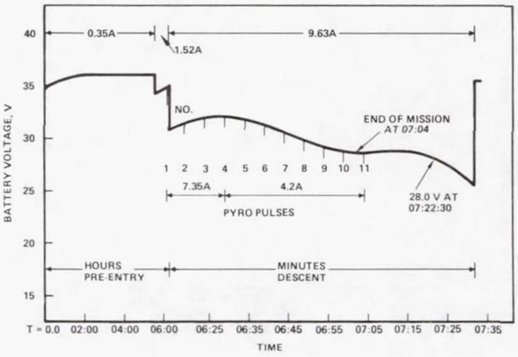


Figure 2-6

PERFORMANCE AND SAFETY CHARACTERISTICS OF Li/BCX and Li/CSC SYSTEMS

R. Murphy
Electrochem Industries

I should like to talk about the performance and safety characteristics of the lithium BCX and lithium CSC battery systems as developed at Electrochem Industries.

First, I shall talk about the BCX system.

It has a high open circuit voltage of 3.9V, energy density of about $1Wh/cm^3$, and an operating temperature of -40 to 72 C.

Most of the talk on the BCX will be concerned with safety, but next is a typical discharge curve for 72 to -40 C at loads ranging from one ohm to approximately 10 ohms.

(Figure 3-1)

The discharge curves are for D cells and represent typical values for the D cells.

(Figure 3-2)

Safety is of the utmost importance; this slide shows D cells forced discharge at 5A and 1 A. Note the temperature increases at 5 A to about 125 C, and at 1 amp to slightly less, especially since both cells go into reverse and the temperature increases very drastically. However, after reversal and at equilibrium cell voltages equilibrate out along with the temperatures.

It has been reported in the literature by Dr. Day, that such cells as these become percussion sensitive. As a result, the particular cell at the 5 A rate was taken out and shot three times with a shotgun; there were no hazards or explosions, and not even a venting.

(Figure 3-3)

The next cell is a C cell, force discharged at 0.5 A. Again, it lasts for about seven hours and the temperature increases to about 30 C and then steadies out.

Of particular interest to many people would be the effect on the safety aspects of a series of cells going into reversal.

(Figure 3-4)

Figure 3-4 shows a series of seven C cells force discharged at 3 A; the cell voltage will increase by about 20V, and after 30 minutes will go into reversal with the attendant increase in temperature. Again the temperatures and the voltage level out after about 60 hours.

We have also tried the same string of C cells with the first cell being a fully discharged cell.

(Figure 3-5)

The temperature on Figure 3-5 plot is the temperature of that fully discharged cell, which is being forced at approximately 3 A. Again the cell voltage will increase to about -0.8V. The temperature steadies out at about 30 C. This is for a time of about 20 hours.

(Figure 3-6)

Figure 3-6 shows the voltage and temperature of a D cell force discharged at 1 A, and subsequently charged at 1 A. Note that as the cell goes into reversal, there is again a temperature rise. After approximately 18 hours, the cell is charged at 1 A; approximately 6 hours later the voltage begins to fluctuate drastically.

We have simulated this by using a reference electrode in one of the cells and it appears that the reason is dendrite formation in the cell. The cell voltage will increase to approximately 4.03 V and steady out at 3.85 V. Again, there is no problem.

(Figure 3-7)

Figure 3-7 shows the typical short-circuit temperature curves for a C and a D cell. The D cells short circuit at approximately 18 A, and the C cells at about 14 A. As you would expect, the temperature increase is rapid, but then steadies out to ambient temperature.

Secondly, I should like to talk about the lithium CSC system (chlorine and sulfuryl chloride), which has a high-volt conservative voltage, again about 3.93 V. The energy density is approximately 1 W h/cm^3, operating temperature range is about -30 to 150 C slightly higher. The energy density, of course, is dependent upon the rate.

Typical D cell discharge curves are given in Figure 3-8.

(Figure 3-8)

These cells were discharged at 1-150 ohm loads. Note at the one-ohm load; approximately 3.1 A yields about 12.3 A h. These represent a very narrow capacity band and range in efficiency, based on sulfuryl chloride and chlorine, of approximately 80-95%.

The low temperature discharge curves at -32 C for 3 ohms and 5 ohms are shown in Figure 3-9.

(Figure 3-9)

At the 1 A, or 900 mA, rate the cells receive about 10 A h, and at 600 mA it receives, approximately 12.3 A h.

(Figure 3-10)

These cells have also been discharged at 76 C, and higher. They have been discharged at 3,5 and 20 ohms. This yielded 12.8-14.3 A h for the various loads.

Specially designed D cells can be discharged at 150 C .

(Figure 3-11)

These cells have been discharged at 3, 5, 10, 20 and 40 ohms, yielding approximately 10.5 Ah for the 3-ohm load; this represents approximately 92% efficiency based on both the chlorine and sulfuryl chloride in the battery. These capacities are to a 2 C cutoff.

The safety characteristics for this battery system, the CSC, is such that the batteries can be incinerated without explosion. The short circuit is typical. Results of a short-circuit test would be loss of contact through the lead being disintegrated. Again, we force discharged and charged the cells.

(Figure 3-12)

This one is for a 1 A charge, force discharged, and then charged for approximately 24 hours. The temperatures is shown by the dotted line, and it maintains at about 42 C at 1A charge. After a while we became impatient and charged it at 10 A, and it vented after about 4 minutes.

We have recently begun to force discharge these cells at rather high rates of 3 A.

(Figure 3-13)

The initial polarization is exaggerated. For example, after two minutes the cell voltage reading would be about 2.95 V, and after about 4.35 hours at the 3A rate the cell will go into reversal and remain at equilibrium, slightly below zero. A typical value would be -0.45V.

We are continuing both the safety studies for the BCX and the CSC.

DISCUSSION

BRO: Do you have any storage data on these?

MURPHY: Yes. I have both data after on year and data after storage at 74 C. At the end of, say, 30 days at 7 for a D cell, I see no loss in capacity. The rate capability is somewhat hindered. For example, at 3 ohm load the capacity for one of those cells stored at 74 C is about 14 A h. However, the load voltage is about 3.0V versus 3.2-3.3V for a fairly fresh cell.

In any of the tests, even after one year storage at ambient temperature, casual storage, we always find that there is very little or no loss in capacity, but a loss in rate capability.

GALASSIE: At that one cell, you had a voltage fluctuation due to dendrite formations?

MURPHY: Yes.

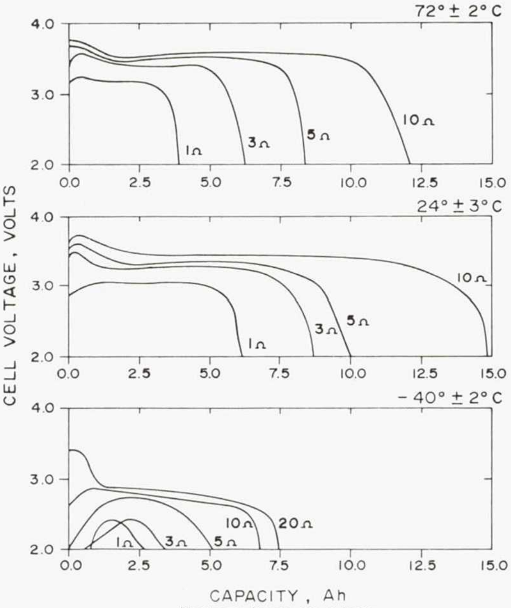
GALASSIE: Then the voltages increased and leveled out? What happened to the dendrites? Were they burned away, broken?

MURPHY: They burned away and then reformed. I think that is the near or for the voltage fluctuation. You gave the figure for the volumetric energy density of the CSC system. Do you have one for the gravimetric energy density?

MURPHY: It is approximately 400 w h/kg for a 1 ohm discharge for a D cell, and 600 w h /kg for a lesser rate, say 20 ohms.

MUELLER: You also gave some data here on your short-circuit incineration. Did you do any of this after shock vibration to see if there was any effect of shock vibration on the `system at all?

MURPHY: Not for the CSC.



Discharge Curves for D Cells

Figure 3-1

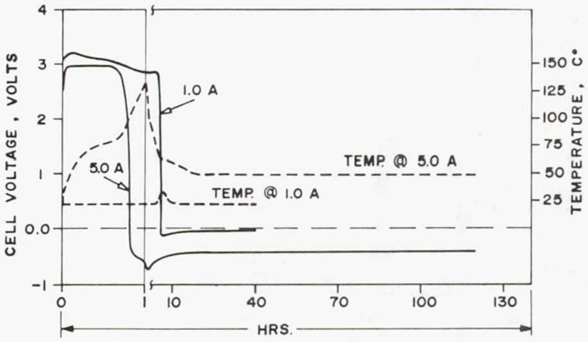


Figure 3-2

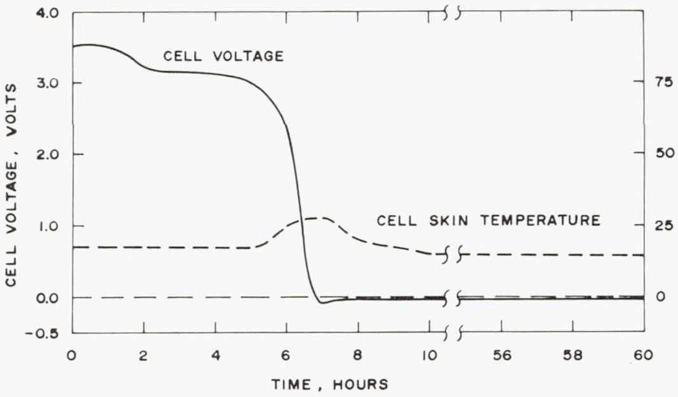


Figure 3-3

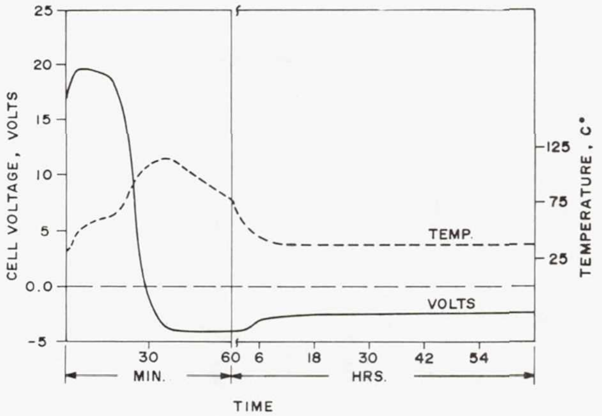
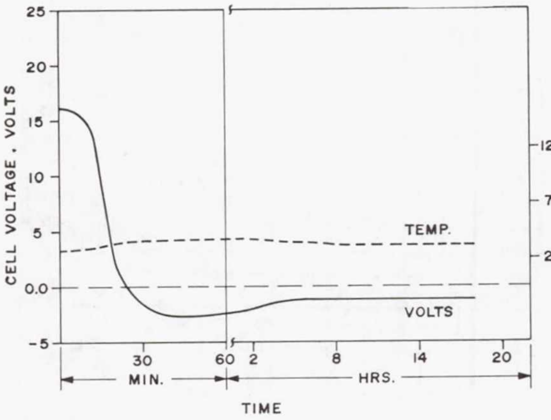


Figure 3-4



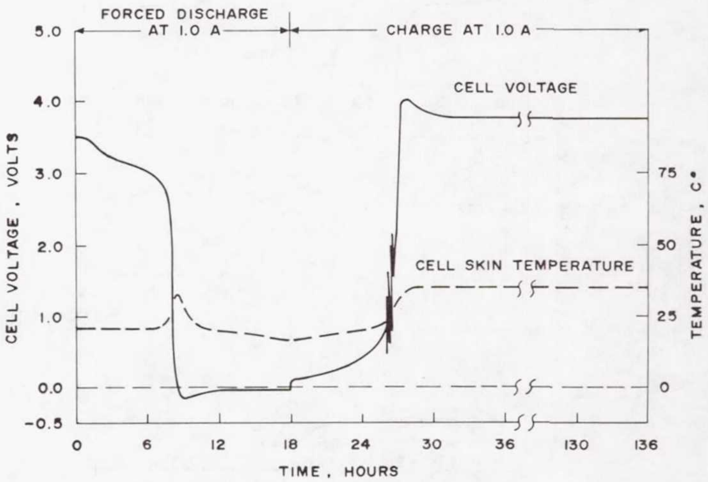
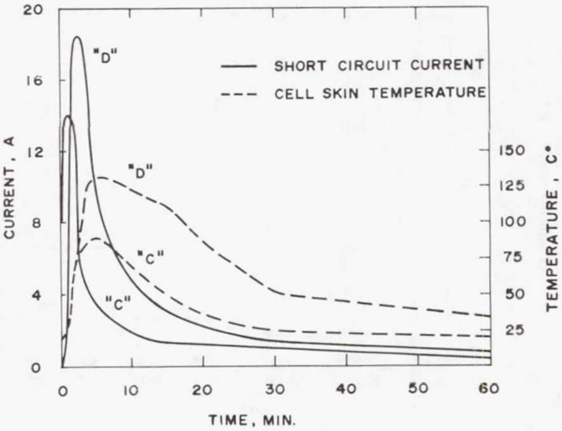


Figure 3-6

Figure 3-5



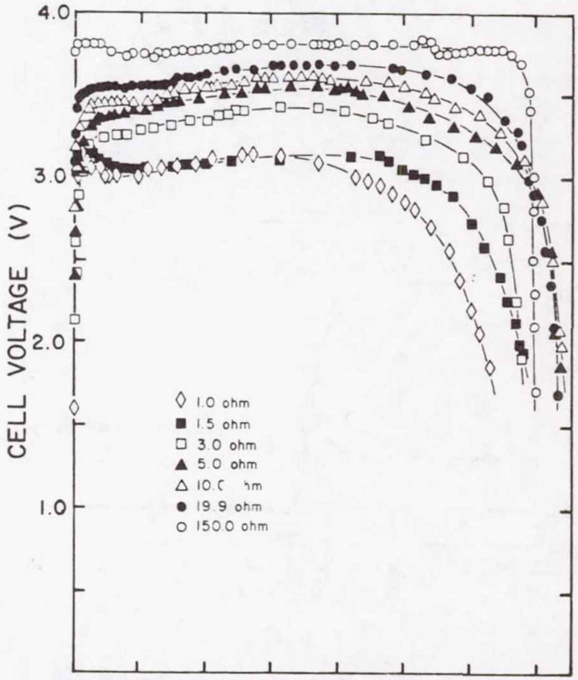


Figure 3-7

Figure 3-8

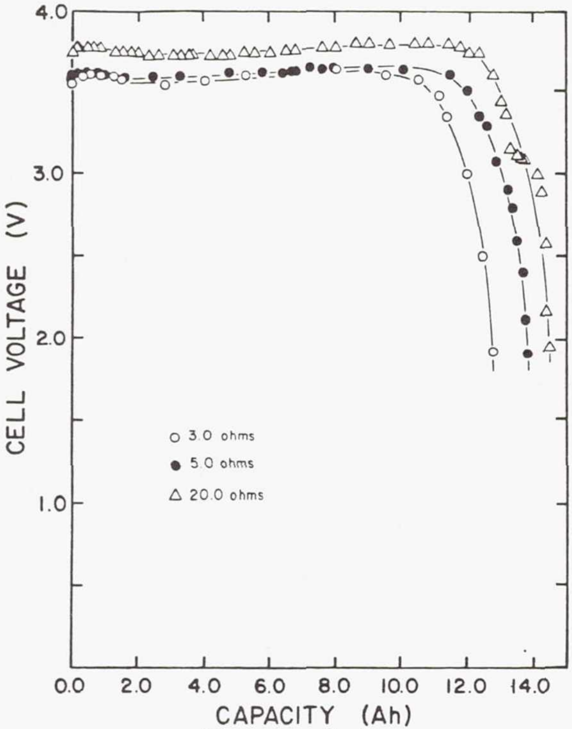


Figure 3-9

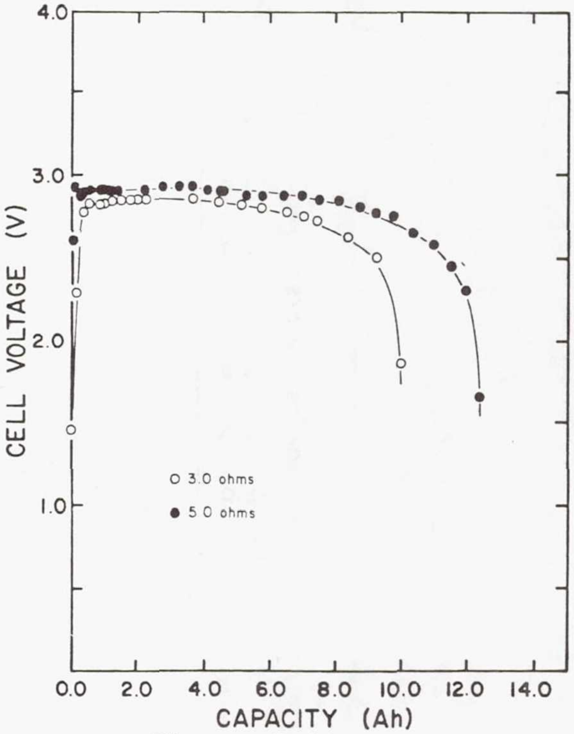


Figure 3-10

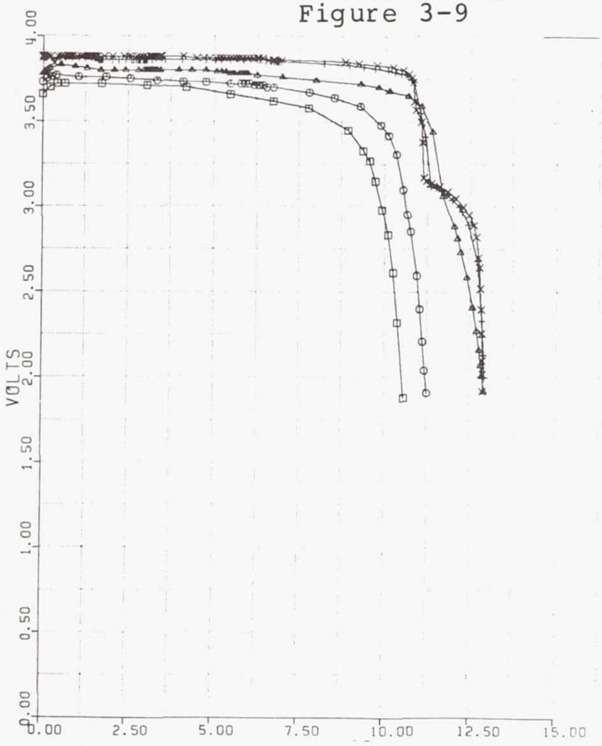
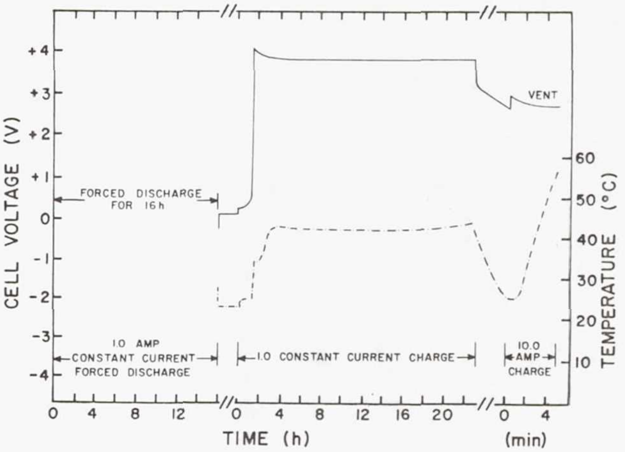


Figure 3-11



Safety Characterization of a D Cell Force Discharged at 1A, Charged at 1A, and, finally, Charged at 10A.

Figure 3-12

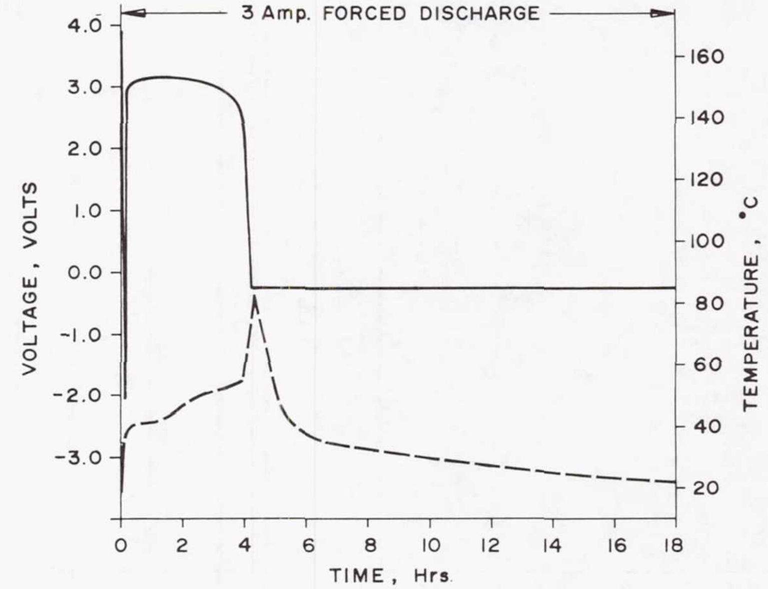

3 Amp. FORCED DISCHARGE
VOLTAGE, VOLTS
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
TEMPERATURE, °C
160
140
120
100
80
60
40
20
0
2
4
6
8
10
12
14
16
18
TIME, Hrs.

Figure 3-13

THERMAL MODELING OF LITHIUM SYSTEMS

K. Kim
Honeywell

Honeywell has been engaged in research and development of the high rate lithium batteries for a number of years. In an effort to resolve safety problems, we have conducted thermal remodeling studies and calorimetric studies. I would like to talk about the heat generation during cell discharge and its distribution, and the effects of casing materials, thickness of current collectors, discharge environments, and entropies. In addition, we have also carried out calorimetric experiments to quantify the heat during cell discharge.

Why should we do all this? We have only one reason that is to provide the necessary heat transfer requirements for high rate lithium bipolar-battery design. For this modeling, we have made an assumption, that is, all the cell components should stay unchanged through the discharge operation period. Even though this assumption is far from the reality, it is indispensible due to the lack of knowledge of cell discharge mechanisms and due to the complication of differential equations. Utilizing thermodynamic relations, the internal heat is derived in equation 1.

$$q_{int} = I\ [(E - E_L) - T\ (\partial E/\partial T)_p]t\ ,$$

In this equation, the heat is considered to be from both overpotential and entropic contributions. For this study, the current density is taken to be 150mA/cm^2 which is considered about the higher limit of discharge rate. Since the $(\partial E/\partial T)_p$ value is not available for acidic electrolyte, we utilized the data from neutral electrolytes. One of Honeywell batteries happens to be circular-cylindrical (Fig. 2) with dimensions as shown in the cm unit. The cell is longitudinally located between insulators and metal supports.

The initial temperature of this battery is 71 C (160 F) and the axial environment is taken as 25 C. The radial environment is taken as either forced convective air at 71 C or forced convective water at 0 C.

The 20-bipolar cell battery is hypothetically divided into 500 pieces for modeling (Fig. 2), in which heat transfer is considered in radial and axial directions only. One of the typical volume-elements is represented as (i,j), and the temperature-rise at this volume-element depends on radial and axial heat flows and its own heat generation. This is mathematically described in equation 2.

$$\frac{\partial T}{\partial t} = \frac{1}{\rho C_p}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r k_r \frac{\partial T}{\partial r}\right) + k_a \frac{\partial^2 T}{\partial a^2} + \dot{q}_e \pm \dot{q}_c\right\}$$

The $\partial T/\partial t$, namely the temperature change at the volume-element during an infinitesimal period is a function of heat capacity, radial and axial heat transmissions, and electrochemical and chemical reaction heats. The chemical reaction heat is not considered for this study due to lack of information on it. The differential equation is solved for steady-state and the transient-flow technique is applied to realize the unsteady-state heat transmission. Calculation was carried out with Honeywell Multics Level 68 Computer.

As a typical result, Table 1 shows heat distribution and temperature-rise for different casing materials for the same radial environments of 71 C. The discharge heats for both casings are approximately 200 kcal, however, the temperature-rise at the center are 189 C for the teflon casing and 99 C for the metal casing. The temperature profile in case of teflon casing is plotted as a function of radial and axial distances from the center (Fig. 3). When $(\partial E,\partial T)_p = -0.70$ mV/ K, the ΔT value at the center is approximately 280 C while the T is only about 110 C if $(\partial E/\partial T)_p = 1.03$ mV/ K. It is noticed that the temperature gradient is rapid through the teflon casing. In Fig. 4, the temperature profile for the metal casing is plotted. In this case, the T values are lower than those of teflon casing and the skin temperature is higher than that of teflon casing. This implies that more heat should be lost through the metal casing into the environment. Also different ΔT's are observed depending on $(\partial E/\partial T)_p$ values.

When the battery is discharged against the 0 C environment of forced convective water, the radial temperature profiles with $(\partial E/\partial T)_p = -0.7$ mV/ K are presented in Fig. 5, in which rhombuses and circles represent the teflon and metal casings, respectively. The thiner the current collector is, the higher the temperature-rise is obtained in this simulation study. This is because the current collector plays an important role both as heat sink and as heat conductor.

The central temperature-rise is plotted as a function of discharge time for metal casing in Fig. 6, in which the discharge against 71 C environment is plotted with circles for comparison. When the discharge starts against 0 C water environment, an initial temperature surge is obstained followed by a gradual cooling due to the conduction to the low temperature environment. A steady state is observed after about 8 minutes of discharge. Here, we can see the effect of $(\partial E/\partial T)_p$ again. In case of $(\partial E/\partial T)_p = 1.03$ mV/ K, the central temperature drops below initial temperature. As we have seen, the entropic contribution is very important for the calculation of temperature change during discharge. If the discharge reactions are known, it is possible to estimate the $(\partial E/\partial T)_p$ value using a thermodynamic relation. The possible electrochemical reactions are shown in equation 3.

$4\ Li + 2\ SOCl_2 \longrightarrow 4\ Li\ Cl + So_2 + S$ $\qquad \Delta H$
$8\ Li + 3\ SOCl_2 \longrightarrow 6\ Li\ Cl + Li_2So_3 + 2S$-90.8
Average $\Delta H\overset{o}{r}$-90.5 kcal/mol

Either or both of these reactions may be predominant, depending on discharge conditions.

The thermodynamic relation is

$$T(\partial E/\partial T)_p = E + \Delta H_r/nF,$$

where T = 298K, E = 3.60V (measured), $H,_r$ ΔH_r = -90.5 kcal/mol), n = 1 and F = 96490. Then $(\partial E/\partial T)_p$ = 1.09 mV/K.

Either or both of these reactions may be predominant depending on discharge conditions. The estimation of enthalpies of reactions leads to -1.09 mV/ K of $(\partial E/\partial T)_p$ value. since some uncertainties may be introduced to this kind of estimation, however, we carried out the discharge experiments on a small $Li/SOCl_2$ laboratory cell with $3cm^2$ of electrode area using our home-made calorimeter (Table 2). Discharges at the rates of 5 and 10 mA/cm^2 were conducted at 3 hours of cell activation with a neutral electrolyte and total discharge heats were directly measured using the calorimeter. The heats from overpotential were calculated from open-circuit potentials and discharge potentials. "Heats from other sources" are taken from the differences between total heats and overpotential heats and are assumed all from entropic contribution to derive $(\partial E/\partial T)_p$ = 1.01 ± 0.06 mV/ K. This happens to be in good agreement with the estimated value inspite of the assumptions.

Table 3 shows comprisons between neutral and acidic electrolytes with regards to activation heats and overpotential heats. The activation was initiated by introducing the electrolyte into the dry cell components and the activation-reaction heat lasted for several hours. Due to large amounts of heats over a long period, accurate activation heats are not available at this time. However, the approximate values will give an idea how significant the activation heat is compared with discharge heats. This fact implies that the activation process may be one of the most serious safety-hazard processes. For the meutral electrolyte under conditions shown, overpotential heat is about a half of the total discharge heat while, for acidic electrolyte, the overpotential heat is the major portion of the total heat.

I wish to express my appreciation to Professor R. Lovrien for his help in calorimetric instrumentation.

DISCUSSION

DI MASI: Did you consider dissipation of heat to the surroundings?

KIM: Yes.

DI MASI: Were they included?

KIM: Yes. As a function of time, the heat is conducted to the outside.

DI MASI: Was that considered in your equation? I thought you solved it for a steady state?

KIM: Yes. The environment is constant, less the environment of the system.

DI MASI: The reason I ask that is because usually there is not a constant loss of heat to the surroundings.

KIM: That is correct.

DI MASI: That is why I am a little unsure as to what you did, whether you considered just steady state, or unsteady state.

KIM: It is unsteady state. The surrounding is constant, or infinite heat sink. The heat loss rate is different according to the temperature of the skin. The skin temperature affects the cell component inside. So that is all constant.

DI MASI: So you assume that was constant?

KIM: Yes.

DI MASI: So the heat loss is very small?

KIM: Yes. For Teflon casing, it is not large. All heat temperature rises, although the heat sink Teflon casing itself and other cell component and electrolyte.

Heat Distribution and Temperature-rise

$(\partial E/\partial T)_p = 0.17$ mV K^{-1}
(average of 1.03 & -0.7)

	Casing	
	Teflon	Metal
Discharge heat, kcal	198.7	200.6
Heat used for core heating, %	58.5	28.6
Heat used for non-core heating, %	41.3	66.5
Heat loss, %	0.2	4.9
ΔT at center, °C	189.3	98.6

Table 4-1

Cell Discharge

Electrode area: 3 cm^2
Electrolyte: 1.8 M $LiAlCl_4$ in $SOCl_2$
Temperature: 25°C
Time: 300 sec

Discharge	1st	2nd	3rd
Open circuit potential, E	3.61	3.60	3.60
Discharge potential, E_L	3.26	3.34	3.26
Current density, mA/cm^2	10.0	5.0	10.0
Total discharge heat, J	6.12	2.46	5.61
Heat from overpotential, J	3.15	1.17	3.06
Heat from other sources, J	2.97	1.29	2.55
$(\partial E/\partial T)_p{}^*$, mV/°K	-1.12	-0.96	-0.95

average $(\partial E/\partial T)_p = -1.01 \pm 0.06$ mV/°K

* "Heat from other sources" is assumed all from entropy contribution.

Table 4-2

$A = 3\,cm^2$
$t = 300$ sec
$T = 298°K$ (77°F)

HEATS OF CELL DISCHARGE

ELECTROLYTE	NEUTRAL		ACIDIC
ACTIVATION(J)	~ 28 (for 4hrs)		~ 370 (for 8hrs)
E (V)	3.60		3.80
$I\,(mA/cm^2)$	5.0	10.0	10.0
E_t (V)	3.34	3.26	3.33
$\Delta H_{obs}(J)$	2.46	5.61	4.66
$\Delta H_{(E-E_t)}$	47.7%	54.6%	90.7%
$\Delta H_{(other)}$	52.3%	45.4%	9.3%

Table 4-3

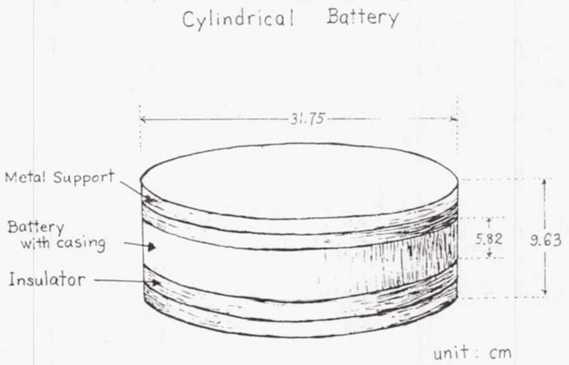


Figure 4-1

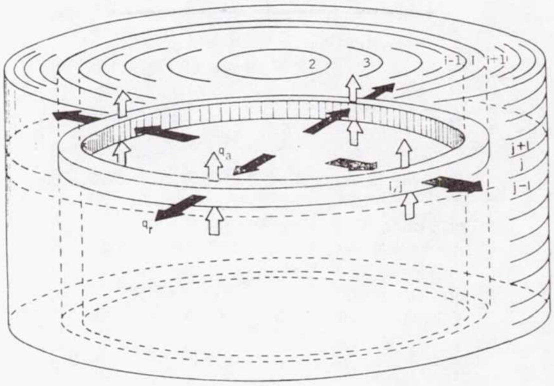


Figure 4-2

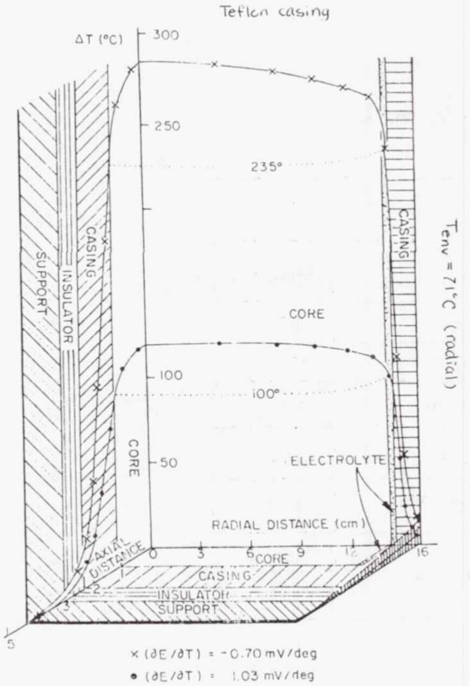


Figure 4-3

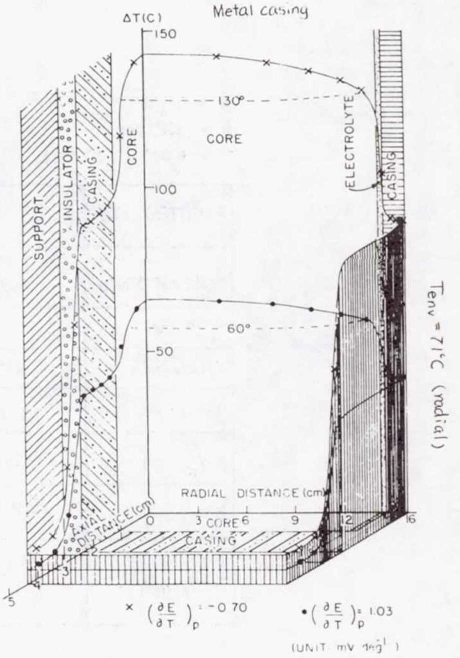


Figure 4-4

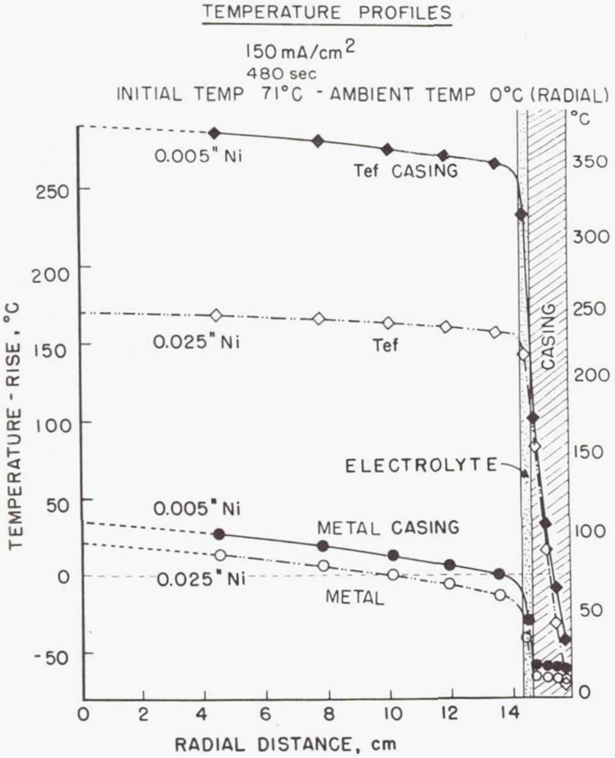


Figure 4-5

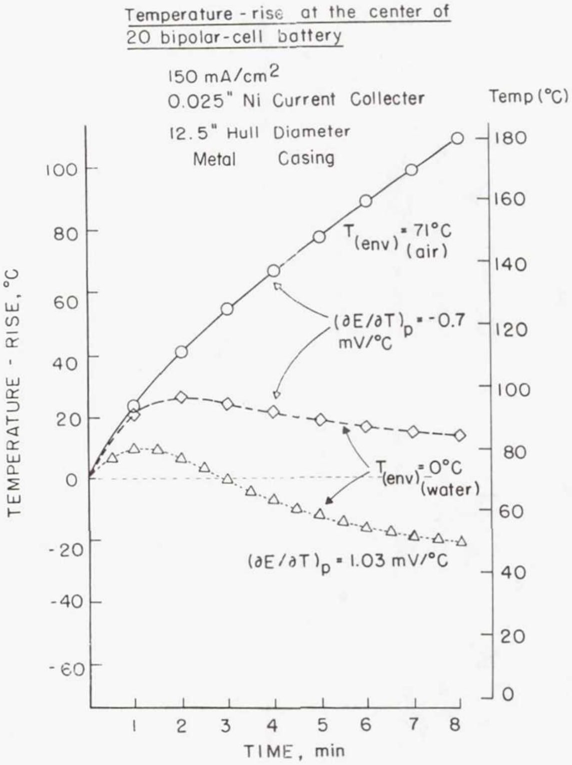


Figure 4-6

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Li/SO_2 CELL LOT TO LOT VARIATIONS AND SOME DESIGN COMPARISONS

R. Walk
Bedford Engineering Corporation

I should like to present some data that Bedford Engineering Corporation has collected on Li/SO_2 cells over the past four years. I shall talk about two different cell designs. One is referred to as the standard cell, which has very high $Li:SO_2$ ratios (1.5 or 2:1). The other is known as the balanced design, where the $Li:SO_2$ ratio is 0.9-1.1:1 on an ampere hour basis.

Unfortunately, all the data are from one manufacturer, and only on D cells. We have tested cells from other manufacturers, and we believe these data to be typical.

These cells were put on test three to six months after the manufacturer's date, except where we indicate that there was some planned storage.

(Table 5-1)

The first column on the left shows 14 different manufacturers' lots that were given Bedford Engineering lot numbers as they came in. In some places you will see two different lines, two different tests of the same lot number. This is because in some cases the lot came in in two different shipments and we obtained the test data on those shipments.

There are 5-15 cells in a test, and we have listed here the maximum capacity, the minimum, the median cell for the test, the mean and standard deviation; i.e., two-thirds of the lot tested fell within the ampere hours.

For example, the first column is within 40 mA h ± 30 mA h of the standard cell. The coefficient of variation is simply the standard deviation divided by the mean, to give us a feel for the spread of the capacities delivered by that lot.

The key feature about these data is that out of the 14 lots and 90 cells, the performance was quite tight. The median cell was normally around 9.5 A h; these are all at 33 ohms, or about 85 mA load.

At the low temperature, 23 C (-10 F) there is also very uniform performance, with the median cell value lower than at room temperature.

(Table 5-2)

Table 5-2 shows some data for two of the lots at approximately 1A drain on the D cell. At room temperature the median cell is about 0.2 A h lower than 85 mA h rate. At -10 F, however, it is down by about 3 A h.

The data are still pretty uniform. In some cases, such as at -10 F, the standard deviation and the coefficient of variation are rather high. We had some information on thi one lot at six months, one year and eighteen months at both temperatures, and essentially, within experimental error, the data are the same as before storage. The storage temperature, of course, is 24 C (75 F).

(Figure 5-1)

Figure 5-1 shows the variation over approximately 90 cells at 85 mA h, and roughly 20-25 cells at -10 F. For example, at 1A the spread in capacity over the 90 cells is about 1 A h. At the lowe current the spread is about 3 A h.

(Table 5-3)

There are fewer lots for the balanced cell. It is a newer cell. Here we are providing data as a function of temperature an discharge rate.

The first striking thing is that the capacities at room temperature (75 F) are about 3 A h lower than for the standard cell, and in all the cells the capacities are down. The standard deviations are higher for standard cells, and the coefficient of variation at room temperature are very high.

In some cases, such as 0 C (*32 F), the capacity of the median cell for the 2 A data is higher than the capacity at 1 A. We are not sure if this is accurate, but it was typical for that test. Of course, these are results from just one lot; we must do more testing to be sure of this information.

The discharge rate, of course, is in hours.

I shall show some of the discharge curves for the balanced D cells. Essentially these are the same as for the standard cells. They are flat at 33 ohms. When they reach the ends of capacity, the voltage drops very rapidly, -10 F data and 120 F data at this low current figure, 5 mA is the best, 140 F data is low.

We have seen this in sulfur dioxide cells before. At 120 F they seem to stay pretty good, but above that point the rate of degradation seems to accelerate.

(Figure 5-3)

For the 1 A data, at 2.8 ohms, the median cells of each test are shown in Figure 5-3. The 32 F data gave the lowest capacity, as you might expect in these higher current. The discharge curve sloped, rather than dropped off rapidly; this occurred for all the cells in that particular line.

(Figure 5-4)

All I want to show on Figure 5-4 is that these are the points on the balanced cell at the four temperatures, and at the four different discharge currents. By plotting ampere hour capacity on the Y axis, and current in amps on the X axis, we obtain these straight diagonal lines that represent the discharge rate. I think this is an interesting and good way to present a lot of data from a small amount of data, and be able to get a lot of information on one chart. For example, if you want to know how these cells would operate for 15 hours and deliver 7 A h, you can see that the cell, running at 500 mA or less, would give the 15 hours. Running above that at the higher currents, it would deliver less than 15 hours.

It is also possible to get a feel for the capacity delivered under conditions where data are not available, say 1.5 A, at -10 , by looking at the -10 curve for 1.5 A.

(Figure 5-5)

Figure 5-5 is just a comparison of the 75 F data with the standard cells. This point, this range is the standard cell at 85 mA. This is the standard cell at lA, and this is the spread and data for the balanced cell at these three currents of 85 mA, 0.5 A and lA, with the has line being the median cell for that particular set of date.

I have the discharge rate lines going these also, you can see the approximate time.

(Figure 5-6)

Figure 5-6 presents the data somewhat differently. I have taken the balanced cell data and broken them down into a little graph for each temperature, and then put the performance range for the group of cells from that one lot. For the low temperature data, and also for the room temperature data, I have put the range of the standard cell.

The lines all show approximately what data were delivered.

I shoud like to thank Mr. Florido Pey and Mr. Mel Anderson of Bedford Engineering Corporation for collecting most of the data.

DISCUSSION

HUBER: I notice a greater apparent spread in the data on the last few figures for the balanced cells versus the standard cells. Is this simply because that represents the smaller sample quantity? Or, does it represent less control of the manufacturing technique or some other variation in the application of the balanced cell exposed to the higher degree of variability?

WALK: First of all, it is a small sample. There is also a price to pay in capacity by going to a lithium-limited cell and trying to make it safer. I do not know the exact reason for the larger spread in this particular cell.

HUBER: Obviously, the lesser capacity is recognized as one of the penalties to be paid for the balanced cell, but my conceren was the greater variability in the data, and the probable or possible reason.

WALK: I am sorry, I do not know.

DI MASI: Do you know if the balanced cells have any anode term connecting capability? In addition to the ordinary anodes, was these a current collector?

WALK: No, there was not.

DI MASI: That could make a difference in the capacity.

WALK: Yes.

STANDARD "D" CELL LOT TO LOT VARIATIONS
(DISCHARGE LOAD = 33 OHMS)

BEC LOT #	# CELLS	MAX	MIN	MEDIAN	MEAN	STD. DEV	COEFF OF VAR
				75°F			
154	5	9.62	9.51	9.57	9.57	.040	0.40
155	15	9.67	9.30	9.50	9.50	.119	1.30
98A	5	9.64	9.08	9.28	9.30	.236	2.54
72A	15	9.45	9.25	9.38	9.37	.051	0.55
33A	5	9.85	9.71	9.81	9.79	.054	0.55
34A	3	10.02	9.71	9.76	9.83	.166	1.69
103A	5	9.71	9.56	9.59	9.63	.071	[illegible]
55B	5	9.56	9.43	9.46	9.49	.059	0.62
139A	5	9.69	9.52	9.55	9.57	.068	0.71
11	5	9.65	9.19	9.60	9.54	.195	2.04
22	5	9.80	9.68	9.74	9.75	.046	0.47
2	5	9.65	9.51	9.60	9.59	.056	0.58
21	5	9.83	9.59	9.73	9.72	[illegible]	1.12
24	5	9.65	9.51	9.58	9.59	.052	0.54
				-10°F			
154	5	[illegible]	8.76	[illegible]	[illegible]	.094	1.10
155	15	8.99	8.73	8.85	8.85	.075	0.84
98A	5	8.90	8.33	8.89	8.78	.250	2.85
72A	15	8.97	8.34	8.57	8.59	.158	1.84
33A	5	9.08	[illegible]	8.96	[illegible]	.077	[illegible]
34A	3	8.79	8.05	8.58	8.47	.381	4.50
103A	5	9.32	8.68	9.00	9.10	.209	2.30
55B	5	9.38	9.14	9.23	9.22	.095	1.13
139A	5	9.31	9.13	9.28	9.30	[illegible]	0.95
11	5	8.83	8.65	8.77	8.74	.084	0.96
22	5	9.31	8.90	8.99	9.01	.184	2.04
2	5	8.36	[illegible]	8.56	8.54	.218	2.55
21	5	[illegible]	8.52	8.81	8.76	.201	2.29
24	5	8.76	7.08	8.61	8.24	.696	8.45

Table 5-1

STANDARD "D" CELL LOT TO LOT VARIATIONS
AND EFFECT OF STORAGE
(DISCHARGE LOAD = 2.7 OHMS)

BEC LOT #	# CELLS	MAX	MIN	MEDIAN	MEAN	STD. DEV	COEFF OF VAR	STORAGE TIME @ 75°F
				75°F				
185	10	9.66	9.15	9.38	9.37	.164	1.70	
185	5	9.36	8.98	9.18	9.15	.160	1.75	
72A	8	9.87	9.25	9.63	9.58	.206	2.15	
AFTER STORAGE AT 75°F								
185	10	9.53	9.01	9.29	9.28	.160	1.70	6 MONTHS
185	5	9.74	9.14	9.29	9.34	.240	2.60	6 MONTHS
185	10	9.48	9.03	9.31	9.29	.170	1.84	1 YEAR
185	5	9.50	9.04	9.19	9.23	.159	1.72	1 YEAR
185	10	9.31	8.98	9.09	9.11	.131	1.44	1 1/2 YEARS
185	5	9.52	9.11	9.17	9.22	.166	[illegible]	1 1/2 YEARS
				-10°F				
185	10	5.92	4.24	5.49	5.22	.633	12.13	
185	5	5.38	4.29	5.09	4.98	.503	10.10	
72A	3	4.21	3.61	3.88	3.91	.241	6.16	
22	15	5.12	4.27	4.68	4.66	.350	7.51	
AFTER STORAGE AT 75°F								
185	10	6.16	4.87	5.66	5.63	.440	7.80	6 MONTHS
185	5	5.76	4.34	5.30	5.21	.540	10.36	6 MONTHS
185	10	5.97	4.73	5.40	5.43	.404	7.45	1 YEAR
185	5	5.45	3.97	4.40	4.62	.643	13.93	1 YEAR
185	10	6.15	4.04	5.52	5.47	.661	12.10	1 1/2 YEARS
185	5	5.70	4.25	5.28	5.18	.561	10.84	1 1/2 YEARS

Table 5-2

BALANCED "D" CELL PERFORMANCE DATA
AS A FUNCTION OF
DISCHARGE RATE & TEMPERATURE

DISCHARGE RATE	DISCHARGE RATE	TEMP	# CELLS	MAX	MIN	MEDIAN	MEAN	STD. DEV	COEFF OF VAR
5	2A	-10	8	3.894	3.630	3.795	3.780	.094	2.479
10	1A	-10	7	5.207	4.733	4.967	4.966	.181	3.649
20	500	-10	7	6.476	5.627	6.024	6.034	.253	4.195
118	85	-10	8	7.629	5.510	6.317	6.442	.635	9.864
5	2A	32	8	6.399	5.311	5.919	5.834	.400	6.849
10	1A	32	8	4.953	4.303	4.441	4.475	.202	4.525
20	500	32	6	7.289	5.173	6.575	6.570	.773	11.768
118	85	32	7	6.795	4.948	5.531	5.736	.729	12.716
5	2.0	75	8	6.582	5.937	6.325	6.311	.240	3.803
10	1.0	75	8	7.206	5.597	[illegible]	6.212	.637	10.262
20	500	75	7	7.532	5.094	5.748	5.960	.899	15.090
118	85	75	7	7.273	5.146	6.018	6.312	.818	[illegible]
5	2.0	120	5	7.574	7.098	7.206	7.253	.188	2.597
10	1.0	120	5	7.545	7.095	7.346	7.370	.185	2.516
20	500	120	4	[illegible]	6.434	6.451	6.567	.243	3.706
118	85	120	4	[illegible]	6.172	6.715	6.622	.311	4.689
10	1A	140	5	7.534	[illegible]	[illegible]	7.278	.201	2.782
20	500	140	4	7.104	[illegible]	6.767	6.705	.462	[illegible]
118	85	140	4	6.140	5.253	5.454	5.616	.465	8.283

Table 5-3

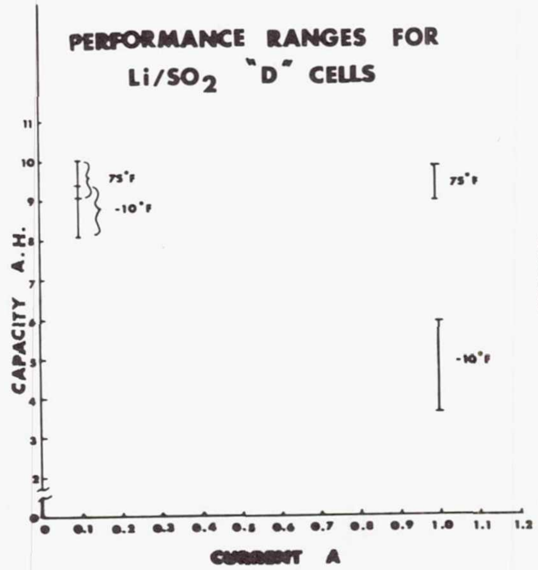

Figure 5-1

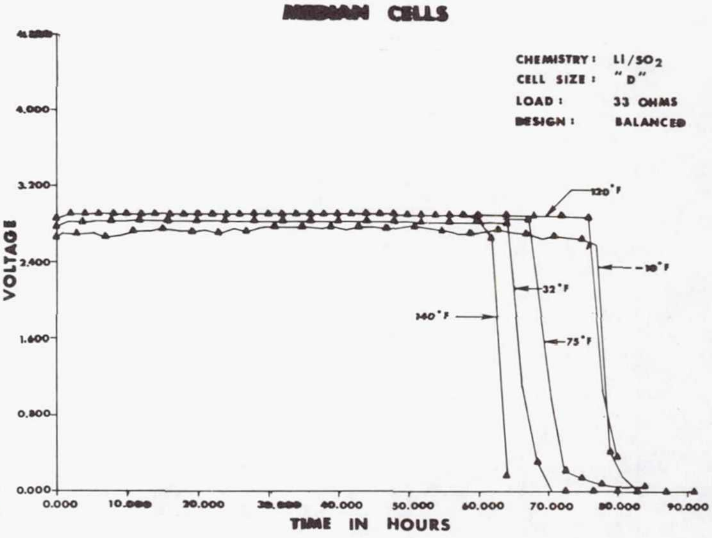

Figure 5-2

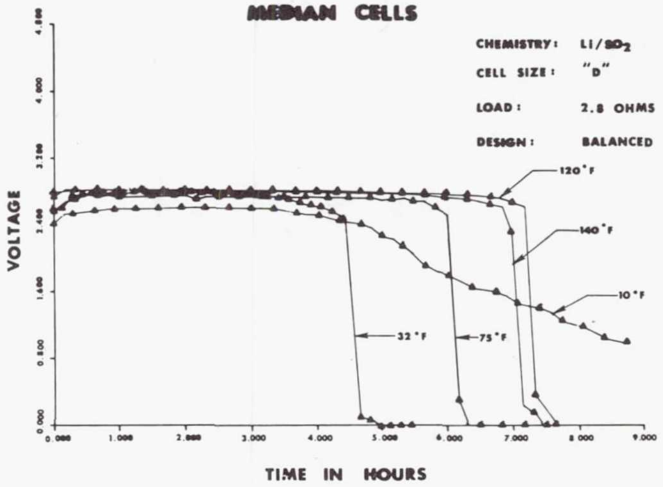

Figure 5-3

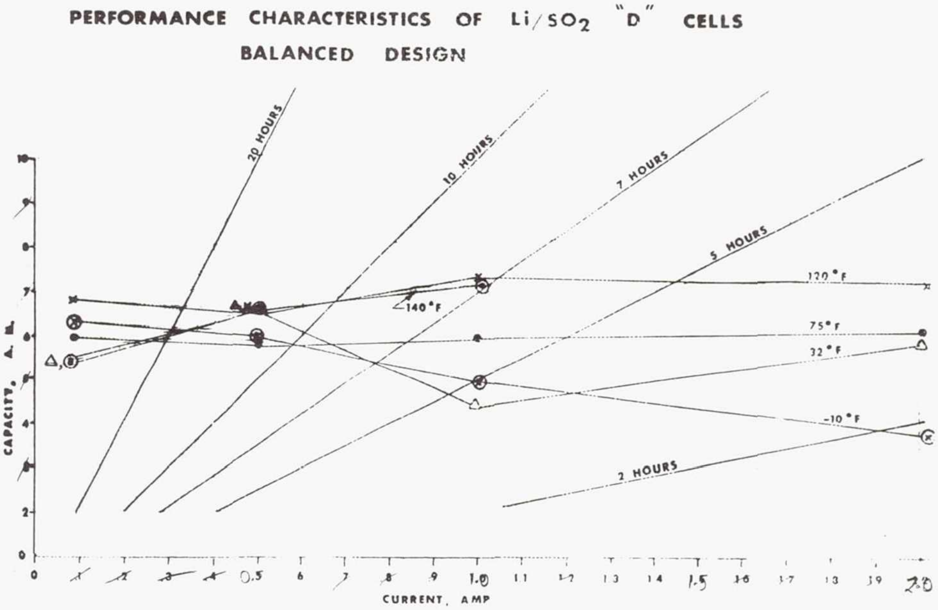

Figure 5-4

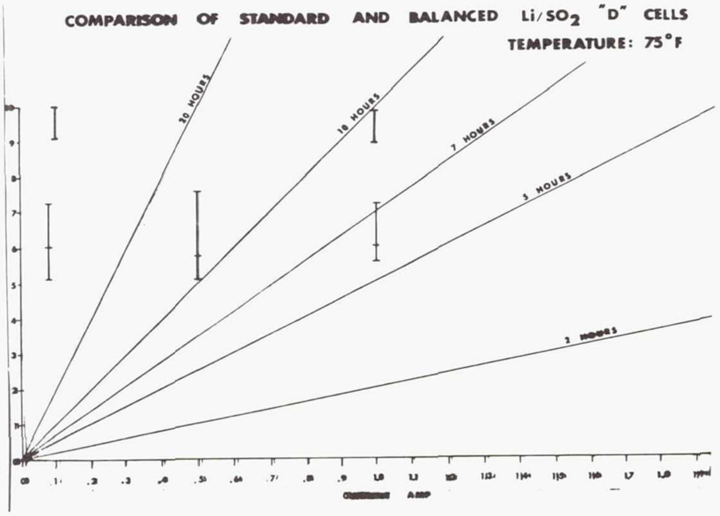

Figure 5-5

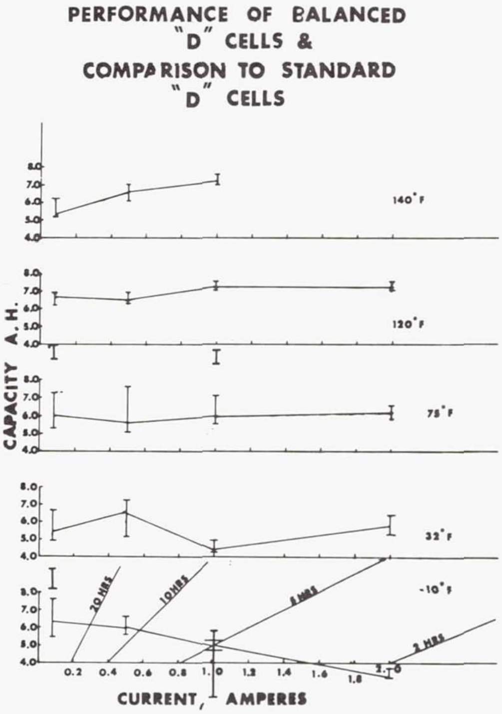

Figure 5-6

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LONG LIFE Li/SO_2 CELLS

S. Levy

Sandia Laboratories

Sandia Laboratories has had several applications recently for a long-life battery (one that could operate continuously for periods of at least five years).

When these applications first came about we did many calculations, talked to a lot of people and decided the lithium sulfur dioxide system would be the best system for our particular applications. However, there were no data available for these very long-life discharges and so we obtained a number of cells from several manufacturers, and placed them on a long-term storage and dishcarge test.

We found that after about eighteen months on tests, we started getting premature failures. A study was initiated and we found several specific problem areas that caused these failures.

(Figure 6-1)

Figure 6-1 illustrates what we found. Probably the most serious problem was corrosion of the glass in the glass-to-metal seal. This can result in two specific modes of failure.

First, a conductive film can form on the underside of the glass; this eventually allows the cell-to-cell discharge. Secondly, in some particular configurations, as the glass corrodes, stresses in the glass (due to the compression seal in that header) result in the cracking of the remaining good glass, thus allowing the sulfer dioxide to escape.

Another problem is the welding of the positive lead. The positive lead in these cells is an aluminum cathode tab, spot welded onto a tantalum pin through the glass insulator. We found that the tantalum was corroding, particularly on high temperature storage, eventually resulting in an open circuit condition.

The final problem was corrosion or selected utilization at the lithium contact with the can. This would result initially in the formation of a resistive film on the lithium, leading to the loss of rate capability for these cells and eventually causing an open circuit condition.

The stress corrosion was not something that we discovered, but was pointed out to us by one of the manufacturers. It is a serious problem, and we are working on it with the manufacturers. It should be solved failrly soon.

We initiated a study to try and find solutions for these various problems. One of our programs was at the point where we had production, and we did have a fairly tight schedule, so that we had to find a solution to these problems fairly quickly.

We did find several solutions for each of the different problems, and ran an accelerated test afterwards. We examined these cells very carefully and came up with a remedy for each problem, we are now going into production. This morning I should like to talk very briefly about our program, how we came up with these different remedies, the results of the accelerated test, and to show you what our modified cell looks like.

The first area we investigated was that of the glass corrosion. We did some rate studies, analyses of the corrosion products, and from on this information we devised a model for this corrosion reaction. The model is based on the underpotential deposition of lithium metal from the electrolyte onto the glass, and the subsequent attack by the lithium on the glass and the further attack by the various products that were formed.

From this model we determined a range of compositions for glasses that should be more resistant to this type of corrosive attack. We then looked through the commercially available glasses to see if we could find any that were in this composition range, and found that the Corning 1723 fell within it. We also started some studies in-house. We formulated a number of different glasses at our glass shop and came up with one that looked promising. We refer to it as TA 23 glass.

We also went to the manufactureres we were working with and asked them if they had any solutions to this problem. One suggested the use of Fusite 108 glass, and the other suggested the use of the Corning 1723 glass, doped with aluminum oxide to change the expansion properties and obtain a better compression seal with the tantalum pin. Both manufacturers are using coatings on the glass to pevent contact of the electrolyte with the glass and thus hinder this corrosion reaction. They are both using a fluoropolymer reaction, one Halar and the other Edathon. We are investigating both of these.

In addition, one of the manufacturers is looking at a tantalum washer polypropylene O-ring arrangement, again designed to keep the electrolyte from contacting the glass.

We looked at all these variations in our accelerated test, along with some standard tests. In the next series of slides I shall show you these glasses after these cells came off of the accelerated test.

(Figure 6-2)

Figure 6-2 shows a standard header. It shows the main body of the header or the outer conductor. The dark areas are the glass and the center pin.

We can see from the dark color on the glass that the corrosion has proceeded across the entire glass surface. And indeed, on these standard glasses we did measure resistances as low as 5 ohms across from the outer conductor to the center pin.

(Figure 6-3)

Figure 6-3 shows the Fusite 108 glass. There is a significant improvement over the standard glass. Corrosion has occurred approximately 50% of the way across the surface of the glass.

These tests were run for five months at 60 C.

(Figure 6-4)

Figure 6-4 shows the Corning 1723 glass doped with aluminum oxide. Roughly 10% of the glass surface has been corroded after five months.

(Figure 6-5)

Figure 6-5 shows a 1723 glass. This particular header was made at Sandia and the molds we used result in these heel marks when the glass is fused. There are also some grooves in the molds, which result in these concentric rings on the glass. The glass is also recessed somewhat, causing some shadows. There is approximately the same amount of corrosion as on the alumina doped 1723 glass.

(Figure 6-6)

Figure 6-6 shows a Sandia TA 23 glass. Unfortunately, we did not have time to fabricate these headers and get them back to the battery manufacturers in time to be incorporated into batteries for the accelerated test, and so we ran some ampules tests with this particular header, by placing the header in a glass ampule, holding the outer conductor at the lithium potential, covering it with electrolyte, sealing it and placing it in a temperature chamber.

We had a more severe test on these particular headers than on the others for two reasons First, there is an excess of electrolyte, which is bad. Secondly, we kept them at 70 C for the five months, while the batteries in the accelerated tests only saw a constant temperature of 60 C for the five months.

We can see again, because there are no shadows, that there does not seem to be any corrosion on this glass after this time at 70 C.

(Figure 6-7)

We did do some resistance measurements on these headers when they came off test, and I shall summarize our observations.

As I mentioned earlier, the standard glass we measured had resistance as low as 5 ohms. Here I am showing the minimum resistance we measured on any particular glass or any particular header from the test.

This next group showed a significant improvement over the standard glass. We found in particular, with the fluoropolymer Edathon, that when we removed the fluoropolymer coating, there was no visual evidence of corrosion on the glass. We believe that the reason for this somewhat lower resistance is the absorption of the electrolyte into the fluoropolymer coating, lowering the resistance of the polymer.

I inadvertently omitted the tantalum washer polypropylene O-ring arrangement from this graph. We found that there was some leakage through the O-ring and that corrosion had begun to occur on the glass, and we found a resistance of about the same order of magnitude as these.

Finally, for the TA 23 glass, we found minimum resistance, of the order of 10 to the 10th ohms; this is what one would normally expect for glass that does not exhibit any type of corrosion.

The next area we investigated was that of tantalum corrosion. It appeared, from observations through the scanning electron microscope, that this was a grain boundary attack. It looks very much like a typical halogen attack on tantalum. Our analytical work has shown that there is indeed high concentration of bromines at the grain boundaries. Because of the very tight program schedule we were not able to study the mechanisms in detail, but our metallurgists did suggest that molybdenum would be better material for use as a center pin because it should be less susceptible to this type of attack.

We therefore decided to use a molybdenum pin, and the two manufacturers used different means of making contact. One was using an arc percussion weld of the aluminum cathode tab directly to the molybdenum pin, and the other one was drilling a hole in the molybdenum pin, forcefitting an aluminum rod into it and spotwelding the aluminum cathode tab to the aluminum rod.

In both cases we were not using the tantalum foil (which is used in the standard arrangement), since this seemed to be where the break occurred.

(Figure 6-8)

I have some scanning electron photomicrographs of some of these pins after the cells came off of the accelerated tests.You can see here the area where the foil had been spot welded to it. Notice the general pitting on the entire surface of this tantalum pin.

(Figure 6-9)

If we look at this front area under a still higher magnification, we can see definite evidence of the grain boundary attack over the entire surface.

(Figure 6-10)

Next, we have a molybdenum pin that was under exactly the same test conditions. Here we see no evidence of pitting on the surface, simply the remnants of the arc percussion weld aluminum tab; And it looks like a good weld.

(Figure 6-11)

Again, if we look at this top surface area under still higher magnification, we can see no evidence of corrosive attack. As a matter of fact, we can still see some of the scratch marks that were formed on to the surface of the pin when it was manufactured.

(Figure 6-12)

When we looked at the cells with the force fit aluminum rod, we saw no evidence of corrosion. However, in some instances, as is seen here, we noticed a radial crack formed across the molybdenum pin.

On this five-month test we saw no evidence of any problem, except for this cracking. However, we feel that for a five-year application this is a potential problem area that we should avoid if possible.

The next area that we considered was that of the lithium nickel corrosion, or selective utilization. We did some corrosion studies, of lithium versus a number of supposedly corrosion resistant metals in the standard electrolyte (acetonitrile lithium bromide with sulfur dioxide dissolved in it).

We found that of all the metals studied, nickel had the lowest galvanic corrosion current with respect to lithium. Therefore, we feel that nickel is the metal to use in the anode.

Again, because of the short time that we had to come up with remedies, we felt the best way to prevent an open circuit condition in cells was to place a grid in the anode and then make contact directly from the grid to the can.

We looked at two different variations on the grid. One had lithium pressed onto one side of the grid; and the other had lithium pressed on both sides of the grid, essentially having the grid sandwiched between the two strips of lithium.

One of the manufacturers also suggested the use of a reaction barrier in the separator. This involves heat-treating a narrow strip of each separator so that it becomes impervious to ions in the electrolyte. Thus, when a cell is discharged, the lithium directly behind this barrier does not become oxidized, resulting in a conductive strip of unreactive lithium running the full length of the anode right into the area where the contact is made with the can.

We found that cells with a grid or anodes with a grid, had a much more uniform utilization of the lithium. We did not notice any significant difference between cells with the reaction barrier in the cathode and those with the standard electrode.

In the standard anodes we again found corrosion or selective utilization at the point of contact with the nickel.

(Figure 6-13)

Figure 6-13 shows a microscopic shot of a portion of the electrode contact.

Here we have the lithium background. This is a nickel tab embedded into the lithium for contact. We can see many areas along the surface where the contact with the lithium is completely gone on both sides. Eventually this will lead to an open circuit condition. We also found that there was a non-uniform utilization of the lithium in these cells.

(Figure 6-14)

Looking at an area of high lithium utilization we can see many areas, as shown in Figure 6-14, where a portion of the lithium becomes physically isolated from the main body of the anode. Thus, this lithium is lost to the cell and we get very poor utilization of the anode.

Cells having the grid in the anode, as I said, showed a much more uniform utilization of the lithium. Looking at them under the microscope, we really could see nothing. These are all cathode-limited cells. We did have a few balanced cells on test, in which virtually all of the lithium was used up during the discharge.

(Figure 6-15)

We looked at one of these cells with the grid. This area is the main nickel contact to the can. You can see that there is no selective utilization. At the end of life, in areas out in the bulk of the anode, where the lithium becomes separated from the rest of the anode, there is still electrical contact to the tab via the grids. There is a much more efficient utilization of the lithium when there is a grid in the anode.

We did not really see any significant difference between anodes having the lithium pressed onto one side of the grid, or having the grid sandwiched between two pieces of lithium. However, for a long-term application such as we are interested in, we feel that having lithium on both sides of the grid is advantageous for several reasons.

(Figure 6-16)

First, if we look at another balanced cell having the grid, we see that there are many areas of unused lithium in between the grid matrix. Thus, it is apparent that we get much better utilization of the lithium where it is directly in contact with the nickel. By putting lithium on both sides of the nickel, we have more lithium in contact with the nickel, which should give a better utilization. Also, by pressing the grid onto one side of the lithium, we are effectively blocking off part of the anode surface. In one of our particular applications, we have to pull a fairly high current from these cells somewhere near the end of life. By blocking off part of the anode, we are operating at a higher current density than normal which is a bad situation, particularly at the end of life.

Anyway, from the results of this accelerated test, we have come up with a modified cell design for long-life applications.

In it we have the Sandia TA 23 glass in the glass-to-metal seal in the header, the positive pin is molybdenum, with the aluminum cathode tab arc percussion welded directly to the molybdenum.

In this particular area I think we violated Murphy's Law, because the molybdenum, in addition to being less prone to corrosive attack in this environment, also makes a better compression seal with the TA 23 glass. The coefficient of expansion of molybdenum matches the TA 23 much better than does tantalum.

Finally, through the anode, we are using the nickel-expanded metal grid with lithium on both sides. Contact will be made directly from the grid to the can. We have ordered cells of this design from two different manufacturers, and should receive them early next year.

At this time we cannot guarantee a more reliable five-year life. However, I feel confident that these cells will show a significant improvement over the standard cells available for purchase.

DISCUSSION

DI MASI: I Was wondering if you knew the increase in efficiency with the lithium, with the grid and without the grid? Did you make any analysis on that?

LEVY: We really did not have time on this study. We only had five months.

DI MASI: Could you venture a guess as to the increase?

LEVY: I should rather not at this time, until we can run some tests on it. We plan to do that.

FELDHAKE: You mentioned stress corrosion. Was that stress corrosion of the can?

LEVY: It was stress corrosion of the can at the outer radius on the bottom. It only occurred in the cells that were of the nickel-plated cobalt steel design. We did not see it in the stainless steel cells.

MARCOUX: What was the lithium bromide concentration in your final design?

LEVY: We are using the standard electrolyte of each manufacturer.

MARCOUX: You were not involved?

LEVY: We did not look at the electrolyte.

AKERS: You had a list of corrosion-resistant glasses up there. Did you categorize them as conductive glasses or nonconductive glasses?

LEVY: The glasses themselves are not conductive.

AKERS: Why not?

LEVY: It was after corrosion or after some time in this battery environment that they became conductive.

AKERS: Did you actually test that?

LEVY: From the center pin to the outer conductor.

AKERS: Thank you.

CHODOSH: Is the TA 23 glass formulated by your laboratory?

LEVY: Yes.

CHODOSH: Is it proprietary?

LEVY: It is not proprietary. There is a patent disclosure pending. Within the next month it should be filed and will be made public.

We are actually arranging for one of the glass manufacturers to make the glass for us as soon as the patent is filed. We are trying to get out of the glass-to-metal seal business.

SCUILLA: Can you offer a reason why that TA 23 glass is more corrosion resistant?

LEVY: Because of the composition.

SCUILLA: Is that from a thermodynamic standpoint, or kinetics?

LEVY: It is basically from a kinetic standpoint. All the network-forming oxides used in glasses are thermodynamically unstable in the presence of lithium. There are certain compositions, though, in which the diffusion rate of ions into the glass is inhibited. This usually entails reduced silica content and high boron, calcium and/or barium content.

As I have said, we have come up with some composition ranges that should be more corrosion resistant.

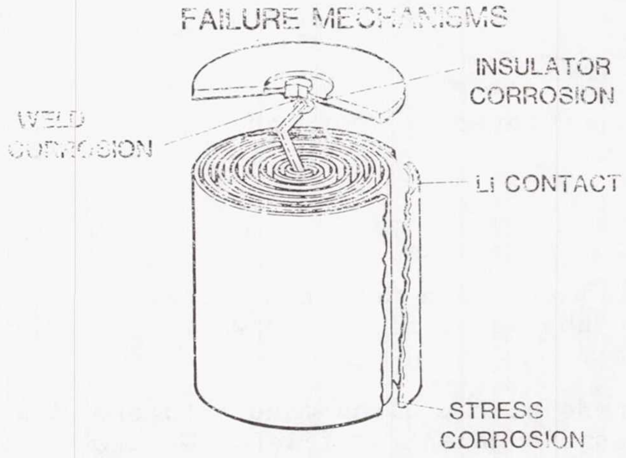
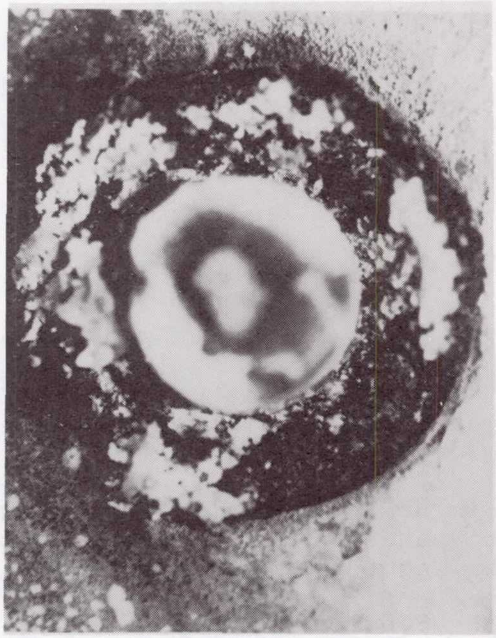


Figure 6-1



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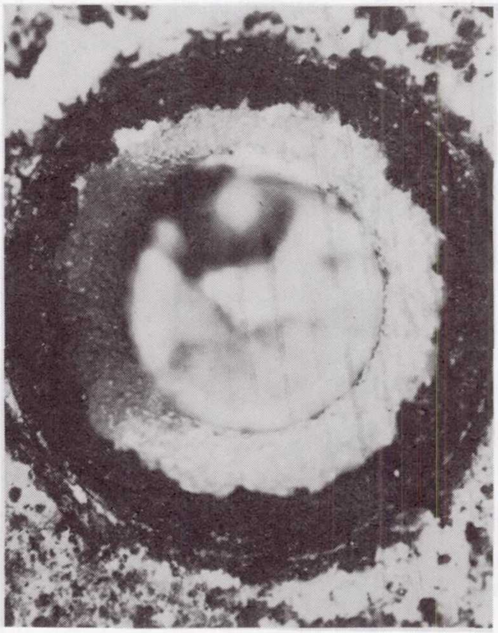

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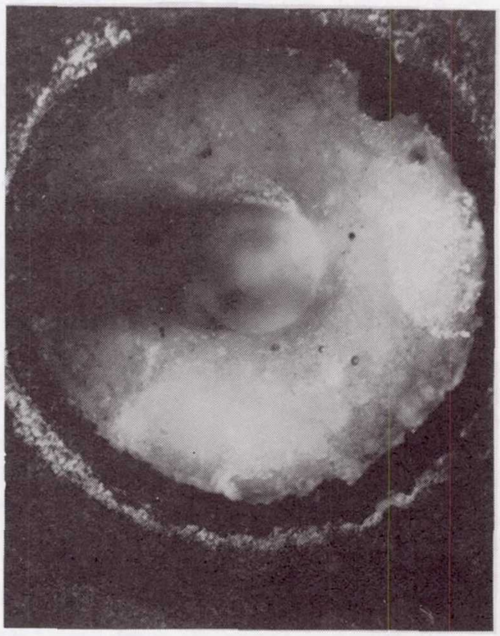

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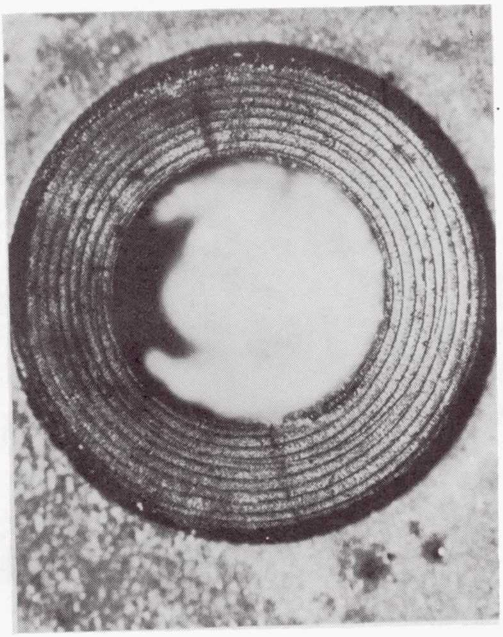

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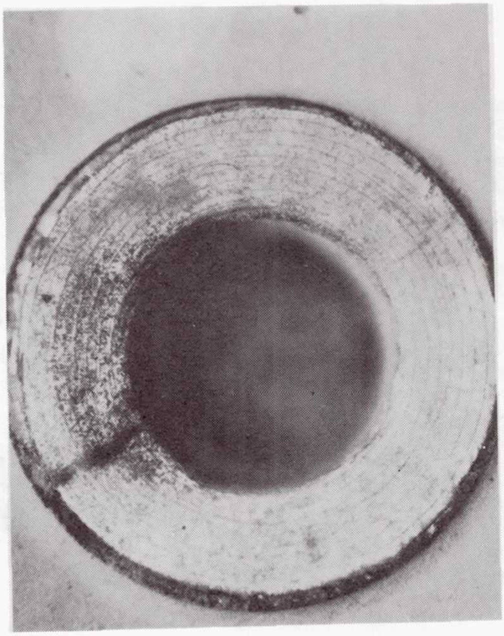

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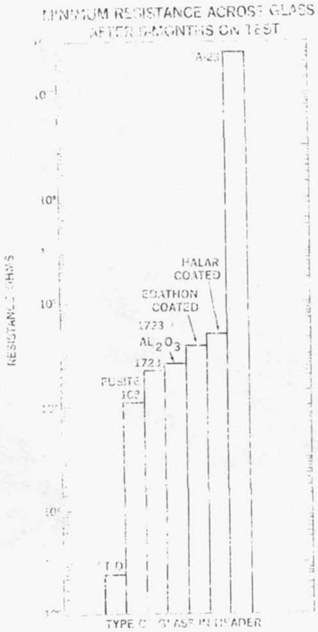

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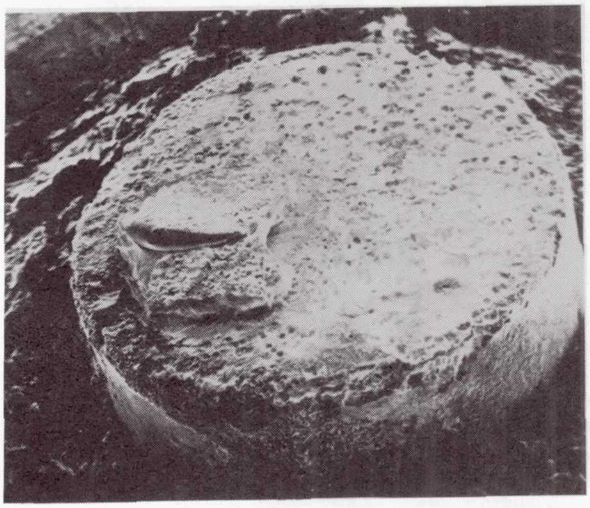

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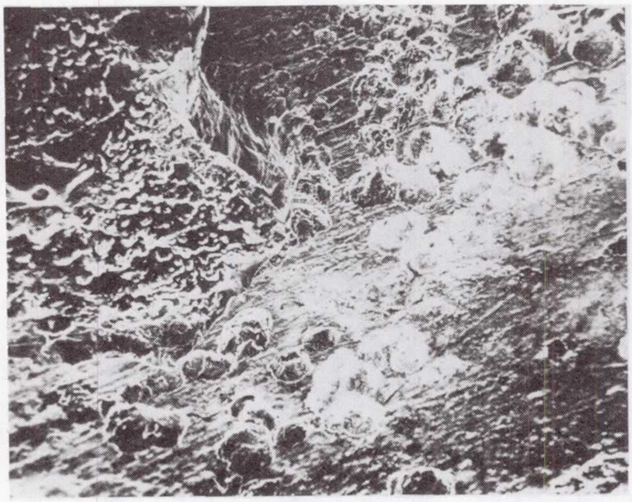
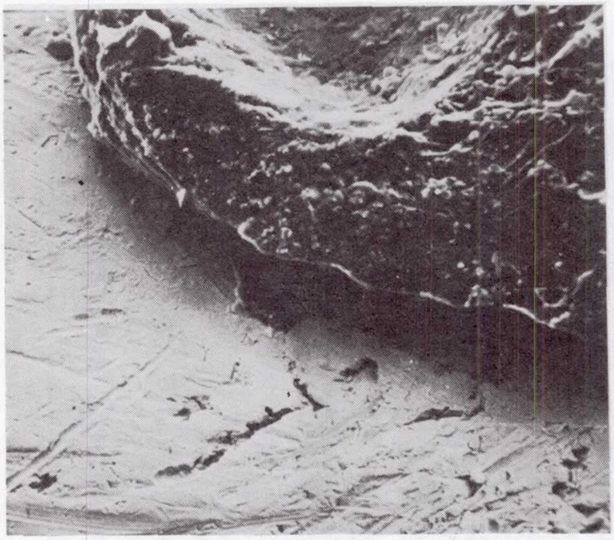


Figure 6-9

Figure 6-10



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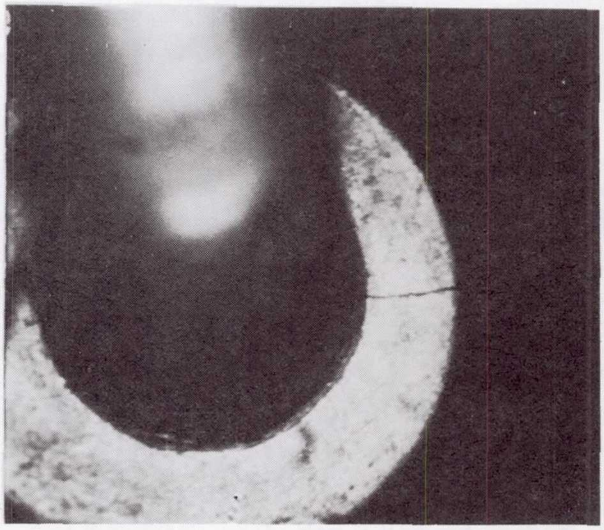

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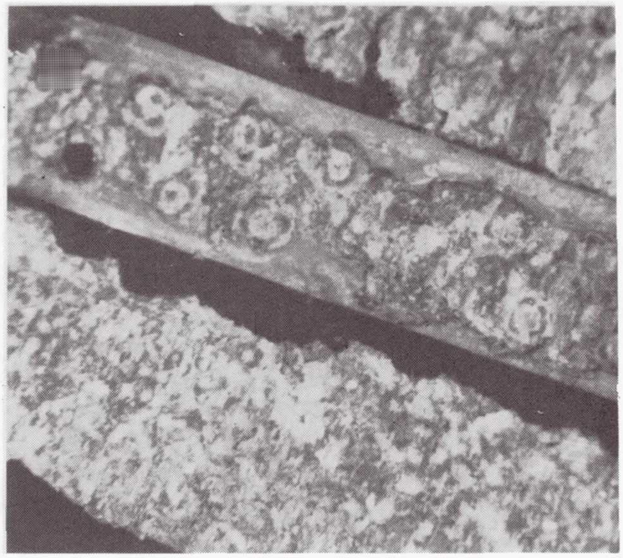

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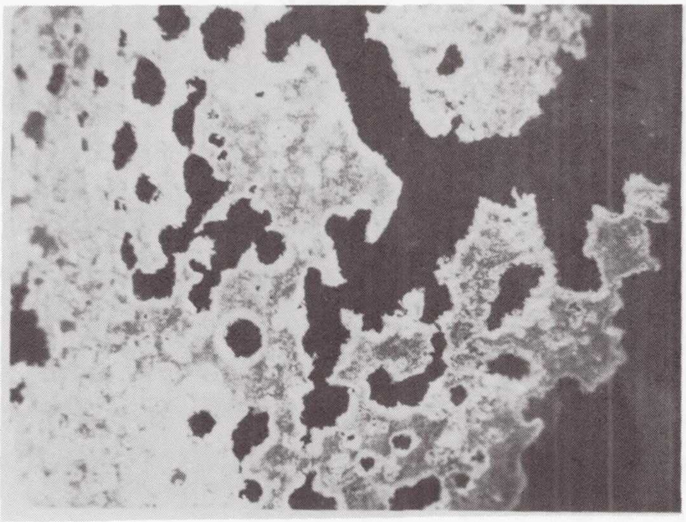

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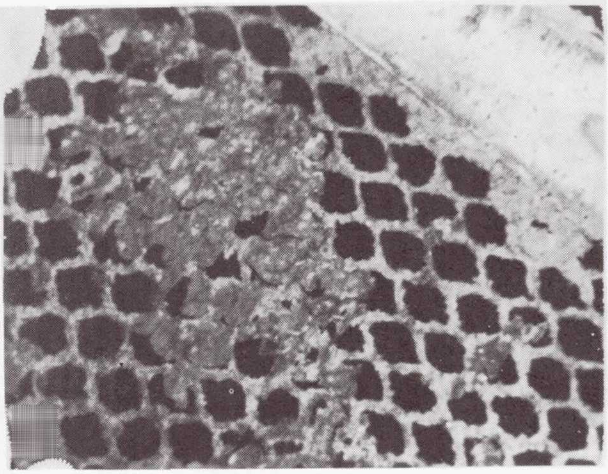

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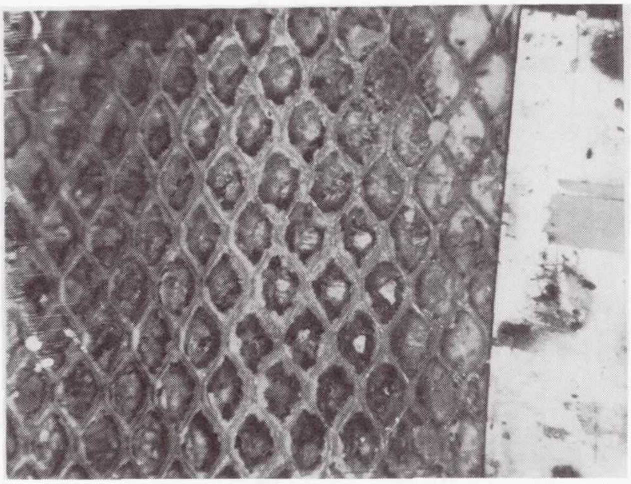

Figure 6-16

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PERFORMANCE, STORAGE, SAFETY AND DISPOSAL OF Li/SO_2 CELLS

G. Di Masi and J. Christopoulos
ERADCOM

Power Sources Division
US Army Electronics Technology and Devices
Laboratory (ERADCOM)
Fort Monmouth, New Jersey 07703

Previous studies[1,2,3] have shown that the electrochemical balance between the anodic and cathodic reactants affects the performance of the cell with regard to safety when it is overdischarged. It was also stated that a lithium-limited D-cell, having sufficient carbon capacity, could be discharged at a 0.5 to 5 ampere rate even into voltage reversal without any serious incidents. In another report[4] anomalous results were indicated without any consideration of the cell stoichiometry. Other studies [5,6,7] have reported cell performance characteristics and general abuse tests.

These investigations include an evaluation of cell performance characteristics after storage at room temperature and 71 C, as well as, some cell failure modes. The performance of cells at low temperatures (-30 C) even into voltage reversal is also considered. The correlation of Li/SO_2 coulombic ratio with generated free cyanide (CN^-) in forced discharged D-cells is also included.

Experimental Procedures

The D and SqD-cells employed for these investigations were of a number of different designs, both internally and externally. The main components were the lithium anode, a polypropylene separator in most cases, and a carbon/teflon cathode pressed upon an aluminum grid. These three components were in a spirally-wound configuration within a steel can. The organic electrolyte was composed of lithium bromide dissolved in acetronitrile and sulfur dioxide, which also served as the cathodic reactant. The cell closure employed was a glass to metal hermetic seal. The cell venting designs were of several types. The internal cell components also varied in physical dimensions and design. The lithium anode had a range of thicknesses and surface areas. Anode current collectors were employed in some designs, and <u>not</u> in others. The cathodes were composed of carbon/teflon having 5% teflon. The methods used to press the carbon/teflon mixture into the aluminum grid was by rolled-pressing in which both sides were covered with the mix. Subsequent drying of the cathodes was performed at 150 to 200 C usually under vacuum.

The cell discharge tests were performed with a North Hills Constant Current Source. High currents were obtained from a Kepco Power Supply. The current was measured through a Weston 50 mV shunt with a Keithley Digital Voltmeter. A type-T thermocouple was attached to the outside steel casing of the cell to measure the temperature. A Standard (TB/2) Environmental Chamber was used to control the external temperature of the cell.

Water determinations were performed in a Karl Fischer Aquameter (Photovolt Aquatest II). This apparatus performed the titrations, coulometrically, and the results, in micrograms of water, were automatically recorded on a digital meter. Vacuum drying at various temperatures and weighing of solids was another method used for water determinations.

The internal resistance was determined by applying a constant current pulse through a mercury-wetted relay (Clare HGS-5114); the voltage and current traces were tracked with a Tektronix 556 scope and photographed for record.

The free cyanide (CN^-) content of forced discharged cells was determined by a spectrophotographic (Beckman Mdl DU) method[8]. Each discharged cell is mechanically disassembled and its internal components placed into one liter of approximately 1 N sodium hydroxide solution. An aliquot of this solution is buffered to pH6 then oxidized with 1% chloramine T to form cyanogen chloride (CNCL); subsequently, the cyanogen chloride formed is reacted with the acidified barbituric acid-pyridine solution. The resulting pink colored solution representing a cyanide complex has an absorption maximum near 580 nm. Absorption measurements of samples are compared with standard curve for (CN^-).

Results and Discussion

Storage

The experiments were performed to evaluate the cells after long-term room temperature storage. In Table 1 the data for fresh cells is given for comparison purposes. The lithium sulfur-dioxide cells, stored for two years, were of three types: 1. excess lithium, 2. balanced and 3. lithium-limited. Another variable considered was that the balanced cells with respect to lithium and sulfur-dioxide (stoichiometrically) contained a continuous current collector along the complete anode. As shown the cells, after storage, rtained a large amount of capacity. The cells discharged at 0.5 amperes, however, showed less degradation. Those cells which had the continuous collector also outperformed the lithium-limited cells having isolated tabs as current collectors.

The cells stored for five years were hermetically-sealed and also contained an anode with a continuous current collector. These cells delivered a capacity of 9 Ah at a medium rate of 0.5 amperes and 5.9 Ah at a moderately-high current of 2 amperes. Though, the higher rate appeared to have a greater effect on the capacity retention, the overall cell storageability was rather remarkable at room temperature. Figure 1 shows a comparison of three squat-D cells having a Li/SO_2 ratio of 1.0, 1.1 and 1.47, discharged at 0.5 amperes after four years storage at room temperature. The capacity obtained was 7.8, 8.7, and 9.5 Ah, respectively, which represents more than 95% of the initial capacity.

In Table 2 the effects of high temperature storage are presented; the cells were discharged at 2 amperes. A decrease in available capacity was obtained from cells, having been stored at 71 C, after previous storage for almost two years at room temperature; a comparison with the two year room temperature data in Table 1 makes this quite evident for both the lithium-limited and excess type cells. A further room temperature storage of seven months following 1 month at 71 C shows that the cells underwent a further loss in capacity. This most likely indicates that the reactions initiated at the high temperature continued at a lower rate at room temperature.

Further evidence of this phenomena is presented in Table 3. This group of cells is of a different lot than those in Tables 1 and 2. These cells were also discharged at 2 amperes after having undergone two types of storage. The data obtained initially showed a relatively good capacity for lithium-balanced cells. However, after storage at 71 C, the cells showed a capacity decrease greater than ten percent which is more than expected after high temperature storage. An even greater decrease in capacity was obtained from these after waiting an additional period of two and one-half months at room temperature. These cells, however, showed a greater randomness and an increase in internal resistance.

Some possible reasons for this large capacity loss are: 1) A current path was formed across the glass to metal seal; 2) The electrolyte decomposition which commenced during storage at 71 C continued further at room temperature; and 3) An anodic poisoning or contamination took place which was irreversible. Analysis of the cells (Table 3) indicated that the fresh cells contained water, as much as, 4000 to 5000 parts per million as compared to the normal cells range of 1000 to 2000 parts per million. A further examination of the stored, undischarged cells revealed that a grayish-green viscous liquid had formed; these cells also displayed very little pressure. These findings seemed to indicate that electrolyte degradation had taken place! Also, internal resistance measurements of these cells indicated that a substantial increase had occurred as shown in Table 3. A further study of the glass to metal seal showed that in some cells a current path had been formed between the positive post and the header. The above observations seem to indicate that self-discharge had occurred in some cells only.

An analysis of other cells showed that less than a milligram per milliliter of iron was present in the solution. To determine the effects of iron on the anode, experiments were conducted with a solution of lithium bromide, acetronitrile, sulfur dioxide, and 0.5 milligrams per milliliter of the ferrous ion. A lithium anode was placed in the solution and open circuit potential versus a 0.01 molar silver nitrate, silver electrode was monitored. Within a period of one hour the potential began to decrease. The lithium metal was left in the solution for 72 hours at which time a current-voltage profile was determined. These measurements are shown in Fig. 2. A fresh lithium anode was then introduced into the solution; the current-voltage curve was also measured. A comparison of the two curves shows that large differences in potential between the fresh and stored lithium occurred above 1 milliampere per square centimeter. Current-voltage curves of stored cells, (71 C-1 mo., 2.5 mo - RT) with and without iron appear to correlate wilth the lithium anode studies. Although, the contamination of the lithium anode with iron (possibly causing local cell action) cannot be put forth as the only cause of the cell degradation, it is a possibility in cells which are contaminated wilh water and having iron available. It has been previously reported[9] that water enhanced the reaction of sulfur dioxide with the bromide ion; whereas other work[10] concluded that less than 100 parts per million did not contribute to this reaction. Therefore, in addition to its effect on the electrolyte of the cell, water and iron also appear to contribute to the degradation of the lithium anode.

Temperature Performance and Safety

The previous studies[2] have discussed the correlation derived experimentally between lithium-sulfur dioxide stoichiometry and the rate of cell discharge at room temperature. However, as the temperature was decreased the efficiency of the carbon cathode was found to decrease. An example of this is shown in Fig. 3. The cells were discharged at -30 C under 2 amperes constant current. The capacity to the 2 volt cut-off was found to be slightly greater than 4 Ah. This represents about fifty percent of the room temperature capacity. However, the voltage did not reverse until almost 8 Ah had been discharged from the cell. This factor was rather important because the cell did not overheat and the formation of dendritic lithium did not take place. At the point of the voltage inflection about eighty percent of the available lithium had been consumed; hence, the remaining sulfur dioxide served as a protective layer even at the increased temperatures. When the current was increased to 3 amperes (Fig. 3) and temperature maintained at -30 C the polarization through voltage reversal occurred at 4.5 Ah. Under these conditions the available lithium was in excess of fifty percent. The deposition of dendritic lithium at the cathode further contributed to the overall reactions. Hence, when the voltage deflected (negative direction) and then inflected (positive direction), a near tangential temperature rise took place. The cell vented following the positive voltage inflection; carbon deposits were observed at vents. Hence, it appears that the current limitations at -30 C are more restrictive than at room temperature.

In Fig. 4, the stoichiometric (coulombic) ratio of lithium to sulfur dioxide was correlated to current density for D-cells and smaller under forced overdischarge into voltage reversal. The data gathered at -30 C and room temperature are representative of a number of experiments. The relationship between stoichiometric ratio and current density, rather than current, was found to be more meaningful in that other cell sizes could also be related. In this figure two solid lines are shown which represent room temperature and -30 C data. The safe region for the -30 C curve favors a lower ratio as compared to room temperature and only extends to 7 milliamperes per square centimeter. This was due to the greater and more rapid polarization of the carbon cathode and the total cell; hence, an inordinate amount of electrical energy was converted to harmful heat energy. The unstable region (room temperature) represents mixed results in which some cells operated safely while others did not; reasons for this may be due to the deviations from the mean cell stoichiometry, in the negative manner. As was previously communicated, the carbon cathode capacity was found to be an important parameter in the overall cell design. The third region, designated as unsafe, represents the discharge of a poorly designed cell.

Disposal

The previous studies[2] found that to obtain a safe operating cell over a wide range of currents, temperature and even into voltage reversal, the Li/SO_2 ration should be 0.9 to 1.0. In addition to this it was reported that these (0.9 - 1.0) ratio D cells yielded the lowest amount of free cyanide (CN^-) upon analysis[2,11]. In an attempt to determine approximately the minimum concentration of sulfur dioxide needed to protect a certain geometric area of lithium anode, a more precise method for predicting conditions and amounts of cyanide evolved. In Table 4, three groups of 4 squat D cells from the same lot with Li/SO_2 ratios of approximately 1.24 were discharged at 0.5A rate to various voltage cut-off points (2V, 1.7V, OV and 2 hours in reversal). To better understand the rate of cyanide generation in situ, a group of cells were disassembled for (CN^-) analysis at post discharge times of 14,168 and 672 hours. In Table 4 cells; 3, 10, 11 and 12 all show values of (CN^-) between 0.8 and 2.7 mg per cell and approximately the same capacity to 2V cut off (7.65 Ah ave). By subtracting this average capacity from 9.5 Ah (ave SO_2 capacity) the amount of SO_2 remaining in these four cells may be estimated as 1.85 Ah or 4.4 g SO_2; since the geometric area (450 Cm^2) of the anodes and the cyanide (CN^-) concentrations of these cells are approximately the samé, the minimum amount of SO_2 for protection is postulated to be approximately 10 mg per square centimeter (geometric area) of lithium. In Fig. 5 an example of how one may predict the cyanide concentration (CN^-) is shown.

In Fig. 6 the coulombic (stoichiometric) ratio of lithium to sulfur dioxide D cells was correlated to the milligrams of free cyanide (CN^-) theoretically generated when sulfur dioxide is depleted in the presence of acetonitrile solvent in situ. Experimental findings of free cyanide (CN^-) in forced discharged D cells agreed within 15% of theoretical (Fig. 6) for Li/SO_2 ratios 1.0 to 1.25. Cyanide (CN^-) content of Li/SO_2 ratio 0.9 to 1.0 was 0.1 - 2 mg. This cyanide was probably generated from suspended lithium due to discontinuous anodes during discharge. At Li/SO_2 ratios greater than 1.25 the (CN^-) findings were limited to 1,200 - 1,300 mg per cell. This may be due to a diffusion limitation of the acetonitrile from the cathode though the cell separator (incrusted with reaction products: B-imino -nbutyronitrile, and lithium cyanide) to the anode or lithium.

Environmental Protection Agency's (EPA) minimum concentration of (CN^-) in fresh water is 0.2 mg (CN^-) per liter.[12] Also, EPA in their studies of ground water pollution from subsurface sanitary fills indicated that approximately 41 liters of water per cubic meter of compacted solid would be needed to obtain this saturation point in a landfill.[13] From this data it is thus possible to calculate the concentration of (CN^-) which could be tolerated per cubic meter (m^3) of landfill: 8 mg (CN^-)/m^3. From Fig. 6 it appears that a balanced cell design could be disposed of both safely and economically. ERADCOM presently procures the balanced Li/SO_2 ratio cell and batteries. A sample lot of these cells both fresh and discharged were tested by Wapora, Incorporated for ERADCOM according to EPA requirements for hazardous wastes and found nonhazardous under EPA guidelines, Federal Register (18 December 1978)[14].

Conclusions:

It has been shown that lithium-sulfur dioxide cells can be stored at room temperature for five years without a significant loss in capacity. Storage at 71 C can cause the cells to degrade at a faster rate especially if the cells contain a significant quantity of water. These effects were observed on both capacty retention and higher voltage polarization.

The safe operating range of current densities at -30 C appears to be more restrictive than at room temperature when a cell was discharged into voltage reversal. This limitation is most likely due to the polariation of the carbon cathode.

It has been postulated that approximately 10 mg SO_2 is needed to sustain each cm^2 (geometric area) of lithium ribbon anode from reacting with acetonitrile at room temperature. Also it was shown that the balanced Li/SO_2 ratio can be disposed of both safely and economically in sanitary landfills because of the low (CN^-) generation (0.1 - 2 mg CN^-) including cell design variations and because it is nonhazardous according to EPA guidelines.

DISCUSSION

BALLARD: What was the ferrous ion contamination?

DI MASI: It was 0.05 mg/ml of solution. I found about 1 or 2 mg of ion in the cells with the ferrous ion; these were the ones that failed.

TABLE 1

Room Temperature Storage

Storage Conditions	Discharge Temperature	Discharge Current	OCV	Service to 2V	Capacity	Comments	Quantit
	°C	A	V	h	Ah		
Initial	RT	0.5	2.96	18.7	9.4	excess lithium	4
		2.0	2.97	4.1	8.2	"	4
		0.5	2.98	17.4	8.7	Li-SO_2 balanced cont Anode collector	3
		2.0	2.98	3.95	7.9	"	3
		0.5	2.98	14.1	7.0	Lithium-limited	3
		2.0	2.98	3.82	7.6	"	4
RT 2 yrs		0.5	3.01	17.4	8.7	excess lithium	4
		2.0	3.00	3.82	7.6	"	4
		0.5	3.00	15.4	7.7	Li-SO_2 balanced cont Anode Collector	4
		2.0	3.00	3.65	7.3	"	4
		0.5	3.00	13.4	6.7	Lithium limited	4
		2.0	3.00	3.55	7.1	"	4
RT 5 yrs		0.5	2.99	18.0	9.0	Slight excess Lithium Cont Anode collector	2
		2.0	2.99	2.95	5.9	"	2

Table 7-1

TABLE 2

Room and High Temperature Storage

Storage Conditions	Discharge Temperature	Discharge Current	OCV	Service to 2V	Capacity	Design
	C	A	V	h	Ah	
22 mos-R.T., 1 mo. 71°C, 2 mos-R.T.	RT	2	2.99	3.31	6.62	Lithium limited
		2	2.99	3.45	6.90	"
		2	2.95	2.74	5.48	Lithium excess
		2	2.89	2.46	4.92	"
		2	2.89	2.60	5.20	"
		2	2.89	2.65	5.30	"
22 mos-R.T., 1 mo. 71°C, 7 mos-R.T.		2	2.92	2.05	4.10	Lithium limited
		2	2.91	2.0	4.0	"

Table 7-2

TABLE 3

Room and High Temperature Storage

Storage Conditions	Discharge Temperature	Discharge Current	OCV	Service to 2V	Capacity	Internal Resistance	Quantity
	$^{\circ}C$	A	V	h	Ah	Ohms	
Initial	RT	2A	2.97	3.9	7.8	0.21	4
1 mo @ 71°C	"	2A	3.01	3.22	6.4	0.39	4
1 mo. 71°C, 2 mos.-R.T.	"	2A	2.90	1.08	2.2	1.2	1
			2.89	1.35	2.7	1.1	1
			2.90	1.0	2.0	1.3	1
			2.90	0.67	1.3	1.3	1
			2.92	2.48	4.96	0.7	1

Table 7-3

TABLE 4

FREE CYANIDE (CN^-), SQ D CELL, 0.5A - CC DISCHARGE RT

$Li/SO_2 = 1.24$ CAP SO_2 = 9.49 AH

CELL No.	POST DISCHARGE 24 HR.		POST DISCHARGE 168 HR.		POST DISCHARGE 672 HR.		COMMENTS
	CAP AH	(CN^-) MG	CAP AH	(CN^-) MG	CAP AH	(CN^-) MG	
5	7.75	13.7					2 HR REVERSAL
7	8.66	38.1					0 VOLT CUTOFF
8	7.9	4.7					1.7 VOLT CUTOFF
6	8.68	54.6					2 VOLT CUTOFF
1			(7.45)	2.7			2 HR. REVERSAL
2			8.4	28.6			0 VOLT CUTOFF
3			(7.54)	0.83			1.7 VOLT CUTOFF
4			8.3	1.6			2 VOLT CUTOFF
9					8.73	1,224	2 HR REVERSAL
10					(7.5)	2.2	0 VOLT CUTOFF
12					(7.86)	1.8	1.7 VOLT CUTOFF
11					(7.71)	1.9	2 VOLT CUTOFF

Table 7-4

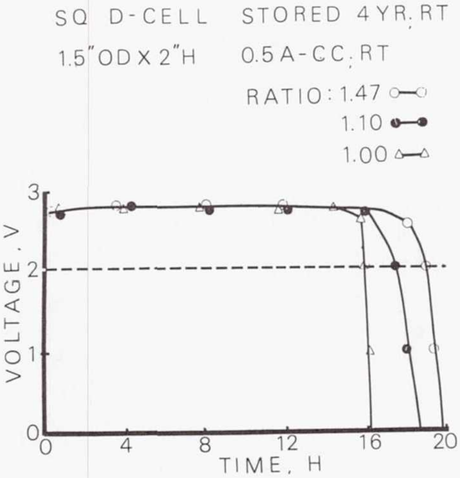

Figure 7-1

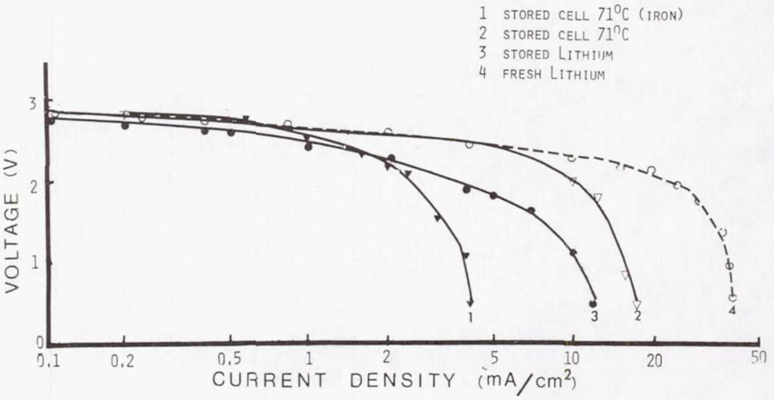

Figure 7-2

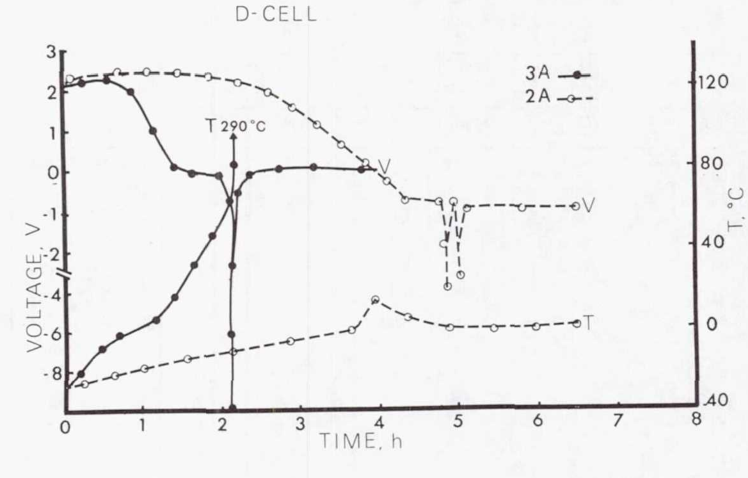

Figure 7-3

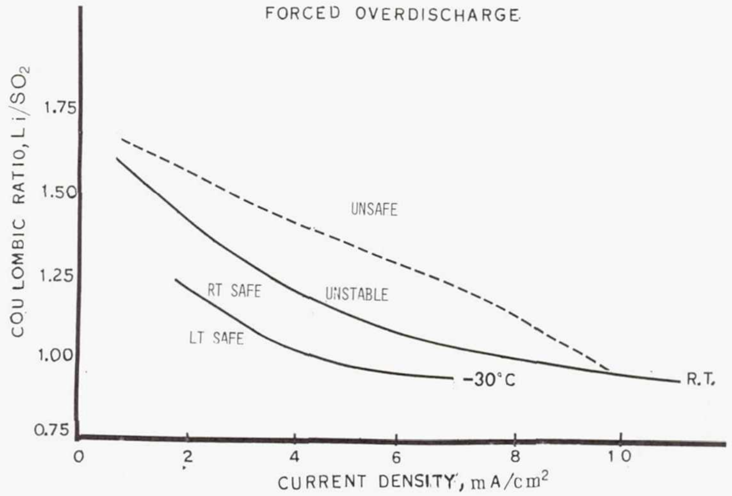

Figure 7-4

Sq D cell $\frac{\text{Li}(11.76)}{SO_2\ (9.49)} = 1.2 \pm 0.1$

Predicted concentration of cyanide (CN^-) based on the chemical reaction of excess anodic lithium with acetonitrile in the absence of sulfur dioxide (SO_2):

$$2\ Li + 3\ CH_3CN \rightarrow LiCN + CH_4 + CH_3CN\text{-}CH_2CN^- + Li^+$$

Calc: Theorectical Li 11.8 Ah
Theorectical SO_2 9.5 Ah
Excess Li 2.3 Ah

$$\frac{(2.3\ \text{Ah Li})\ (26\text{g}^{CN^-}/\text{mol } CN^-)\ \ (1\ \text{mol } CN^-)}{(3.86\ \text{Ah/gLi})\ \ (2\ \text{mol Li})\ \ (6.939\text{gLi/mol Li})} = 1.10\text{g}\ (CN^-)$$

Note: Acetonitrile available in excess

Figure 7-5

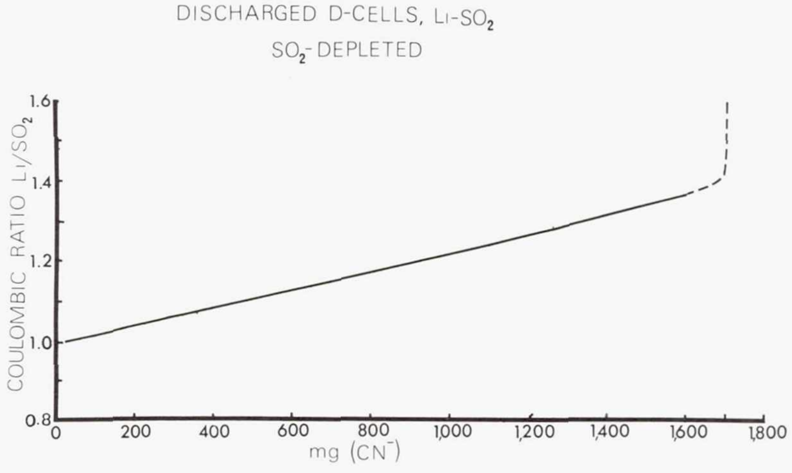

Figure 7-6

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Li/SO_2 CELL PERFORMANCE

S. Cloyd
Air Force Aeropropulsion Laboratory

I should like to report on the results of testing a pilot production cell that was generated for the Air Force under a manufacturing technology program.

To give some background, the Air Force Materials Laboratory awarded a contract to Honeywell Power Sources Center in 1976. The final report was published in 1979.

The Materials Laboratory was very patient with the Aeropropulsion Lab in that we did go through several design changes during this program. We went through a baseline of first and second engineering prototype cells, and then a final pilot production type cell, which was generated in 1979.

The testing of both the first engineering prototype cell and the pilot production cell was accomplished at the Aeropropulsion Laboratory at Wright Paterson. There are a considerable number of interesting differences between the two types of cells.

As a summary, the key features in the pilot production cell were as follows. Early on, all the industries found that the glass-to-metal seal was important and so that is included.

The pilot production cell also included a lithium-limited composition approach to coulombically balanced chemistry; I shall give you some of the numbers so that you can put this cell on Mr. Di Masi's chart.

Over a year ago the Air Force felt that the grid structure in the lithium anode was going to be an important feature. So, we have been working since October 1979 with the grid structure, and I think some of these results will fit directly with Mr. Levy's work. One of the other interesting things that the Air Force require from the cell was an intermittent storage capability at 98 C (205F), because the greenhouse effect in the canopy of an aircraft on a flight line in the desert, for example, can reach this temperature. At that time cells were not capable of withstanding such temperatures. Another interesting feature was that we decided that no voltage delay whatsoever could be tolerated, and so we strove for an instantaneous voltage response. Specifically, this cell was designed in a D/2 configuration to be used initially in the PRC 112 Triservice Emergency Radio. Since then this technology passed on to a A-size cell.

These features resulted in a very high-reliability, high-integrity cell with slightly decreased energy densities, gravimetric and volumetric: we realized approximately 90 watt hours per pound and 6 watt hours per cubic inch. We were willing to suffer these for the sake of the added safety features.

(Figure 8-1)

The first engineering prototype was entirely different from the cell that we actually ended up with. The prototype had some features that I want to point out to you specifically -- this is how we came across some of our unique characteristics. It did not have 205 capability, the instantaneous response. I want to point out exactly which things we did change drastically in the production lot.

First , the volume is very close to a D/2 type size cell. There was no grid.

By looking at the numbers, you can see that it was very definitely a non-lithium-limited type configuration.

The other key feature, which may have had several ramifications, is the fact that the first engineering prototype contained a 72% (by weight) sulfur dioxide; there are some drastic differences when that concentration is changed. I was interested to see that Mr. Levy did not deal with any of the concentrations of sulfur dioxide in that regard.

(Figure 8-2)

Figure 8-2 shows the fresh cell performance of the first engineering prototype. It looks terrible. There was absolutely no capacity at the cold temperature at, say, 400 mA in a D/2.

Voltage delay was very evident below -29 C (-20 F) and in some cases down around -46 C (-50 F), -51 C (-60 F).

If you will just keep this picture in mind when I show you the production lot, you will see what a drastic difference we did realize.

(Figure 8-3)

Figure 8-3 is the last chart for the first engineering prototype, and you must also keep this in mind when I show you the production lot testing. This shows a rate capability that is really not very good. I do not have all these in the form of current density, but approximately 57% of rating capacity is realized; this is only 750 mA. The triangles either side of the points indicate plus or minus one standard deviation from the arithmetric average (the points) of six cells.

(Figure 8-4)

I have more data on the pilot production cell, to show how some of these differences caused improved performance. As far as the physical characteristics of the pilot production cell are concerned, we did increase the volume; we gave the electrolyte more room to expand; we made it a safer cell; and it can now stand intermittent storage at 205 F without venting.

There were also changes in the cathode, and I have a comparison chart for that. There was a grid in the anode, which was definitely lithium-limited and approaching a balanced cell, if not truly limited.

The other key feature -- I am beginning to believe this is more and more apparent -- is a 64.4% (by weight) sulfur dioxide concentration in the electrolyte. I really do believe that this is now starting to show up in other ways than just an improvement in voltage delay . I shall point it out again as we come to it.

(Figure 8-5)

Figure 8-5 is a chart of the comparisons between the first engineering prototype, with the core performance, and the pilot production cell. As you can see, there were several structural changes in the cathode.

(Figure 8-6)

Now, refer back to Figure 8-2. Figure 8-6 shows the fresh cell performance for the pilot production cell. There is a decrease in capacity at the upper end of the temperature scale, but we knew this. The capacity delivered through a range of temperatures was leveled out. I think two things had a bearing here: both the grid and the fact that we had a lower concentration of sulfur dioxide in the electrolyte. There was only one data point in this graph that showed any voltage delay whatsoever. It was a true data point at -70F at 400 mA; it showed approximately a 5 second voltage delay. All the other points showed no voltage delay in the fresh cell performance.

(Figure 8-7)

I included this computer plot to show that in fact is was the only point showing any voltage delay in fresh cell performance at true -70F.

(Figure 8-8)

Figure 8-8 shows a plot of discharge versus vapacity for the first engineering prototype. We only went up to 750 mA with the first engineering prototype. This chart demonstrates that the grid structure drastically improved the rate capability of this cell. There was statistically no loss in capacity from 50 mA up to 1A, and this is with a D/2 cell. The current density is doubled. At 2 A we were getting 70% of the rated capacity, 4.2 A h. Again, the current density doubled from a D. At 4 A it was

53% of capacity, and at 5 A and a D/2 cell, we still realizing approximately 2 A h.

(Table 8-1)

So that you would have the actual numbers in the proceedings, I wanted to include Figure 8-1. It is just a graph of the same thing I showed you last time. During all this excessive rate discharge testing, there were no cell failures, there was no voltage delay, they were all at room temperature, and all cells had had approximately a year of room ambient random orientation storage before the test. It also gives the maximum temperatures they reached at the end of the discharge.

I should like to briefly summarize and just present some data that I generated under the Abuse Test Type Commissions.

(Figure 8-9)

Figure 8-9 shows the cell short-circuit test. Unfortunately it got a little too big. Voltage and current are on the left, and cell temperature is on the right.

This cell was short-circuited at room temperature and it did vent at this point, approximately 1.75 minutes into the short circuit at a maximum temperature of about 47 C.

Several cells were tested this way, and the temperature at the venting was within a degree for each cell, showing a very high reliability in the vent mechanism.

(Figure 8-10)

We did most of our abuse tests at room temperature and at -40 to see what differences would occur owing to inefficiencies in discharge. The only things that occurred differently were in the -40 C test: the venting that did occur was delayed by about 1.25 minutes owing to the cell being soaked at -40 and then brought out into the room for the test. The maximum temperature was 22 C. It took a little longer to warm up, and so the current did not increase as fast as at room temperature.

(Figure 8-11)

We had been working with the PRC 112, and so we had four cells in the battery. I put four of these D/2 cells together into the four corners of a square configuration and tried the test in this four-cell series string.

Two cells vented at approximately 1.75 minutes and 1.9 minutes into the short circuit. We approached 25 A; I believe that 22.5A was the maximum current demonstrated.

I have some temperature data here. One of the cells vented at 64 C, and one at 65 C; the maximum temperature of the battery was 65 C. That also shows the open-circuit voltage at the end.

(Figure 8-12)

Figure 8-12 shows the data at -40; the results are the same, except that the battery tended to warm up a little more at the end of the test.

The vents were delayed till 2.5 or 2.6 minutes; it took them a little longer to warm up. One cell vented at 60 C and one at 72 C.

The maximum temperature was actually higher than the maximum one that vented. It warmed up for a little while after it had been short circuited.

(Figure 8-13)

We also went through a cell puncture test at room temperature and at -40 , and puncture occurred actually where the voltage started to decrease. We did get some noise. There were temperature increases of approximately 13 C. The cell did not vent. This would simulate a piece of shrapnel going into a radio.

(Figure 8-14)

Figure 8-14 shows the results of a -40C puncture test. The interesting feature is that the temperature increased to a maximum of 23 C, and it tried to heal itself. I assume that this is from corrosion around the nail that was left in.

(Figure 8-15)

Figure 8-15 shows the results of forced discharge testing at 300 mA constant current. I have a summary chart, so I shall not linger on any of these.

All I want to say here is that, besides there being absolutely no reaction at a 300 mA reversal to approaching 100% of the capacity itself, the reason for the temperature decrease was that the technician opened the door; apart from that, it did not cool off during discharge.

There was no reaction. The cell did not vent. The temperature increased approximately 6 C during the time of the reversal, to a maximum of 24 C. Excuse me, a minimum or a maximun negative voltage of -2.5V. Again, there was no reaction at 300 mA.

(Figure 8-16)

At 1A there was an increase of 8 C during discharge. The maximum temperatue attained was approximately 54 C. However, even though this chart suggests that venting occurred, a videotape recorder playing during the test showed that there was no venting.

Some people may remember that during reversal a very erratic voltage pattern can be seen. The grid structure did not allow for a lot of noise, but did provide that current path during reversal testing; it just leveled off, and so we shut it off eventually.

(Figure 8-17)

For the 2 A reversal we did have cell venting, followed by a very slight amount of flame. The whole venting process lasts for only about 3 seconds. This D/2 cell increased 13 C during discharge, and a maximum temperature of 67 C was reached at the time of venting.

(Table 8-2)

To summarize the forced discharge test, I should like to point out the current densities involved. This maximum temperature occurs during the reversal process. 300 mA is the rated voltage of the cell. We shall delay reversal at -40 to connect with Mr. Di Masi's. I think these would be viable data points to include on your chart.

(Figure 8-18)

The sulfur dioxide concentration will be important as regards storage. We have shells of the production type, lithium with a grid, on cold storage, and we have completed the hot tests at this point. Again, the top and bottom points from the dot represent plus or minus one standard deviation. These are at 0 C, and statistically there is no decrease in capacity over one year.

I think we do have cells on tests for five years in each condition ; the test includes testing of six cells.

At room temperature there is one thing that I cannot describe.

(Figure 8-19)

First, statistically there is only a slight decrease over the one year of storage; the cells are all stored upright at room temperature.

I am starting to see a slight increase in the variation in the cells; this makes sense. However, I cannot explain that point. I do not know why it did that. It must have been simply the statistical sample. We shall also be doing this test for five years. Here is where the interesting part comes in.

These all used the blue glass, Honeywell's old standard seal, but have now switched to a new standard white Fusite glass. I have just a few comments about this.

(Figure 8-20)

Figure 8-20 shows the elevated temperature storage at 71 C (160 F) not 60 C (140 F); the two curves represent capacity at 300 mA load at room temperature and at -40 . I am missing that point there, but this was actually stored at 71 C (160 F) for that time, and then cold soaked and discharged at -40 .

I am going to mention a few characteristics that we observed here. First, there are six cells per condition. During all the testing, through the nine months of high-temperature storage, we had not one venting. We detected no leakage. These cells were checked about once a week.

There was no real significant variance in their discharges until about the sixth or seventh month, when it started to grow. This is a little better than what Dr. Levy had shown.

That is the key feature about the 64% sulfur dioxide electrolyte.

At eight months the average was only 38% decrease in capacity from our fresh cells, at room temperature.

Now for some of the bad parts:

As early as the second month we did observe one cell with open circuit voltage about 3.34V, and so we are starting to get this reaction. That cell only showed a decrease in capacity of about 12% of what the rest of them had.

So at that time, event though it had the open circuit voltage high, it was not greatly affecting the capacity.

At the -40 discharge, the first time we had seen a voltage delay was during the fourth month. This was at 300 mA. Thus, these points at the second and third month at 40 , after 71 C (160 F) storage, showed no voltage delay. The fourth month discharge at -40 was the first one, and showed a delay of about five seconds.

During the fifth month at the 70 discharge, we lost our first cell owing to no capacity.

During the seventh month at the 70 discharge, they were all good, and showed no delay. One cell did have an open-circuit voltage of 3.26V. However, that turned out to be the highest capacity cell of the group.

And so I think that implies that this higher open-circuit voltage does have to exist for a while before it affects capacity. We ended up with a capacity of 2.99 A h.

During the ninth month at the 70 discharge, there were three cells with 70% of fresh capacity, which I thought was truly remarkable.

I have one other comment before concluding. We did want to verify the 86 C (205 F) capability.

(Figure 8-21)

As such, we went through temperature cycling. Unfortunately, at this point in the tests I did not have many cells left, and I only had four cells with the old blue glass. And one with the new seal as I show it, as the white glass, Fusite glass.

All the cells had the one-year ambient storage at random orientation before they were put through this temperature cycling regime: from room temperature overnight to two hours at 160 F up to one hour then at 205 F, back down to 160 F for two hours, and then back to room temperature overnight.

This temperature cycling regime was followed five days per week for a total of four weeks. At the end of each week the five cells were removed. No voltage delay was ever experienced. These were all dishcarged at 300 mA. There was no venting, and no leads, and the standard deviation of these cells was very similar to that of our one year room ambient storage. I think this does definitely demonstrate the 205 F storage capability.

In conclusion, we realize that we were going suffer some energy densities over what could be obtained from lithium sulfur dioxide. However, the Aeropropulsion Laboratory felt that what we wanted to put out into the field was the safest, most reliable cell we could generate.

We said that we have a good energy density. We were able to reduce it a little and keep it so that it wants to stay in the can even at 205 F.

Therefore, with the use of the grid, as Mr. Levy has described and maybe with this 64% electrolyte, you can see a tremendous performance in lithium sulfur dioxide.

DISCUSSION

DI MASI: Do you attribute that good capacity retention only to the reduction of sulfur dioxide and the grid, or are there other things that you think may have contributed, as well as almost the elimination of the voltage delay?

CLOYD: I really do believe that the voltage delay was directly associated to the 64% (by weight) of sulfur dioxide. In conversations with Mr. Levy, he says that at 68% they definitely see it. Well, at 64% I definitely did not, but I did at 72%. So I think that has a definite bearing on voltage delay.

As far as capacity retention is concerned, I think the storage of the glass-to-metal seal could be affected by the smaller amount of sulfur dioxide in the electrolyte. If a slightly decreased capacity can be tolerated, these data may show that we can store them for a long time with standard glass. The new glass will make it even better.

DI MASI: Do you think that other contaminants may affect that? Were these cells not specially made, in a sense, with regard to cathodes?

CLOYD: Changes were made in cathode structure. One thing that made them special was that they had waited so long that they had to go through an additional drying step in the cathode.

So, it could be that there was lesser a smaller amount of water in what a normal production cell. That is really the only different thing. It could very well could have had that effect.

FRANK: Did you measure your voltage raise on a timescale of less than a millisecond?

CLOYD: No. Our computer only goes down to about one second when we are reading several cells. However, we can see it if it lasts longer than one second. In some situations we did see that it was less than one second. We did not have the capability to measure it instantaneously.

CHODOSH: Would you care to comment on how the optimum concentration of 64% was selected?

CLOYD: I have no idea. Mr. Blagdon from Honeywell may be able to answer that. I do know that they are now around 68%. So what we have here is different from what they are putting out at this point as far as percentage of sulfur dioxide by weight. We have a decrease in sulfur dioxide concentration.

CHODOSH: If I understand you correctly, they are now using 68% sulfur dioxide?

CLOYD: I think so.

SUMMARY OF
HIGH RATE DISCHARGE TESTING

CURRENT (AMPS)	CURRENT DENSITY (MA/CM2)	MAX. TEMP (°C)	CAPACITY TO 2.0 VOLTS (AH)
1.00	3.47	23°C	4.12
1.50	5.21	28°C	3.85
2.00	6.94	32°C	2.83
2.50	8.68	32°C	2.95
3.00	10.42	39°C	2.68
3.50	12.15	39°C	2.16
4.00	13.88	42°C	2.22
5.00	17.36	49°C	1.80

Table 8-1

SUMMARY OF
FORCED OVERDISCHARGE TESTING

CURRENT (AMPS)	CURRENT DENSITY	CAPACITY TO 2.0 VOLTS	OPERATING VOLTAGE	MAX TEMP °C	OBSERVATIONS
0.30	1.04MA/CM^2	4.27 AH	2.8 VOLTS	24°C	NO REACTION
1.00	3.47MA/CM^2	4.10 AH	2.7 VOLTS	54°C	NO REACTION
2.00	6.94MA/CM^2	2.83 AH	2.5 - 2.6 VOLTS	67°C	VENTING/SLIGHT FLAME

Table 8-2

PHYSICAL CHARACTERISTICS OF HALF "D" CELL

FIRST ENGINEERING PROTOTYPE

PHYSICAL	
Outside diameter	1.324 in.
Length	1.190 in.
Volume	1.64 in^3
Weight	47.8 g
Case thickness	0.017 in.
ELECTRODES	
Cathode	
Length	16.00 in.
Width	0.65 in.
Thickness	0.016 in.
Mix weight	3.2 g
Cathode area	134 cm^2
Anode (no grid)	
Length	18.5 in.
Width	0.65 in.
Thickness	0.016 in.
Weight	1.68 g
Capacity	6.50 AHr
Separator	
Length	19.0 in.
Width	0.85 in.
Weight	0.84 in.
Electrolyte - 72 wt % SO_2	
Volume	15.0 cm^3
Theoretical capacity	5.7 AHr

Cell Case and Header Materials:	304 Stainless Steel
Terminal Pin Material:	Tantalum (0.125 in O.D.)
Separator Material:	Celgard 2400 (Polypropylene)
Glass Seal:	Hermseal Type GC SO_2 Resistant Glass
Anode Lead:	316L Stainless Steel
Cathode Lead:	1145 Aluminum

Figure 8-1

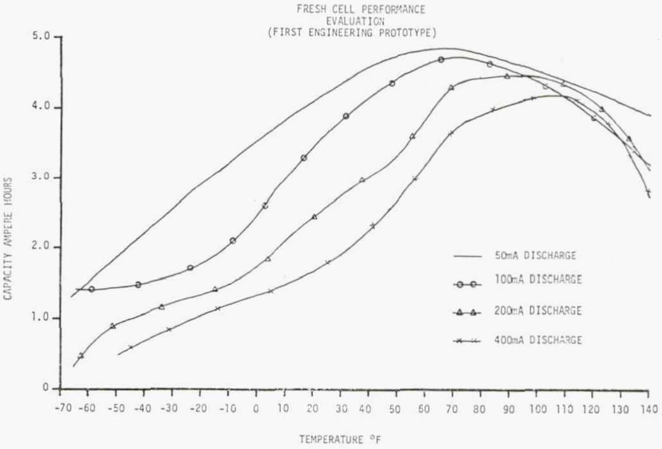


Figure 8-2

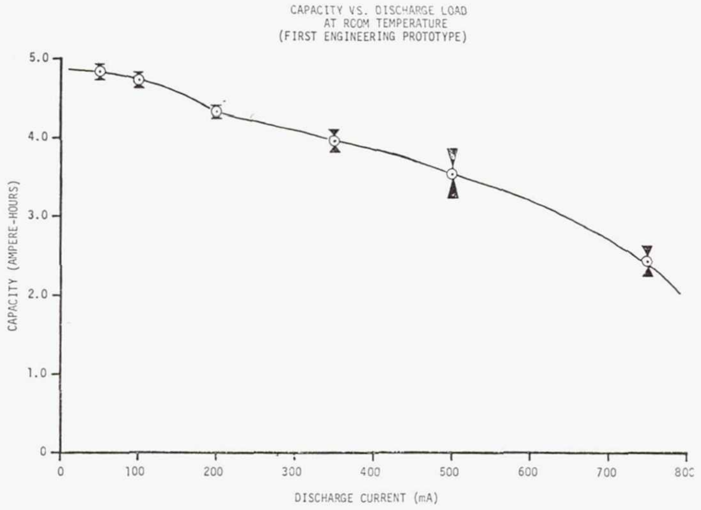


Figure 8-3

PHYSICAL CHARACTERISTICS OF HALF "D" CELL

PILOT PRODUCTION

PHYSICAL	
Outside diameter	1.324 in.
Length (nom.)	1.427
Volume	1.98 $in.^3$
Weight	58 gms.
Case thickness	0.017 in.
ELECTRODES	
Cathode	
Length	28 in.
Width	.92 in.
Thickness	.03 in.
Mix weight	4.25 gms.
Cathode area	332 cm^2
Anode	
Grid (nickel metal) weight	2.0 gms.
Length	24.5 in.
Width	.92 in.
Thickness	.0070 in.
Weight	1.33 gms.
Capacity	5.14 AH
Separator	
Length (avg.)	28.9 in.
Width	1.125 in.
Weight	2.0 gms.
Electrolyte (64.4 Wt. % SO_2)	
Volume	16.4 cc
Theoretical capacity	5.5 AH

Figure 8-4

COMPARISON OF PHYSICAL CHARACTERISTICS

(FIRST ENGINEERING PROTOTYPE VS. PILOT PRODUCTION)

	1st EPC	PRODUCTION
CATHODE		
Carbon/Teflon	80/20	95/5
Length	16.00 in.	28.0 in.
Width	0.65 in.	0.92 in.
Thickness	0.016 in	0.03 in
Area	134 cm^2	332 cm^2
Drying Conditions	No Heat Treatment	Heat Treatment (Additional Drying)
ELECTROLYTE	72.0 Wt. % SO_2	64.4 Wt. % SO_2
ANODE		
Theoretical Capacity	6.50 AH	5.14 AH
Current Collector	No Grid	Nickel Grid

Figure 8-5

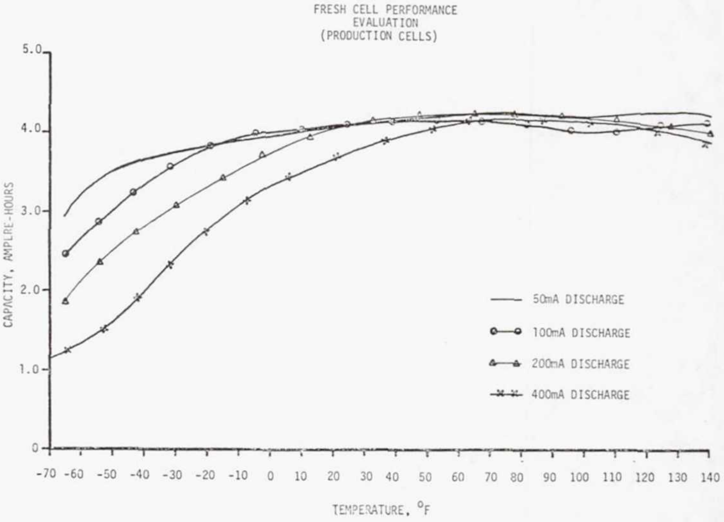
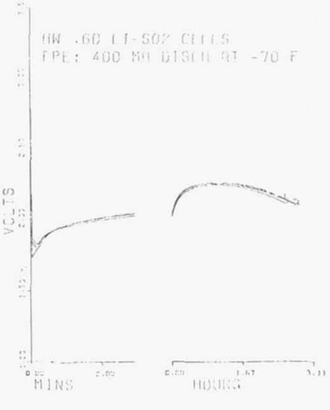


Figure 8-6



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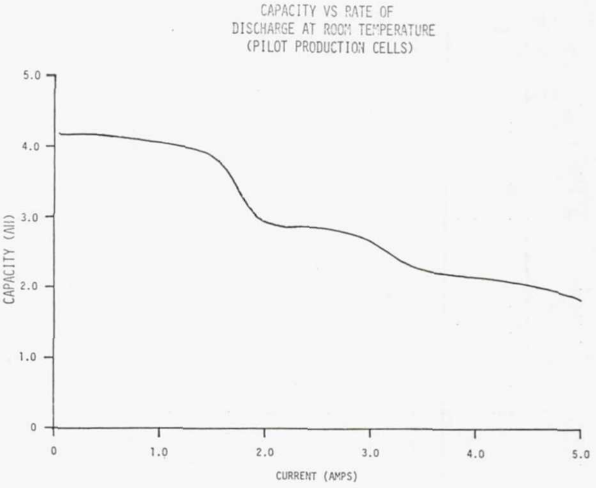

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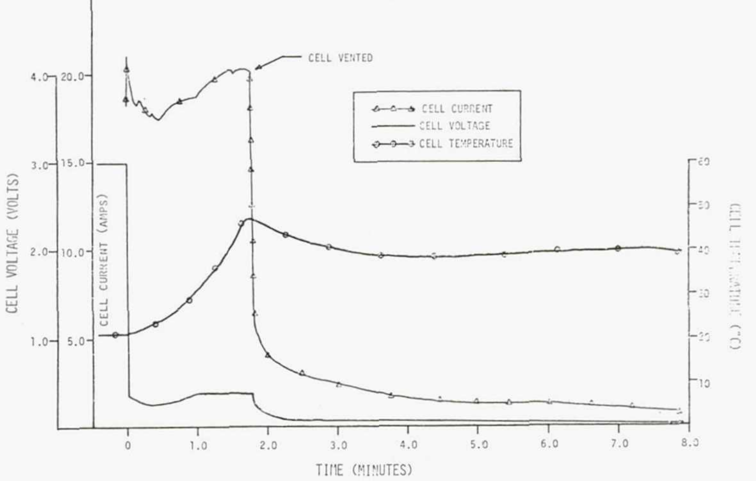

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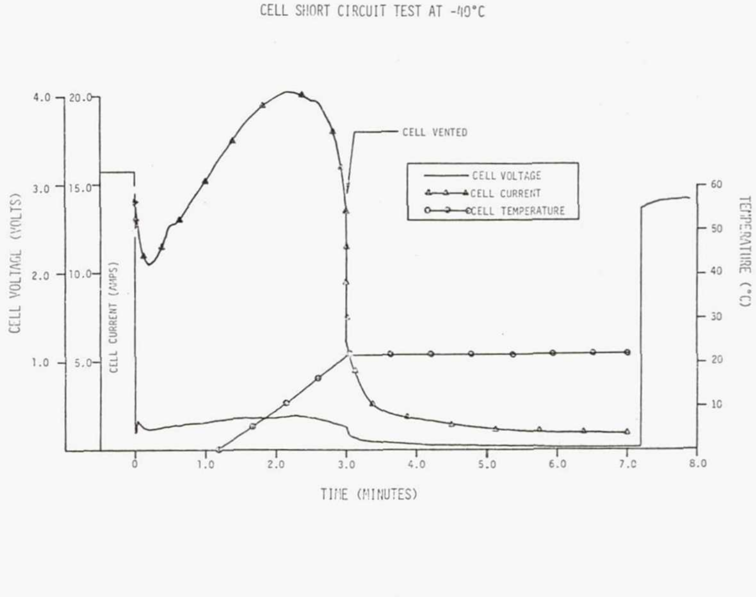


Figure 8-10

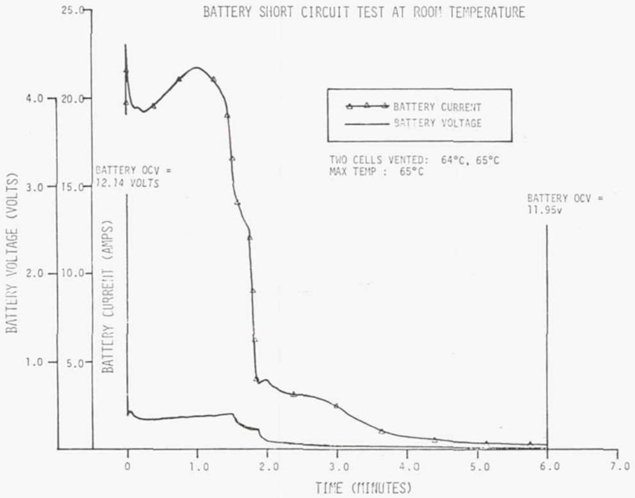


Figure 8-11

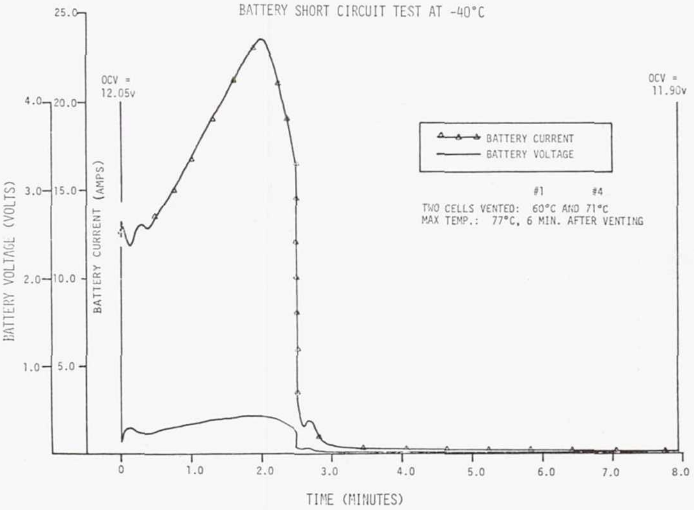
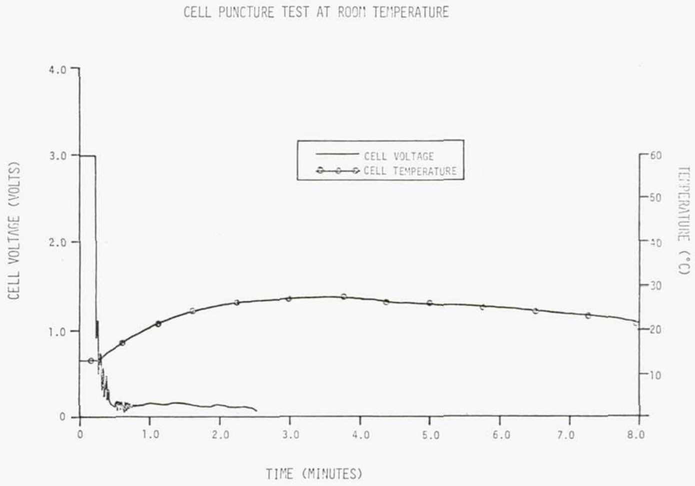


Figure 8-12



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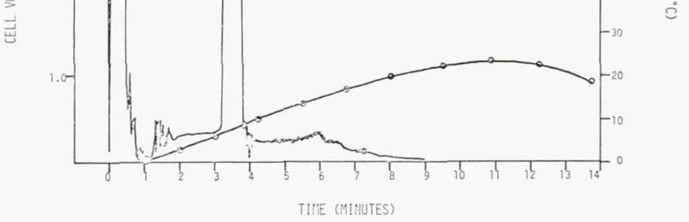

Figure 8-14

FORCED OVERDISCHARGE TEST AT
300mA CONSTANT CURRENT

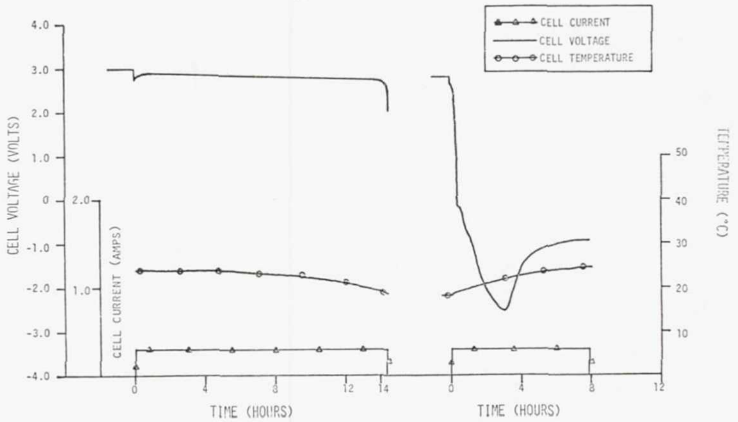

Figure 8-15

FORCED OVERDISCHARGE TEST
1.0 AMP AT ROOM TEMPERATURE

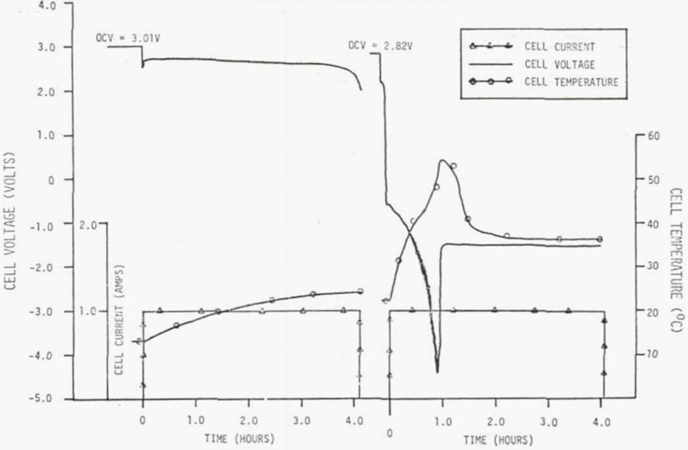

Figure 8-16

FORCED OVERDISCHARGE TEST
2.0 AMP AT ROOM TEMPERATURE

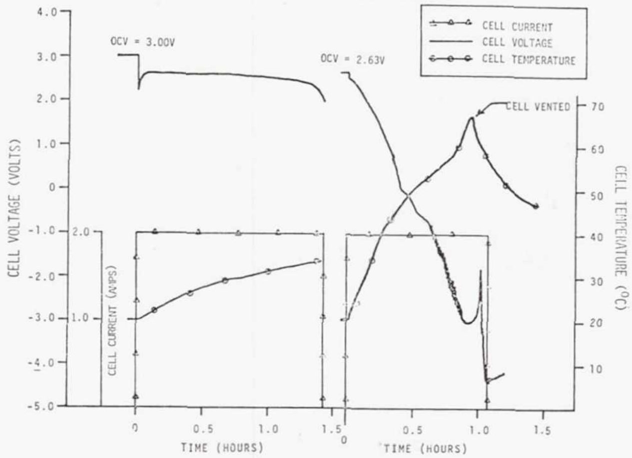

Figure 8-17

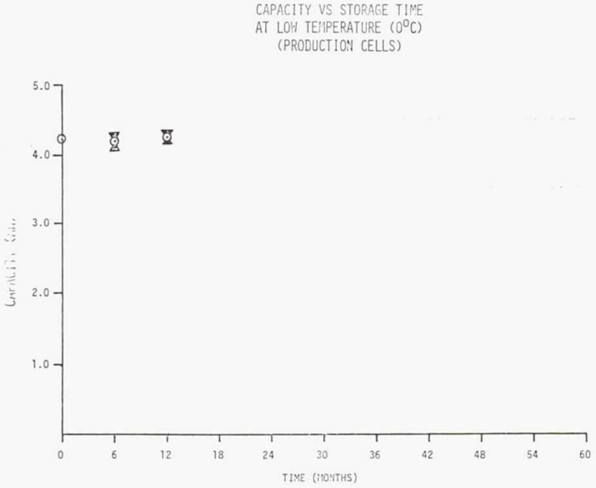

Figure 8-18

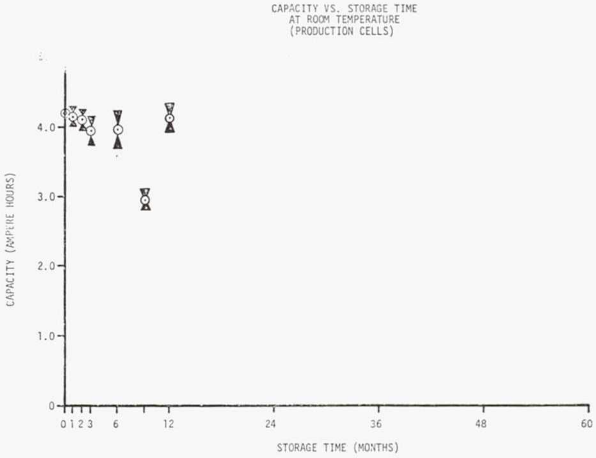

Figure 8-19

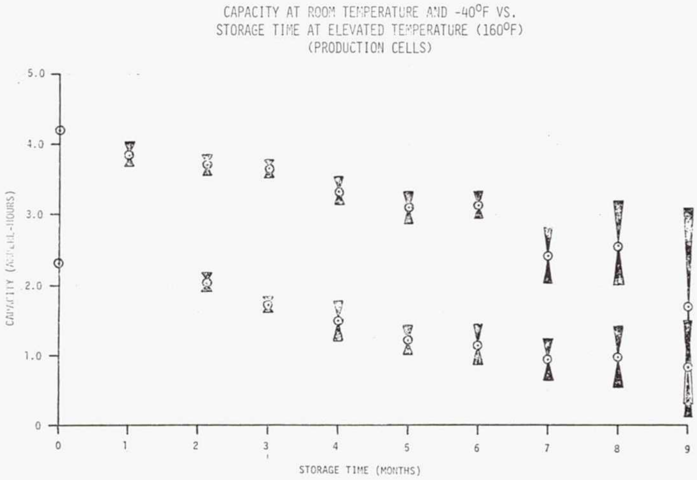

Figure 8-20

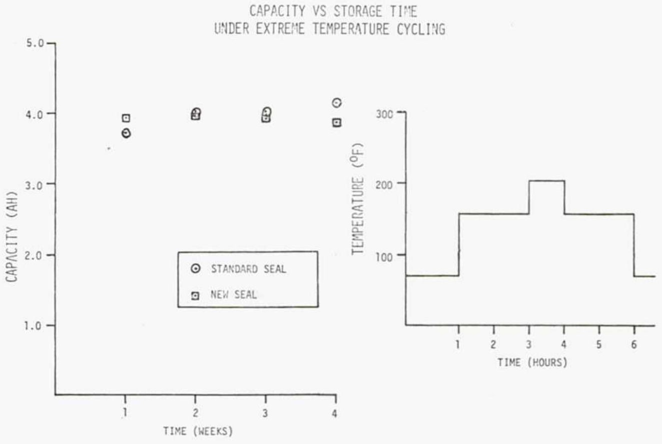

Figure 8-21

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ALTUS SMALL BUTTON CELL PERFORMANCE

C. Freeman, F. Bis, D. Warburton
Naval Surface Weapons Center

I should like to discuss the results of some testing we performed on Altus lithium thionyl chlordie (Li/SOCl$_2$) cells manufactured in 1978. These tests were to evaluate safety and performance under a realistic set of fleet conditions.

Since the manufacture of these cells, the Altus technology has undergone a lot of improvement. However, these results are still important in that they serve as a benchmark for the evaluation of the new technology.

We tested 60 disc-shaped cells of 0.2 and 1.5 A h capacities; twenty each of the 101 low rate, the 101 high rate, and the 402 cells.

(Figure 9-1)

Figure 9-1 shows the two cell sizes. The 101 low rate and the 101 high rate have a capacity of 0.2 A h and the 402 cells have a capacity of 1.5 A h.

The test plan we followed simulates the mine environment. It involves non-destructive testing, ruggedness testing, destructive testing and a storage program (which we could not implement because of ceramic seal problems).

The non-destructive testing involves open circuit voltage measurements initially on all the cells, alternating current resistance measurements initially on all the cells and closed-circuit voltage pulses, 20s on and 20s through 1000,100,10 and 1 ohms at temperatures of -54, -36, -18, -1, 21, 32, 54 and 71 C. The purpose of the non-destructive testing was to indicate any cell-to-cell variation or product variability before we implemented the rest of the test program.

The ruggedness testing involves low-frequency vibration, high-frequency vibration and two-phase water entry shock at temperatures of -54, 25 and 71 C. It also involves thermal shock, in which the cells were brought from a chamber condition at -64 C to a condition at 71 C. The low-frequency vibration simulates vibration encountered in truck and ship transportation, the high-frequency vibration simulates vibration encountered in aircraft transportation, and the two-phase water entry shock simulates the two shock phases involved in free fall from a plane (the first phase is impact with the water and the second phase is the drag forces).

Finally, the destructive testing involves single cell discharge at the one-hour rate followed by multi-traversal of the DC power supply; single-cell discharge at the four-month rate; short-circuit testing at room temperature through 0.01 ohms; and oven heating of the cells.

I should like to present some of our test results.

(Figure 9-2)

Figure 9-2 shows the 10 ohm pulse data as a function of temperature for the three cell types. Each pulse represents 20 seconds. Voltage recovery begins around -18 C. Below this temperature, the polarization effects were too great for voltage recovery.

These spikes represent a voltage delay of approximately 2 seconds; at some mine applications this is not acceptable.

(Figure 9-3)

From our pulse data we generated polarization curves. However, owing to the proprietary nature of the Altus technology, we were unable to accurately calculate current densities. Therefore, we generated our curves as a function of resistance loads rather than current densities. Current densities, however, are increasing.

Figure 9-3a shows a comparison of the 101 low rate and 101 high rate cells. The solid lines represent the low rate cells, and the dotted lines the high rate cells. Figure 9-3b shows results for the 402 cells. Here again you can see that voltage recovery begins around -18 C.

(Table 9-1)

Following ruggedness testing at -54, 25 and 71 C, there was cell degradation, which appeared greater at the higher temperatures. However, owing to our limited sample size, we were unable to determine the individual effects of each ruggedness test and temperature. The third column shows the discharge data at the one-hour rate, of the cells that were vibrated and shocked. The third column shows the capacity calculated to a test voltage of 2V. We can see that all th cells achieved capacities well below their nominal values of 1.5 A h for the 402 and 0.2 A h for the 101. We can also see the general trend of decrease in capacity with increase in temperature.

(Figure 9-4)

In the destructive portion of our test program, we discharged nine fresh cells at the one-hour rate and then drove them into voltage reversal with the DC power supply. Figure 9-4 shows a typical discharge, for a 402 cell, with cell ptential as a function of time. There is our voltage curve and our temperature. In all cases no cell vented during discharge at the one-hour rate. However, several cells did vent during voltage reversal at currents equal to or exceeding 1A. In all cases, the cells had been driven to at least 100% of their capacity in reverse before venting was achieved. In this case, the first current during voltage reversal was 1A. We held this current for five hours, and nothing happened. We then increased the current to 2A, and after about 4 1/2 hours we achieved a violet vent. By this I mean that rather than a simple cracking of the ceramic seal, the cell visibly swelled and there was expulsion of the ceramic seal. However, I should like to emphasize again that in this case the cell was driven to roughly ten times its capacity to reverse before venting was achieved.

(Table 9-2)

Table 9-2 shows the capacities of the cells discharged at the one-hour rate. The first column show the three cell types: 402, 101 high rate, and 101 low rate; the fourth shows the fixed resistance discharge load; in one case we had a constant current discharge of 2A. The discharges took place at room temperature. The third column shows the capacities calculated to a test (Table 9-4)

Moving on to the short-circuit data, we short-circuit discharged nine fresh cells to 0.01 ohms at -18,25 and 71 C, to indicate the cell performance in the event of an accidental short. Table 9-4 shows, for the three cell types, the discharge temperature, the maximum current achieved by each cell, the maximum temperature achieved by each cell, and whether or not the cell vented. From this table we can see that no cells vented at -18 C. Also, no 101 low rate cells vented at any temperature. However, the 402 cells and the 101 high rates both vented at 25 and 71 C. In all cases venting was very mild, a simple cracking of the ceramic seal. In only one case was there swelling of the cell.

Finally, we heated six fresh cells from 45 C to 1000 C at a rate of 15 per minute. All cells vented midly at temperature above 180 C. Venting was accompanied by a small flame at temperatures above 600 C.

In summary, the limited ata obtained indicates the following:

The specific energy and the voltage regulation are to the mine environment.

There is cell degradation with ruggedness testing. However, we need to further investigate the individual effects of each ruggedness test and temperatures.

In terms of safety, the test results from the voltage reversal, the short-circuit testing and the oven-heating tests are consistent with the vendor's claims of safety in the $Li/SOCl_2$ system.

The product variability needs improvement. However, again, this is not uncommon in the early development of the new technology.

Finally, our results warrant more investigation. We shall be investigating the Altus technology further on the 5 A h cells and larger.

CAPACITIES OF CELLS DISCHARGED AT THE ONE HOUR RATE
FOLLOWING SHOCK AND VIBRATION

CELL TYPE	SHOCK AND VIBRATION TEMPERATURE (°C)	DISCHARGE TEMPERATURE (°C)	CAPACITY TO 2 VOLTS (AH)
402	-54	40	0.581
402	25	25	0.480
402	71	0	0.044
101 HR	-54	40	0.082
101 HR	25	25	0.055
101 HR	71	0	0.001
101 LR	-54	40	0.104
101 LR	25	25	0.060
101 LR	71	0	0.078

Table 9-1

CAPACITIES OF CELLS DISCHARGED AT THE ONE HOUR RATE

CELL TYPE	SERIAL NUMBER	CAPACITY TO 2 VOLTS (AH)	FIXED RESISTANCE (OHMS)	CONSTANT CURRENT (AMPS)	DISCHARGE TEMPERATURE (°C)
402	11	0.754	3	--	25
402	55	0.440	3	--	25
402	25	0.200	--	2	25
402	9	0.713	3	--	25
402	32	0.567	3	--	25
101HR	3	0.052	10	--	25
101HR	53	0.065	20	--	25
101LR	117	0.082	40	--	25
101LR	111	0.032	20	--	25

Table 9-2

CAPACITIES OF CELLS DISCHARGED AT THE FOUR MONTH RATE

CELL TYPE	SERIAL NUMBER	FIXED LOAD RESISTANCE (OHMS)	CAPACITY* TO 2 VOLTS (AH)
402	56	6500	1.59
402	26	6500	1.62
402	45	6500	1.62
402	73	6500	1.64
402	49	6500	1.62
101HR	2	50K	0.143
101HR	33	50K	0.177
101HR	14	50K	0.182
101HR	36	50K	0.181
101HR	57	50K	0.128
101LR	162	50K	0.212
101LR	171	50K	0.204
101LR	189	50K	0.210
101LR	161	50K	0.217
101LR	166	50K	0.212

* MANUFACTURERS ADVERTISE CAPACITIES FOR 402, 101HR, 101LR AS 1.5 AH, 0.2 AH, AND 0.2 AH RESPECTIVELY

Table 9-3

CELL SHORT CIRCUIT TEST DATA

CELL TYPE	DISCHARGE TEMPERATURE (°C)	MAXIMUM CURRENT ACHIEVED (AMPS)	MAXIMUM TEMPERATURE ACHIEVED (°C)	COMMENTS
402	-18	5.7	130	NO VENTING
402	25	11.5	135	VENTED
402	71	13.1	150	VENTED
101HR	-18	2.7	108	NO VENTING
101HR	25	2.8	135	VENTED
101HR	71	4.7	166	VENTED
101LR	-18	0.28	10	NO VENTING
101LR	25	0.70	52	NO VENTING
101LR	71	0.60	96	NO VENTING

Table 9-4

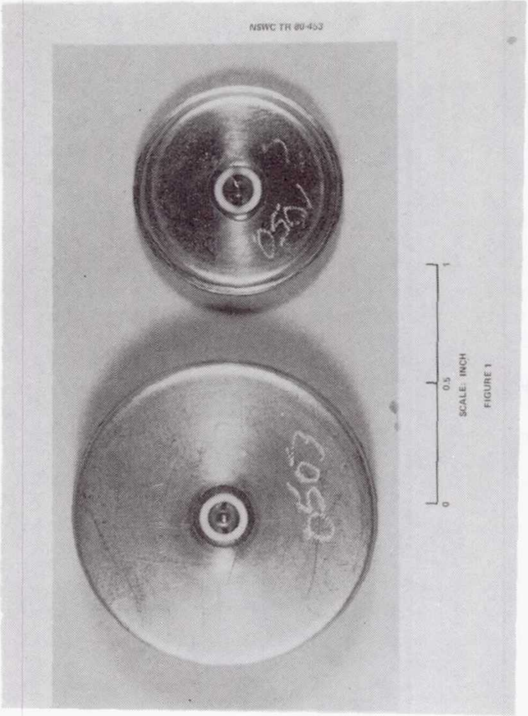
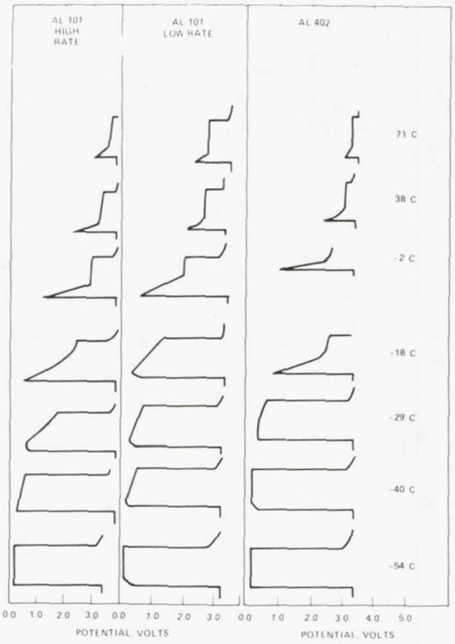
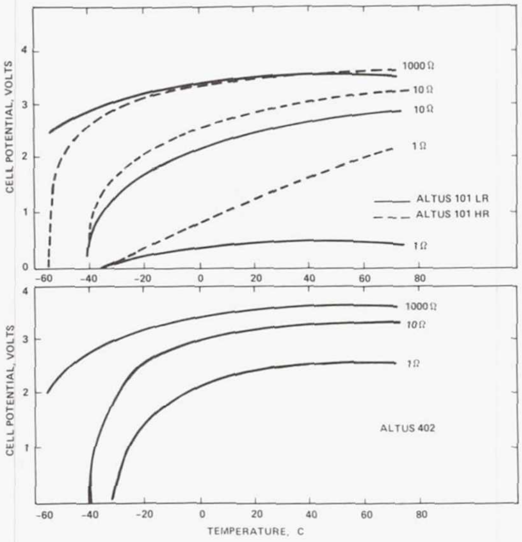


Figure 9-1



10 OHM PULSE DATA AS A FUNCTION OF TEMPERATURE 20 SECONDS PER PULSE

Figure 9-2

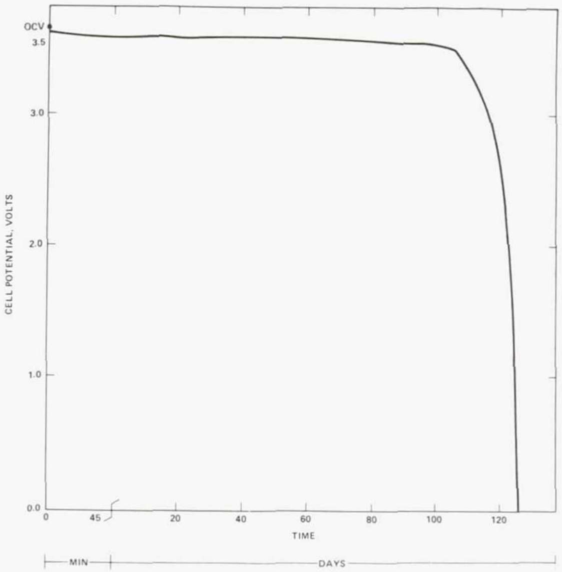


POLARIZATION CURVES OF 101 LOW RATE, 101 HIGH RATE, 402, AND Li/SO_2 CELLS

Figure 9-3

DISCHARGE CURVE OF 402 CELL DISCHARGED THROUGH THREE OHMS AT ROOM TEMPERATURE AND DRIVEN INTO REVERSE WITH A D.C. POWER SUPPLY

Figure 9-4



DISCHARGE CURVE OF 402 CELL DISCHARGED THROUGH 6500 OHMS AT ROOM TEMPERATURE

Figure 9-5

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CATASTROPHIC EVENT MODELING

H. Frank

Jet Propulsion Laboratories

The purpose of this presnetation is to introduce a new model for the catastrophic failures in lithium thionyl chloride batteries. It could also be applied to other types of primary lithium cells.

By the term "catastrophic failure," we mean failure where either venting or explosion of the cell occurs.

The model was developed by Professor Alan Herman from Tulane University, a consultant for JPL. I shall explain the background for the model, present the model itself, show how we plan to verify it, and show its practical applications.

(Figure 10-1)

We shall start with the background for the model. Those of you who attended the meeting of the Electrochemical Society last month in Florida will know that there was a great deal of discussion about the nature of the film on the lithium anode. We have what is known as the dual layer film of lithium chloride on the lithium anode. This consists of a compact layer of lithium chloride, represented by the dashed marks, and then a porous outer layer, represented by the segmented areas along with the dashed marks. These represent lithium chloride. There is quite a difference in thickness of the two layers. The compact layer is extremely thin, about 100 A, while the outer layer is much thicker, about 100 microns.

As soon as the lithium anode is immersed in thionyl chloride the inner layer grows rapidly for only a fraction of a second, whereas the outer layer continues to grow over several days or weeks at a diminishing rate.

The growth of the outer layer occurs by lithium ion diffusion through the compact inner layer, with simultaneous electron tunneling, followed by reaction with the solvent.

Now, the model states that cracks develop in the compact inner layer; they are represented by these little open areas. They develop because of one or more reasons.

First, they may be a difference betweenthe thermal coefficient of expansion of the lithium metal and the lithium chloride film. Secondly, there may be stresses caused by entrapped gases and impurities in the compact layer. Thirdly, there may be lattice defects formed in the compact layer during the film-forming process.

One piece of evidence for the existence of these cracks is that on open circuit, it has been shown that these cells generate small amounts of heat on a microcalorimeteric basis.

Now, formation of a crack and repair by the chemical reaction of the bare lithium with the solvent is a dynamic process. The model states that this reaction is exothermic in nature, and during the condition of open circuit, the rate of crack formation and the rate of heating are very low. However, one places the cell on discarge, there is a critical current density above which the cracking and repair reactions occur at a markedly increased rate. This heating associated with the cracking and repair reaction is over and above the battery heat that we described this morning from the polarization and I^2R losses. Thus we have two types of heating effects: That from the chemical reaction, plus the I^2R, plus polarization losses which were calculated from the thermal neutral voltage.

Now, for very short periods of time, adiabatic conditions prevailed. Therefore, if the specific heats of the various components are known, the temperature rise may be calculated.

The model states that when the temperature reaches the melting point of lithium, 186 C, then add this is the reason for explosions there is a breakdown of the film and thermal runaway, subsequently leading to venting or explosion.

(Figure 10-2)

Next we shall present the model itself. Figure 10-2 shows the final and most useful equation for the model. If anyone is interested, I can send you a copy of the derivation. The equation relates battery discharge current to the time required to reach the melting point of lithium. One can use this by specifying a given current and calculating the maximum time to reach the melting point of lithium and explosion, or conversely by selecting operating time and calculating the maximum safe discharge currents.

There are seven constants in the equation, K1 through K7. Some of these are quite straightforward; one is simply the melting point of lithium. Some are related to the thermal conductivity, specific heat capacities and the enthalpy of the repair reaction which is known.

Others are not quite so straightforward and they deal with rate constants of the chemical repair reaction. They may be determined by calorimetric studies. This equation is used to compute the safe operating limits for the cell. We plan to try to verify this model.

First, we plan gross type of verification, which will be accomplished by purchasing some high rate spiral wound D cells instrumented with thermocouples, and subjecting them to high-rate discharge.

Before doing this we shall have made calorimetric measurements to determine all the constants. We shall make predictions of operating times and temperatures, and compare them with the measured values. We shall also predict the conditions under which explosions can occur, and establish whether or not they actually do occur.

The second part of the verification involves testing an important assumption within the model by identifying cracks witin the compact inner layer. This will be no easy task, since the layer has such small dimensions. We plan to meaaure the AC impedance during the course of discharge, and expect to see a sharp decrease inte capacitance portion, which we will try to associate with the formation of the cracks.

As regards, the practical significance of the model, it maybe used to predict safe operating currents and times for the thionyl chloride cells; it may also be applied with different consequences to other cells, chloride cells.

We have also suggested methods for minimizing the explosion hazard. One is the application of protective films to the lithium anode. These films would conduct lithium ion, and would inhibit the corrosion reaction and minimize the heating from that effect, thus extending operating limits.

We have examined one such type of film and have attained some degree of success in examining crown ether films for the lithium anode. Other types of materials that might be considered are polyvinylpyrrolidone, or jelled polymer electrolyte, such as hexafluoropropane vinylidene. There are also polyethylene oxide and polypropylene oxide.

From reading the patent literature it is apparent that some companies are employing some of these types of films, not necessarily from the safety point of view, but from the point of view of minimizing the passivation. However, we believe that they have an impact on safety as well.

We shall try to give a report on our verification as soon as possible.

There is one additional point, not necessarily related to the model here, but related to the safety aspects of primary lithium batteries. It deals with the characterization of the Shawinigan carbon black, which is commonly employed as the cathode material for these primary lithium batteries.

In our recent studies, we conducted four-year transform infrared (FTIR) investigations of the Shawinigan carbon black. In these investigations we observed the existence of carbon double bonds. Hence we can say that the Shawinigan carbon black is not plain carbon, but contains appreciable amounts of carbon double bonds. As we all know, materials such as chlorine or other components of the electrolytes can react quite rapidly and exothermically to add to these double bonds.

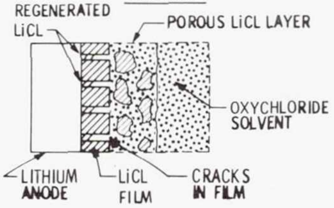
We shall be pursuing this investigation further. I simply wanted to present it at this time because I think it might be related to the next paper.

CATASTROPHIC FAILURE MODEL FOR PRIMARY LITHIUM CELLS

THEORY

- CRACKS CONTINUOUSLY DEVELOP IN THE LiCl FILM FOR MANY REASONS
- CRACKS ARE CONTINUOUSLY REPAIRED BY CHEMICAL REACTION OF SOLVENT WITH Li TO FORM LiCl
- THE CHEMICAL REACTION IS EXOTHERMIC (EVOLVES HEAT)

SCHEMATIC



- THE RATE OF CRACK FORMATION AND REPAIR IS VERY LOW DURING OPEN CIRCUIT, AND AT LOW CURRENT DENSITIES. HENCE INTERNAL HEATING IS VERY LOW UNDER THESE CONDITIONS
- THE CRACK FORMATION RATES INCREASE MARKEDLY WITH CURRENT, BEYOND A CRITICAL CURRENT DENSITY. HENCE INTERNAL HEATING IS QUITE HIGH UNDER THESE CONDITIONS
- FOR RELATIVELY SHORT PERIODS OF TIME, ADIABATIC CONDITIONS PREVAIL AND INTERNAL TEMPERATURE RISE CAN BE COMPUTED
- WHEN THE TEMPERATURE REACHES THE MELTING POINT OF LITHIUM (186°C), THE FILM BREAKS DOWN AND VENTING OR EXPLOSIONS OCCUR

Figure 10-1

CATASTROPHIC FAILURE MODEL FOR PRIMARY LITHIUM CELLS

SIMPLIFIED VERSION OF MATHEMATICAL MODEL

$$I = \frac{k_1 - k_2 t - k_3 e^{-k_4 t}}{k_5 t - k_6 e^{-k_4 t} + k_7}$$

WHERE: I = DISCHARGE CURRENT, amps

t = TIME TO REACH MELTING POINT OF LITHIUM, sec

k_1 THRU k_7 = SUMS AND PRODUCTS OF SEVERAL CONSTANTS CONSISTING OF CELL MASS AND SPECIFIC HEAT, INITIAL CELL TEMPERATURE, MELTING POINT OF LITHIUM, RATE CONSTANTS FOR THE CRACKING AND REPAIR OF THE ANODE FILM, ENTHALPY OF THE REPAIR REACTION, AND A CRITICAL CELL CURRENT ABOVE WHICH FILM CRACKING INCREASES WITH CURRENT

Figure 10-2

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CARBON CATALYSIS OF REACTIONS IN THE LITHIUM $SOCl_2$ AND SO_2 SYSTEMS

W. Kilroy
Naval Surface Weapons Center

Certain hazards associated with lithium batteries have delayed widespread acceptance of these extremely attractive power sources. As eager consumers of these batteries, it seems to us that no specific chemical explanation has been given for these safety hazards. We have been trying to throw some light on the safety problems for both the sulfur dioxide and thionyl chloride cells.

Lithium by itself is quite inert to thionyl chloride or sulfur dioxide even under conditions of vigorous mechanical shock. However, we have found that when it is mixed with carbon black there is a dramatic change -- spontaneous ignition on mixing and explosive energy release on shocking become common, especially with the thionyl chloride electrolyte. Since there are plausible scenarios by which the lithium and carbon in these batteries can become intimately mixed, we decided to look into this effect.

The work was performed in a dry room of less than 0.5% relative humidity at approximately 24 C. We used primarily Shawinigan acetylene black and $SOCl_2$ - 1.6M Li Al Cl_4 or SO_2 - AN - $LiAsF_6$ electrolyte.

The basic reaction involved mixtures of lithium and carbon with battery electrolyte. We examined various parameters that influenced this reactivity: the nature and the freshness of the carbon; the freshness, the purity and the conductive salt of the electrolyte; the effect of Teflon or moisture, etc.

We found that the reactivity was relatively low and variable if the lithium and carbon were merely lightly pressed together. However, prior grinding of the lithium/carbon mixture significantly raised both the level and reproducibility of the reactivity. Therefore, we routinely ground approximately 7 mg of lithium with various amounts and types of carbon in standard Pyrex ignition test tubes and proceeded to add approximately 100 mg (about three drops) of electrolyte. Relative reactivity was then assessed with a qualitative scale of numbers from one to ten.

(Figure 11-1)

Figure 11-1 shows the effect of varying the lithium/carbon mass ratio in ground lithium/carbon mixtures on their reactivity to battery electrolytes. Curve A is for the thionyl chloride electrolyte, and curve B for the sulfur dioxide electrolyte. The points in Figure 11-1 represent the average reactivity vaues based upon four repetitive runs. A "one" on the relative reactivity scale represents no reaction with increasing heat evolution until sparks are observed at a "six." A "ten" can best be described as a Roman candle with a shower of sparks and flame, often ascending five feet in height. Remember that this is only a small ignition test tube, 3 in high, containing about 7 mg of lithium and an equal amount of carbon. Such intense flammability from relatively small amounts of material were impressive; but it is disturbing to think of this reactivity scaled up to the size of a D cell.

Figure 11-1 shows that an increase in the lithium: carbon mass ratio led to a fall in spontaneous flammability. It also reveals that the thionyl chloride electrolyte had a higher average reactivity than the sulfur dioxide electrolyte. At high lithium: carbon ratios (about 7:1), even though there was no spontaneous flammability, the mixtures were often shock sensitive. Light probing of unreacted mixtures with a 6 in, 25g steel needle often produced explosive reaction accompanied by loud report.

We examined many variables to see what effect they might have on the observed reactivity. We added water to the electrolyte, we added Teflon to the carbon, we compared LiBr with Li As F_6, $LiALCl_4$ with mixtures of LiCl and $AlCl_3$, and we examined the effects of different $SOCl_2$ fractions. No major effects were noticed, and details will be presented in a forthcoming paper.

(Table 11-1)

Table 11-1 shows the effect of carbon type on the reactivity of these ground lithium/carbon mixtures with thionyl chloride battery electrolyte. We studied a variety of carbon blacks, graphites, and even some activated carbons to try to correlate the reactivity with the surface area, purity and crystallinity at both low (1:1) and high (7:1) lithium: carbon ratios. Purity had no discernible effect. However, particle size appeared to play a significant role.

The Desulco graphite, whose particles were 5 microns in diameter, were much less reactive than either the Sterling or the Shawinigan carbon blacks. BET measurements were approximately comparable.

The most obvious trend in this table is illustrated by Figure 11-2.

(Figure 11-2)

Figure 11-2 shows the relative reactivity of the ground Li-C-SO cl_2 electrolyte mixtures as a function of the surface area of various carbon blacks. For both the high and the low carbon ratios, the reactivity rises with increasing surface area. When the surface area is approximately 100 m^2/g, the reactivity levels off at approximately nine, i.e. with consistently vigorous fires. We conclude that an extensive lithium/carbon interface is required. This can be accomplished by either having a small proportion of high area carbon or a large proportion of lower area carbon.

Lithium/carbon mixtures were also prepared electrochemically by constant current discharge of a cell containing a lithium anode, carbon cathode in an aprotic solvent such as propylene carbonate and containing no cathode depolarizer.

(Figure 11-3)

A typical voltage time plateau is shown in Figure 11-3. These plateaus are thought to involve undervoltage deposition of lithium to form lithium-carbon intercalates. After discharge, the cathode was washed with an inert solvent and vacuum dried at about 25 C. When $SOCl_2$ electrolyte was then added to approximately 1 mg of this material, the mixture became very hot and the electrolyte boiled.

In summary, there are three immediately apparent explanations for the mechanism of this catalysis by carbon. First, a local short itself formed, and the carbon particle in the lithium surface can act as a tiny short-circuited cell. On the other hand, however, we have found ground lithium/carbon mixtures to be equally reactive to thionyl chloride containing no salt.

The second explanation is that active lithium-carbon compounds form. X-ray photoelectron spectroscopy (XPS) has revealed evidence of lithium-carbon compounds. Indeed, we have found that lithium and carbon will intercalate at high pressures at room temperature. The ground lithium/carbon mixture reacts with water to give acetylene, indicating the presence of a carbide. Finally, we showed that cathodically formed intercalates are reactive with the thionyl chloride electrolytes.

The third explanation is that carbon acts as a vehicle for dispersing the lithium to a very large surface area. This is consistent with the observation that first occurred on adding thionyl chloride electrolyte to lithium ground with thermodynamically inert magnesium oxide or aluminum oxide. The thionyl chloride was inert to both magnesium oxide and aluminum oxide.

Both lithium compound formation and the local cell action would seem to be excluded by the inertness to lithium and the high electrical resistivity of these oxides.

In conclusion, we observed a very powerful catalysis by carbon of the lithium battery oxidant reaction. This effect is important because, in polarized cathodes, lithium and carbon may become intimately mixed, (a) by undervoltage deposition to form reactive lithium carbon intercalates that react continuously with the electrolyte, accumulating heat to possibly dangerous levels, or (b) by normal overvoltage deposition of passivated lithium dendrites, followed by shear or shock, grinding the dendrites and carbon together and causing violent reactivity. Furthermore, severe mechanical distortion of fresh or normally discharged lithium batteries could shear lithium and carbon components together with the same dangerous results.

With this in mind, we are testing carbons that have the promise of combining a greatly reduced reactivity in lithium/carbon mixes with unimpaired efficiency as cathodes.

Effect of carbon type on the reactivity of ground Li-C mixtures
with $SOCl_2$ battery electrolyte (1.6M $LiAlCl_4$)

Name (company)	Type of carbon	B.E.T. surface area (m^2/g)	Composition, o/o ww			Reactivity	
			C	H	O	Li/C=1	Li/C=7
Sterling FT (Cabot)	black	15	99.5	0.1	0.4	5.2	1.0
Sterling FT (Cabot) Heat treated at 3000°C	black	15	99.99	0	0	8.0	1.0
Shawinigan (Shawinigan) acetylene black	black	65(.042)[1]	99.5	0.1	0.1	9.2	7.3
Vulcan 6 (Cabot) heat treated at 2700°C	black	88	99.9	0	0	8.7	5.7
Vulcan 6 (Cabot)	black	119	99.0	0.1	0.5	9.0	9.0
Carbolac I (Cabot)	black	878	84	5	11	9.5	9.7
Spectroscopic (Ultra Carbon) graphite USP	synthetic graphite	< 0.1	99.99	0	0	1.0	1.0
Graphite (Asbury Graphite micro 850 Mills)	natural graphite	-15(0.5)[2]	99.8	<0.1	0	6.7	1.0
Desulco (Superior Graphite) #9039	synthetic graphite	30-50(5.0)[2]	99.5	-	-	1.0	1.0
Coconut charcoal (Barnaby-Chaney)	activated	1600				8.5	1.7
Coconut charcoal ash free by HCl, HF wash (Barnaby-Chaney)	activated	1600	96	3.4	0.6	8.0	1.7

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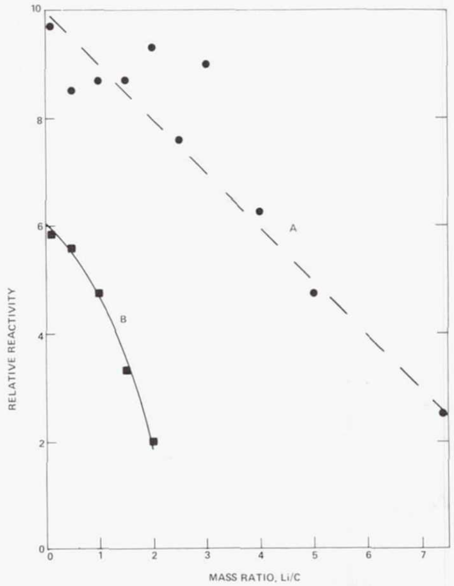
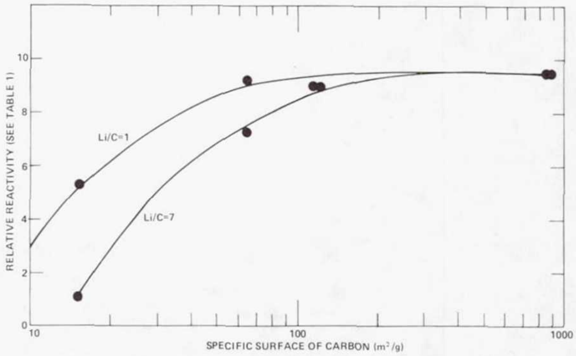
[1] Average particle diameter in microns

Table 11-1



EFFECT OF Li/C RATIO IN GROUND Li–C MIXTURES ON THEIR REACTIVITY TO BATTERY ELECTROLYTES. A: $SOCl_2-LiAlCl_4$ B: $SO_2-AN-LiAsF_6$

Figure 11-1



REACTIVITY OF GROUND Li-C MIX TO $SOCl_2-LiAlCl_4$ VERSUS SPECIFIC SURFACE OF CARBON. UNGRAPHITIZED CARBON BLACKS

Figure 11-2

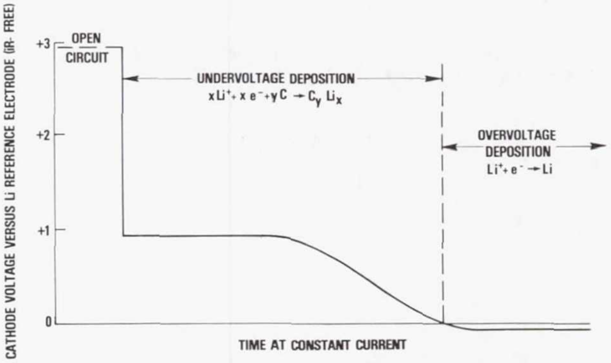


FIGURE TYPICAL VOLTAGE-TIME CURVE FOR CARBON-BLACK (TEFLON BONDED) ELECTRODE CATHODIZED IN APROTIC SOLUTION FREE OF CATHODE DEPOLARIZER

Figure 11-3

SAFETY TESTING OF LITHIUM CELLS

J. Bene
NASA Langley Research Center

A couple of years ago I gave a paper on lithium thionyl chloride safety and showed a horror film. It left everybody in stunned silence for a while. Since then we have done a little work on the subject.

One thing that concerns me is that lithium thionyl chloride systems are built such that they are SO_2 limited, and can be very dangerous. And people continue to use them, and people continue to have problems.

At Langley, the safety testing is basically the same as everywhere else: it consists of a forced discharge to zero volts constant current under isothermal conditions. The temperature that we normally use are -40 to 65 C (40 to 150 F);they are dictated by the projects we are trying to service.

Following the forced discharge, we force the cell into reversal to 100% of available capacity. Again, this is a constant current, and again we maintain the cell under isothermal conditions. Many people argue with that. One of the reasons why use with isothermal discharges is that with the information of how a cell behaves under isothermal conditions, and knowing the cell exotherm and the battery design, one can make a fairly accurate prediction of the battery performance under different conditions.

Following forced reversal, the cells are removed from test environment, and we run what we call chemical reactivity check no.1. We take the discharge cell on open circuit. It is placed in an insulation package and allowed to sit there. We simply monitor the temperature.

After that test, if there is a cell left to test, we go into chemical check no. 2 where we take undischarged, partially discharged or totally discharged cells and heat them, up to 149 C (300 F), depending on the type of cell. Again, we monitor the cell for thermal stability. We run a short-circuit test, and we also run drop tests, and puncture tests to determine exactly how a charred cell might behave if it developed a leak.

Another test that we run is very abusive, and will cause a cell to vent in most instances. We deliberately discharge that cell in an insulated package; a pretty rugged test for a cell. However, in the past, battery packs were designed where cells were stacked like logs. And people insist on potting them up in foam. A cell inside the log structure is almost perfectly insulated. Therefore, we ran that type of test.

When I was here before, I talked about an SO_2 limited cell. I think the $Li:SO_4$ ratio was about 1.5: 1.

During the normal course of the discharge, we found no problems with the cell anywhere from -20 to + 150F, or from currents of 250 mA up to 4 A.

However, following the reversal to 100% of the capacity available, we observed any number of types of vents, and they wer all active. Some were violent, and some cells even exploded. This occurred all the way up to 60 F and down to currents as low as 250 mA. Cells that did not vent under those conditions, went into a thermal runaway condition on heating to 300 F.

While under load in reversal at high temperatures (150 F), a cell would occasionally violently vent. And shorted cells generally vent passively. I say "generally" there because I want to talk about that later on.

Diode reversal protection would not help these cells since the amount of voltage generated in reversal was too small to activate a diode.

Last time we mentioned the gas analysis that we did, and what we assumed to be the problem. We then set about working with Mallory to solve it, and we came up with a series of cell designs that we call SX.

We have gone to a lithium-limited design and looked at excesses of sulfur dioxide, anywhere from 10 to 30%. Again, with this type of cell design we experienced no problems during the normal course of a discharge, from temperatures of -20 to 150 F, and up to 4A.

When we put the cell in an insulation package after reversal, all we get is a minor heating. In other words, the cell comes back up to ambient. It might go up to about 90 , 15 above ambient. This indicates that the chemical activity in that cell is fairly benign or very small.

After on external heating to 300 F no cells vented for any reason.

We still have problems with the lithium-limited cell design under load at cold temperatures, when about 20% of the cells vent. We have only seen this at -20 F. It might happen at -15 F, but we only test at -20 F.

All the vents we have seen were at 2A, except for one, which vented at 1A. These vents, when compared with the old SO_2-limited design, which would undergo a "violent vent" (because if we used "explosion" a lot of people get upset), gave what we call subtle size for a vent.

Again, the shorted cells passively. Diode reversal protection works here because the cell will generally go anywhere from 1.5V to -2V without a diode on it.

Again, for cells with diodes on them, that have been no incidents under any operating conditions, even up as high as 8A.

We looked at Altus's thionyl chloride system, the AL 250, a 5A h cell. The testing has been very limited.

We keep the cell in reversal for the amount of capacity we have. The temperatures we have checked so far are -40 F and -4 F at 0.5A. Following that treatment, when a cell is placed in insulation package, we see heating as high as 310 F in that cell.

It is my understanding from some people at Altus that a safety mechanism, the anti-reversal protection mechanism, in the cell is probably causing the problem.

One cell vented violently on open circuit under those conditions; this cell was discharged a little differently. We started off at 1A and gradually brought it down to 0.25A. We got 1.1 A h out of it, which was typical of these cells. Then the cell was put into reversal at 1A for 4.4 A h, which is more than 100% of what we got out. Discharge was stopped, and the cell sat in the bath at -20 F for two hours. Then it was removed and it exploded.

Another test result we have here, is that after 30 days standing at 160 F all twenty cells showed slight or severe bulging, and 20% of them were dead.

(Figure 12-1)

Figure 12-1 shows how the Altus cell looked after explosion. It threw the terminal, which it is supposed to, and the guts. That shell is empty.

(Figure 12-2)

The hole is much larger than the terminal; there was severe burning around the hole where the terminal was.

Another cell we tested was the lithium bromine, an Electrochem cell. Again, we have just performed limited testing so far. We tested the cell from -40 to 150 F. Again, when it is put in reversal following cold (-4 F) discharge, or even 75 F discharge, and then placed in insulation package, it heats up (235 F). We have not fully explored this on either cell to try and find if there is a critical area. At present, I should say that something chemical or electrochemical is occurring.

One cell vented violently while in reversal at 75 F at 0.5A, after completion of less than 100% of the reversal period. It gave 10 A h at 0.5A at the 80-A h reversal point, it blew.

Again, cells that shorted vent passively around 300 F.

(Figure 12-3)

This is hard to imagine here, but the cells were just put in baux. This is aluminum baux in a forced air chamber. They were just held in place with C-clamps on the baux. There were four cells in the chamber. The cell you see back here was up here when it blew.

There had been a great deal of comment by people saying that it was necessary to reverse SO_2-limited cells in order for them to explode, and that lithium must be deposited on the cathode to form fine granules or find dendrites before there were any problems.

We ran a test of this about two years ago. We reversed this cell, and started with 2 A, never allowing it to go down to zero. We stopped around 0.1 or 0.2V, then continuously dropped the current in steps until we got down to 0.25A until it got near to zero volts. Then the discharge was stopped. At that time about 7.5 A h had been obtained which was what we always got at 0.25A with those cells. When the cell was removed from that -20 F bath and a short was placed on it, it exploded.

(Figure 12-4)

We have only done that with two cells, and both of them did the same thing.

Now, that is not to say that there are no other ways. They only took about 12 minutes to explode after being removed from the bath. I am sure the short was not necessary.

DISCUSSION

HUBER: On your first experiment, did you have the 300 F temperature on the fully discharged cell, and not the fully charged one? It would not have been the same thing.

BENE: Yes. If you did that on the fresh cells, they would vent around 215, 220 F. The cell has been totally discharged. Occasionally, nothing happens to them at temperatures above 300 F.

HUBER: Perhaps you have not considered this aspect. Do you have any answers to a fully discharged cell having any adverse reaction without any abuse testing, such as being heated or crushed, but just being allowed to lie around.

BENE: I have had no cells that blew up as such, or, even vented violently.

I am trying to think back. What you are asking is something we did years ago.

We have heated up cells that have been discharged and not reversed.

HUBER: Yes, I can understand it with the heating. I am looking at a specific problem that I do not want to have myself, and am just checking some testing you have done.

BENE: The last test I showed the cell blown. That has not been abused or reversed.

HUBER: That is true, except that it had been shorted, which can certainly happen.

BENE: The rapidity with which it blew, as fast as the temperature rise was, may not have been caused by a short. Now, you could have a fairly low impedance load on the cell pack, and you would still get the same problem.

I think the point I am trying to make more than anything is that Li/SO_2 cell that are SO_2-limited are dangerous animals once they have been discharged.

HUBER: I recognize that. In my application we only take them down to between 50 and 75% of a fully charged. They are discharging by 50 or 75%. That is the end of their life.

However adverse circumstances, it is possible to discharge them all the way before they are put to their intended use. I think the discharge is going to be probably at about 400 mA rate. It is a little difficult to at present. My personal feeling, from what we have observed so far, is that those vents are due to localized heating while under load or in reversal.

Those cells are much, much safer than any other cell.

PALANDATI: Do you have any idea as to how the thionyl chloride cell or the BSX cells were internally designed as far as lithium versus thionyl chloride, etc?

BENE: No.

JAMES: I was interested in your point that cells do not have to be driven into voltage reversal in order to explode.

As Dr. Kilroy mentioned in the previous talk, it is not necessary to get lithium mixed up with the carbon of the cathode. It is not necessary to be able to plate lithium out as dendrites. Up to 1, maybe even 1.5V, the carbon can absorb lithium at undervoltage owing to the formation of what is probably a lithium carbon intercalate. These intercalates are actually very much more reactive with most solvents than is pure lithium because they are not passivated. It is like you have a tremendous monolayer of lithium in these layers between the carbon sheets. This might be involved in what you saw.

Were the cells that exploded after shorting thionyl chloride cells?

BENE: The one cell that I showed, which exploded, had not been reversed. That was an SO_2-limited cell.

The problems we are seeing with lithium-limited cells is about 1% of those that we had with the SO_2 limited cell. Even though I think some of these things that you mentioned might come into play, the overriding factor with the SO_2-limited cell is the basic balance.

Once the sulfer dioxide is exhausted, the lithium acetonitrile reaction occurs. That, in turn, produces methane (which we covered here two or three years ago.

Our whole approach was to try to get around that problem. The only way to do that is to use up all the lithium and still keep an excess of sulfur dioxide.

Figure 12-1

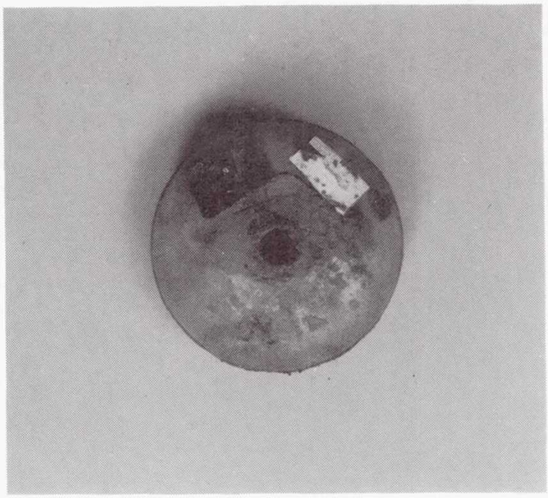


Figure 12-2

Figure 12-3

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PANEL DISCUSSION: SAFETY-- WHOSE RESPONSIBILITY?

Chairman, C. Scuilla
CIA

SCUILLA: How serious is the battery problem? Today we have seen some papers concerning lithium technology, and they describe some violent ventings and explosions, as well as general leakage, which can become a safety issue at times.

I should like the panel discussion not to be limited to lithium battery technology, because approximately 10,000 safety-related injuries from both wet and dry battery types on the commercial market have occurred.

Today we have brought together a panel of product-safety engineers, legal experts, and battery engineers to discuss these particulr questions. We should also like a lot of audience participation

I should now like to introduce the panel members individually. They will each speak briefly and then the panel discussion will start.

Our first member is Mr. Robert Estes, of the Consumer Product Safety Commission, Electrical Engineering Division. He will speak briefly on the function of the Consumer Product Safety Commission, and the National Electronic Injury and Surveillance System (NEISS) injury data base.

ESTES: I am not an expert on lithium batteries. As a matter of fact, I am not even an expert on wet cell or dry cell batteries. I am an electrical engineer with the Engineering Sciences Directorate at the Consumer Product Safety Commission. However, I have been a focal point for contact for people with problems or complaints related to batteries.

I do not know how many of you are familiar with the Consumer Product Safety Commission. The Consumer Product Safety Commission, or Product Act was signed into law in October 1972, and the Commission itself was established as an independent regulatory agency in May 1973.

The purpose of the Consumer Product Safety Commission is to protect the public against unreasonable risks of injury associated with consumer products. The term "consumer product" means an article produced or distributed for sale or use in and around a household or residence, or a school, in recreation or otherwise.

We are excluded from such areas as automobiles, aircraft, foods, drugs and articles not produced for use by consumers. Some of those areas would be covered by OSHA or other regulatory agencies.

The reason for the existence of a Consumer Product Safety Commission is that it is estimated that each year there are approximately 36 million injuries and 30,000 deaths in accidents involving consumer products. The financial cost of the accidents is staggering. It is almost $10 billion annually. Of course, we cannot prevent all these injuries, because many of them are caused by factors out of our control. However, a number of them can be attributed to design probelms, or what we might consider reasonable foreseeable misuse. These are the areas that we try to address.

The primary source of injury data for the Consumer Product Safety Commission is the NEISS system. We collect data from approximately 70 strategically located emergency hospital rooms throughout the United States. I say "strategically" because they are planned to give a broad spectrum of what goes on in the United States. They are not all located in urban or metropolitan areas. Originally there were about 130, but we found that the same quality of data may be obtained from 70. When a person comes into one of these emergency rooms with an injury, certain information is recorded, and at night these data are transmitted to the Consumer Product Safety Commission, where they are tabulated and statistical information gathered.

The NEISS system collects data under such headings as the product involved. We have nearly 1000 different product codes. 'Wet cell batteries' is a product code. 'Dry cell batteries' is a product code. A particular brand would not be a product code. Any data from injuries falling within a particular product code would be recorded under that code. The information would include the product involved: the age and sex of the individual; the type of injury (a cut, a laceration, a thermal burn or a chemical burn). This information is recorded. We also collect data on the part of the body involved.

From the data that we receive from the emergency room we estimate the number of injuries that would be associated with that product each year. Thus the figure of 10,000 battery injuries is predicted from a much lower number of actual injuries.

Also, we can sometimes find out such information as how the product relates to the type of injury, by simply looking at the NEISS data. For instance, most of the injuries caused by lawn mowers would be lacerations; most of the injuries caused by another product may occur to a particular age group, and we might want to put particular emphasis on protecting that age group.

We have other means of collecting data. One is from consumer complaints. Somebody will call in and tell us that some product of theirs malfunctioned, or that it caused an injury. We also collect information from newspaper clippings. Going through those we may see where an injury occurred or somebody was killed because of a particular product. We then make note of that.

As well as NEISS, the In-Depth Investigation Reports are very useful. This is where we actually interview the victim, a relative or a witness. We can get in-depth information on the accident from these reports; this is not available from NEISS, which simply informs us that there was a battery involved in an accident, and a person, perhaps, received a chemical burn.

We thus have many ways of responding to injuries, and then of taking a suitable course of action.

SCUILLA: Our next panel member is Mr. Milan Ruzicka. He is managing editor of Product Safety and Liability Reporter, and is also a laywer.

He will speak briefly on the legal aspects of safety and product liability.

RUZICKA: During this meeting we are discussing the design, production, testing and perhaps selling of batteries.

I should like to talk about what happens after you have let go of your product and it causes an injury. You are, of course, then facing a potential plaintiff.

Under the present law in the United States, you could be sued under several theories: the traditional negligence theory, breach of warranty, strict liability and fraud or misrepresentation.

Under the negligence theory, the oldest theory in the commonwealth system, the plantiff simply alleges that you have been negligent in making the product. To determine negligence, your conduct is compared with that of other battery manufacturers, and if it falls below that standard, you could be found negligent. The same applies if you did not comply with existing standards, whether industrial or mandatory.

Breach of warranties: warranties are express statements that you have made about your product. They can be either written or oral, either yours as manufacturers or your agents'. That is, if you have a network of salesman or distributors, their statements can be imputed to you and you can be held liable.

Strict liability: I believe that this is the most problematic area for most industries, because under this theory the burden on the plaintiff to prove his case has been lowered to a point where it is relatively easy.

Under strict liability, you no longer examine the behavior of the manufacturer and compare that with the behavior of the industry as a whole. Instead, you switch attention from the manufacturer to the product itself.

There are several elements to strict product liability. All these have to be proved by the plaintiff: that product must be found defective; that the defect poses an unreasonable hazard; that the plaintiff has been injured and the injury has been caused by the defect in the product.

The product may be defective in a number of ways. Defects in manufacturing are the easiest and the most frequent examples; they arise when the product was simply not made as designed (when the manufacturing phase did not use the materials or the specifications called for by the design department, or when an imperfection occurred in the product).

Design is one of the most difficult areas of strict liability. A design defect is indicated when, an examination of the product, it performs and functions exactly as intended, and still causes an injury. In the design cases, under the law of most states, the court or the jury engages in a balancing act, balancing the utility of the product as it was designed against the risk. The plaintiff in most jurisdictions must present an alternative design and, through experts, must prove that the alternative is safer and, on balance, does not decrease or destroy the utility of the product.

The third way a product can be found defective is if it is not equipped with sufficient warnings. The product may be perfectly designed and made, and yet pose a hazard for which the warning is insufficient or even absent. I anticipate that in the battery area the warning may be an important topic, and so I should like to say a few words about when the duty to warn arises. This occurs when the product poses a risk; when the risk is known to the manufacturer at the time the product was made; and when it is feasible to give warnings.

There are very few general rules of application about warnings that I could mention. Neither I nor anybody else could tell you what is a perfect warning, but there are several rules.

One of them is that even though the warning you have given complies with industrial or mandatory standards, you can still be held liable for not giving sufficient warnings.

Another general rule is that you cannot use warnings as a means of eliminating a hazard. In other words, you cannot improve the warnings instead of improving the design of your product. Your first duty is to design hazards out of your product, and then to provide warnings for those that remain.

Not only must the risk be known at the time of manufacutre, but you have a duty to test the product to find out what sort of risks it poses. For those of you have heard about the asbestosis cases, most of the allegations are that the manufacturers did not test the product to find out the risks.

The defenses in a failure-to-warn case are as follows: that the risk was not known at the time of manufacture; that tests performed but the state of knowledge and technology were not sufficiently advanced to discover the hazard; that the risk is obvious to a reasonable person; and that plaintiff assumed known risk.

For those of you who market your products overseas, especially in Europe, there is under consideration an EEC directive that would make you liable even though you could not possibly have know about the risk. It may take another year for this directive to be adopted, and it will then become the law of all the member countries of the European Economic Community.

If the risk is obvious, a warning is unnecessary. For example, you do not have to place a sign on a knife saying that it cuts flesh. However, this also varies. I wish I could give you examples of court decisions involving batteries , but there are too few. However, I did hear about a recent case from Utah in which the State Supreme Court held a champagne manufacturer liable for failing to warn about the pressure of the gas inside the bottle. The Court admitted that this sort of risk would be obvious to somebody living in New York, but to people in Utah, who do not drink much champagne, the risk is greater. Therefore, as far as Utah is concerned, champagne bottles must carry warnings.

As regards the defense that the plaintiff assumed known risk, the assumption of risk is very subjective. You can inquire whether that particular plaintiff knew about that particular hazard. If he did, you have proved the assumption of risk and defeated the plaintiff's case.

Another, less frequent, defense is that the plaintiff was an expert and therefore should have known about the hazard. This particular defense is allowed in only a very few jurisdictions.

SCUILLA: Our next panel member is Mr. John Callan, of the NASA/Goddard Space Flight Center, Office of the Chief Counsel. He will speak briefly about the government's unique position in product liability law.

CALLAN: I thank Mr. Ruzicka for that very good presentation on the subject of product liability.

I do not know much about product liability law, as a government attorney, because the United States government is very well insulated from product liability claims. Two reasons for this are:

First, the government is generally not a manufacturer, seller or supplier of goods. It is a user of goods. Secondly, the principle of sovereign immunity allows the government to avoid many liability claims. Sovereign immunity is based upon the old common law principle that the King can do no wrong. This was even carried into our democracy and held to apply to the United States government by John Marshall in a case in 1821. The concept that the King can do no wrong, and cannot be sued unless he gives his consent. The U.S. government gave its consent only in 1946 to be sued under the Federal Tort Claims Act. The Federal Tort Claims Act allows suits; however, against the government you have to prove negligence or some wrongdoing on the part of a government employee acting within the scope of his employment.

The Federal Tort Claims Act is very specific and very strictly construed. If you do not have a claim under the Act as it is very clearly spelled out, then you do not have a claim.

However, product liability law is relevant to government contractors because they are subject to the state product liability laws, which differ in every jurisdiction. It is therefore relevant to us in the government, because when our contractors are used they try to get under the cloak of the government immunity. They also try by lobbying and other means, to make government indemnify them when they are producing something of a hazardous nature for the government.

SCUILLA: We are trying to provide some sort of background to lead into our panel discussion. There are two other people on the panel. The first is Mr. Donald Warburton. He is with the Naval Surface Weapons Center, and has had about 25 years' experience in the development of primary batteries. The other is Mr. Thomas Hennigan, who is retired from NASA/Goddard and now has his own consulting business. He has had 23 years' experience in the development of secondary batteries.

Let me ask the first question. What other types of battery systems have had similar safety incidents?

WARBURTON: All batteries are potentially dangerous if they are used improperly. In the military, of the conventional primary systems, one that has caused considerable problem, again originally because of lack of education, is the magnesium system. People did not really consider the hydrogen that would be generated during the reaction of magnesium and manganese dioxide (magnesium reacts with the electrolyte, water, and forms hydrogen in copious quantities). There have been many incidents in which explosions have occurred. I think that, fortunately, there were not serious injuries. However, conventional systems can, indeed do, cause great hazards.

HENNIGAN: It is difficult to try and remember all the serious problems that have occurred over twenty years. However, I should like to try to explain some of my experience with rechargeable systems.

First, I should like to categorize some of the failure or safety hazard modes that I have seen over the years: the battery design problems; misuse or personnel errors; equipment failure, which is not a battery failure, of course, but may cause a battery to fail; shorting of battery cells owing to metal tools or metal objects on the personnel working with the battery; voltage levels associated with batteries, which may not be important in the batteries we are talking about today, but have been in the past and may be in the future; and a thermal runaway.

I should like to relate some of the problems of batteries I have dealt with over the last 20 years. Most of these are really problems with sealed spacecraft batteries, which we used in tests for satellite programs. Some of them are military problems.

As far as Ni/Cd batteries are concerned, I estimated that in the 20 years, NASA and the Air Force purchase at least 60,000 sealed cells. This is based on a survey made in 1970, when together we were buying 3000 cells a year. The number was much higher in the 1960s, and decreased in the 1970s, and so about 60,000 cells might be near the number.

It is hard to estimate the number of batteries that were made by both NASA and the Air Force, but I think 1000 batteries would be a reasonable number.

I do not remember any serious accidents due to batteries or cell failure in the spacecraft-type batteries. Several occurred in development batteries, including one at Crane which was a development battery using recombination electrodes. One out of approximately 550 cells exploded in accelerated tests, which are pretty stressful; we expected to lose more than that. I won't say there were no leaks.

I heard of one incident where, in the Air Force, a fairly large development cell burst. However, that was due to an equipment failure associated with the batteries. In other words, it was not a commercial charge, but the electronics in the battery itself.

As far as silver cadmium, (Ag/Cd) I should say we used about 1000 cells in this 20-year period, and made at least 60 batteries. One exploded owing to misuse. In that case the wrong type of charger was used (a constant current charger), which overcharged the battery. One rupture was due to equipment failure. In the vented silver zinc (Ag/Zn), of which we did not use many, we flew two satellites with vented batteries where the silver zincs were the main power supply. We had one fire flash explosion due to battery cell problems. I was involved in that investigation. Thre was a fire due to silver zincs on board the submarine. We are not certain the cause because the batteries were burned down or melted down, but the investigation showed that the fire may have been started by a hard short, self shorting. As far as I know, there was no explosion. However, the main problem was that mercury infiltrated the battery compartment and was very difficult to remove.

We did development work on sealed silver zinc cells; we had about 50 cells -- these are potted cells, they are not sealed like the NiCd's -- and we ran 30 of these. Essentially, we had no failures. Now, these do leak at the end of life and start to crack, but I do not really consider that a hazard.

I have not really worked on nickel hydrogen cells, but I have heard the papers and I understand there were some problems in early development with boilerplate cells and a couple of typical cylindrical cells. I have not really heard of any problems lately.

I did make this generalization on these batteries. The Ni/Cd, battery can take abuse, and is not prone to failure of equipment and personnel errors. This does not mean that you can abuse it, but it can take some failures -- such as overcharge for a while, etc. -- and it will live. The system is basically stable, with no dendrite formation as such; if the battery is doing nothing it is very stable.

Silver cadmium cannot take any abuse, and is very prone to equipment failues and personnel errors. It is at least moderately stable. It does not tend to develop hard shorts, but will develop soft shorts during its life. However, these do not seem to result in explosions, simply in cracking of the cell case, because the cells are unbalanced at that time and gas is involved with cells of high voltage.

Now, silver zinc, whether sealed or not cannot take any abuse. They are prone to equipment failure and personnel error. These cells are very likely to develop soft and hard shorts. One major problem with these is hydrogen evolution, especially in enclosed areas. If oxygen is present and an ignition source is available, you can imagine the consequences.

Now, as far as I know, the nickel hydrogen can take abuse as far as reversal and overcharge, and appears to be a rather stable system. From what I have seen of the Air Force Ni/Cd's, they seem to be well engineered, well-controlled batteries.

There are a couple of things here that were potential safety hazards. The first is the voltage levels, which used to be a problem years ago, when 150 or 250V batteries were required. This is no longer a major problem. However, I have noticed that the electric car manufactures are dealing with 72-100V. I do not know whether the DC voltage is dangerous, but I remember seeing a warning in a General Radio instruction manual about not cutting across the 500V terminals; it mentioned that a person was killed by 22-5V. I find that hard to belive, but General Radio did say it. I do not know of any thermal runaway occurring in spacecraft batteries. I think the reason is probably that people usually have quite a bit of monitoring, charging and discharging equipment, etc., and so they do not have that problem.

I am not saying that I know all about the failures in the world since 1955 or 1960, but these are some of the typical ones I have encountered.

SCUILLA: I think we have developed two very interesting points here: the one that Mr. Warburton suggested as far as all batteries being hazardous, and the other about batteries being in the developmental stage as opposed to the production stage.

I should like to ask another question to the panel and the audience. Can we generalize a battery system's hazard potential into, say, two categories: the first being batteries in the development stage having the highest safety potential, and the second being batteries in the production stage maybe having the least? What would a manufacturer consider a qualified production item?

HENNIGAN: I think one of the reasons, especially since the late 1960's that we have been very successful with the Ni/Cd and Ag/Cd is that the manufacturer is subject to quality control to make these cells in the right way. Development cells, which usually come off some kind of development contract, are not usually subjected to this. It is not part of the contract. Then they spend all the money on the development, and do not have very little money left to build cells, and you get what is left.

FRANK: I am going to respond in the form of a question. If we are procuring thousands of these cells, how does the categorization come about as being developmental or production, since there are huge purchases, apparently, of these cells? I can tell you that we are in the research and development stage, and we are purchasing thousands of cells.

BOWERS: I started in the battery business in 1935, and have been familiar with most battery manufacturers in this country.

I do not think that a battery ever stops being developmental. Changes continually take place in any system, as manufacturers consistently try to improve their products. The real problem is that when an improvement becomes an impairment, then you run into some difficulty. However, you cannot talk about something that is in the developmental phase in a battery because it never comes out of the developmental phase.

SCUILLA: I should like to ask some questions about safety testing. Do you basically do enough safety testing? What statistical confidence, if any, should we have in the test results from a legal standpoint? Can I get a legal response to that?

MR. RUZICKA: As far as the product liability law is concerned, as long as you sell the battery, it is of no consequence whether you classify it as developmental or production. once it enters the stream of commerce and is sold as a regular part of the company's business you subject yourself to liability as a manufacturer.

If there are ANSI or ASDM or government testing standards, it is necessary to comply with those. If there are not, and there is an injury, the amount of testing you have done will be considered on a case-by-case basis. The plaintiff will then doubtless find experts to show that testing one battery out of 1000 is statistically unreliable and that it would have been much better to test two out of 1000.

Then, of course, the question of the reliability criteria is up to the jury, and that is basically the problem that product liability law presents today: , that injuries are in effect redesigning your products and changing your quality control procedures after the fact.

Therfore, the answer is basically that it depends on how much the plaintiff's attorney knows about your product. It eventually becomes, as always in design cases, a battle of the plaintiff's experts and the defendant's experts. The outcome depends on whose side the jury buys, and this differs from case to case.

CALLAN: I agree with the answer. I should just like to add that the manufacturer can test to his heart's content and be a completely reasonable and prudent manufacturer, and yet in a strict liability case the plaintiff does not have to prove any negligence on the part of the manufacturer whatsoever. He simply has to prove that there was a defect in the product, that the defect was in the product at the manufacturer's plant, and that the defect was the proximate cause of his injury, and he wins.

LACKNER: Since testing and qualification can be quite costly, what is the responsibility of the federal government to subject all the items to some safety test in their own laboratories, and give them a sort of "Good Housekeeping" stamp of approval, which then may then be used as a reference mark in the courts? Some manufacturers may otherwise simply not have the facilities to do the testing. Heart Pacemaker batteries may be an example.

RUZICKA: There are many answers to this question. Under the product liability law, , even if there are standards, your compliance with them does not immunize you from product liability.

We had quite a few public relations problems with the Tang commercials after one of the first space flights. It is our policy at NASA not really to certify or to endorse commercial products.

WARBURTON: As a product engineer I have to make some assessment of the product that I wish to develop or put into a weapons system. And as a government scientist, I think we are faced with the establishment of a criteria against which we must judge whether this particular chemistry or that particular chemistry is safer than another, if indeed we can.

Somehow we have to establish for these very energetic systems, how, at what rate, and under what conditions this energy is released. If we have that information, then perhaps we can set up some criteria as to the safety and use of these batteries.

This is our predicament. The designs keep changing as money keeps pouring into the coffers to develop new electrochemical systems.

MILLER: Batteries are manufactured for many different applications, from space and military through industrial to consumer applications. Does the law really make a distinction between these types of endeavors?

RUZICKA: In some respects it does. However, if your battery is sold to the Air Force and injures a government employee, he gets some compensation from the government. However, under the sovereign immunity doctrine, he cannot claim against the government, and so he will claim against you. He could then recover under the same laws as could a consumer who bought a D-size battery in a drugstore.

There are some provisions. Because he has not purchased an item himself, there are some differences, but they are very technical. He does not have a course of action for breach of warranties, express warranties especially because he himself has not signed the contract between you and the purchaser.

However, as far as the traditional concepts of negligence and strict liability are concerned, there is no distinction.

TAYLOR: I should like to take a question about the duty to warn. For example, if we as the manufacturer of a lithium battery attach to it a label stating "Do not recharge," and a consumer recharges it and blows himself up, where does that leave us?

RUZICKA: The law of warnings increasingly requires the manufacturer to put as much detail into the warnings as possible not only of why not to recharge, but also of the consequences of not heeding that warning.

TAYLOR: Then, would "May explode if recharged," be sufficient warning?

RUZICKA: You could still be held liable if the consumer recharges it, and if it is proved that that particular warning is not sufficient. However, it is a jury question.

DI MASI: If no contract has been made over batteries carrying the warning, "Do not burn or incinerate, do not recharge," etc., and they are dumped in a sanitary dump, what is the position if some young children find them, set a fire and throw them in. Is the design engineer, who has run all these tests, in any way held responsible for this kind of incident?

RUZICKA: The law requires the manufacturer to make the product safe, either by design, manufacture or by the warnings placed on it for its intended use and disposal, including foreseeable misuse.

If the manufacturer obtains information that children are setting fire to dumped batteries, that risk becomes foreseeable, and the manufacturer is under duty to take that into consideration in designing and selling this product.

Again, these are all factual questions that are decided by juries. A jury in one case may say that the manufacturer has done as much as he could; in another case, in another jurisdiction, the jury may say something else. The unpredictability of the law as it stands is one of the basic problems. That is why your insurance rates have been increasing 700 % the last three or four years.

DI MASI: Even with sufficient warning, then your opinion about this particular incident is that it can still be made into a case?

RUZICKA: Yes, indeed. I have recently come across a case involving a telescope where there was a big warning on the front page of an instruction booklet saying that a Sun filter that came with it had to be properly placed into the telescope and at the proper slot before viewing the Sun. The warning then said that not properly inserting the filter may cause eye damage. One of the purchasers placed the filter improperly, leaving a crack; he was blinded on one eye when viewing the Sun. The opinion of the Court was that to say "May cause eye damage," if it is known to the manufacturer that the result will be blindness, is patently insufficient. Therefore, if you know that a little statement on the battery saying "Do not incinerate" is not sufficient to prevent misuse, you may still be liable.

OTZINGER: I have written and reviewed a number of cell and battery specifications, and I have not seen a safety hazard request or a statement from a supplier. I am wondering if that is something that should be included? We been remiss in the past and perhaps now we should give our suppliers an opportunity to make that kind of a statement, or even require them to disclose to us the hazards and safety issues that are involved in the cells and batteries that we purchased from them.

RUZICKA: Definitely. I think that is a good point.

OTZINGER: To my knowledege it has never been done. I have never seen a safety hazard, on a request for documentation from a supplier.

RUZICKA: The duty to make a product safe is not delegable. In other words, you as a manufacturer cannot rely on somebody else that your product will be used properly. If you sell to a company that does not really care about the way its workers use the product, you may still be faced with liability even though that company or its workers may be found in violation of occupational safety and health laws, for whatever reason. In most states, the employer is immunized by the Worker's Compensation Law from common law suits by its injured workers once compensation benefits have been paid. Because most of the benefits are not sufficient, the workers are increasingly claiming against you as manufacturers, and recovering.

HALPERT: If I were a manufacturer, or even an engineer working with lithium batteries, I should be concerned that, once the batteries were on the market, I could still be held responsible for anything that happened. What kind of incentive can we give these manufacturers to get them to make their products and put them on the market for consumers to use?

CALLAN: The only thing that manufacturers can do is to lobby Congress, because DOD has a statutory authority to indemnify contractors for items that are considered extra hazardous. We at NASA have no indemnification authority, which means that if we receive a defective product that injures somebody, then we relieve the manufacturer of his liability in that defect and we pay.

Hence, the only incentive for a manufacturer is to become involved in extra hazardous manufacturing, if these batteries are as bad as you seem to indicate.

By the way, there is legislation in specific areas to cover extra hazardous activities. One is the Price Anderson Act in the nuclear field. However, that essentially relies on private insurance and group policies. There is the Teton Dam Act, which allowed victims of the dam breaking to make claims against the government. There are other liabilities that are allowed by specific legislation.

MURPHY: I wonder if you could clarify a logistic problem regarding lithium batteries. There is a limit on shipment of lithium cells; I do not recall the weight per cell. However, if these cells were in series, would there be a weight limit?

SCUILLA: The Department of Transportation exemption 7052 does limit the amount of lithium in one sort of shipping container. Thus, if your battery is made up of cells with a large capacity, which would require more lithium, there are instances where the limit would apply. However, any individual may apply for an exemption to ship larger cells, and a number of other lithium battery companies have applied for specific exemptions for shipping lithium cells with 10,000 or 12,000 A h. There have been some other modes of transporation restrictions on those individuals.

It would be necessary to check with the Department of Transportation's Hazardous Materials Operation Section, because the transportation regulations are basically in a state of flux, and it could change tomorrow.

NICHOLSON: Mr. Otzinger made reference to the fact that he had not seen any requirements for battery vendors to file hazard reports and so forth. However, some areas of the government do require this; we have recently been involved in a Navy program where hazard reports have had to be filed. As regards the safety of batteries, we were doing some work recently on very large pocket plate Ni/Cd batteries. As you know, alkaline batteries generate hydrogen; it is possible to find formulae, in the literature, to indicate the amount of hydrogen generated per gram of active material.

In this particular instance, an investigator was doing some charging and discharging at low temperatures in an environmental chamber, which had very sturdy doors. This type of experiment generates a lot of gas, especially in overcharge. He had been running a nitrogen purge, but ran out of nitrogen. He felt that because the battery had been sitting for a while, no hydrogen was being generated. Unfortunately, a lot of hydrogen was being generated, and when he went to resume his tests and did not run his hydrogen purge, he threw some open-type switches inside the chamber. Fortunately, he was standing in the right place. Otherwise, he wouldn't be alive today. His argument was that he had read it in a book and there was nothing in the book that says that can happen. My argument was that not everything is in the book. It is still necessary to be very careful with the batteries.

SCUILLA: How large was the capacity?

NICHOLSON: It was about 200 or 225 A h.

SCUILLA: I should like to ask Mr. Di Masi and some of the Li/SO_2 manufacturers, whether their approach to safety in that system is simply in the lower coulombic ratios.

When we make larger cells, the double Ds and triple Ds, could we infer a shift in that maybe rather than just trying to imply with some of the presentations that the one-to-one ratio is the safest. Should all Li/SO_2 cells be designed to that specific ratio?

DI MASI: My experience is of testing a number of cells, not manufacturing them. As the watt hours of a particular cell are increased, the effects of heat dissipation become a problem.

One is therefore not justified in comparing a cell of 5-10 A h with one of 30, 40, 50, or 1000 A h, because the tremendous amount of heat generated would cause the larger cells to go into violent explosion or venting. It would be like composing a small motor with a car engine. It is therefore not only a matter of design and electrochemistry of a system. There seems to be a jump at about 10 A h, where the heat management becomes critical.

PALANDATI: I believe that this is basically what we have seen for years in the silver zinc area. If you take a 300 A h cell, you have this problem. You cannot even stop the firing once it starts. Several cells in a battery produce an avalanche effect. Again, I think one has to look at the size of the cells.

Cells of O-1 or O-2 kW h are one aspect. Cells of 4, 5, 50 or 100 kW h, which are some of the battery designs of the future, bear no comparison.

I should also like to mention that nickel cadmium and silver cadmium that were low energy density batteries compared with silver zinc, which was the high energy density battery at that time. The energy densities now associated with lithium batteries are obviously that much greater again. The potential hazard is thus even greater today than 15 or 20 years ago.

TAYLOR: I really see no difference between lithium systems and conventional systems. Obviously, the more energy you pack into a system, the greater your problem.

From today's meeting, I feel that many of the problems are simply that people don't understand what can go wrong. Instead, you can talk to us, the manufacturers, about your applications and we can recommend batteries to meet these applications, and how you could safely use them and how you could abuse them.

I think, for example, that what Mr. Bene is doing today is finding conditions to blow cells up. That is useful up to a point, but I think it can indicate a lack of understanding.

It is understood nowadays that you can use lithium sulfur dioxide batteries and lithium thionyl chloride batteries under wide extremes of abuse up to a certain point. If you talk to us we can tell you those conditions, as well as what may happen if they are exceeded. We know that the batteries are safe up to a certain point, which is far beyond that available from past conventional systems.

I should like to dispel this question of the unknown. Many batteries are safe nowadays, under conditions that could have caused problems only a few years ago.

BENE: We do not deliberately try to find ways to blow up sulfur dioxide cells. However, I could mention many assurances I was given, when we became involved in this program, that these cells would not blow up, and would not vent. Very naively, we had some serious problems, and fortunately no one was injured.

The gist of our work has been to find the conditions under which these batteries give problems, and to decide whether we should reasonably expect that type of behavior under conditions of performance and disposal. From that basis, we have pursued different design changes in the cell.

As I pointed out in my talk, one thing I have heard for many years is that it is necessary to reverse a sulfur dioxide cell before it will vent. The evidence I have presented today shows that this is not so. The progress we have made now shows that a Li/SO_2 cell, particularly in a D size, should be designed to consume all the lithium and leave sulfur dioxide in excess (a lithium-limited cell). I think it is that simple.

SCUILLA: I should like to expand on the user misuse problem by commenting on the specification sheets. I have found, in reviewing earlier data sheets on lithium systems, that for some of the abuse test conditions, currents and discharge rates were not mentioned by the manufacturer as presenting some heat balancing rejection problem that allowed the cell to vent.

How can we, the government and the manufacturers come together with some sort of safety statements, and a realization of some of the limitations of these systems, as far as the specification sheets go?

HENNIGAN: Over the years we have had some problems with a number of batteries. However, we never depended on the manufacturer's specifications as far as how to use the batteries; we determined our own, wrote them up and gave them to people.

BIERMAN: At Honeywell we have always supplied at least a hazardous analysis handling, and a special safety sheet, with any cells. I think some other manufacturers have done, or are doing that.

We have taken a strong position on the safety issue and have primarily focused on the aspect of education. Education is the key to safety. I like to draw the analogy that you do not give a lead-acid car battery to a nine-year old child to play with. You also do not give a sulfur dioxide cell to a nine-year old child to play with, because he will find ways in which to cause that cell to vent.

I think there is a key here that people have to realize and understand. They have been used to dealing with batteries as things they can buy in a drugstore and put into a flashlight. This is not true with lithium cells.

I think it is important to understand that most people, and most big companies, only think of batteries when they have completed all the electronics.

We stood up here last year and discussed batteries and how safety features could be designed into them. However, it is necessary to get the manufacturers involved early. They are experts in the field, and are not called on enough for their expertise.

I have suggested in the past, during the Tri-Service Safety Committee, that a movie be made to show the do's and don'ts, because I think that once the users learn how to handle the Li/SO_2 cell, they will find it very safe.

Lithium sulfur dioxide batteries may not be right for all applications. If you are going to put your product out in a drugstore, we should probably say, that these batteries are not suitable. However, if your application is, for example, a space or military application where you can help educate the users, we should be happy to provide batteries.

ESTES: I should just like to mention that in our investigations we did come across one accident involving a lithium sulfur dioxide battery. It was in a smoke detector. I forget the number of batteries in there, but I think there were more than one. I believe that one of them exploded. There was no injury. However, from what I have heard here today it seems to me that there is a lot of research being done in this area. I am antici- pating the time when these batteries become more available to the consumer.

Are you ready to start putting these in the hands of consumers, either in limited number or in large numbers, and what are we waiting for? Is it a safety factor, is it cost? Can we expect to see lithium batteries in consumer products any time in the near future?

MC DONALD: There are already a number of lithium batteries out on the market. Lithium manganese dioxide batteries, for instance, currently power a number of calculators and watches. As far as the sulfur dioxide and the thionyl chloride batteries are concerned, we at Duracell have no immediate plans to put out batteries for consumer use.

ESTES: I suppose you are talking about low-energy sources. Would you sell a battery, assuming that you make a D size, if you knew that somebody was going to use it in a toy, for example? Would you feel you had any responsibility, or would you be hesitant to sell it under those conditions?

MC DONALD: At present we would not sell a D-size sulfur dioxide battery to a toy manufacturer.

OTZINGER: Is it your company that has just been licensed by Sanyo?

MC DONALD: Yes. However, that is in the lithium manganese dioxide system. We would not sell lithium sulfur dioxide batteries.

OTZINGER: Will you be selling the manganese type?

MC DONALD: Yes.

OTZINGER: Do you see any safety hazard at all in connection with that?

MC DONALD: We have not been able to determine any safety problems with that system at all.

HALPERT: The Army Research Office in Charlottesville put out a complete defense, and compliance with that standard in a suit brought in negligence. In a strict liability, compliance with industrial custom does not provide you with defense, because the object of the inquiry is the battery itself, not your behavior.

However, you can introduce the defense that the product you have designed or you have sold is up to the state of the art, and could not possibly have been made safer, or that the cost of making the product safer would have been prohibitive. Then, of course, it becomes a factual question.

As far as compliance with industrial customs, in a negligence case it is a complete defense. However, non-compliance with industrial custom, or with the state of the art, or with voluntary or mandatory standards, will convict you on both theories.

There was a recent case, again not involving a battery. It was a case involving children's sleepwear, where a manufacturer complied with the Consumer Product Safety Commission standard although he knew that that particular standard was so weak that it would have passed as inflammable about 19 different types of paper, including newsprint. Of course, the defense that the manufacturer complied with the standard was not accepted. In fact, it did not prevent the jury from imposing punitive damages against the manufacturer.

BIERMAN: Does not the fact that an agency such as SURCOM, Ft. Monmouth is buying sulfur dioxide batteries in the hundreds of thousands imply that the government at least feels that these cells are safe enough to be used?

CALLAN: You could use that in your defense. However, it is up to your lawyer and how you want to make your case. The fact of our buying a lot of batteries does not make them safe.

If you are in a litgation, you must produce examples of how you sold the item in the past, that it has been acceptable, and that you know of no other injuries or damages. In fact, I received a letter from a company that manufactures containers of liquid nitrogen. It was a form letter that a law firm was sending out to users all over the country; in it they asked whether we had any incidences of damage, explosions, etc. Our answer was that we had not. However, these are just the facts you try to marshall in support of your position in litigation.

LACKNER: What is the secondary liability of the manufacturer? Occasionally we see signs saying that in case of defect, the main product (the battery) will be replaced, but that the manufacturer is not responsible for the transistor radio, for the satellite, for secondary problems that might have occurred owing to a defect. Now, obviously in cases of safety to the human being, there is some moral or legal justification for loss. Is there any legality in the statement "We shall not be responsible for secondary problems"?

RUZICKA: Yes and no. In consumer transactions, warranties have become documents that do not promise remedies, but limit them. That is why nearly all the states have adopted a Uniform Commercial Code, which gives implied warranties in addition to the warranty you get on a product.

It is still possible for a product manufacturer to limit his responsibility for the amount of compensation that he will pay. However, the courts draw a difference between a consumer transaction and a commercial one. In consumer transactions, the courts will set a limitation on the amount of damages for personal injuries, or a disclaimer of liability for personal injuries is per se unconscionable. That means it is given no effect.

As far as the limitation on property damage, such as on an automobile tire that comes with a warranty to say that in case of failure the manufacturer will replace the tire, even though the car may have plowed through ten Rolls Royces, the courts usually look at the way the warning or limitation has been written, in order to give it effect.

Basically, then, you can limit in consumer transactions, consequential damages for property damage. However, you have to be very careful to make it as conspicuous as possible, to put it on the front page of an instruction booklet, or in different type.

In commercial transactions, however, the courts feel that they should not interfere with agreements between companies.

The courts also assume that the two parties to the contract acted at an arm's length basis, and are both considered both experts in what they are doing, and so the courts do not interfere in their contractual freedom.

Therefore, if you, as a company, sign a contract to buy something and the supplier disclaims all liability and you accept this, you are left with it.

HELLFRITZSCH: Where does the government fit in? If the manufacturer sells to the government, does the commercial transaction analogy or consumer transaction analogy hold?

RUZICKA: We are talking about a suit filed by an individual against a company, rather than one company against the other.

HELLFRITZSCH: The distinction I have been looking for here is: what warranty does NASA or the DOD have when they contract with the manufacturer?

That breaks down into two things: their internal use of it, and then, of course, its use in the field, more or less like a production item (the DOD will probably do this more than NASA).

CALLAN: If a dangerous item is sold from a manufacturer to the government, and a civilian employee of the government, or a soldier in the military, is injured, he has no suit against the government. There is a doctrine in the military and in NASA or

civilian agencies, that his compensation, which is exclusive, comes from a Workman's Comp with the government.

As regards the situation between NASA and the manufacturer, when NASA accepts something, it accepts it for everything except latent defects or fraud or misrepresentation.

Once we take it and inspect it and accept it, it is ours, unless there is an express warranty that survives our inspection language.

HELLFRITZSCH: Then it is essentially the case of the commercial manufacturer versus the commercial, where both people know what they are selling and buying and they do it at arm's length?

CALLAN: Yes.

HELLFRITZSCH: I should like to make one general comment about bettery safety. All batteries are, to some extent, hazardous, and always will be. If you ingest the materials that they are made of, they may not kill you immediately, but they are heavy metal oxides. Most of the liquids that can be poured out are corrosive. If gases emanate, they could be deadly. Any aqueous battery with zinc or magnesium anodes can give off hydrogen, possibly causing hydrogen-oxygen explosions. As far as the voltage is concerned, an electrical engineering professor at Wisconsin told me that a sewer inspector in Chicago was killed with an ordinary two-cell flashlight.

These things are never going to change.

SCUILLA: Basically, I should just add that I believe safety is everyone's responsibility.

I should like to thank all the panel members and the audience for a very fruitful discussion.

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SESSION III

FUTURE NEEDS

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HIGH ENERGY DENSITY BATTERIES FOR SATELLITE APPLICATIONS

L. Marcoux, Hughes Aircraft
R. Marsh, AFAPL

I should like very quickly to go over the first year of a study we performed for the Air Force.

The idea of the program was that the Air Force recognized that, in a period starting in 1990, they will require very large (25-100kW in some instances) power systems in space. They also recognized that it was impossible to embark on a battery development program for those kinds of power systems.

They knew that DOE had been pumping several million dollars a year into high-energy batteries for terrestrial applications, and so their ideal was to see where the performance requirements of DOE differed from the aerospace requirements, and to establish whether or not these systems showed any promise in aerospace application.

The objective of the program was to determine the suitability of those advanced systems, to narrow them down to those showing the most promise, and then, in the second year of the program, to conduct preliminary design studies.

(Table 14-1)

An interesting way to begin the study is to look at the similarities and differences in the battery requirements themselves.

The total energy requirements of the Air Force aerospace applications are very similar to those of the electric vehicle, and, of course, are dramatically different from those of load leveling. Specific energy requirements, operating voltages and baseline power requirements are again comparable with those of the electric vehicle. The peak power requirement, indicated as a peak power of 100 kW, seems fairly innocuous and straightforward. However, when evaluated in terms of the peak power to baseline energy ratio, it is an appalling power requirement, and it is considerably more rigorous than those of the electric vehicle. The advanced battery systems are very low in power. The rest of the characteristics, with one exception, are very similar. The charge-discharge times are, of course, a little more rigorous for the space application. The calendar life for space applications may be not as rigorous as that of the DOE terrestrial applications. The time frame is the same. The great advantage that we enjoyed in this study was that we were not held to the $30-100/kWh that is characteristic of the terrestrial application. However, we do have cost constraints.

Our plan was to spend the first year in technology assessment (battery technology evaluation, prelininary engineering studies and system selection), and the second year in technical design (cell design, battery design and battery integration). Most of the first year was to be spent in selecting of system around which to perform those designs.

The battery evaluation was fairly straightforward, consisting of data base generation (literature search, technical meetings, and meetings with battery developers and development sponsors), system comparison (preliminary data packages, state of the art battery comparison and preliminary system selection) and performance projection (identification of historical development pathways, problem areas and possible problem resolution). This third area was the most important because it became clear immediately that there were no systems today in which state of the art technology was adaptable to the aerospace application.

However, we knew that, in the past, many decisions have been made in the development of these batteries whereby cost had been minimized at the expense of performance, and we felt that performance could be optimized if more money were made available for the systems. This proved to be the case. Our conclusion was that, for the high-temperature batteries, we should pursue technology that was being discussed four years ago, because the performance capability was probably there.

At the same time, we thought it was important investigate the engineering aspect. We knew that there was a high probability that the systems under consideration for integration into the spacecraft would be high-temperature batteries, 400 - 500 C devices. This is not as outrageous as it sounds. The people working on nuclear power systems for spacecraft had the same problem. We did, in fact, carry out a preliminary set of studies to evaluate the alternative control and isolation technologies.

Because we recognized quite early that we had a severe power problem, we felt we should also evaluate hybrid technology. Our conclusions were that, in very strange duty cycles, it could conceivably be of some benefit, especially in the case of a flywheel which could be integrated with the attitude control system. However, the Air Force power requirement is for a large, prolonged burst, and there the energy storage capability rejects the flywheel concept, and also the concept of using very high power peaking Ni/Cd or Ni/H_2 batteries.

Finally, we felt that the Air Force guidelines were certainly a good beginning. However, we needed to narrow down those mission constraints further and examine real missions because of the diversity of the guidelines.

(Figure 14-1)

As shown in Figure 14-1, with the guidelines and the mission requirements, we established battery requirements. We then used various inputs to project battery capability. We also considered the engineering constraints on the battery, and traded those off against one another to develop a system.

The advanced battery literature is at best a swamp, with many strange beasts in it. We needed criteria to reduce the number of batteries under consideration. This was done in conjunction with our evaluation of the literature. We found that systems to be considered for use in the 1990s would have to be under active development now. We needed systems in which real cells had been demonstrated. We felt it would be an advantage if two of those cells had been discharged and charged together, that 200 or 300 cycles should have been demonstrated on the system, and that there should be a large enough data base available for us to work with the systems.

Using those criteria, we were then able to group the advanced systems into three major categories that typify their electrochemical behavior, namely the molten salt cells, which had unique advantages and unique problems; organic electrolyte cells, which are characterized by their complex chemistry and high resistance; and aqueous cells, which, on examination, appeared considerably better than we would have ever imagined.

We then broke the categories down and considered the systems available within each one. We first considered the molten salt cells; these included sodium cells with beta alumina separators, antimony trichloride systems and the various sulfur systems that Mammantoff is working with, the lithium sulfur systems in their various forms; and the older lithium halogen systems. Of that first set we were able to eliminate all but sodium sulfur and lithium metal sulfide.

We had approached the organic electrolyte cells (sodium cells with beta alumina separators, and lithium chalcogenide cells) with enthusiasm until we reached the conclusion that they were probably one major scientific breakthrough away from being applicable. We wanted to limit ourselves to technology that we felt was applicable to our 1990 target date. Therefore, although these cells have considerable advantages and are much easier to integrate than the high-temperature batteries, it would be premature to consider them at present.

Finally, we considered the aqueous systems. We investigated the redox systems by using standard aqueous redox potentials, and found that specific energies, of course, could never meet those of our requirements. We then examined the zinc chlorine and zinc bromine systems, found out that zinc bromine had all of the advantages of zinc chlorine and none of the disadvantages, and decided to concentrate on the zinc bromine systems.

(Table 14-2)

Six months ago, when we had narrowed our systems, we had arrived at the strengths and weaknesses indicated in Table 14-2.

Our activity in battery evaluation occupied the second six months of the program. We then concentrated on these systems in an attempt to extrapolate their technology to 1990 and to develop a program plan that would allow us to reach that point.

The thermal management study was a fairly straightforward engineering study in high temperature materials and heat transfer. It included evaluation of battery packaging alternatives (insulation and configuration), provision of preliminary radiator sizing estimates, evaluation of the impact of the operating temperature on heat rejection system weight, and, most important, evaluation of three methods of thermal control: louvers, heat pipes and fluid loops.

(Figure 14-2)

The conclusions, shown in Figure 14-2, were that the weight advantages of louvers were significant. However, their control was not as tight; the thermal stratification was greater. The heat pipes and fluid loops offered the same weight type characteristics. However, heat pipes were considerably more reliable because they did not require the active mass transport of pump fluid loops.

Other conclusions of the thermal study were: surface area optimization of the battery package design reduces heat leaks and weight; dual radiator designs reduce system weight; alkali metal (Cs) heat pipes have potential for control flexibility and reliability; the most effective insulation material is the DOE developed multifoil vacuum insulation; and, of course, the thermal management system components require additional development.

We entered the mission analysis task with the attitude that it would be a straightforward evaluation of shuttle launch requirements along with projected Air Force and NASA missions, in order to specify baseline power, peak power, weight constraints, capacity, cycle life, calendar life, duty cycle, launch and safety requirements, spacecraft interfaces and vulnerability requirements. We found that the Air Force missions were not well defined and that the NASA missions were too well defined. They were very large Ni/Cd systems for low-Earth application. We were therefore not able to talk about specific aspects of the mission.

We therefore sorted the various requirements into three categories. The first was the set of primary requirements, which would be limiting. Not surprisingly, after a year's work we concluded that specific energy was going to be critical. The set of secondary requirements were those related to lifetime (duty cycle, cycle life, calendar life). We felt that the battery system technology was such that those were no problems. Finally, we did go through the shuttle launch requirements, safety requirements, vulnerability requirements and spacecraft integration. Again, we felt that everything here could be done. If we do not have the power and energy in the right weight package, we have no mission anyway.

We also tried to make some generalizations, largely from the Lockheed high-voltage high-power study conclusions, and from some work done at Wright Field, on what the Air Force general mission requirements should be. They are rather interesting. They gave us good reason to concentrate on synchronous orbits and ignore low-Earth orbits, where the advanced systems have less promise. As for the baseline power requirements, with the window that we knew about, the peaking capability required is still outrageous (up to ten times the baseline), and I doubt if these systems can meet it as stated. I feel that what will ultimately evolve is a compromise between what the Air Force requires and what it can have; the problem is largely a definition of peak duration. It is the energy under the peak that is limiting.

The weight aspects are the most interesting. Very large communication satellites for synchronous orbit today run somewhere between 7 and 8% battery weight. That is conventional technology. For power satellites, considering all the components necessary to keep them orbiting, it is possible to go up to 20% for battery weight, and that is fairly generous, as well as probably cheating a little on the power electronics.

Our assumption was that the systems were going to be shuttle-launched into synchronous or 12h elliptic orbits. That meant we could use 2260-2720kg (5000 or 6000 lb) for the on-orbit weight of the spacecraft.

(Figure 14-3)

If we do that, we see for the baseline power requirements (the abcissa on Figure 14-3) that at 7.5% of the spacecraft devoted to battery weight (assuming that in 1990 we can achieve 160 Wh depth of discharge), this is a very optimistic sort of cell performance. Those numbers are derated for thermal isolation and control by 20%, and by 20% for converter inefficiencies. There is another derating factor which I do not recall. These are fairly conservative numbers. Thus, a conventional spacecraft should be capable of about 15kW, or perhaps 20 - 25kW for a good design.

(Figure 14-4)

That changes considerably when the Air Force's peak power requirement is applied. A spacecraft with 15% battery weight is then capable of, say, 20kW. Thus, with the current battery technology, the original idea of a 50kW device in synchronous orbit is unrealistic.

The conclusions of these considerations were that the zinc bromine system simply did not have the specific energy to be considered for synchronous orbit. We feel that it is a very interesting system, and appears to be capable of extremely long life. It is not as complex as it might appear superficially, and probably deserves further consideration for use in very large power systems and low-Earth orbit. For the synchronous and elliptical applications, lithium metal sufide and sodium sulfur are probably the only systems consistent with the requirements of 20 - 30kW higher orbit missions. They appear to be indistinguishable, and both have individual strengths and weaknesses.

In terms of specific energy, both systems are essentially equivalent, and both require substantial increase for use in satellite application. The specific energy requirements of the space mission are such that lithium aluminum iron sulfide will have to become lithium silicon iron disulfide, with considerable chemical changes. At present the sodium sulfur system probably has as high a specific energy as a one-tube, one-cell sort of device can ever have. Consequently, to meet the specific energy requirements, a major development in cell design is necessary, to replace the one-tube, one-cell configuration.

Both systems are power poor, but the changes necessary to meet specific energy will also increase the power capability. The peak-to-base power capability will probably never exceed 2:1.

The operating temperature, oddly enough, favors the higher temperature system (lithium metal sulfide), simply because it reduces the radiator size. One of the problems in thermal control was that the vast difference in temperatures between the batteries and the electronic heat dissipation would require two separate thermal control systems. The thermal control aspect of the high-temperature battery will be minor because of the extremely high operating temperature.

The sodium sulfur system has a much longer lifetime than the lithium metal sulfide system. However, by the 1990s, the lithium metal sulfide system will probably meet the 1000-cycle requirement for the space mission. Extended calendar life is not demonstrated for either system, but this will be no problem if batteries can be frozen between eclipse sensors.

Because of the one-cell, one-tube arrangement of the sodium sulfur battery, it is difficult to put into a battery configuration. Obviously that system will have to be replaced, simply because it will be impossible to carry enough container material to meet the requirements with current cell technology.

Both systems are fragile. We do not think that this is a major problem. We should be able to launch the system frozen, and packaging will reduce the problem.

Our feeling for the way the program should go in the next ten years is that, because of the integration problems in batteries of this type, we cannot simply jump from a cell-development phase to a battery-development phase, but that we must go through an intermediate development of the battery module, which we assume will be thermally and electrically independent.

(Table 14-3)

The program would probably have three phases, as shown in Table 14-3, the zero phase being our own study program, the next a cell-development phase, followed by a module-development phase, and finally, a module demonstration phase.

The module-development phase would simply test the various control aspects of the module and would not result in the demonstration of the module. It would simply be sub-module component development, and would also continue cell development through that phase to a point where the cells were qualified for flight. The final phase, module demonstration, would be a qualification phase for the battery modules.

I think one of the interesting things was that, at least during the early phases of this program, we sat down and carefully evaluated the costs. I think those numbers are conservative, and, are some four or five times larger than the Air Force ever thought they would be. However, the important aspect of the study is that the development of this type of battery system is expensive, is not straightforward and is going to take a long time.

(Table 14-4)

I think the schedule is very tight. In fact, it indicates that a very successful program would be necessary to make the 1990 mission initiation date.

The major conclusions in the study have come out during the discussion. They are as follows. The missions will be 10 - 100 kW type power requirements in higher orbits. Thermal problems appear to be manageable. The hybrid concept does not appear to be useful for military spacecraft. The most promising systems for the Air Force application are the alkali metal sulfur systems.

It is clear that, because of the specific energies obtainable in the near term, we must work very carfully with the spacecraft designers and integrators because we need 12 - 15% of the spacecraft weight for battery.

Finally, I must point out that this has been an extremely optimistic study. I think it has to be, because the need is real, and will probably drive the development. However, all our projections are acknowledged as optimistic.

DISCUSSION

LEAR: I noticed that you had a separator problem with the zinc bromine system.

MARCOUX: It is a separation problem, not a separator problem. The difficulty, which is solvable, is that the zinc bromine system in its present configuration requires gravity in that the bromine is separated on charge from the electrolyte flow by an organic complexing agent, a quatenary ammonium bromide that forms a polybromide in an admissible phase.

Dr. Lim at Malibu has said that this is no problem, and that these molecules are like anion exchange resins. He has shown that we could get about three molecules of bromine. It can be done with a solid bromine complexer rather than a liquid type. That would be a disadvantage for space, but probably not for mass.

LEAR: Did you look at a packaging concept for this particular system?

MARCOUX: We did not have to. Exxon has a very nice one. Their EV battery looked as though it could simply be put into a spacecraft.

HALPERT: You were talking about synchronous orbits. Then you mentioned a 1000-cycle requirement.

MARCOUX: That is for ten years.

BATTERY GUIDELINES

SPECIFICATION	USAF/HUGHES HED BATTERY PROGRAM		DOE AND EPRI PROGRAMS	
	LOW EARTH ORBIT	GEOSYNCHRONOUS ORBIT	LOAD LEVELING	ELECTRIC VEHICLE
TOTAL ENERGY, KWH	5.8, 14.6, 29.2	12, 30, 60	100,000	25 TO 40
SPECIFIC ENERGY, W-HR/KG	66	100	[8 KWH/FT^2]	140
OPERATING VOLTAGE, V	28 TO 150	28 TO 150	1,000	50 TO 100
BASELINE POWER, KW	10, 25, 50	10, 25, 50	10,000	20
PEAK POWER, KW	100	100	10,000	50
PEAK POWER/TOTAL ENERGY, HR^{-1}	17.2, 6.85, 3.42	8.33, 3.33, 1.67	0.1	1.2 TO 2.0
CALENDAR LIFE, YR	5	10	10 TO 20	3 TO 10
CYCLE LIFE, CYCLES	29,200	1,000	2,500 TO 5,000	800
CHARGE TIME, HR	0.916	22.8	10	1 TO 6
DISCHARGE TIME, HR	0.583	1.20	5	2 TO 4
COST, $/KWH	600,000 TO 700,000	600,000 TO 700,000	30	50
TIME FRAME	1,990 TO 2,000	1,990 TO 2,000	1,985 TO 1,990	1,985 TO 1,990

Table 14-1

MAJOR CANDIDATE SYSTEMS COMPARED

SYSTEM	STRENGTHS	WEAKNESSES
LiAl/FeSx	STATE OF CELL DEVELOPMENT SYSTEM ENGINEERING PROGRESS ENERGY DENSITY	HIGH TEMP OPERATION CYCLE LIFE SPECIFIC POWER
Na/S	CYCLE LIFE LIQUID ANODE AND CATHODE EXTENT OF DEVELOPER INTEREST	HIGH TEMP OPERATION SPECIFIC POWER FRAGILITY
$ZnBr_2$	CYCLE LIFE LOW TEMP OPERATION	Br_2 SEPARATION PROBLEM SPECIFIC ENERGY

Table 14-2

PROGRAM COMPONENTS

PHASE	DESCRIPTION	TIME FRAME	ROM COST, $K	OBJECTIVES
0	HEDB PROGRAM	1979 TO 1981	400	EVALUATE FEASIBILITY OF CONCEPT IDENTIFY CANDIDATE BATTERY SYSTEMS DEFINE CELL AND BATTERY REQUIREMENTS IDENTIFY CANDIDATE MISSIONS DEVELOP CONCEPTUAL DESIGNS
I	PHELIMINARY CELL DEVELOPMENT	1981 TO 1985	3000	DESIGN, DEVELOP, AND TEST CELLS DEVELOP HIGH PERFORMANCE COMPONENTS DEMONSTRATE FEASIBILITY AT CELL LEVEL
II	BATTERY MODULE DEVELOPMENTS	1984 TO 1987	3300	DEFINE FINAL BATTERY REQUIREMENTS DEVELOP AND DEMONSTRATE FLIGHT CELLS DEVELOP MODULE COMPONENTS DEMONSTRATE MODULE COMPONENTS DEVELOP FINAL MODULE DESIGN
III	BATTERY MODULE DEMONSTRATION	1987 TO 1990	2500	FABRICATE MODULE QUALIFY MODULE DEMONSTRATE MODULE (LIFE TEST)

Table 14-3

PROGRAM SCHEDULE

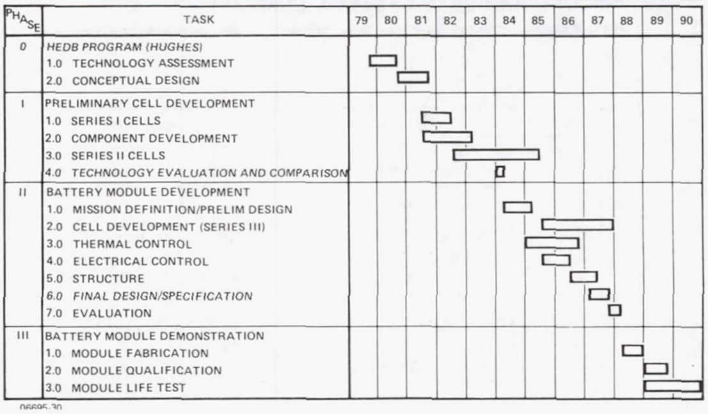


Table 14-4

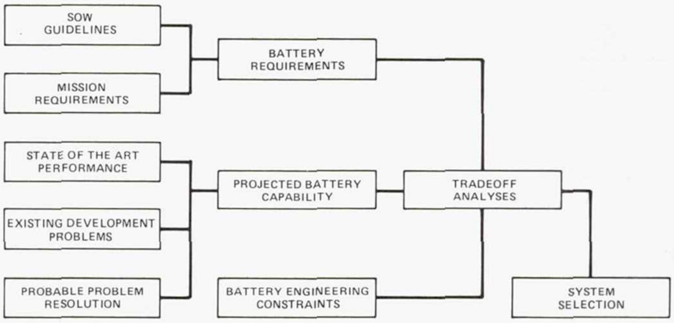
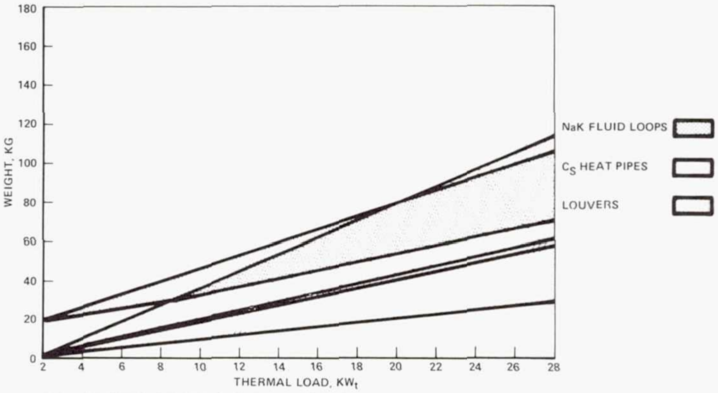


Figure 14-1



*CELL MOUNTING IN SINGLE 3 x 3 ARRAY ASSUMED

Figure 14-2

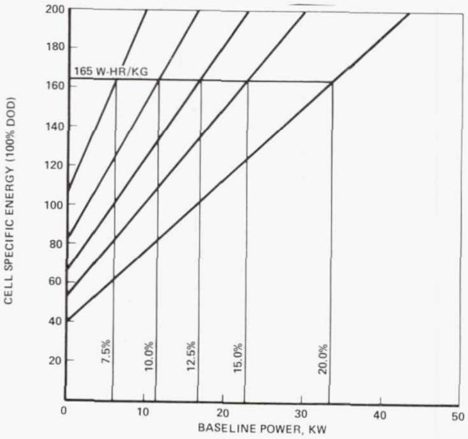


Figure 14-3

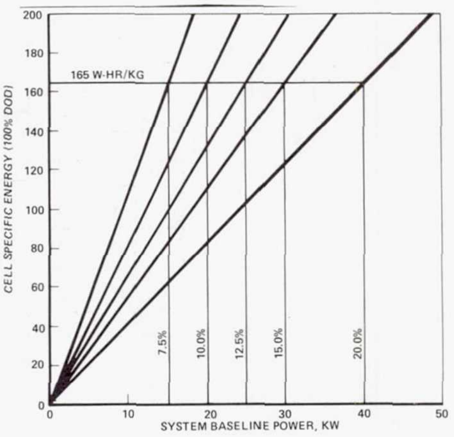


Figure 14-4

SESSION IV

ELECTRODE/MATERIAL TECHNOLOGY

G. Halpert, Chairman
Goddard Space Flight Center

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THE STRUCTURES OF THE SINTERED PLAQUE IN THE NICKEL HYDROXIDE ELECTRODE

B. Vyas
Bell Laboratories

The search for longer lasting nickel cadmium batteries is a continuous effort: in recent years there has been a greater emphasis on the sinter in the nickel battery itself.

I shall talk about the sinter in the nickel hydroxide positive electrode and how that affects the lightness ability of that electrode.

(Figure 15-1)

Figure 15-1 is a presentation of the various failure mechanisms that have been identified for the nickel electrode. The nickel sinter is involved in all these failure modes. The first one, chemical attack by carbonate, nitrate or other electrolyte components, involves corrosion of the nickel sinters. The second is the physical mode, which involves swelling of the electrode, and physical shifting of the sinter in the electrodes. The third is the mechanical failure mode, and is due to fatigue (the increase in volume of the nickel hydroxide as it charges and discharges), or to the oxygen pressure that causes deformation or fracture of the sinter. The important point is that all these involve the sinter in the electrode. Therefore, if we are able to understand what happens to the sinter, we may be able to understand how long the electrode is likely to last. What we have tried to do is literally to look at the sinter as the electrode is cycled. I am going to show a very preliminary study of that sort.

(Figure 15-2)

Figure 15-2 shows a GE sinter made by the conventional slurry technique. Figure 15-2(a) is a picture at low magnification; Figure 15-2(b) is at a magnification of x5000. This is the magnification at which most of the pictures have been taken. One can see that the sinter as prepared is a conglomeration of round particles. Figure 15-2(c) shows the same sinter after exposure to solution. We have removed the active material from a nickel electrode by dissolving the electrode, or a 1 inch disc from it, in a solution of EDTA in ammonia. This shows that when the sinter is dissolved it is not attacked by the solution. This was confirmed by weight loss measurements. One can see on the picture that there is no attack of the sinter as such. Therefore, the technique used to look at the sinter does not affect the sinter in any way. Figure 15-2(d) shows the same sinter, after being wet oxidized at 350 C for 20 minutes. This is a step used in the electrochemical deposition of nickel hydroxide as a measure to prevent corrosion. Again, this sinter looks quite similar to the untreated one above. There is no further sintering, reshaping or structuring of the sinter in this oxidation step.

(Figure 15-3)

Figure 15-3 shows commercial electrochemically deposited electrodes. We removed the active material and now we are just looking at the sinter. It looks quite similar to those shown in Figure 15-2. There is no damage. Nothing has happened. Figure 15-3(b) shows the same electrodes after 270 cycles at room temperature in a flooded cell in 30% KOH. Again, the sinter looks quite the same. This indicates that the prepassivation step, the oxidation step, was used to form the passifer which prevents the corrosion of the sinter. Thus, as this as-received sinter electrode is cycled, it is not damaged. This is very important but nothing new. What is important is that there is no control on this corrosion, which leads to a variation of corrosion from one lot to the other.

(Figure 15-4)

From Figure 15-4 you can see that the lot 12 sinter seems to be the closest to the starting sinter, and the lot 19 is the most damaged sinter. Lots 17 and 18 fall in between them.

(Figure 15-5)

The same is true after 66 cycles at the C rate at room temperature in a flooded cell: the lot 12 sinter is still quite similar to the starting sinter, while lot 19 shows many joints that have been broken over. Again, lots 17 and 18 fall somewhere in between. Thus, by looking at the sinters, one can see which are stronger. In this case, lot 12 is the strongest, and lot 19 the weakest. If the growth or destruction of these electrodes are dependent on the strength of the sinter, the life of the electrode may be assessed by looking at the sinter.

(Figure 15-6)

Bernhart and Maurer have also run growth studies on these, again cycling them at the C rate at room temperature in flooded 30% KOH. The growth rate of lot 19 is the highest, that of lot 12 is the lowest, and lots 17 and 18 fall in between. This is consistent with saying where the strength of the sinter lies. Hence, there seems to be a qualitative comparison between the strength of the sinter and the growth rate observed in these electrodes.

(Table 15-1)

To get a more quantitative idea of the destruction of the electrode we measured the resistance of the sinter after removal of the active material. The GE sinter has a resistivity of 110, whatever that related number means. Then lots 12, 17, 18, 19 have values of 212, 187, 226 and 215 respectively. The R, the change in resistance due to corrosion and bond breaking, is almost 100% for chemically deposited electrodes, while for the electrochemically deposited electrode it is very small, which is again consistent with corrosion occurring during the impregnation step of these electrodes.

On cycling these electrodes for 100 cycles, there is a slight increase in the resistance. Again, lot 12 and lot 18 have values of about 16. Lot 19, which is the weakest, has attained a resistance of about 51. Thus, a semiquantitative idea of the mechanism of destruction of the sinter and the life of this electrode is possible.

(Figure 15-7)

Figure 15-7 shows electrode plates taken from real cells that have been cycled. Lot 12 was cycled rapidly for about 8000 cycles; the plate looks the same as before cycling. Lot 19 was run through high-temperature overcharge and rapid cycling. This is an accelerated test, which is equivalent to about eight equivalent seasons of orbital cycling. All the active material and the sinter have just fallen off, leaving only the screen.

We then decided to look at the sinter of these small chunks on the plate. These batteries had nylon separators.

(Figure 15-8)

The sinter in the lot 12 plate from the cell seems to be damaged, but it is still there. Most of the sinter in the lot 19 plate has disappeared, just as the active material. The most interesting thing was the etching of the sinter on the boundaries. That intrigued us because it was different from normal corrosion, which is seen during the impregnation process where the whole material simply dissolves. Here, there seems to be preferential attack at the sinter bonds. It is quite different. The third cell (c) is also made with electro-deposited electrodes. Again, in these cells with nylon separators, the sinter in the electrochemical electrode is also being destroyed. There is slight etching, but much less pronounced.

It therefore seems that cells with nylon separators attack the sinter preferably at the grain boundaries. To check that, we ran lot 19 electrode in 30% KOH for about 292 cycles.

(Figure 15-9)

Although the sinter is corroded, it looks very similar to the impregnated sinter. The bonds are broken up all over the place. There is no obvious preferential attack, simply a general destruction of the sinter.

However, when we cycled a lot 12 electrode in a solution of 3.5M KOH and 1.8M K_2CO_3 etching occurs at the grain boundaries, and is very similar to the etching observed in the sinter from real batteries that were run under accelerated tests.

Thus it seems that carbonate seems to form this preferential attack. It is well known that carbonate corrodes the nickel in these cells. However, it is significant that the attack is preferential. This can be more harmful because it tends to break the sinter bond faster. Again, Maurer and Bernhart have shown that the rate for electrodes cycled in carbonate solutions is an order of magnitude greater than for KOH.

In the cells, of course, nylon degradation occurs, and one of the products of this decomposition is carbonate. This shows that the carbonate is causing this damage. However, it also produces nitrate and ammonia, and these could affect this kind of attack, too.

To summarize: in the electrochemical process, the sinter remains unchanged during the impregnation process. It is relatively strong. However, in a chemical deposition there is tremendous uncontrolled corrosion, which leads to a weak sinter. This also causes lot-to-lot variation. During cycling, the sinter is damaged, the bonds are being broken, and, if there are impurities like carbonates present in the electrolyte, they tend to attack the sinter preferentially, leading to a faster breakdown of the sinter bonds, higher growth rates and a low life for the electrodes. Finally, it is possible that the resistivity measurement of the sinter could lead to a better understanding of the attack on the sinter as the electrode is being cycled.

DISCUSSION

DUNLOP: Do you have any explanation of the carbonate attack on the nickel sinter and the preferential attack?

VYAS: We are investigating this preferential attack, but I can report nothing at present.

LEAR: You have said that nylon accelerates the failure rate. Would you like to expand on that?

VYAS: I showed pictures of the sinter that was preferentially attacked in these plates.

(Figure 15-8)

Figure 15-8 showed preferential attack of the sinter bonds, and these cells had nylon separators. It is also known that the nylon separator decomposes to carbonate, and carbonate causes such preferential attack. Therefore, one could conclude that the nylon separator may cause the preferential attack.

These are accelerated tests, where a high-temperature overcharge is given to the battery, and then rapid cycling is carried out as a means of accelerating what would happen in a real life orbital test.

LIM: Could you comment on how you take the active material out, and the possibility of the nickel sinter dissolution during that process?

VYAS: We take a lin disc, dissolve it in hot solution of 4 mg EDTA, 10ml ammonium hydroxide and 60ml water, and leave it for a couple of hours. That removes all the active material. We have checked this by weight loss: we have left the sample overnight, and there is no change in weight. And we looked SDM and the sinter looks the same. Thus we have confirmed that that does not attack the sinter very much.

HENDEE: I think you said that you were only looking at the very outside of the plaque. Have you looked to see if this corrosion starts at the outside and works inward through to the substrate during cycling?

VYAS: It happens all over. We mainly investigated the surface of the electrode after we dissolved it, but we have broken some up and tried to look on the inside. For instance, this lot 19 is corroded all the way down to the substrate. We could not see any corrosion of the substrate as such.

HENDEE: Are you saying that it corrodes evenly throughout with time?

VYAS: No. I am saying that the corrosion is uniform over the complete surface of the sinter at any given time.

HENDEE: It is not uniform from surface down through to the substrate?

VYAS: No, it does not seem to start at the surface and then keep going in. However, this is only a preliminary investigation of the sinter. In cycling, the breaking of the bonds may be preferential.

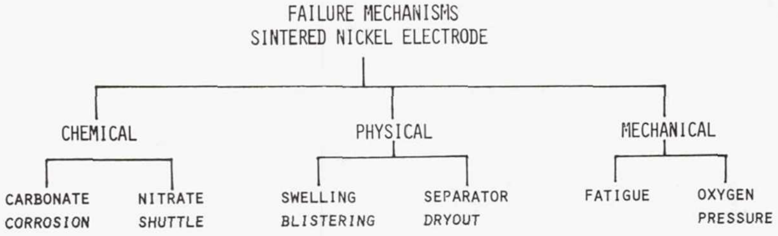


Figure 15-1

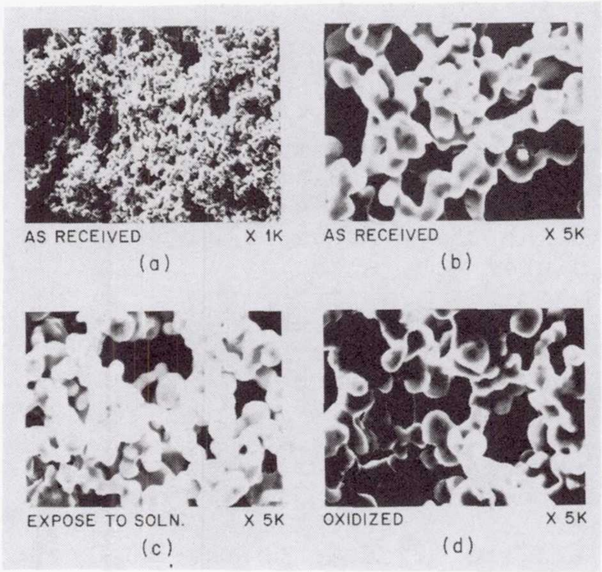


Figure 15-2

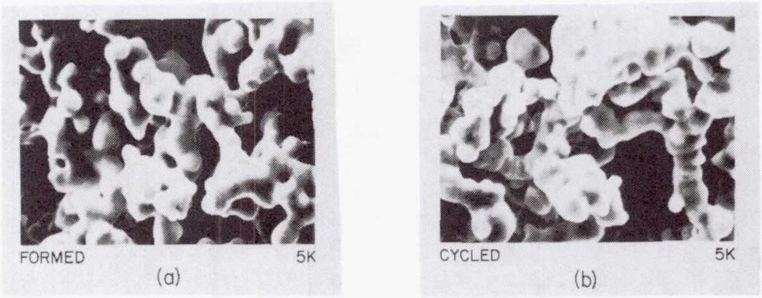


Figure 15-3

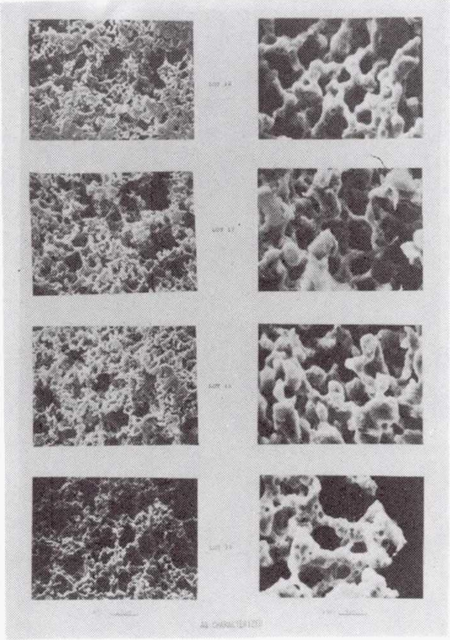


Figure 15-4

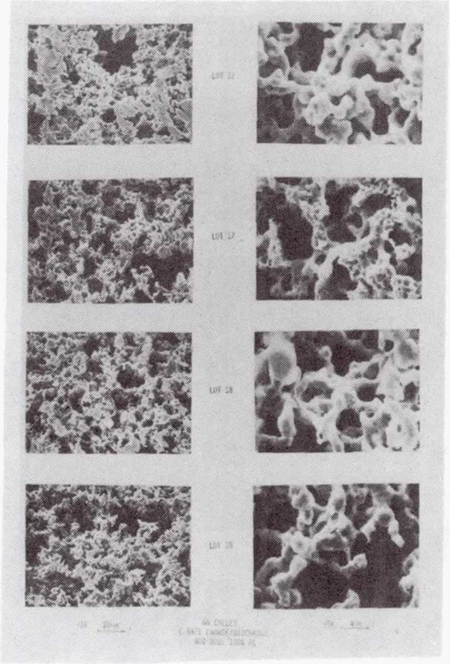


Figure 15-5

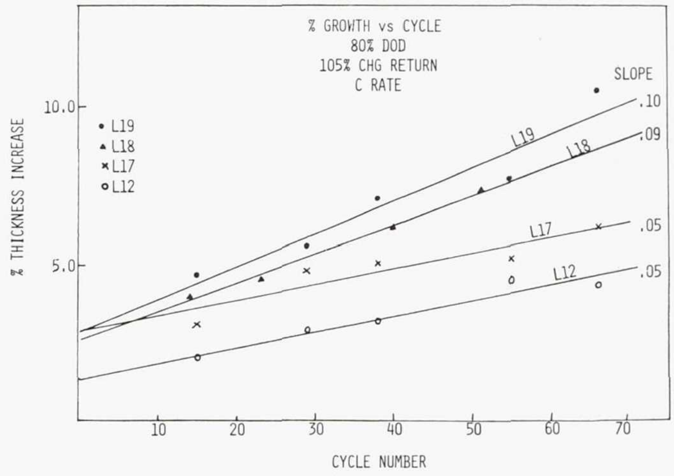


Figure 15-6

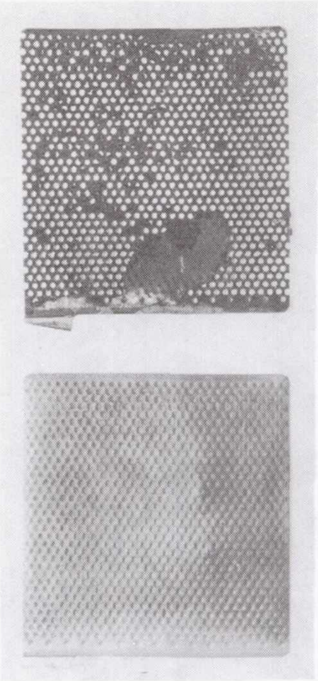


Figure 15-7

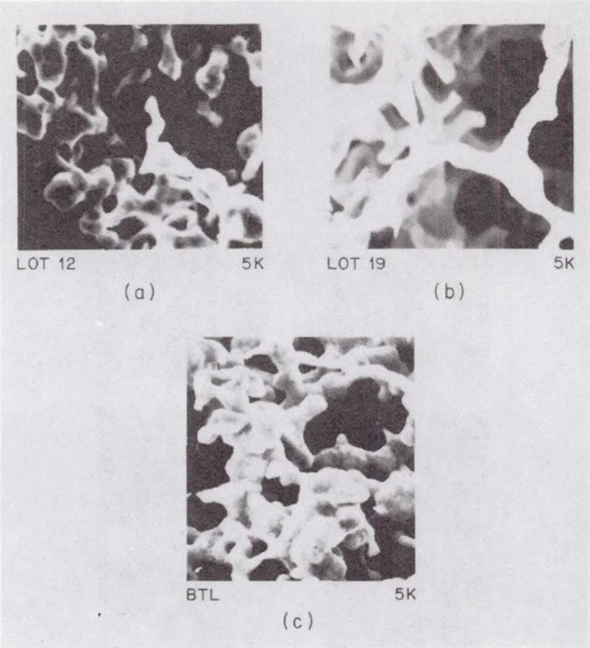


Figure 15-8

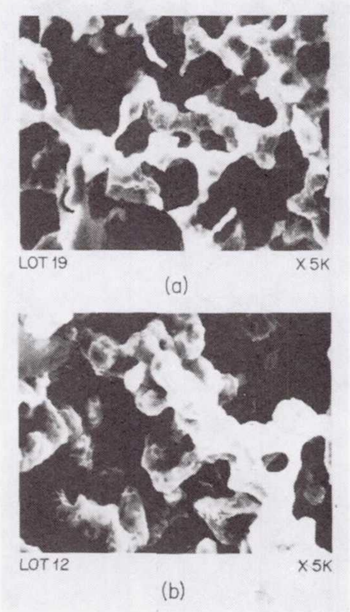


Figure 15-9

CHANGE IN APPARENT RESISTIVITY AND THICKNESS OF NICKEL SINTER UPON IMPREGNATION AND CYCLING

	THICKNESS			RESISTANCE			
				IMPREGNATION		100 CYCLES	
	t_i (in)	T_f (in)	Δt $(in \times 10^4)$	Ri $(\Omega-cm)\times10^6$	ΔR_{imp} $(\Omega-cm)\times10^6$	Rcy $(\Omega-cm)\times10^6$	ΔR_{cy} $(\Omega-cm)\times10^6$
G. E. Sinter	0.0285			110			
L 12-60 X	0.0308	0.0314	6.0	211	101	226	16
L 17-50 XX	0.0297	0.0302	5.0	187	77	214	27
L 18-50 IV	0.0291	0.0294	3.0	226	116	242	16
L 19-67 IV	0.0293	0.0316	23.0	215	105	266	51
BTL*	0.0291	0.0289		133	23	146	14

---

*10c rate charge/discharge for 192 cycles.

Table 15-1

INITIAL CAPACITY CONDITIONING ON ELECTROCHEMICAL NICKEL HYDROXIDE ELECTRODES

D. Fritts
Air Force Aeropropulsion Laboratories

I should like to discuss what might be causing the initial capacity build that is frequently observed with electrochemically impregnated plates.

(Figure 16-1)

The problem is that we really do not know the final capacity of a given electrode until after 40 or 50 cycles. This, in turn, can cause capacity imbalances between the plates within the cell, and between the cells. The causes are not known at present. The purpose of this investigation is to clarify the situation.

I should like to introduce some new terms that are used by electrochemists. For these terms, conditioning is defined as the initial cycling where cell capacity is usually unstable.

C is the capacity obtained during discharge of an electrode from fully charged to 0.4V.

C_T is the theoretical capacity based on weight gain after formation cycling.

is the total electrode strain or mechanical strain during discharge.

$_T$ is the theoretical strain for a fully conditioned electrode; it is based on empirical data.

C/C_T is the utilization fraction of active material.

$/_T$ is the strain observed during conditioning of the cell divided by the strain expected for the fully conditioned electrode. $/_T = 1$ for no mechanical conditioning.

The experimental approach that we took was as follows. First, we fabricated gridless electrodes (no current collector). The reason for this was to ensure mechanical homogeneity, so that a strain measured in one direction would be typical of a strain measured in the other directions.

(Figure 16-2)

Another parameter that was measured, which is a little out of the ordinary, was the plaque hardness. Figure 16-2 shows our hardness tester. Here is the half-inch diameter ball I was talking about. The plaque is slipped under there. Effectively this weight then drops on to this balance arm, putting on 100g tear load. This weight then follows putting on a 400g test load. This LVDT is used then to measure the displacement into the plaque. The LDVT will essentially measure about 10^{-6}in displacement, which is much more sensitive than necessary for the depressions that we observed, which are about 2×10^{-3}in. The apparatus is shown in Figure 16-2. Essentially, we took a half-inch diameter ball and compressed it into the plaque, and took the hardness as being the inverse of the distance that the ball sunk into the plaque.

The next thing we did was to electrochemically impregnate these plaques by using the Pickette process. We used 50% ethanol solution, pH 3.5, with 10% cobalt nitrate added to the impregnated solution.

We used the cycling regime from 25% overcharge to 100% depth of discharge. This was based on the theoretical capacity, based on weight gain. The 100% depth of discharge is based on a voltage of 0.4 versus the cadmium electrode. We measured some of the obvious parameters: the cell current, so that we could determine our amp hours; the voltage of the nickel electrode versus the cadmium third electrode, so that we could make sure that we are nickel limited; and the electrode growth in situ.

(Figure 16-3)

The in situ growth measurements were accomplished by this sort of situation. Figure 16-3 shows the gridless plaque, with a tab weld at the top. The tab is fixed to the cell case, and that essentially becomes our fixed plane for all our measurements. From the bottom of the plaque is the ferrite core from an LVDT suspended from that. The differential transformer is set outside the cell, and it indeed picks up where that core is. Again, the maximum sensitivity of a strain measurement is 3×10^{-7}, about two orders of magnitude greater than necessary.

(Figure 16-4)

A characteristic strain behavior of the gridless electrode is shown in Figure 16-4. The troughs represent shrinkage of the electrode, and the peaks represent growth. Therefore, the electrode does shrink on charge. Essentially, the 100% charge point is in here, indicating that there is some growth on overcharge. We then go to the start to discharge. It will stay flat. This varies from electrode to electrode. It may stay flat out here until about 40%. Then relatively dramatic growth occurs, and then charge process is started again, and the electrode shrinks. The properties for this particular electrode are: thickness = 1 mm, loading = 1.47 g/cm^3 void, plaque hardness = 34.8, plaque porosity = 83%.

(Figure 16-5)

What was the importance of the hardness parameter that I put there before?

The ordinate shows the strain, and the abscissa the capacity. Those have been removed from the electrode. That is the strain on discharge. This is the discharge portion of the cycle. Those are the data that we obtained. They are basically linear. Thus, our empirical fit to that data, $_T$, is shown by the dashed lines. This is for the fully-conditioned electrode, by the way, and not in the conditioning part of the process.

(Figure 16-6)

Figure 16-6 essentially shows an electrode that is conditioning. The left-hand ordinate is effectively the mechanical conditioning parameter, and the right-hand ordinate is the utilization. Hence, both of these things are conditioning simultaneously. In fact, the mechanical conditioning seems to be rather more dramatic than the electrochemical conditioning. However, the most important point here is that they both stabilize at the same time. If I had plotted this for about 100 cycles, those lines would be parallel all the way out.

(Figure 16-7)

I have three more figures, sililar to this, just to show that this sort of mechanical conditioning behavior is repeatable and that they both end up going parallel about the same time; or, at least, that the capacity becomes stable.

(Figure 16-8)

(Figure 16-9)

We get the same sort of a thing, and so we end up in this continuous capacity mechanical conditioning.

I should like to make another comment here. These are gridless plaques, and the effect is much more dramatic when a grid is present, because it adds to additional mechanical rigidity and the electrochemical conditioning is a slower process under those circumstances. I have not shown that here because I have no data to give you E_T for this situation, and so I could not plot E_T.

(Figure 16-10)

Now, taking this knowledge and putting together a kind of logic chart, we arrive at Figure 16-10: what we have observed, why we think we observe it and what sort of conclusions we can arrive at.

The rigid plaque has greater strain per amp hour. We saw that the harder the plaque, the greater is the strain for the amount of capacity obtained from it. This effectively says the amount of mechanical work done by the active material is related to the amp hours we get out and to the rigidity of plaque.

The second conclusion is that the rigid plaque has poor utilization. This can be seen by looking at Figures 16-6 to 16-9. Effectively, more mechancial work is required per amp hour in the rigid plaque. This is not to imply that this rigid plaque is absorbing that much mechanical work out of the essentially electrochemical charging process. I believe that the rigid plaque is essentially limiting the amount of molar volume change that the nickel hydroxide can go through, essentially shutting down the discharge in a mechanical fashion.

The third conclusion is that the electrodes mechanically condition. That was fairly obvious in the data that show that active material is doing work on the plaque via molar volume.

The fourth conclusion, probably the most important, is that these two utilization parameters stabilize together. This implies for a given cycling limits, essentially, puts less strain on the plaque and you could not see any dramatic growth on the electrode.

DISCUSSION

DYER: Do you see a correlation at lower loading levels between the strain and the capacity?

FRITTS: Yes. I'll go back to this one chart.

Each of the lines on Figure 16-5 were essentially six different electrodes made out of one plaque sample, and each one was loaded to a different level so that each point here represents a full 100% depth of discharge.

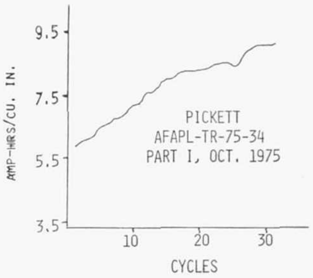
HALPERT: Can you give us one more definition of rigid plaque with limits in terms of hardness and so on?

FRITTS: The plaques that I have shown here are effectively very rigid in terms of what we see commercially. These plaques were fabricated in house. Typical commercial plaque has a hardness, as I have defined here, that runs from about 24 to about 35. These are at the very upper end of the scale.

INITIAL CAPACITY CONDITIONING OF
ELECTROCHEMICAL $Ni(OH)_2$ ELECTRODES

PROBLEM

- INITIAL CAPACITY BUILD FREQUENTLY OBSERVED.
- ACTUAL FINAL CAPACITY OF ELECTRODE NOT PREDICTABLE.
- CAUSES CAPACITY IMBALANCE BETWEEN PLATES IN CELLS AND BETWEEN CELLS.
- CAUSES OF CONDITIONING NOT FULLY EXPLORED.



PICKETT
AFAPL-TR-75-34
PART I, OCT. 1975

PURPOSE

INVESTIGATE MECHANISM OF INITIAL CAPACITY CONDITIONING

Figure 16-1

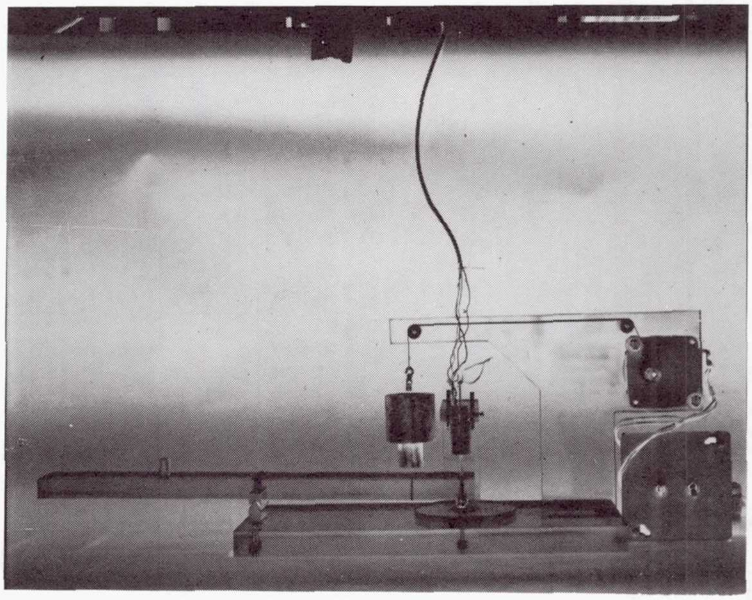


Figure 16-2

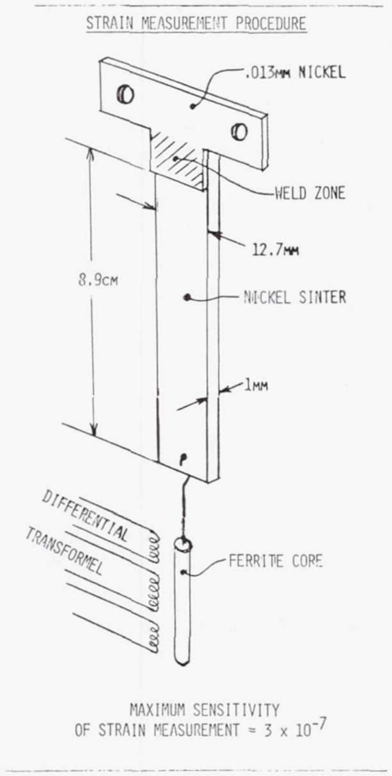
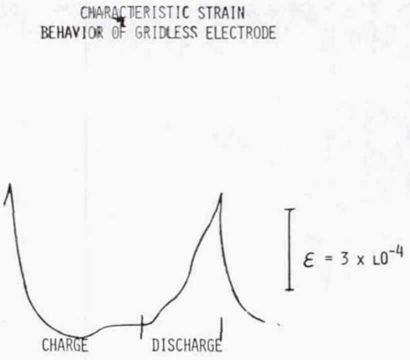


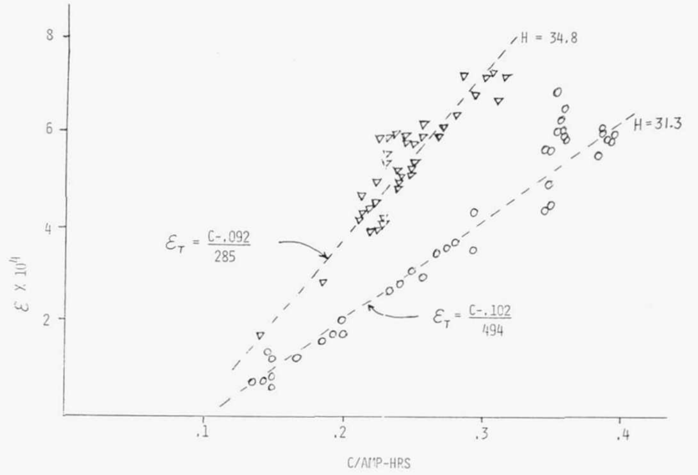
Figure 16-3



ELECTRODE PROPERTIES

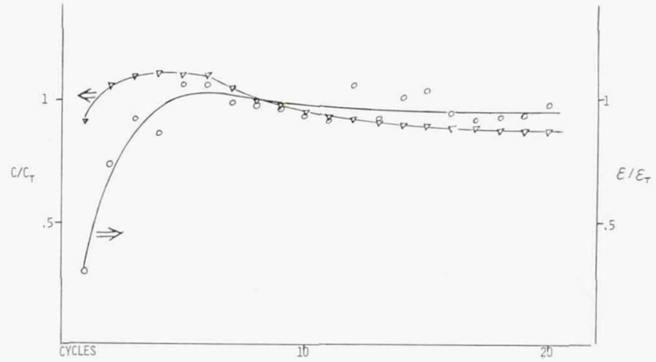
THICKNESS	1MM
LOADING	1.47 GMS/cc VOID
PLAQUE HARDNESS	34.8
PLAQUE POROSITY	83%

Figure 16-4



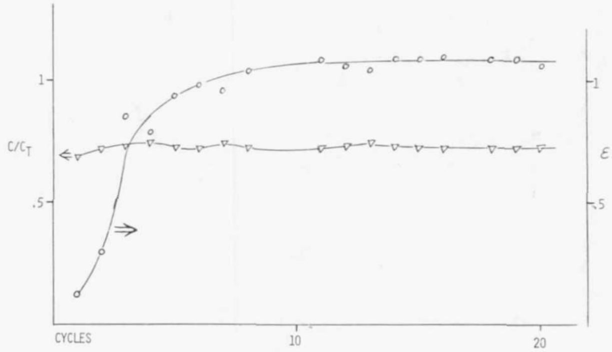
ELECTRODE STRAIN DUE TO DISCHARGE VS. CAPACITY FOR FULLY CONDITIONED GRIDLESS ELECTRODES

Figure 16-5



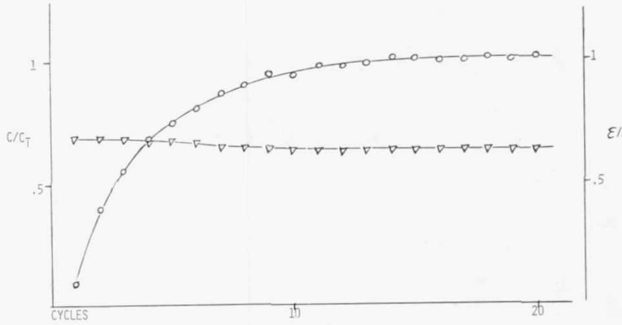
CHARACTERISTIC CAPACITY AND STRAIN CONDITIONING
ELECTRODE NO. 1, H = 31.3, L = 1.2 GMS/CC VOID

Figure 16-6



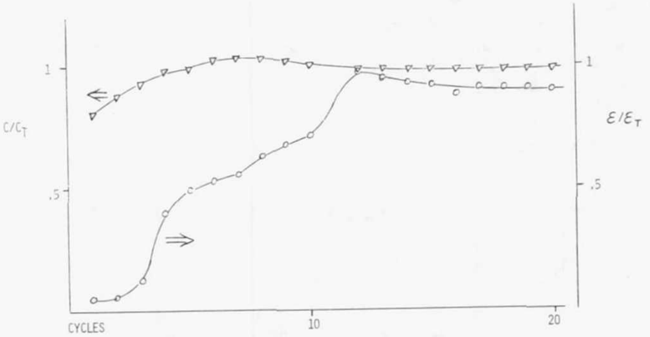
CHARACTERISTIC CAPACITY AND STRAIN CONDITIONING
ELECTRODE #2, H = 34.8, L = 1.23 GMS/CC VOID

Figure 16-7



CHARACTERISTIC CAPACITY AND STRAIN CONDITIONING
ELECTRODE #3, H = 34.8, L = 1.47 GMS/CC VOID

Figure 16-8



CHARACTERISTIC CAPACITY AND STRAIN CONDITIONING
ELECTRODE #4, H = 34.8, L = 1,34 GMS/CC VOID

Figure 16-9

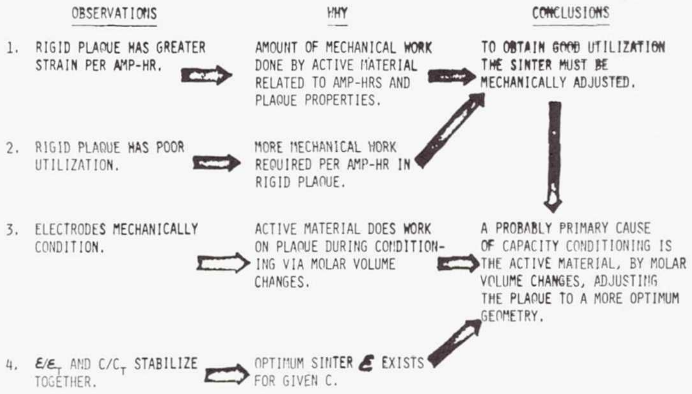

OBSERVATIONS
WHY
CONCLUSIONS
1. RIGID PLAQUE HAS GREATER STRAIN PER AMP-HR.
AMOUNT OF MECHANICAL WORK DONE BY ACTIVE MATERIAL RELATED TO AMP-HRS AND PLAQUE PROPERTIES.
TO OBTAIN GOOD UTILIZATION THE SINTER MUST BE MECHANICALLY ADJUSTED.
2. RIGID PLAQUE HAS POOR UTILIZATION.
MORE MECHANICAL WORK REQUIRED PER AMP-HR IN RIGID PLAQUE.
3. ELECTRODES MECHANICALLY CONDITION.
ACTIVE MATERIAL DOES WORK ON PLAQUE DURING CONDITIONING VIA MOLAR VOLUME CHANGES.
A PROBABLY PRIMARY CAUSE OF CAPACITY CONDITIONING IS THE ACTIVE MATERIAL, BY MOLAR VOLUME CHANGES, ADJUSTING THE PLAQUE TO A MORE OPTIMUM GEOMETRY.
4. $\mathcal{E}/\mathcal{E}_T$ AND C/C_T STABILIZE TOGETHER.
OPTIMUM SINTER $\mathcal{E}$ EXISTS FOR GIVEN C.

Figure 16-10

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EXPANSION OF THE NICKEL ELECTRODE

H. Lim
Hughes Aircraft

Before going into the details of nickel electrode expansion studies, I should like to tell you briefly about our program. We have an ongoing program, the battery study. Its objective is to understand the failure mechanism of nickel cadmium and nickel hydrogen batteries. The program started around 1974, and we thought the weakest component of the nickel cadmium battery at that time was the nylon separator. Therefore, we started a study of the stability of the nylon separator, and we found that the separator is not stable. The next phase of the program was to develop a stable separator for nickel cadmium and nickel hydrogen batteries. We developed several new separators that are stable in KOH electrolyte. One of our colleagues, Scott Verzwyvelt, will describe one of the separators later this morning.

The next problem is the cell failure mechanism in the nickel electrode area. My talk describes a part of the nickel electrode studies; the program is still in progress.

One of the difficulties in studying nickel electrode expansion studies is the timescale. As you know, to observe a reasonable amount of expansion, we need months or years in actual batteries. Therefore, we devised the technique of what we call the electrode bending experiment, which is shown in Figure 17-1.

(Figure 17-1)

We have a flooded plexiglass cell with a sample electrode. This is a GE foil substrate. Active material is taken off the sample electrode on one side, and left only on the other side with a cadmium counter electrode.

With this configuration, if the active material expands, the electrode will bend convex -- concave towards this direction. This very small bending may be easily detected with light deflection. In this case we used a laser beam to project it on the screen through a mirror attached on the electrode. We can thus make a very sensitive measurement of a very small expansion. The electrode sample we used is a standard GE chemically impregnated electrode. We used 23.7% KOH solution.

(Figure 17-2)

When we look at the single charge-discharge behavior, we found that during the charge, the active material contracts from the fully discharged electrode as shown in Figure 17-2; this is slightly different from that shown by Mr. Fritts. We did not observe a bump here. My guess is that owing to the electrolyte concentration difference, we used 23.7% by accident; we intended to use 31%, but when we proceeded with half of the experiment, we found out there was some calculation mistake, and so we just proceeded with 23.7% solution. We are intending to study a concentration effect. During discharge, the electrode expands.

(Figure 17-3)

When we look at the continuous cycle behavior (Figure 17-3), the end of charge deflection was almost the same for each cycle, but the end of discharge deflection is continually changing. We expect that during charge and discharge the amplitude should remain the same, but because during the shrinkage the plaque resistance may not go down fully, it only shows up on the discharge end.

When we plotted this discharge deflection versus a number of cycles on a log scale, we found a good linear relationship. When we discard the data points, roughly below 20 cycles, the linear correlation function is better than 0.99 for all these curves at the various depths of discharge.

(Figure 17-4)

When we plotted the bending against the number of cycles, we defined the slope of this curve as a rate of bending (Figure 17-4).

(Figure 17-5)

When we plotted the rate of bending against the depth of discharge on a log/log scale(Figure 17-5), we found a good linear relationship, with a slope of 2.2. We have no explanation for the 2.2, but what is important is the linear relationship between this bending rate and the depth of discharge. Therefore, when we know the rate of bending at one depth of discharge, we shall be able to extrapolate to find the bending rate at another depth of discharge. Also, all these experiments take only about a week instead of months or years in the actual battery observation.

I shall just mention a little of our speculation about the mechanism of the electrode expansion.

(Figure 17-6)

We are speculating about two different expansion mechanisms. One is the oxygen bubble pressure. When an oxygen bubble forms inside a capillary in the active material, the maximum bubble pressure difference is dependent on the radius of the capillary. It is therefore possible, if the maximum pressure is really obtainable in the battery, to get $1.7\text{-}6.9 \times 10^5 N/m^2$ (25-100 psi) or greater. However, if the oxygen bubble pressure increases, the solubility of oxygen in the KOH is growing, and if the solubility goes up, the rate of diffusion from the bubble to the outside will be high. We are fairly sure this kind of pressure is not reached, actually observed in the battery. But this kind of mechanism is not totally ruled out at this point.

(Figure 17-7)

Another speculated mechanism is the density change. It is reported that the density of active material in the charge state is 4.6, and in the discharge state is 4.16. Hence, there is a sizable density change during charge and discharge. If the active materials shrink and expand reversibly, you would expect the permanent expansion of the active material. However, there is at least one mechanism you can think of.

Figure 17-7 shows the nickel sinter and is a mass of active material. That is not a single crystal, but a polycrystalline structure. During charge, if the active material particles shrink and one of the particles changes configuration from this position sideways, the next time it expands one of the particles has to move out of the plane. Because of the resistance of the sinter, the weakest point to move out is in the direction A, and it will expand there. At this point, we think this is the most likely mechanism.

DISCUSSION

FOUGERE: You have talked about expansion during charge and discharge. Are you considering overcharge?

LIM: Yes, but not in this case. We do not have the data on overcharge in the figures. We are planning to do some experiments to find out the effect of overcharge. We should like to vary only the overcharge portion, leaving the other part constant. However, we have not yet reached that point.

SEIGER: The gas bubbles that are coming off the electrode towards the end of charge, are they uniform, or do they come off from discrete points?

LIM: Visually they are coming out from almost everywhere in the electrode in that geometry. However, with the electrode that has active material on both sides, initially the bubble comes from the front side, which is facing the counterelectrode, and starts from the rear side. I think the front side is always heavier.

Other than that, we observed no other spatial distribution. That is just a visual observation.

MAURER: We found the lot-to-lot variation on the growth rate is much larger than what you find from even the depth of discharge. Have you started to look at that variation to see which of these parameters change, whether it is the slope of that line of rate of bending versus depth that changes, or some other part of it?

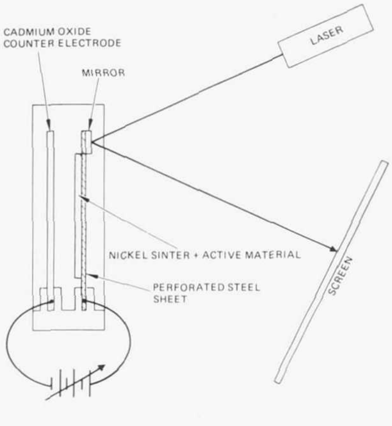
LIM: I am aware of that problem. We are trying to avoid it by staying in the same lot. All these electrodes are from the same lot, but this is not the same lot or same electrode. As you can see, we can count 14 data points. Some of the points are from the same electrode. We took out the same specimen. We can make four specimens from one electrode. These are thus not from the same electrode. However, the linear correlation function we have here is better than 0.99. Therefore, we do not have electrode-to-electrode variation. This is a rather surprising linearity, but we do not have lot-to-lot variation data here.

RITTERMAN: I should like to point out that if you have a lot-to-lot plot, the sensitivity to that is somewhat limited, regarding your statement about linearity.

LIM: We did not analyze mathematically what the variation means. However, looking at Figure 17-5, the mathematical arm of that is exactly in the same form of Pat McDermott's analysis for DOD dependence. This is an exponential DOD. Therefore, we were trying to fit in that form -- or log versus linear -- but it came out linear to about this point. However, for the higher depth of discharge area it did not fit. This log/log scale fits much better.

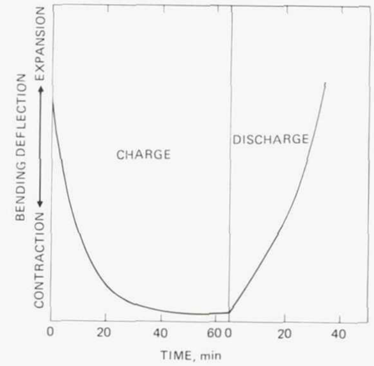
ROGERS: I wonder whether in the relationship of voltage to pressure, the overvoltage required would cause the oxygen to be generated at the surface instead of inside a small core, because the voltage would be around 60, 70mV for the high pressure you suggested, which is unlikely to occur deep down inside an electrode when the surface is available for oxygen generation.

LIM: Certainly that plays a role in reaching the equilibrium pressure. I think that is probably one of the reasons why the equilibrium pressure does not reach, what's close to equilibrium pressure. I think you are absolutely right that the oxygen evolution is concentrated at the surface because of the ohmic drop in the latest state of charge.



APPARATUS FOR ELECTRODE BENDING EXPERIMENTS

Figure 17-1



BENDING DEFLECTIONS DURING A SINGLE CYCLE (ACTIVE MASS ON ONE SIDE; C–RATE)

Figure 17-2

BENDING DEFLECTIONS FROM CONTINUOUS CYCLING (C RATE; 18.3% DOD)

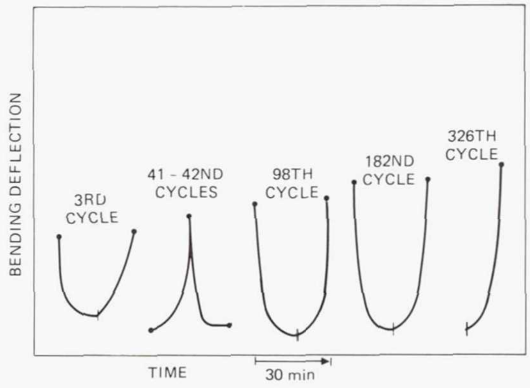


Figure 17-3

CORRELATION OF ELECTRODE BENDING VS DOD

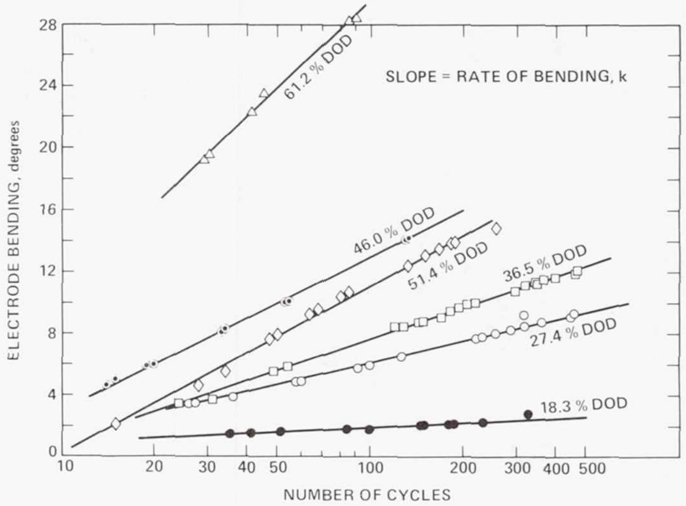
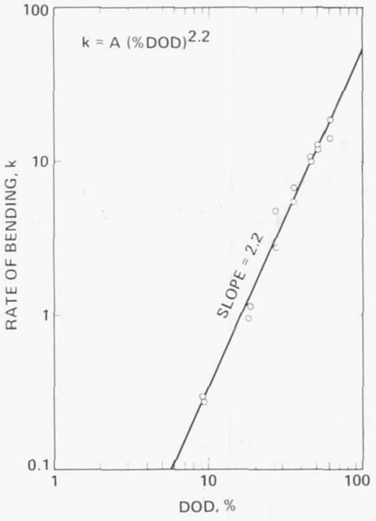


Figure 17-4



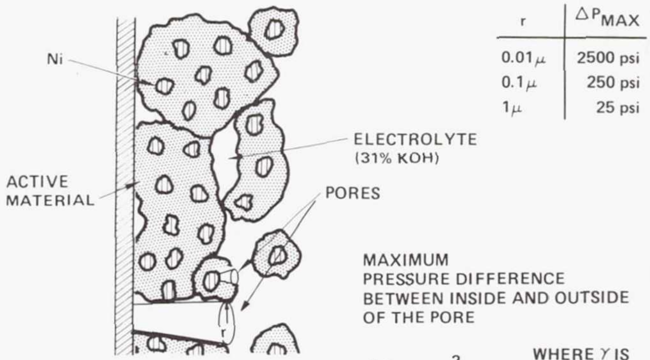
ELECTRODE BENDING RATES AT VARIOUS DOD

Figure 17-5

O_2 BUBBLE PRESSURE MODEL

ASSUME γ = 87 DYNES/CM AT 25°C

r	ΔP_{MAX}
0.01μ	2500 psi
0.1μ	250 psi
1μ	25 psi

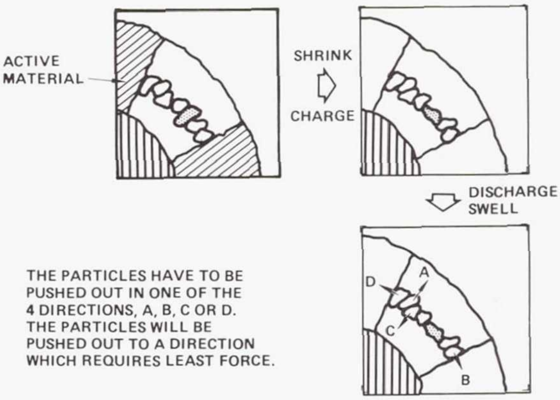


MAXIMUM PRESSURE DIFFERENCE BETWEEN INSIDE AND OUTSIDE OF THE PORE

$\Delta P_{MAX} = \frac{2}{r} \gamma$ WHERE γ IS SURFACE TENSION OF ELECTROLYTE

Figure 17-6

A POSSIBLE MECHANISM OF ELECTRODE EXPANSION BY DENSITY CHANGE



THE PARTICLES HAVE TO BE PUSHED OUT IN ONE OF THE 4 DIRECTIONS, A, B, C OR D. THE PARTICLES WILL BE PUSHED OUT TO A DIRECTION WHICH REQUIRES LEAST FORCE.

Figure 17-7

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THE CMG NICKEL ELECTRODE

R.A. DePaul and I. Gutridge
MPD Corporation

I should like to introduce, to those of you who are not already aware of it, a new nickel electrode called the Controlled Microgeometry (CMG) electrode. It is a product of battery research at Inco's European Research and Development Center in Brimingham, UK. It has been developed to the stage of small scale production and, since early this year, has been commercially available from MPD Technololgy both in Europe and the U.S. MPD Technology is the company set up by Inco to commercialize new products resulting from research and development.

In this presentation I first want to describe the concept of the CMG electrode and its advantages over the more conventional type of electrode, and then to present some results that we have achieved with CMG electrodes in nickel cadmium cells.

(Figure 18-1)

Figure 18-1 shows diagramatically the construction of the CMG electrode. The basic element is very thin perforated nickel foil. The perforations in the foil are both accurate and regular. Each foil is coated either on one side or both sides with a layer of nickel hydroxide active material, leaving the holes clear. An electrode is produced by stacking foils together, usually 20-100 foils, so that all the small holes are in register. There is thus a sandwich-like construction of foil/active mass/foil, with cylindrical channels passing through the electrodes.

The next two figures show actual electrodes.

(Figure 18-2)

Figure 18-2 shows an ordinary view of a CHG electrode.

(Figure 18-3)

Figure 18-3 shows an expanded view. There are two different patterns of holes; their significance will appear later.

It is important to get a feel for some of the numbers involved. Typical values for the critical dimensions of the electrode are as follows: the foil thickness is about 4 m; the active mass thickness is 60 m, about 15 times the foil thickness; the hole diameter is about 0.5mm, the edge-to-edge hole spacing is about 0.75mm; the average perforated area is 15%, and the electrode thickness ia about 3mm.

(Table 18-1)

Table 18-1 shows the characteristics of a typical electrode that we are currently producing. The important thing to note is the ratio of active mass to foil, which is something over 2.5:1.

One advantage of such a construction that will have been obvious from Table 18-1 is a higher number of ampere hours per kilogram. A typical specific capacity for a CMG electrode is 190A h/kg and 350A h/l. The best figures obtained to date are 220A h/kg and 450A h/l. I think you will agree that 140A h/kg and 450A h/l would represent a fairly good sintered electrode. The main reason for this improvement is that we are using this very thin nickel foil substrate, which combines low weight with good strength and conductivity. Whereas a typical ratio for a medium loaded sintered electrode may be equal weights of active mass to support, we have a ratio of between 2:1 and 3:1.

The second advantage of this construction is really what led to the coining of the name "controlled microgeometry." All the parameters that control the performance of the electrode (the size of the holes, the distance between the holes, thickness of the foil, thickness of the active mass, the porosity and composition of the active mass) can be individually controlled over a wide range. Therefore, the electrode may be designed to give the optimum performance for a given duty cycle. The purpose of the design may be high energy density or high rate performance. To illustrate this, Figure 18-4 shows the effect of changing the pattern of holes.

(Figure 18-4)

Two 24A h electrodes are shown. In one, the area of holes is 13%. In the second it is 20%. When the electrodes are discharged at the C/5 rate, there is little difference between the two electrodes, as shown by curves 1 and 2. However, when the discharge rate is increased to the 2C rate, then the electrode with the finer 20% hole pattern shows a marked improvement both in capacity and discharge voltage.

Figure 18-4 just shows the effect of two different hole patterns. When you consider that we can vary the hole area from 5 to 45% and the hole diameter from 0.4 to 1mm, I think you will appreciate that we have scope to design for widely different discharge profiles. In fact, the examination and optimization of this aspect of electrode design is the subject of a Department of Energy contract that has recently been awarded to the Inco R&D center.

The third significant advantage of CMG electrodes is the ability to make them over a wide thickness range. Conventional electrodes are usually limited either by practical or by economic considerations to a thickness range of about 0.5-3 mm. CMG electrodes may be made by using just a few foils, or up to about 140 foils to give an electrode 6mm thick. We have an electrode that is 36mm thick, 15cm by 30cm, with a capacity of just over 100A h for a single electrode. Thick electrodes have obvious benefits for high energy density moderate rate batteries, whereas the ability to make an electrode, say, 0.2mm thick combined with optimization of hole pattern offers the scope for very high discharge rates, in the 100 C range.

So much for the idea. Does it work?

During the research and development work on this electrode, we have made and tested several thousand electrodes, and the properties I have quoted so far are based on test results of many hundreds of electrodes. However, tests on single electrodes are of limited interest, and so I should now like to show some results achieved in cells. I shall concentrate on nickel cadmium cells, since I believe they are of most interest to this audience; however, the electrodes can and are being used in both nickel iron and nickel zinc systems.

The next few figures show the results of laboratory tests in nickel cadmium cells using CMG nickel electrodes and commercially available sintered cadmium electrodes. These results were first published in a paper presented by Dr. Turner from the Inco Research Labs at the recent Power Sources Symposium in Brighton.

(Table 18-2)

Three cells were built, and the constructions are shown in Table 18-2. The CMG electrodes varied in thickness from 0.67mm to just under 2mm. The cadmium electrodes were either 0.6 or 0.8 mm thick, and we used a number of different separator systems and two electrolyte concentrations.

Figure 18-5 shows the first few cycles of these cells.

(Figure 18-5)

All three cells require about ten cycles to reach full capacity, but a substantial portion of the capacity is available after five cycles. Cell A stablized at 111% of theoretical capacity after 12 cycles. Cells B and C leveled out at about 90% of theoretical capacity after about 15 cycles. One of the differences between cell A and the other two is the electrolyte concentration, which was 30% in cell A and 20% in the other two. At cycle 26 in cell C, the electrolyte was changed to 30% KOH, and the capacity rose to 100% of theoretical.

The formation of these cells was done in excess electrolytes. The cells were cycled without a bottom on the case, in about 20 liters of electrolyte. After cycling in this way for about 50 cycles, the cells were removed from the tank and bottoms were fixed to them. The electrolyte volume was then 3-7cm^3 A h.

(Figure 18-6)

Figure 18-6 shows the next 40 cycles of cell A. Initially the cell showed a marked fall in capacity. This highlights an important factor in the use of CMG electrodes. It is necessary with these electrodes to provide sufficient support to the electrode to prevent swelling. For the first few cycles of this cell, the plastic cell case was unrestrained and the cell case wall bulged. At cycle 70 the cell was clamped back to its original dimensions and see the capacity recovered, showing that this loss was not permanent. It is therefore very important, in the design of cells using CMG electrodes, to ensure that sufficient pressure is exerted to maintain the electrodes within their original dimensions. This can be done by designing the cell and battery stack to be close packed and providing the necessary clamping from the battery box. Alternatively -- and clamping is not possible in all cells -- for a freestanding electrode, the separator and electrode may be stitched at regular intervals. A little energy density is lost, but for some applications this approach is most appropriate.

(Figure 18-7)

Figure 18-7 shows the performance of the cell at different discharge rates. At 50% of theoretical capacity (132A h) the cell voltage at 40A drain is 1.26V, falling to 1.21V for 160A drain. The delivered capacity at 40A was 220, falling to 200A h at 160A.

(Figure 18-8)

Figure 18-8 shows the charge acceptance of one of these cells. The upper curve shows the discharge capacity expressed in both ampere hours and ampere hours per kilogram versus the charge capacity. The lower curve shows charge capacity versus charge factor. To maintain a capacity of 120A h, a charge factor of 1.03 is necessary, whereas to maintain 140A h a charge factor of 1.16 is required. Conversely, if a specific battery application requires a maximum overcharge of, say, 10% then the design parameters for this cell should include the value of 155A h/kg for CMG nickel electrodes of this particular construction.

That is a quick survey of the sort of properties that we have achieved. I shall summarize them in the next two tables.

(Table 18-3)

Table 18-3 shows the electrode properties (a) in excess electrolytes, (b)when the electrolyte was restricted to 3 - 7 cm^3/Ah, and (c) after 300 deep discharge cycles (by which I mean 100% depth of discharge every cycle), after which the capacity of the nickel electrodes is 160A h/kg and 320A h/l.

(Table 18-4)

Utilization of the nickel hydroxide is 85 - 90% after deep cycling for nearly 300 cycles, as shown in Table 18-4.

I hope I have managed to arouse your interest in this electrode, and that you may see possible applications in the aerospace field.

DISCUSSION

SENDERAK: What are the maximum discharge rates that you can get out of this type of electrode?

GUTRIDGE: You can design this electrode for very high rate applications. The standard electrode that we make (15mm thick, 15 by 30), can easily be cycled between C/1 and C/3 rates. However, with a higher area of holes and the right hole pattern, you can make a thin electrode with fewer holes in it, which can be discharged at 15 - 100 C. Thus, you design to determine the internal resistance of the electrode, and you have control over all the critical numbers that you need to design to do that.

SENDERAK: Would you cycle these cells as vented or sealed?

GUTRIDGE: The results I just described were in vented cells.

LIM: I have a related question about the rate and the amount of the electrolyte. I am not sure whether I missed something. Can you comment about the amount of the electrolyte and the rate capability? I am asking the question because you have relatively large holes, and if you are running the cell in start the condition, there would be a rather thin electrolyte connection between the active material and the separator area.

GUTRIDGE: The numbers I gave were between 3 and 7cm^3/A h of electrolyte in these vented cells. As far as the discharge rate in these cells was concerned, we went to the 2 cm^3 rate, and we were already starting to have problems with the cadmium electrode. Therefore, we were restricted by that in the rates at which we could discharge the cells.

As far as the volume of electrolyte is concerned, the porosity of the active mass is quite high. We essentially have sufficient electrolyte within the confines of the electrode to discharge or to cycle this electrode at moderate rates.

ROGERS: Am I right in thinking that the active material is packed between the sheets?

GUTRIDGE: Yes.

ROGERS: In that case, as you mentioned, you get a pressure exerted during expansion of the active materials. What pressure are we talking about? Is it sufficient, for example, to flatten the usual polypropylene or felted nylon separator?

GUTRIDGE: Let me make a comment before I answer the question about expansion. We are not looking at something that will destroy the strucutre of the electrode. However, the problem you may get is the one you mentioned. If you do not restrict the dimensions, you can put pressure on other parts of the cell.

We defined a pressure which we pressed the electrodes before we start cycling at something like $1.38 - 2.76 \times 10^4 N/m^2$ (2 - 4psi). We do not have figures for the pressure that is likely to develop in a particular cell arrangement. That depends on the design of the cell. We try and keep the electrode within its dimensions and prevent the swelling, rather than let it swell and see what happens to the cell.

ROGERS: If you do restrict it in, say, battery design as we do in an aerospace battery, then if the electrode swells the separator material is going to flatten out and you are not going to have a separator any more, you are going to have almost a solid sheet. It is an extreme case.

GUTRIDGE: We have not seen that sort of problem. One of the cells that I have described had only two layers of four-mil felted nylon. That was the only separator material. That cell performed quite satisfactorily.

BOWERS: For battery C, did the replacement electrolyte contain lithium hydroxide?

GUTRIDGE: Yes.

BOWERS: Have you discharged cells without lithium hydroxide additive?

GUTRIDGE: We have. We find that the number of cycles for formation is greater if lithium hydroxide is not present.

LEAR: Table 18-3 up there showed 300 cycles. Did you continue cycle testing?

GUTRIDGE: Yes, these cells are still being cycled, and they are up to 400, 450 cycles now.

MAURER: The figures raised a lot of interest to those of us who were involved in those previous three papers. In Figure 18-6, where you showed the capacity fading with cycling, you said that was a result of the cell bulging; then you had to squeeze it down and the capacity went back up. Why was it bulging? Was it because the active material was falling on the surface and causing an increase of thickness, and then you squeeze it back so that the resistance goes down?

GUTRIDGE: The active mass was growing. It was not actually falling off the structure, because we were able to get the capacity back, but you would finish up with a much lower density electrode if you did not hold it together.

MAURER: Then the active mass is actually increasing and you are able to squeeze it back?

GUTRIDGE: Yes. If you were to continually cycle without having some applied pressure, you would start to lose active mass. However, that was not what we observed in that short time, because we were able to get the capacity back.

GARLOCK: Have you done any temperature work with this new electrode?

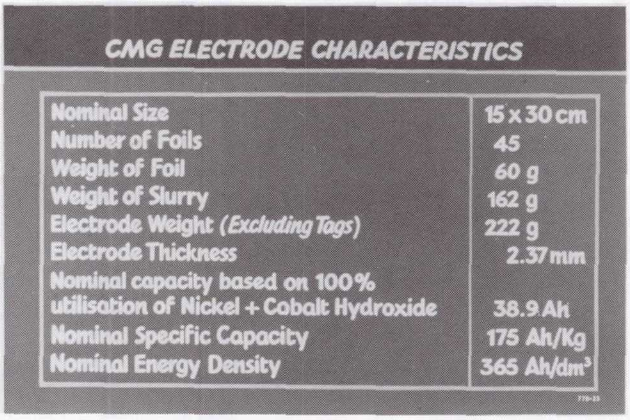
GUTRIDGE: All our tests have so far been done at room temperature.

FRITTS: I was wondering if you found any problems with severe overcharge, oxygen pressure between the layers?

GUTRIDGE: No. In fact, the overcharge that we have used in a lot of our cycling tests is probably a lot higher than you would choose to use in other electrodes. We have cycled electrodes at 60, 70% overcharge continually in our early experiments. The overcharge that we use now is a standard, 30% overcharge. High overcharge is no problem.

BOGNER: How did you deposit the active material, and did it contain an additive like cobalt?

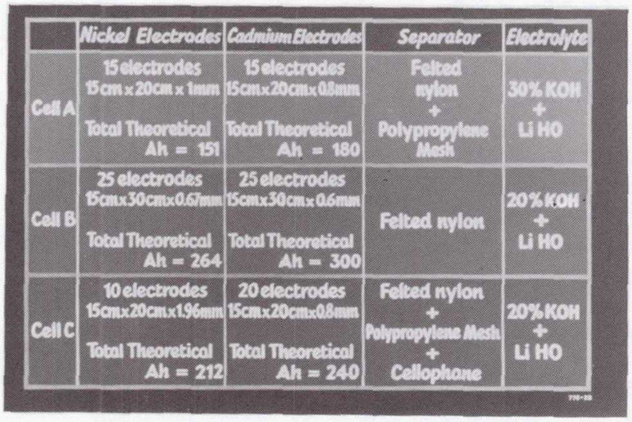
GUTRIDGE: It is deposited by a slurry coating method. Yes, it does contain cobalt.



CMG ELECTRODE CHARACTERISTICS

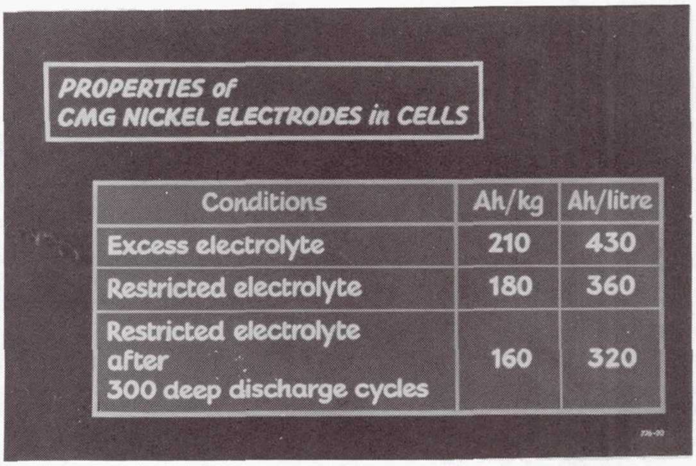
Nominal Size	15 x 30 cm
Number of Foils	45
Weight of Foil	60 g
Weight of Slurry	162 g
Electrode Weight *(Excluding Tags)*	222 g
Electrode Thickness	2.37 mm
Nominal capacity based on 100% utilisation of Nickel + Cobalt Hydroxide	38.9 Ah
Nominal Specific Capacity	175 Ah/Kg
Nominal Energy Density	365 Ah/dm^3

Table 18-1



	Nickel Electrodes	*Cadmium Electrodes*	*Separator*	*Electrolyte*
Cell A	15 electrodes 15 cm x 20 cm x 1 mm Total Theoretical Ah = 151	15 electrodes 15 cm x 20 cm x 0.8 mm Total Theoretical Ah = 180	Felted nylon + Polypropylene Mesh	30% KOH + Li HO
Cell B	25 electrodes 15 cm x 30 cm x 0.67 mm Total Theoretical Ah = 264	25 electrodes 15 cm x 30 cm x 0.6 mm Total Theoretical Ah = 300	Felted nylon	20% KOH + Li HO
Cell C	10 electrodes 15 cm x 20 cm x 1.96 mm Total Theoretical Ah = 212	20 electrodes 15 cm x 20 cm x 0.8 mm Total Theoretical Ah = 240	Felted nylon + Polypropylene Mesh + Cellophane	20% KOH + Li HO

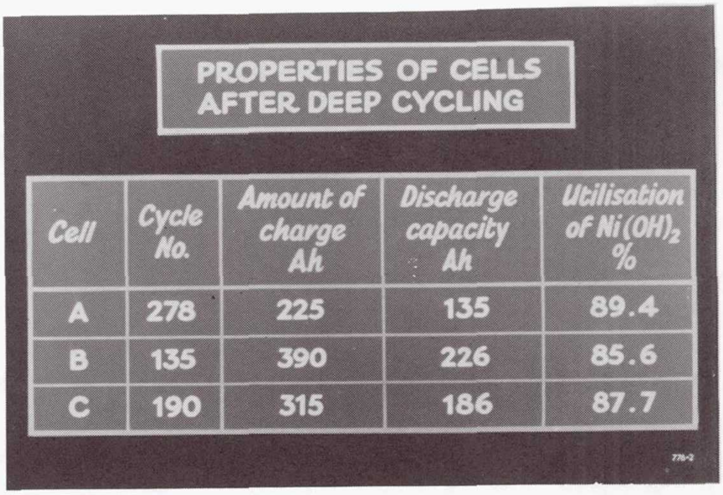
Table 18-2



PROPERTIES of CMG NICKEL ELECTRODES in CELLS

Conditions	Ah/kg	Ah/litre
Excess electrolyte	210	430
Restricted electrolyte	180	360
Restricted electrolyte after 300 deep discharge cycles	160	320

Table 18-3



PROPERTIES OF CELLS AFTER DEEP CYCLING

Cell	*Cycle No.*	*Amount of charge Ah*	*Discharge capacity Ah*	*Utilisation of $Ni(OH)_2$ %*
A	278	225	135	89.4
B	135	390	226	85.6
C	190	315	186	87.7

Table 18-4

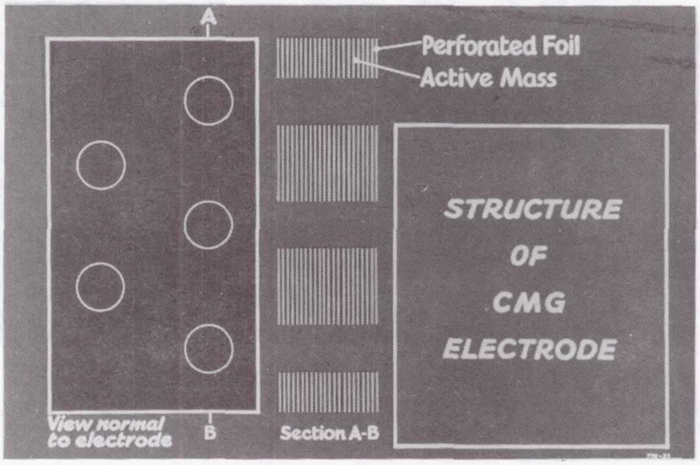


Figure 18-1

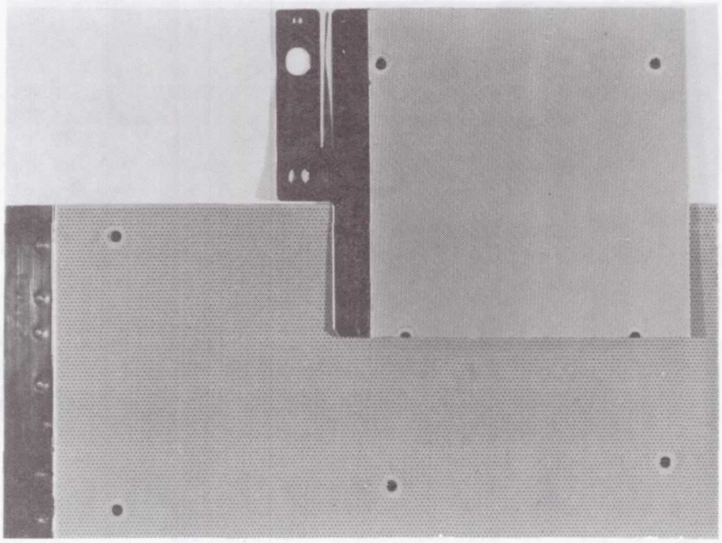


Figure 18-2

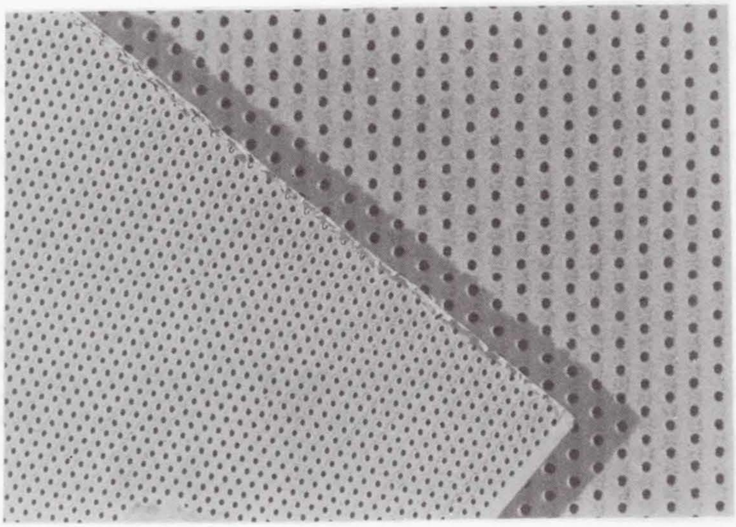


Figure 18-3

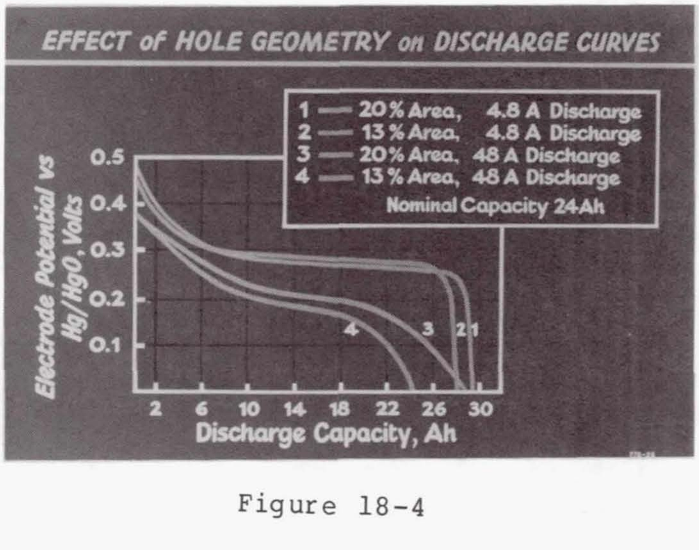


Figure 18-4

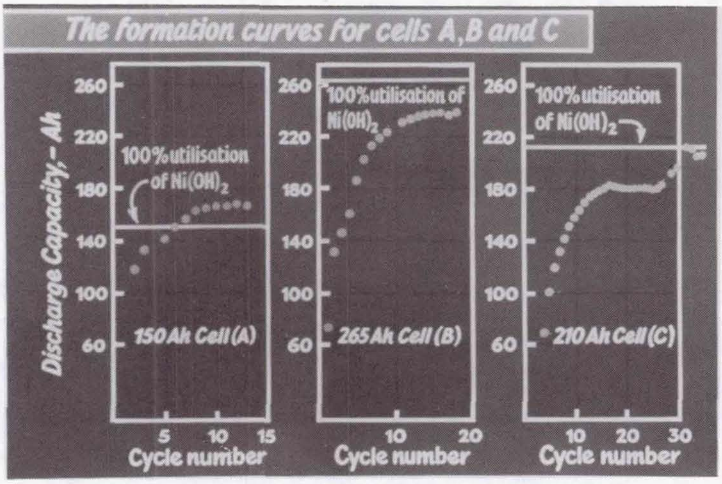


Figure 18-5

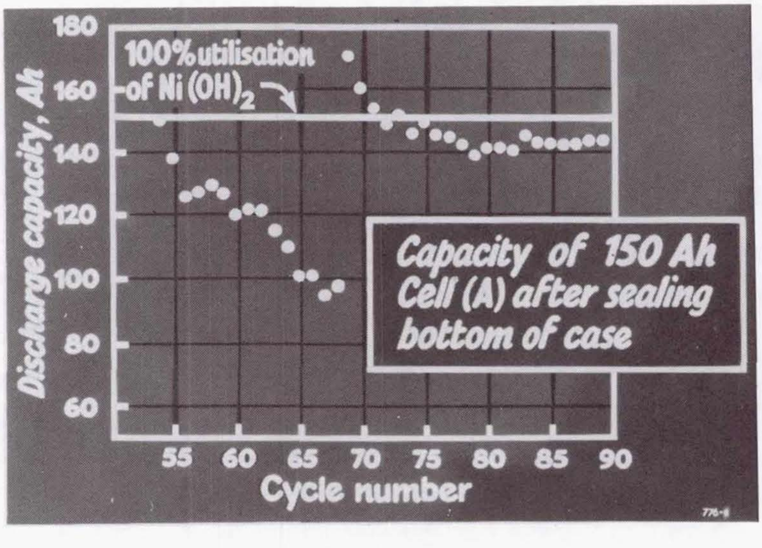


Figure 18-6

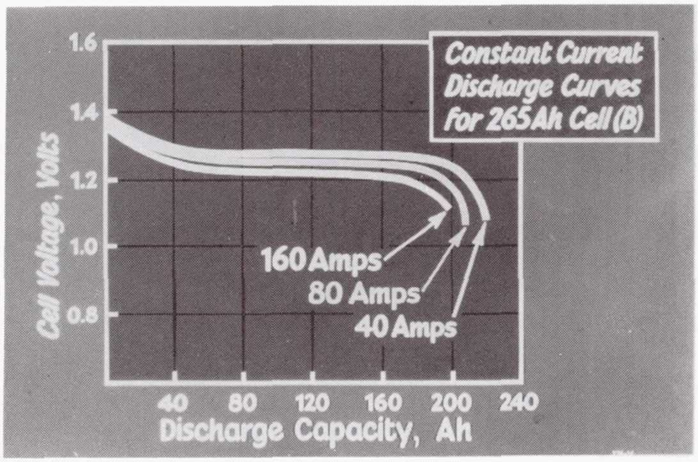


Figure 18-7

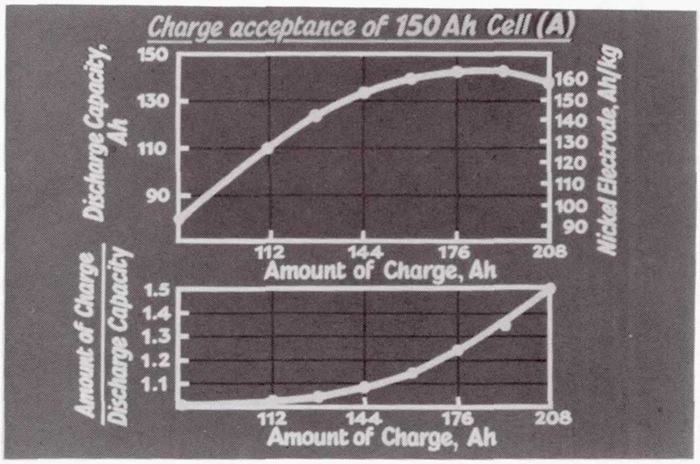


Figure 18-8

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LIGHTWEIGHT COMPOSITE CADMIUM ELECTRODES

R. Sutula and W. Ferrando
Naval Surface Weapons Center

We are reporting preliminary work on a cadmium electrode and its lightweight composite cadmium electrode. The work has been done over the last few months, and so is relatively new. I stress the preliminary aspect of it.

(Figure 19-1)

Figure 19-1 shows the way we make one of these. This is another approach to making electrodes. It is a sintered electrode. We start out with a thornel highly graphitized mat fiber; I believe this was made by Union Carbide. We take this mat fiber in several layers, and coat it with an electrolus nickel coating. The coated mat material is called a composite. Then we place it on a screen, put it under compression and sinter it.

The screen we are using is very primitive at present. It just consists of strips of nickel wire. After sintering, we call it the graphite composite precursor. Then we activate it by using the Pickette method of activation, with a 2M cadmium nitrate solution with 50% ethanol and water. The half cell reaction is

$$Cd + 2OH^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} Cd(OH)_2 + 2e^-$$

We used a flooded cell with no additives at all in the electrolyte. We are using the commercial positives in this case surrounding the cadmium negative. We use one wrap of hermion and one wrap of nylon separator material. The compression on this is rather low and somewhat variable at this time, and so we are not under high lateral pressure.

(Figure 19-2)

Figure 19-2 shows the voltage versus the theoretical capacity for the eleventh charge cycle on cell 52. The charge rate is 1.87 C. It is a 2A h capacity plate, and the voltage starts out at 1.35V. As it reaches 100% of capacity, it goes up to about 1.7. There is not much gassing; it does not use excessive amounts of water.

I might say a few more things about it. There is some question about the carbonate being generated by the fiber underneath the nickel coating. We did carbonate tests on this after 480 cycles, and after several hundred cycles at high rate. The amount of carbonate was too low to be measured. It was just present in trace quantities due to the plaque.

You can see the overcharge, about 300% on that; the rate is 1.87 C, which is a pretty high rate overcharge.

(Figure 19-3)

Figure 19-3 shows the same cell on discharge at three different rates: 0.25C, 2C and 8.2C. At the lower rate you get virtually 100% of the theoretical capacity in this particular cycle up to about 1V for 4.5 hours. Then as the rate is increased 2C, you get about 88 to 90% for 29 minutes. Then, as you raise the rate even more you are getting about 45% and 3.2 minutes.

(Figure 19-4)

Figure 19-4 shows a different plate, no. 64 (we ran about six or seven of these plates during the short time we have had to do this). The capacity of this is 1.46A h, the charge is about 125% of C, and the discharge 0.5C on this one, 0.73A. You can see what the utilization does on this particular plate. It starts out a little above 80% and levels out at about 75%. The fluctuations are mostly caused by the cams you cut on and off in the instrument used for cycling. Thus it went out about 90 cycles, and it looks quite good. We can compare that with Figure 19-5 (work by S. Gross, Review of electrochemical impregnation for nickel-cadmium cells, Boeing Aerospace Co. Report, August 1977).

(Figure 19-5)

This shows a review of an aerospace report on the cadmium electrode efficiency of different impregnations of plaques. The chemical impregnation for commercial use has the lowest efficiency, and for aerospace application it has higher efficiency. The electrochemically impregnated electrode is at the top. You can see that we are within that range, although, it is below 80% there, and at 50 cycles it is probably about 70 or 75%.

(Table 19-1)

Table 19-1 shows the percentage utilizations of active material, and amp hours per kilogram, for two plates at different discharge rates. This is a cutoff at 0.9V.

I went back and checked data on some of the other cadmium plates we have done up to about 60 cycles. We had done up to about 120A h/kg at 50 to 60 cycles. I stress that. In my conclusions I shall say a few things about that.

The bottom line on Table 19-1 shows data for commercial negative. We just tried that (at the same rate) to see what we would get by comparison. It is an unfair comparison, of course, because that is the older chemical impregnation method, and I know that there are newer ones available now. Some of the conclusions that we can draw are that by this composite plate method we can make a cadmium electrode that appears to be rather good. We measured the thickness of a couple of plates after about 100 cycles, and if anything they were thinner than they started out. This shows that they do not swell in the electrolyte, and they do not produce carbonate in the electrolyte. As far as the process goes, we feel it would be a minimal step to mass production. In other words, we can roll these off rollers and through vats and cut them up. They have potentially low cost. The mat fiber is maybe $7.50 per pound, but you can make about 100 plates with it. We substituted some of the nickel in the plate with carbon, and we feel that it would possibly be a good approach from that point of view. As for its life, it looks promising. As I said, they have not gone for thousands of cycles yet.

As far as future work is concerned, we shall be pressing hard with this. Several things can probably be done to raise the amp hours per kilogram. We think we can raise it by 10 - 15% by putting a proper kind of current collector in here. The current collector we use at present is rather crude. One thing we must use now is a proper type of nickel screen. This was not available to us from the start, and so we are going to come back to that.

Then we can start refining. We must do more studies on these plates, similar to the things we have presented in previous papers. We can refine the fiber diameter here; in other words, we were using this mat fiber with a diameter in the range 6 - 16 m, averaging around 9 m. I think that if we used a somewhat smaller fiber diameter (around 6 m with the same 0.5 m coating that we have, we may be able to raise the power-to-weight ratio 15 - 20% over and above what we can do by changing the screens.

We have quite good loading. This loading is not a problem. We can get high loadings and we can change the porosity on these plates at will. I have made some plaques that are 40mm, and are quite good and highly porous. I can make them so porous that I can see through them, although I am not sure whether that is an advantage. I can vary the porosity over 90%, and it retains its strength like a fiber tennis racket would.

DISCUSSION

RAU: Have you used pre-impregnated graphite fiber for coating?

FERRANDO: No, we are just using the graphic mat. We work from the mat as we see it. It is a thornel type of fiber. It is not primarily used for batteries, but we are making this application for it.

RAU: Could a carbon-carbon composite be used in place of this as a plaque?

FERRANDO: It is nickel coated. That is critical in here.

RAU: A carbon-carbon composite with 80% porosity will absorb the purpose.

FERRANDO: I do not think so; I think it will swell.

RAU: I should like to know the properties of the graphite mat fiber.

SUTULA: This is commercially available Union Carbide fiber. It is VMA grade thornel type P. The current cost is about $7.50 per pound.

RAU: Is it a high-modulus or a high-strenth fiber?

SUTULA: It is a high-strength fiber. It has a surface area of about $0.4m^2/g$ and I believe its density is about $2.1 g/cm^3$.

RAU: Is it made from rayon fibers?

SUTULA: It is thornel type P. I believe it is a petroleum by-product.

RAU: I should like to know some details of the coating process of nickel.

SUTULA: We can give you the patent number (the patent was issued in July of this year), and you can look it up in there. It explains in complete detail how to coat the fiber properly with nickel.

RAU: As such, these fibers would be quite brittle, and so the electrode plaque cannot have good strength.

SUTULA: It does. In fact, the load-to-failure runs between 90 and $100kg/cm^3$.

RITTERMAN: You showed in Table 19-1 that there was 95% utilization of cadmium at constant current at C/4. Is that correct? Usually I should expect about 80% utilization.

SUTULA: Yes, I agree. However, 95% is what came out for that C/4 rate.

RITTERMAN: The theoretical equivalent of 1g of cadmium hydroxide is 0.366A h. You are getting about 0.1A h. Taking about 80% utilization of theoretical, and taking about 50% of that for the inert material, you get 0.15A h. Your 0.1A h, even with a 20% improvement, still falls short of the standard sintered plate. You are getting about a quarter of theoretical.

SUTULA: What is currently the best ampere hours per kilogram for plate weight of a cadmium electrode?

RITTERMAN: It is 0.15A h/g, which is 150A h/kg.

SUTULA: We believe we can achieve 150A h/kg with no problem as far as changing some of the current collectors and also improving the fiber diameter. The other thing it would allow you to do is to come up with a commercially viable process so that you can mass produce these things very rapidly and more cheaply than at present.

RITTERMAN: You would have to have some sort of weight for your grid; I really wonder if it is feasible to go from 100 to 150 A h/kg?

SUTULA: Currently we have ones on test that are achieving 135 A h/kg, and these are very crude ones.

RITTERMAN: Do they have the grids?

SUTULA: Yes.

DISCHARGE CHARACTERISTICS OF COMPOSITE CADMIUM ELECTRODE

CELL NO.	DISCHARGE RATE, A	% UTILIZATION	AHr/Kg
62	0 25 x C	95.3	93.3
62	2 x C	85.0	89.2
62	4 x C	85 6	89.9
62	8 2 x C	43.1	45 2
66	0.15 x C	92.0	55.1
66	0.25 x C	95.0	102.4
66	1.2 x C	86.6	93.3
66	4 x C	63 0	67.9
COMM.	0.5 x C	77.0	31.5

Table 19-1

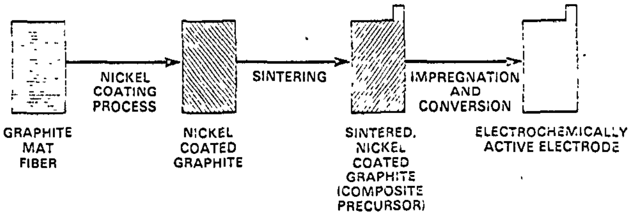
HOW TO MAKE A LIGHTWEIGHT ELECTRODE

Figure 19-1

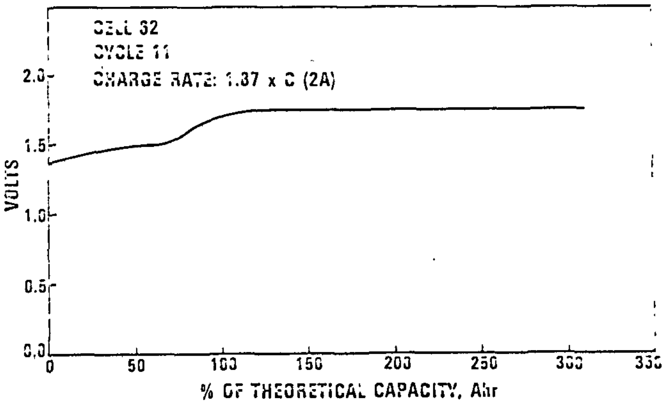
CONSTANT CURRENT CHARGE

Figure 19-2

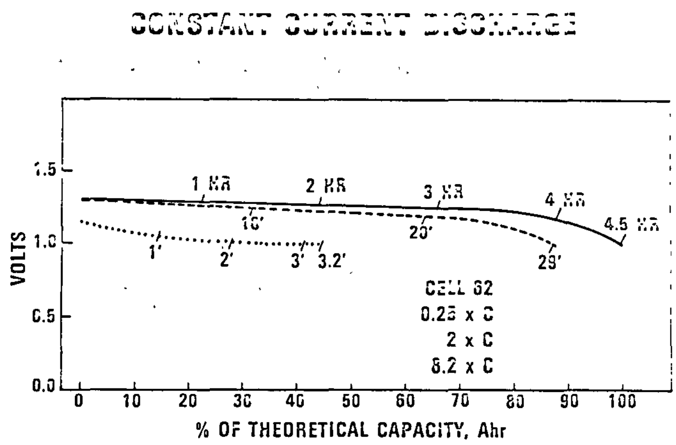

Figure 19-3

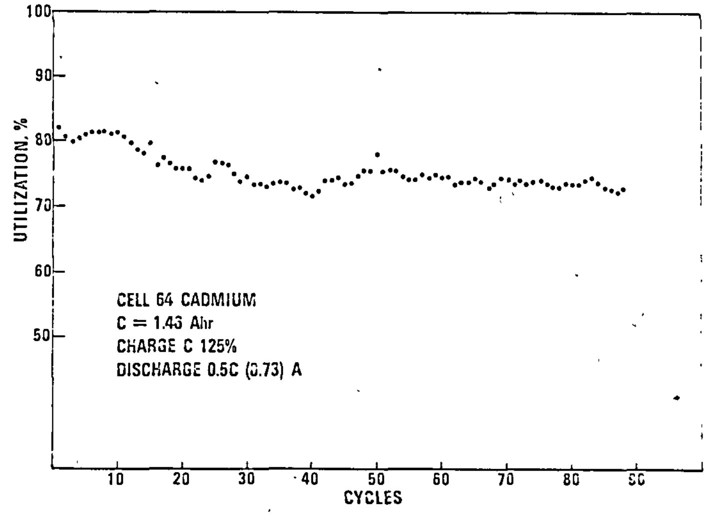

Figure 19-4

CYCLING DEGRADATION OF CADMIUM ELECTRODES

BASIS:

- CHARGE C/2 FOR 4 HOURS (5 HOURS FOR AEROSPACE ELECTRODES)
- DISCHARGE C/2 TO 1.0 VOLT
- COMMERCIAL AND BELL TELEPHONE LABS ELECTRODES-REF 8
- AEROSPACE ELECTRODES - BOEING SPACECRAFT CELLS

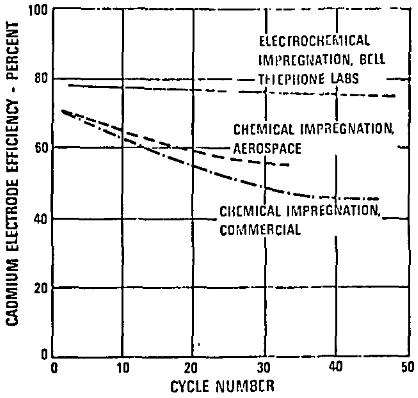

Figure 19-5

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ELECTROLYTE DISTRIBUTION STUDY IN SEALED NICKEL CADMIUM CELLS

V. KUNIGAHALLI
Coppin State College

At the outset I should like to thank Mr. Halpert and Dr. McDermott for their assistance in carrying out the investigation.

The purpose of the study was threefold: first, to find an alternative method of estimating and extracting the electrolyte content in a cell; secondly, to understand how the electrolyte is distributed in the cell components (the positives and the negatives and in the separator material); and thirdly, to discover whether the electrolyte is associated mostly with the positives and negatives or the separator. In the last Battery Workshop, the question was raised as to whether the electrolyte content is more towards the positive or negative in the nickel cadmium cell.

I should like to say that this is purely exploratory work, and the results are very preliminary.

It is known that the thermal conductivity can decrease significantly with electrolyte distribution, causing an increased internal thermal resistance. It is also known that variations in the charge behavior, sometimes attributed to the different separator materials like polypropylene or nylon, can also be attributed to differences in the amount of electrolyte present and its characteristic distribution among the cell components. The presence of adequate and well distributed electrolytes can cause the initial signal behavior in the auxiliary electrode to be normal and particularly it will behave the same for both the perpendicular and the parallel configurations. These observations stress the importance of electrolyte distribution among the cell components in the positives and negatives.

Let me say a few words about the experimental approach, how the cell was opened and how the analysis was carried out. First, the cell was tested for leaks. Then it was opened in a dry lab filled with dry nitrogen. The positives, negatives and separators were separated from the cell pack. The wet weight of each component, each individual positive, negative and its separator, was recorded by using a balance already placed inside the dry lab.

Each component was then immersed in a beaker containing exactly 250ml of deionized water. The system was allowed to stand for about 3h in the inert atmosphere, taking care to see that there was a positive pressure of nitrogen in the dry lab. Then each component was taken out of the beaker, allowing sufficient time for most of the electrolyte to drip off the surface of the plate or separator. After this, the positives were collected together, the negatives were collected together, and the separators were collected together and put in three different soxhlet extractors. The soxhlet extraction was carried out with 1000ml deionized water for about 24h. After this extraction, when we tested the soxhlet extract, it was not basic in nature. This clearly indicated that the extraction had been completed in the immersion technique. In fact, this soxhlet extraction was intentionally carried out to cross check and ascertain whether the extraction of the electrolyte has been completed or not. Lastly, the electrolyte extracted from each component was analyzed by the volumetric method, and the content of potassium hydroxide and potassium carbonate calculated.

I should like to add that the utmost care was taken to prevent all possibility of contamination, particularly that of carbonate from external sources including the atmosphere. The only time the solutions were exposed was during the titration, which was done very quickly.

(Table 20-1)

Table 20-1 gives a brief history of the cells studied here. The first two columns show two 6A h cells and two 8A h cells and the manufacturer's name. For the cycled cells we have given the Crane pack number and the percentage DOD, the temperature, and the total number of cycles that have gone into the cell.

(Figure 20-1)

Figure 20-1 shows the content of potassium hydroxide and potassium carbonate in the individual cell material. N stands for the negative plate, S stands for the separator, and P stands for the positive electrode. For convenience, positives are given the even numbers, negatives odd numbers, and separators are given continuous numbers.

We can see that in each of the set of components, the average potassium carbonate is shown by this dotted line. It is 12.67 for the negatives, 15.06 for the separators, and 9.49 for the positives. One of the tables that I shall present later shows the standard deviation, which is pretty good.

From Figure 20-1, we can see that the percentage of potassium carbonate associated with the separator is larger than that for the positives and negatives. Also, there seems to be approximately uniform distribution of the electrolyte in the cell component in all cases. The cell is an 8A h cycle cell, which has undergone 23,748 cycles; it is non-Teflonated.

(Figure 20-2)

Figure 20-2 shows the results from the next cell that we analyzed, an 8A h cell that had undergone 23,772 cycles. The only difference between this and the previous cell is that this cell is negative base Teflonated. The trend is very similar to the one we saw in Figure 20-1, in that the percentage of carbonate in the separators is larger than in the positives and negatives, and there is uniform distribution. It is interesting to note that in the positives, the negatives and the separators, the percentage of carbonate is correspondingly lower than in the cell in Figure 20-1. This probably indicates that the degradation of the separator is slightly less in a Teflonated cell than in a non-Teflonated cell.

(Table 20-2)

Table 20-2 shows component weights of an 8A h cell. While the cell pack was disassembled, the wet weight was recorded for each negative, separator and positive. After immersion and drying, we took the dry weight of the components; the difference is the weight of the electrolyte. There is a pretty good average for the electrolyte and a very uniform distribution. The standard deviations are within 0.1, 0.2 in this particular case.

(Figure 20-3)

Next, we took another cell that was available to us, a 6A h cell, which had undergone again 37,726 cycles. In this case the separator material was very sticky, adhering to the negative plate, and so it was not possible to separate them. Therefore, we took the positives and the combination of negatives and separator, and analyzed these in the same way as the others.

Here again the carbonate associated more with the separator and negative combination than with the positives. The distribution is approximately uniform, but, there is a slightly greater deviation than for the 8A h cell. However, in general, the pattern is more or less similar.

(Figure 20-4)

Lastly, we took a 6A h uncycled cell, and there we could remove the separator material very easily. Again we found that the carbonate content was very high in all the cases in general. There is one that is very difficult to reason. Secondly, there seems to be a sort of pattern from one side of the cell to the other. You can see, particularly for the separators, that the carbonate content (shown by the dotted area) and the potassium hydroxide content (which is shown by the shaded part), are increasing from one side to the other. I have no explanation for this kind of behavior. One could only speculate, perhaps, that if there had been a tiny hole on one side of the cell, which has been lying there for years, then probably the component that was exposed to the atmosphere would have undergone more oxidation, and therefore the carbonate content would have been greater and would go on decreasing as you reach the other extreme. Another speculation could be that owing to differential compression, it is possible that some of the electrolyte has been accumulated on one side of the cell.

(Table 20-3)

Table 20-3 summarizes the results shown in Figure 20-1 to 20-4, for the purpose of comparison. For example, and for 8A h cells, we have given the standard deviation which is pretty good. It is only ±1% by weight.

In the 6A h uncycled cell, the deviation was 3%. This clearly indicates that cycling has contributed to more uniform distribution of the electrolyte among the cell components. As we said, the carbonate content is mostly associated with the separator.

(Table 20-4)

Table 20-4 shows the absolute weights of the electrolyte associated with the positive, separator and negative plates in each of these cells. We can see that in each case the negative is associated with the greatest proportion of electrolyte, followed by the positive, and the separator has the least.

DISCUSSION

WEINER: With regard to the cell that was lying around uncycled, do you have any information as to how long it was in storage, at what temperature it might have been kept and, whether it was discharged during that period of time?

KUNIGAHALLI: I tried to collect as much information as was available. I gathered that all these cells were manufactured in the early 1970s, and were all lying in a cabinet at room temperature.

HALPERT: Then we do not have its exact history?

KUNIGAHALLI: No. In fact, I tried to locate it but I could not.

RITTERMAN: I see you have values for the interelectrode spacing. How did you calculate that?

KUNIGAHALLI: After opening I took the can along with the lining material, and measured the dimensions. Then, by the number of plates, I calculated the separator material dimensions. I just wanted to see whether that would give me some information.

ROGERS: I am wondering whether you took into account that when you take a nickel cadmium cell out of a battery pack that is now under a strain, and cut it open, you must get an electrolyte redistribution, which may or may not relate a great deal to how it was in the cell. Have you taken that into account?

KUNIGAHALLI: No. This is just a preliminary approach. We are still doing work on it.

SCOTT: Teflonation of negatives is reputed to cause less electrolyte to be absorbed by the negative plates. Your data do not seem to indicate that that was the case with the Teflonated cell. Would you care to comment on that?

KUNIGAHALLI: The carbonate content is less in Teflonated cells than in non-Teflonated cells.

SCOTT: What about the total electrolyte content?

KUNIGAHALLI Among the two 8A h cells, the last one is a Teflonated one and it does have more electrolyte than the non-Teflonated cell. I think that is the meaning of the trend.

SCOTT: That may or may not be true. That is not the way I understand it. However, regardless of how much total electrolyte is added to this cell, the process of Teflonating a negative is reputed to prevent the negative from flooding as much as in negatives that are not Teflonated. Your data do not show that.

KUNIGAHALLI: That is true. I have no explanation at present.

ELIASON: It is a little better to use a humidified rather than a dry nitrogen atmosphere when dissecting the cells. This prevents dryout of the electrodes. We found this quite some time ago.

What was the total electrolyte in the cell? You obtain this number by taking the weight prior to dissection and then adding up your weights and seeing how that comes out with the rest of your total electrolyte. Did you do that? Did you have any numbers like that?

KUNIGAHALLI: We did not know the weight that was put in when the cell was manufactured. I could not get that data because these are very old cells. In fact, I did want to cast it with my analysis result whether it would be anywhere near to the amount of electrolyte that was added to the cell when it was manufactured.

ELIASON: You can get that number experimentally by starting with your cell weight and then adding up all the weighted components afterwards.

KUNIGAHALLI: We did not do that.

ELIASON: How did the concentration of the electrolyte compare with their manufacture? I assume you probably used about 30, 34% weight. I see some of your numbers were 32 - 33% KOH by weight, or 34%, which is a little high. You probably lost some water, which gave the higher concentrations calculated by your experimental procedures.

There is a standard procedure. Dr. Rogers had commented on it earlier. We have dissected many cells over the past six or seven years, and they do show a very reliable and consistent distribution of the electrolyte in the nickel electrodes and cadmium electrodes and in the separator after dissection. This has been very consistent over the number of years.

HALPERT: We have also been doing that work for quite some time, and the water problems have been discussed previously.

TABLE 1
HISTORY OF CELLS

RATED CAPACITY (Ah)	CELL MFGR.	NWSC/ CRANE PACK #	DOD (%)	TEMP (°C)	TOTAL CYCLES	INNER DIM OF CAN (MILS)	AVG. SPACE PER SEP (MILS)
6	GE	*	–	–	–	758.8	10.98
6	GULTON	58D	25	0-40	38,150	755.3	6.0
8	GE	18E	25	20	23,748	839.76	8.76
8	GE	18F	25	20	23,772	841.15	5.8

*UNUSED CELL OF THE TYPE USED IN PACK 201A - 207A.

Table 20-1

TABLE 2

CELL ANALYSED:
GE 8AH CELL PACK 18F , 23772 Cycles

I.D.	WET WT. (g)	DRY WT. (g)	WT. OF ELECTRO-LYTE (g)	I.D.	WET WT. (g)	DRY WT. (g)	WT. OF ELECTRO-LYTE (g)	I.D.	WET WT. (g)	DRY WT. (g)	WT. OF ELECTRO-LYTE (g)
N_1 *	11.68	9.84	1.84	S_1	0.67	0.24	0.43	P_2	9.67	8.79	0.88
N_3	11.77	10.29	1.48	S_2	0.97	0.31	0.66	P_4	10.03	9.05	0.98
N_5	11.55	9.68	1.87	S_3	0.93	0.32	0.61	P_6	10.02	9.01	1.01
N_7	12.06	10.14	1.92	S_4	0.98	0.32	0.66	P_8	10.02	9.02	1.00
N_9	11.80	9.91	1.89	S_5	0.92	0.32	0.66	P_{10}	9.89	8.90	0.99
N_{11}	12.15	10.19	1.96	S_6	1.00	0.33	0.67	P_{12}	9.94	8.98	0.96
N_{13}	12.18	10.21	1.97	S_7	1.17	0.36	0.81	P_{14}	10.08	9.08	1.00
N_{15}	12.15	10.07	2.08	S_8	1.12	0.35	0.77	P_{16}	9.83	8.83	1.00
N_{17}	12.06	10.15	1.91	S_9	0.83	0.26	0.57	P_{18}	9.66	8.75	0.91
N_{19}	12.17	10.26	1.96	S_{10}	1.08	0.32	0.76	P_{20}	9.95	8.94	1.01
N_{21}	12.11	10.21	1.90	S_{11}	0.80	0.28	0.52	P_{22}	9.80	8.79	1.01
N_{23}	11.70	10.11	1.59								

Table 20-2

TABLE 3

RATED CAPACITY (Ah)	NO. OF CYCLES	POSITIVE			SEPARATOR			NEGATIVE		
		WT. % KOH	WT. % K_2CO_3 (AS KOH)	TOTAL	WT. % KOH	WT. % K_2CO_3 (AS KOH)	TOTAL	WT. % KOH	WT. % K_2CO_3 (AS KOH)	TOTAL
6	–	16.56	16.94	33.5	11.94	19.12	31.02	13.38	16.63	34.01
6	38,150	10.26	20.86	31.12	–	–		11.33	22.44	33.77
8	23,748	22.08	9.49	31.57	12.38	15.06	27.44	20.44	12.67	33.11
		** ± 1.098	± 0.905		± 1.037	± 0.648		± 0.655	± 0.387	
8	23,772	23.33	9.04	32.37	16.5	12.63	29.13	20.65	11.59	32.211
		** ± 0.37	± 0.48		± 0.59	± 0.80		± 0.62	± 0.67	

*VALUES FOR NEG-SEP COMBINATION

**STANDARD DEVIATION

Table 20-3

TABLE 4

RATED CAPACITY (Ah)	NO. OF CYCLES	WEIGHT OF ELECTROLYTE IN GMS			
		POS	SEP		NEG
6	–	8.66	6.93		8.78
6	38,150	9.3		*17.01	
8	23,748	9.65	2.18		20.64
8	23,772	10.75	7.12		22.37

*VALUE FOR NEG-SEP COMBINATION

Table 20-4

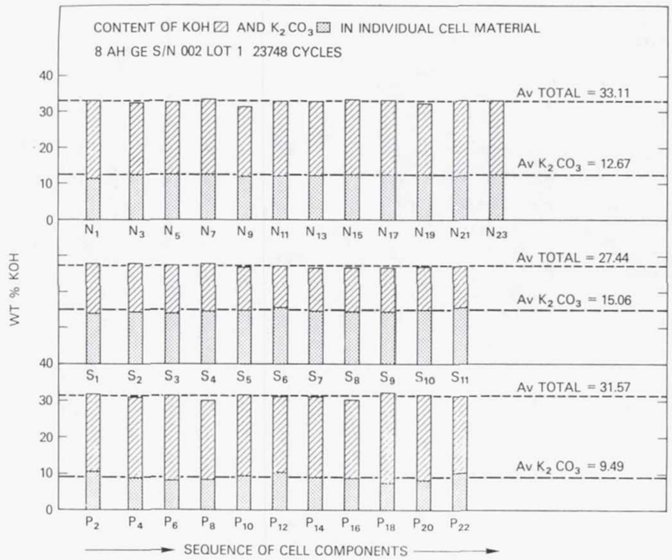

Figure 20-1

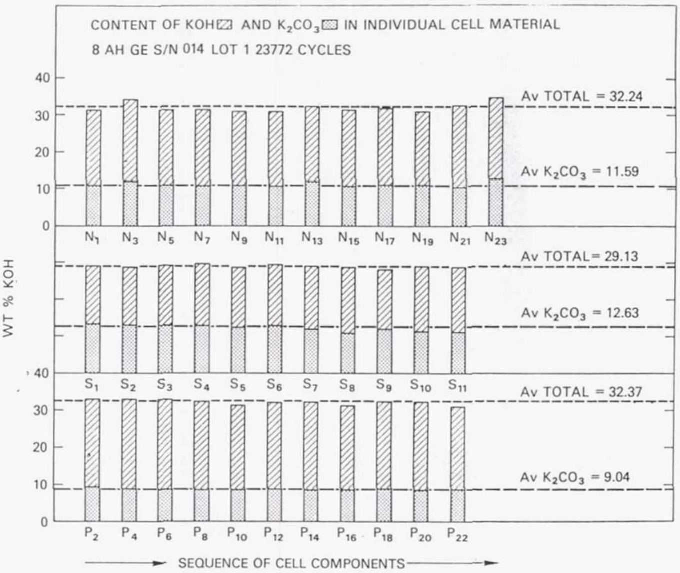

Figure 20-2

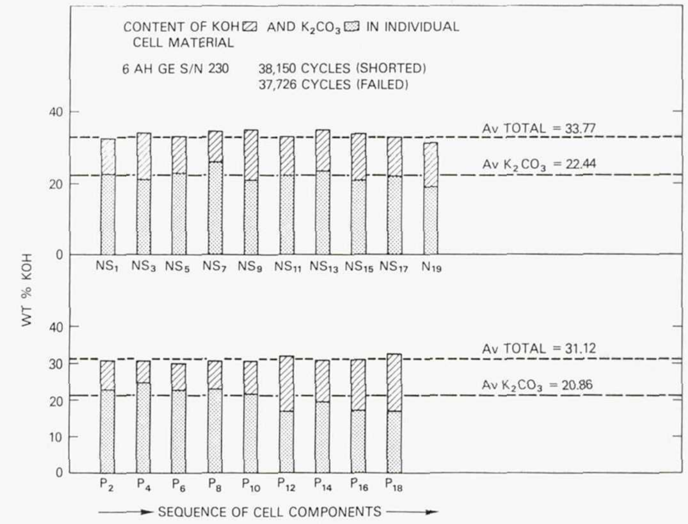

Figure 20-3

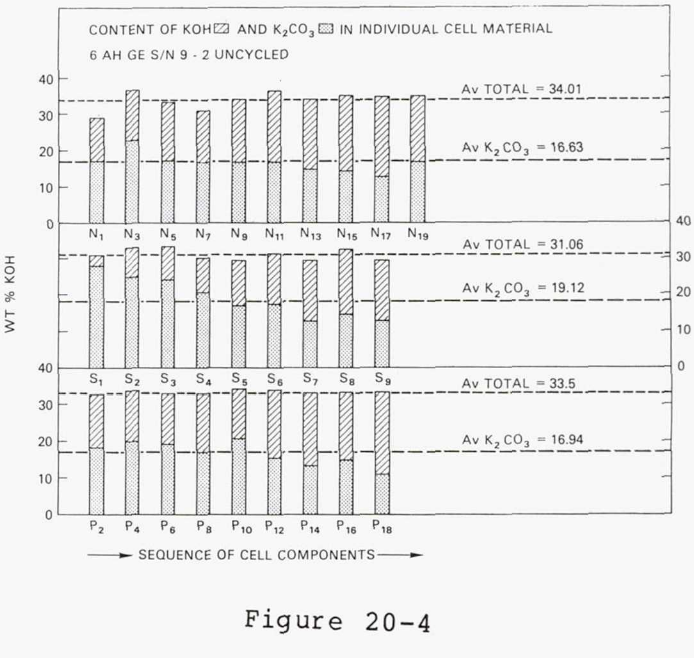

Figure 20-4

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PBI TREATED POLYPROPYLENE BATTERY SEPARATOR

S. Verzwyvelt
Hughes Aircraft

As we completed our nylon degradation study, we started to look for new separator replacements in nickel cadmium cells, and later in nickel hydrogen cells. This paper is concerned with one of those replacement materials. It is a PBI treated polypropylene felt separator for nickel cadmium cells.

Some of the desired properties that we considered in fabricating the new separator material for Ni/Cd cells were good mechanical strength, good chemical stability, good wettability to the electrolyte, high electrolyte retention, and gas passage. Furthermore, we wanted all these properties to be stable to the life of the Ni/Cd cell. This is obvious. We felt with the state of the art in nylon separators, these parameters were changing.

State of art separators in use currently are nylon felt and polypropylene (PP) felt. Both of these had good mechanical properties and good gas permeability. The electrolyte wettability and retention of nylon is very good. However, polypropylene itself is intrinsically unwettable, and so it needed a wetting agent. That raised the problem of the stability of the wetting agent, which comes into the chemical stability. We feel that nylon has very marginal chemical stability, and this has been brought out in previous papers. The carbonate problems associated in nickel electrode failure are obvious by now. The chemical stability of the polypropylene material itself is excellent, but the wetting agent on the material has very questionable stability. From our own experience, it washes off in acetone or in boiling water. It even comes off in repeated immersion in potassium hydroxide.

The new material that we came up with for Ni/Cd cells is a substrate of polypropylene. The wetting agent is a PBI surface coating. PBI (polybenzimidazole) is unique in that it is wettable and stable in KOH.

A generalized procedure for fabricating the separator is as follows. Basically, we immerse a clean polypropylene felt in a 7% solution of PBI, and remove the excess PBI solution by passing it through Teflon-coated rubber rollers or by plotting. We then immerse it in a hot water bath to precipitate the PBI onto the polypropylene fibers. The remaining water is dried off in an air oven.

(Figure 21-1)

Figure 21-1 shows the apparatus used to measure electrolyte distribution, and is primarily included to explain the data shown in Figure 21-2. This apparatus is generally used in the industry to measure electrolyte distribution of the components. It consists of a weight that sits upon a stack of components, which are saturated with electrolyte; increments of electrolyte are removed with a number one Bachman filter paper, and then the components are weighed, the whole thing reassembled and the experiment gone through in a series of steps.

(Figure 21-2)

This procedure yields curves as shown in Figure 21-2, in which the total electrolyte in the component stack is plotted against the electrolyte for a component. Basically, we are withdrawing electrolyte. The nickel electrode contains its electrolyte very well. Only under very starved conditions does it lose its electrolyte. Pellon 2505, the nylon we were using, starts out with excellent electrolyte retention but loses it rapidly, while the new separator, polypropylene PBI, starts out at a lower initial electrolyte retention but is much more stable in its release of electrolyte.

To look at this graph in perspective, from our own measurements a typically loaded nylon cell has a value here of about 15mg/cm^2 of KOH per square centimeter of separator, which is almost around its intersection. This is typically where you would make a new Ni/Cd cell.

If you cycle the battery, the nickel electrode expands, it increases its void volume, the large pore structure becomes a small pore structure and there is a tendency to dry out the separator. You can see the obvious advantage polypropylene has over Pellon. It has much more electrolyte and gives it up much more slowly to an expanding nickel electrode.

(Table 21-1)

As for the stability of this new material, we have run a number of tests on it. In the first test, we measured the weight decrease after reaction in 34% at 100 for 80 days. "Powell" is the manufacturer of the material. In this condition, the standard Powell felt as received lost 3% of its weight, while PBI impregnated Powell felt lost a little over 4% of its weight. I might say something about PBI cloth. Its main manufacturer is Celanese Corporation. They fabricate the material for a fire-retardant garment, and so, when it is sold commercially it is going to be much more inexpensive than it is at present. The cloth itself lost 9.6% of its weight. In both cases the potassium hydroxide had a light yellow tint to it. I shall come back to this yellow tint solution in Figure 21-5.

If you compare the stability of these polypropylene PBI materials with that of nylon, nylon in comparable conditions would be a total loss after 80 days. The only fibers that were left would be floating in the solution. It would lose 10% of its weight in 3 days, and 60% in 10 days.

As far as the electrolyte retention in terms of long term standing in the battery, after the first reaction the electrolyte retention is still good (better than nylon under the conditions for measuring here versus the polypropylene PBI separator before the experiment). On the bottom two lines we have a different polypropylene substrate material. Its results are much the same. It has a slight loss of retention, but vastly improved over nylon. Furthermore, the last two lines are for material under a different test. They were at 110 in an oxygen atmosphere over the potassium hydroxide for 17 days.

(Figure 21-3)

As a visual demonstration, two cells that were held at 80 for 26 days. The upper cell has a nylon separator and the bottom has polypropylene PBI. The nylon separator is disintegrating; its mechanical strength is really quite limited now. You can see fragments of it adhering to the positive electrode. The polypropylene PBI, however, is really in excellent condition. It is almost unchanged.

(Figure 21-4)

Now the question arises as to how this actually works in the cell. Is it a good separator for application in battery cells? The curve shown is Figure 21-4 is generated by using GE 24A h chemical deposited nickel electrodes. We fabricated boilerplate cells with polypropylene PBI separators, with separator spacing of 274 m. As electrolyte loading is increased, we have a well-controlled method of loading. As you increase that, the capacity C at about 2.75 mils levels off. This is rated to be 120 minutes. We are well above rated at about 2.75 mils.

While the internal resistance R of these cells by AC impedance measurement levels off at the same place, they coincide. The pressure levels P built up as you increase the loading, come in at about 3 mils. For comparison, nylon has very comparable curves, except that the pressure buildup is more abrupt. The actual resistance here is high because it is measured in the actual boilerplate cell, and is released at the boilerplate -- or the vast majority of this resistance, the separator, the actual electrode stack actually has a few milliohms resistance.

(Figure 21-5)

Figure 21-5 shows the work being conducted at the Space and Communications Facility at El Segundo. These were cells fabricated for Hughes by General Electric with our separators and some other variables. This graph is included for three points. It shows a charge, and end of charge, and the discharge voltages after the fifth eclipse season. These are in geosynchronous orbits in accelerated-type tests. It basically shows that the polypropylene battery is a workable battery. It is very comparable to nylon after the fifth eclipse season. Also, one of the purposes of this test is that in the tenth or twelfth eclipse season, we expect to see the nylon battery fall out. As nylon degrades, we expect to see that perhaps the nickel electrode will fail; we expect the polypropylene to keep going until some other mechanism has its effect.

The third point is that there was one a yellow solution tint on reaction for 80 days at 100% in 34% KOH. After the fifth eclipse seasons, we have seen no effect of that small soluble component of PBI. As you can see now, there is no catalytic effect due to the PBI. It is used as a wetting agent on the polypropylene.

DISCUSSION

GASTON: At what temperature did you conduct an accelerated life testing? Was it also 80 C?

VERZWYVELT: That test is actually being carried out at El Segundo. I really do not wish to talk much about it, other than to mention the three points that we have now. There is some degree of temperature acceleration. If somebody responsible at El Segundo wishes to talk more about the particulars of that, he is welcome to do so.

GASTON: If I use the polypropylene material, the temperature becomes very important. Certainly, if I raise the temperature of polypropylene it will outperform nylon.

VERZWYVELT: There might be some embrittlement, but it depends on the temperature you go to.

LEAR: Did you treat the polypropylene separator with heat treatment before you used it?

VERZWYVELT: No. All we did to the polypropylene material is to remove Herculon 90 Surfactant with acetone or with boiling water.

SCHEMATIC DRAWING OF ELECTROLYTE DISTRIBUTION MEASUREMENT APPARATUS

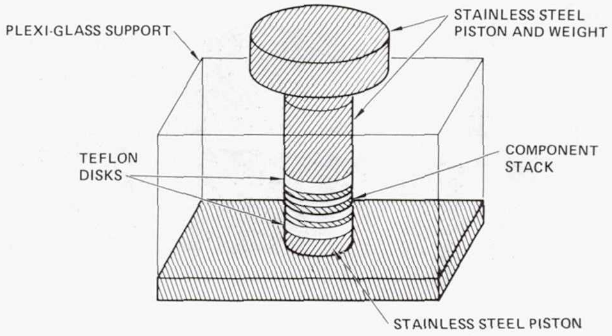
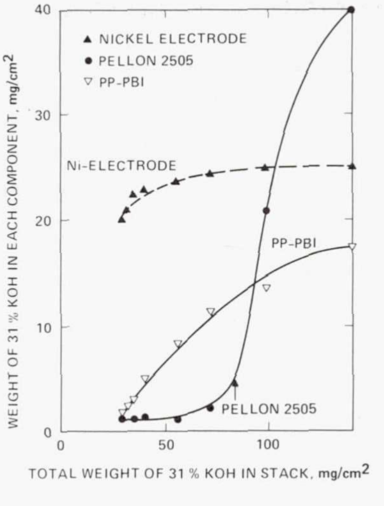


Figure 21-1



ELECTROLYTE DISTRIBUTION IN A MULTI-COMPONENT STACK

Figure 21-2

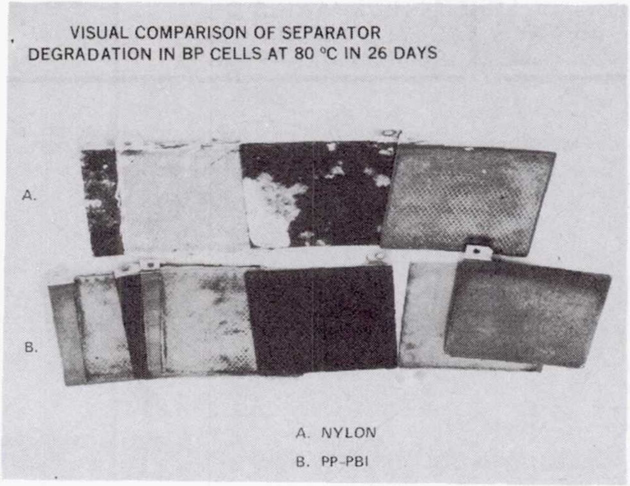

VISUAL COMPARISON OF SEPARATOR DEGRADATION IN BP CELLS AT 80 °C IN 26 DAYS

Figure 21-3

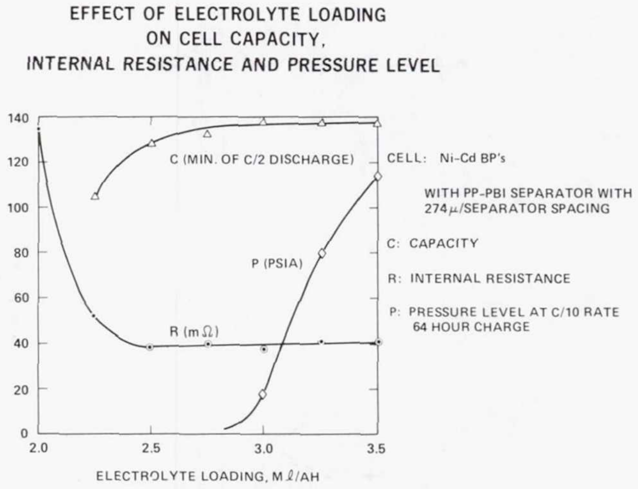

EFFECT OF ELECTROLYTE LOADING ON CELL CAPACITY, INTERNAL RESISTANCE AND PRESSURE LEVEL

Figure 21-4

ACCELERATED LIFE TEST DATA
12AH CELLS

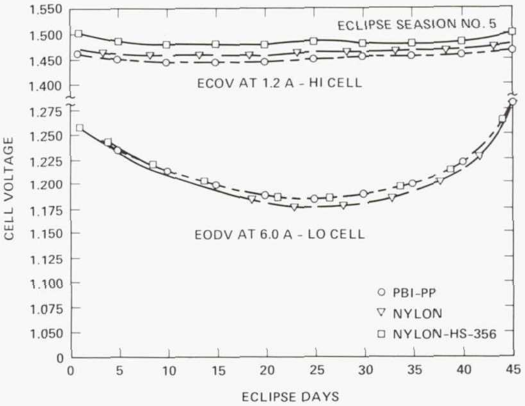


Figure 21-5

STABILITY OF PBI

I. WEIGHT DECREASE AFTER REACTION IN 34 % KOH AT 100 °C FOR 80 DAYS

PP-FELT (POWELL	ΔW = 3.0 %	
PP-PBI (POWELL)	ΔW = 4.4 %	YELLOW KOH SOLUTION
PBI-CLOTH	ΔW = 9.6 %	
PELLON 2505	TOTAL LOSS	ΔW = 10 % IN 3 DAYS 60 % IN 10 DAYS

II. ELECTROLYTE RETENTION, O/W

PELLON 2505	34 %
PP-PBI (POWELL)	96 %
PP-PBI (POWELL) AFTER HEATING IN KOH*	62 %
PP-PBI (GAF)	142%
PP-PBI (GAF) AFTER HEATING IN KOH**	110 %

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* 80 DAYS IN 34% KOH AT 100°C IN N_2 atm

** 17 DAYS IN 31% KOH AT 110°C IN O_2 atm

Table 21-1

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LIGHTWEIGHT 50A H CASE DESIGN

L. Miller
Eagle Picher

As the title indicates, my presentation is concerned with a program to develop a lightweight 50A h cell case. This could be considered an extension of some seven-year-old technology that we developed back in the NATO 3 days, which we fabricated in house. We developed very lighweight cell cases, and incorporated thin or small lightweight terminal assemblies with these to achieve high energy density.

This was a very small cell, under 20A h. When we tried to scale it to the larger 50A h cell, we encountered a few problems primarily associated with the width or thickness of the cell. When you have large areas of thin material in a flat geometry during a pressurization part of the overcharge, deflection or rounding of these surfaces tend to occur. It does not look very good. In the battery structure you might get some pressure on some of the support members that tend to get a little displacement. If one of these units comes out, you can probably anticipate early battery performance degradations. You have to do something about the structures, the support mechanism, and Figure 22-1 will show you the approach taken.

(Figure 22-1)

The cell on the left has what we call a strengthening rib around the outside of the container. For comparison, a standard cell is shown on the right. It is actually a little taller, and has slightly higher capacity, but will serve for the purpose of comparison. Statistically, the purpose of the program was to reduce the weight in the cell container, and also to incorporate the compression seals that you see on the cell on the left, which was standard design in our nickel hydrogen cells.

Design geometry is basically the standard NASA 50A h geometry, roughly 4 88 in is approximately 55A h. The program was carried out with NASA/Goddard under the direction of Mr. Halpert. The material was 304L; it was 12 mils in thickness. The fabrication was entirely done in-house at Eagle Picher, including the terminals and the compression seals. This allows us much better control over the production scheduling process.

As for testing, the unit has actually been pressurized to 100 psig. The deflection measured is considerably less. We certainly did not achieve the yield point of the material. It is considerably less than the much thicker standard cell, which is around 25 mils. There is, however, a problem with it. The first design we came up with did not work so well. It actually showed a deflection of both the cover and the bottom of the assembly.

(Figure 22-2)

We packaged up one of the test units back to Mr.Halpert; he and his associates did a structural analysis and were able to point out the error in our ways. We had to move those ribs out as close to the edge of the container as the tuning would allow. Then we had to put more ribs on the cover assembly, particularly around the two terminal areas.

As for achievement, this case weighs approximately 150g. You could consider the standard cell case to weigh around 300g, maybe a little more, depending on the terminal assembly. If you add this up on a 22-cell battery, you have a saving of around 3.3kg (7.25 lb) which is significant. However, when you place a number of batteries on a satellite, these values add up quite quickly.

Just as an example, on the 25kw power module program, where you might assume there were to be 60 or 70 batteries, you could probably anticipate a weight saving of about 227kg (500 lb).

DISCUSSION

TASEVOLI: Have you done any cell burst pressure measurements on the cell design?

MILLER: We may have, but I do not have that information with me. The last time I talked to the people in that group they were doing some work in that area.

GOLER: Could we compare the deflection of the narrow edge of this 12 mil can with the dimples with a 12 mil can without the dimples?

MILLER: I could, but I do not have the data here. We have done that.

HALPERT: I should say it expanded like a balloon. It became trapezoidal rather than square; and this thing stayed square with 100 psi.

GOLER: What's the possibility of going with --

MILLER: It is a very obvious improvement. As Mr. Halpert said, even the heavy-duty case would swell up. This one stayed virtually flat.

GOLER: Would it be possible to go to an 8 mil material then and still have suitable performance?

MILLER: It is possible. You just have the simple fabrication, the welding of the thin material. We found out, owing to the NATO program, making some 1200 cells, that we could essentially weld 12 mil material. You start getting more problems with thinner material.

GASTON: Is the cover also made of 12 mil material? During the testing, do you have to strain all six sides?

MILLER: The cover is also 12 mil material. In the NATO design it was 15 mil, and the remainder of the container was 12 mil. The only side supporting are the two major flat sides.

LIM: I should just like to make a comment on a question for the previous

It was not the reluctance of our answer or anything. The point of the Figure 21-5 was that the PBI has enough stability for the stoichiometric, that much of the small amount of the weight decrease. Even though the total product is affecting the material balance it does not have enough change. It is therefore safer from that standpoint. There is still a question about the stability of PBI because of the small amount of PBI going into the solution to make the color yellow.

Someone might say that could give a catalytic effect, and some of the battery data are up to five eclipse seasons. The equivalent position compared with nylon shows no adverse effect. We are quite convinced that it does not give any adverse catalytic effect. That was the point of Figure 21-5.

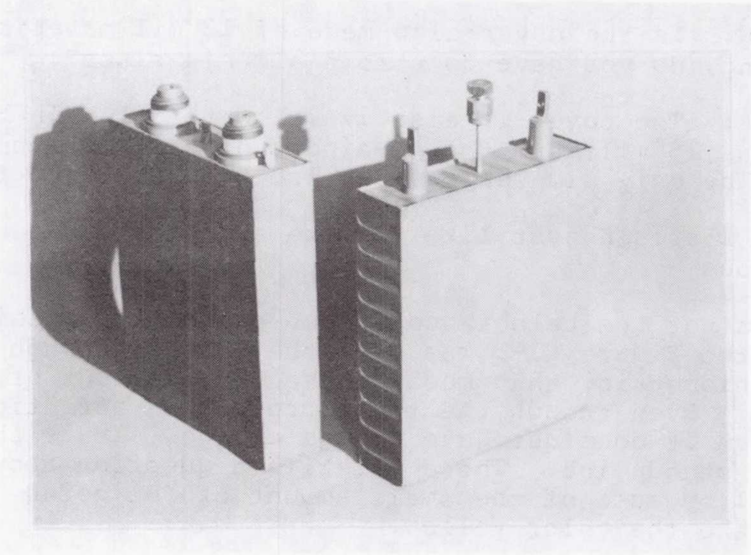


Figure 22-1

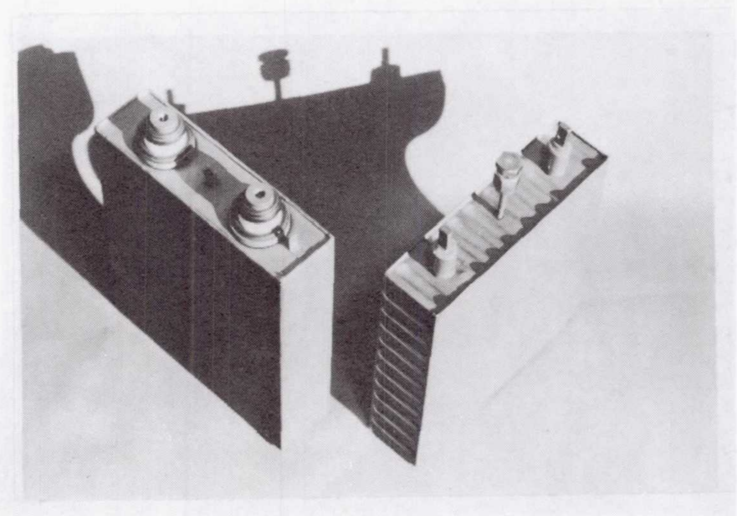


Figure 22-2

ANATOMY OF A SHORT

W. Scott
TRW, Inc.

Some time ago we had occasion to do some testing, under severe conditions, of batteries containing nickel cadmium cells, to see whether we could simulate some strange behavior that we observed in orbit. We did manage to cause one permanent hard short in a cell and several other less permanent so-called soft shorts.

I should like to show you the results of some teardown that we did both on the cell with the hard short, and on some that did not show such hard shorts.

(Figure 23-1)

Figure 23-1 shows how one edge of the hard shorted cell looked when the pack was first removed from the case. The case is shown, as are the header and the comb. Note the area here where the separator is: that melted completely. Whether it is burned or not is a little hard to determine.

(Figure 23-2)

The other side of that same cell looked the same (Figure 23-2). The separators were in essentially new condition, and there was nothing much left -- at least on the outer edges of the several plates near the center of the pack.

We did take the plate stack apart, not by simply pulling the various plates apart as is often done, but by carefully cutting around the edges of all the separator bags with an electrically heated knife, so that we did not physically disturb the bulk of the separator on the negative plates. The separator was, indeed, quite stuck to the negative plates, after several thousand cycles. And so, using an ohm meter, we began peeling off one plate after another until we came to the place where the short was located.

(Figure 23-3)

Figure 23-3 shows the two plates between which the short had occurred. The spot corresponds to the place that we finally located between these two where the short had actually occurred. As you can see, there is a burn spot, or hot spot, whatever you want to call it. Actually, this spot perpetrated itself several plates out in each direction from this one central pair of plates where the short occurred because of the large amount of heat generated when the cell discharged through the short.

By the way, the cell was fully charged at the time the short occurred.

(Figure 23-4)

Figure 23-4 shows the other side (the positive plate side) of that pair of plates. You can see some of the separator that was stuck to this positive plate from the opposing layer of separator material. There is also some iron oxide, arising from the effect of a great amount of heat generated on the iron substrate material.

We then took the pair of plates between which the short occurred, dried them, vacuum impregnated them with a resin, and did some metallographical cross sections. Finally, we arrived at Figure 23-5.

(Figure 23-5)

The lower plate is the positive and the upper one the negative. That thing there is the cause of the short. We were somewhat surprised that it looked like it did, and that we did not see any more heat damage in the surrounding areas. However, we did verify by using a microprobe and measuring resistance between, say, that area and the plates on either side, that there was something of the order of a 1 ohm electronic path between that lump and the adjoining plates. Because of the fact that we did not see much physical damage at that area in comparison with the damage that I showed on those other two plates on the outside where the heat had penetrated, we suspected that this particular lump, although causing a short at the moment, was not the primary cause of the short of the cell. Ultimately we concluded that this particle here was a secondary effect due to the spatting of a chunk of the negative plate material from the underside of this plate, and the lodging of this large chunk between the two plates. By various processes of deduction we concluded that the short had really occurred between this plate and the upper one through the big lump of material. Because of the damage that had occurred during the shorting action, that particular area of short had burned itself free and had produced a secondary short, which was more permanent.

We then removed the positive plate through which the original short had occurred. We were done out of arriving at the true source of the short by the fact that that particular short had disappeared.

(Figure 23-6)

We then made a more careful examination of that cell, and other cells that had gone through a similar type of testing, to see if we could discover the ultimate cause of the short. Figure 23-6 shows one of the plates that had something a little special.

In general, we felt that the overall condition of the separators in these cells was essentially as new, except for a few spots. One of those spots is pretty small, but it is fairly significant. We actually missed that spot when we first sorted through the cell, because it is so small. We finally found it by scanning with a stereomicroscope at about 5 power.

(Figure 23-7)

If you look at the spot under about 20 power magnification, it looks like Figure 23-7, where that is primarily a growth of cadmium coming through the separator.

(Figure 23-8)

Looking at it under a scanning electronmicroscope, it is not too definitive; it is shown in Figure 23-8.

I shall not go on to comment in any detail at present. However, we are mainly trying to understand the physical characteristics of the particular kind of growth through the separator that might cause this kind of short.

(Figure 23-9)

Figure 23-9, by the way, shows one of the other plates from that cell that had the burned edges. As you can see, the whole top of the separators melted off the whole top of the plate. We believe that this effect was produced when the cell discharged through the short and the very high current that passed through the tabs heated up the tabs in the top of the plate to the extent that the separator melted.

You can see, on this particular plate, another little spot which is shown at higher magnification in Figure 23-10.

(Figure 23-10)

Now we are beginning to see something structurally significant. You can see whole areas here where the cadmium, or whatever it is that is growing through the separator, completely obscures the separator fibers.

Interestingly enough, opposite this area and a number of other areas, there was no visible effect on the positive plate surface. There was then essentially an almost continuous cadmium compound path from the negative to the positive, and yet apparently no electrical path was discernible at that time.

(Figure 23-11)

Figure 23-11 shows something a little more extensive. Actually, under a microscope you can see that there was an actual hole burned in this one.

(Figure 23-12)

There is a big chunk of separator missing. In this case we found pieces of separator stuck to the positive plate opposite that hole. However, on this particular cell there was no sign of shorting electrically.

(Figure 23-13)

Figure 23-13 shows a photograph in through the hole at about 250 magnification under a scanning electronmicroscope. You can see that the fibers of the separator surrounding the hole appear to be in good condition. However, there is a hole burned right through the separator at that spot. Again, this was a cell that had not shorted apparently from the external electrical behavior. It therefore looks as though we had some particular form of cadmium growth through the separator in these particular cells. There was general cadmium deposition in the separator. However, in these particular spots there was a unique form of growth, which at least in one case finally produced a massive short in the cell. We do not know what particular physical and chemical conditions are necesssary to convert one of these cadmium growths into a massive electric short.

DISCUSSION

THIERFELDER: What kind of tests were you running that created the shorts? Were they overcharge tests?

SCOTT: Yes. I think the essence of the stress was that we were simulating rather excessive amounts of overcharge at relatively high rates. For example, the control conditions were inadvertently (in the spacecraft at least) allowing up to 130 - 150% overcharge at up to C/3 rates.

LEAR: For those fused plates, where the material was sticking to the positive plate, is it possible that, when you were taking the compression off the plates, you might have pulled it loose rather than burned it loose?

SCOTT: I do not think that pulling could cause the sort of abrupt termination of the separator fibers that were seen around those holes. When you pull it loose you pull whole fibers right out of the separator material. You do not break them off or truncate them, as we are seeing around those holes.

LYONS: Was that a Pellon envelope?

SCOTT: Yes, that was a 2505.

LYONS: Is it possible, in the areas with the holes, that there were weak or thin spots in that material?

SCOTT: I suppose it is possible. However, there was no evidence of thinness in the immediate vicinity of any of those spots. The material was perfectly normal right up to the very edge of those areas.

LYONS: Is it possible, then, that the plates, either the positives or the negatives, were uneven, and owing to that possibly caused a short because of the pressure between the plates on the material?

SCOTT: Yes, that could certainly be a contributing cause, and it may be important. Another cause could be other kinds of more localized flaws in the surface: small bumps or lumps might escape detection during the inspection of the plates during cell manufacture. We are also not absolving the positive plates from some role in this process because of the fact that we saw so many of these areas where the cadmium structure had built all the way through the separator and yet there was no shorting, that we suspect there could be a necessary contribution from the positive plate in just those areas that we did get an actual short.

HENDEE: In Figure 23-13, that is crystalline structure inside the hole, is it not?

SCOTT: Yes.

HENDEE: I assume that is causing the short.

SCOTT: Ordinarily you would say it was cadmium hydroxide?

HENDEE: Yes.

SCOTT: That, on its own, is non-conductive. Therefore, there must be other constituents, and presumably some conductive form of cadmium is also involved. However, it is not obvious.

HENDEE: Yes. It is that now that you have disassembled the cell. However, when it happened, it was not.

SCOTT: Of course, that is the problem. We do not know what happens when the pressure on the separators is released.

Figure 23-1

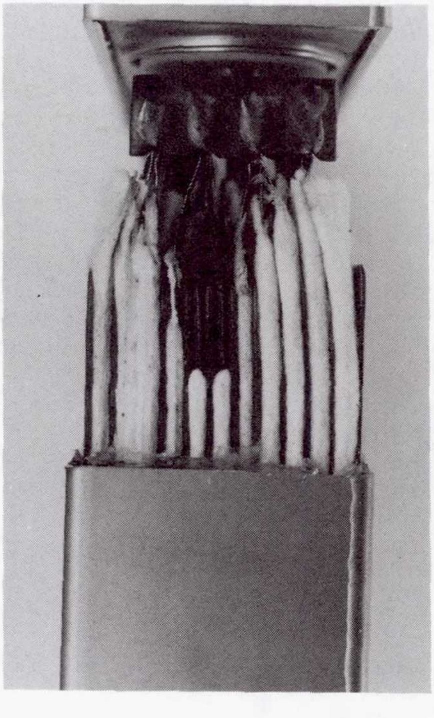


Figure 23-2

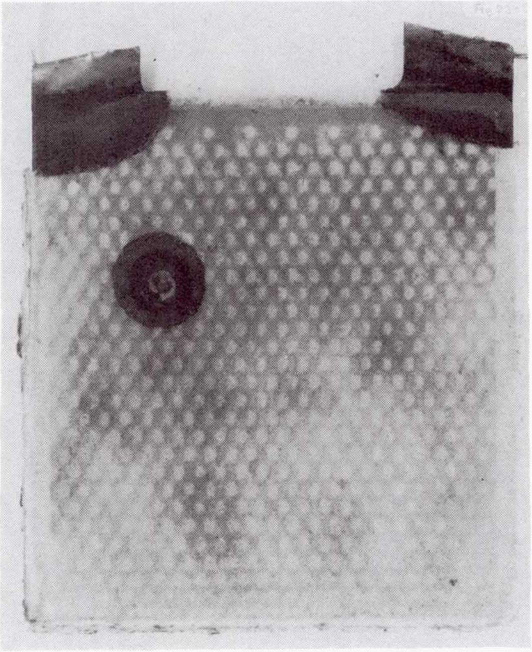


Figure 23-3

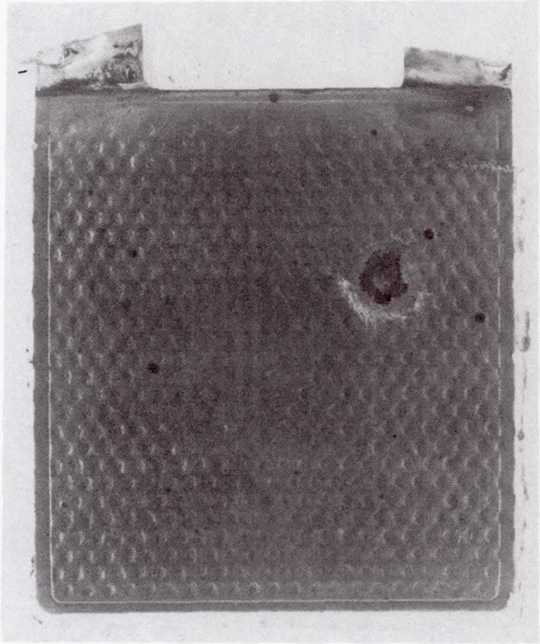


Figure 23-4

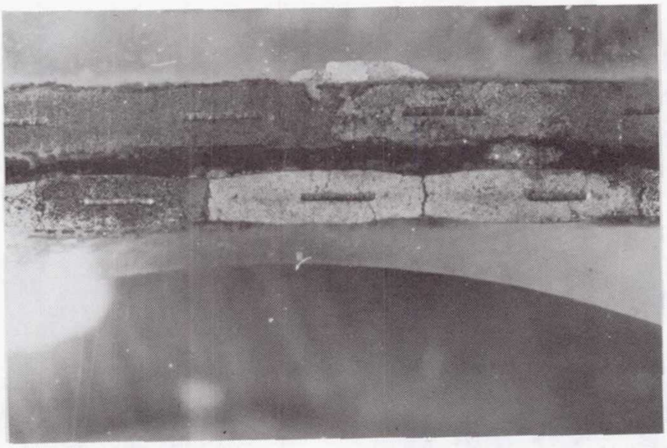


Figure 23-5

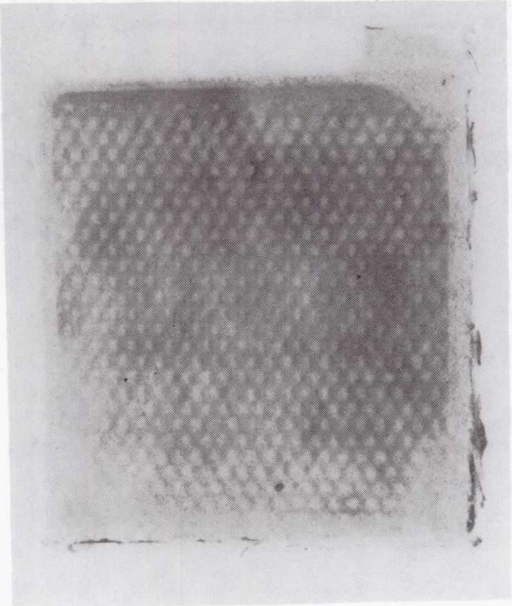


Figure 23-6

Figure 23-7

Figure 23-8

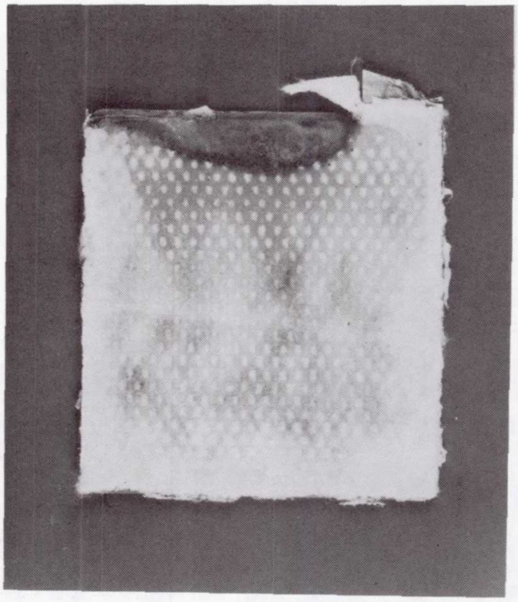


Figure 23-9

Figure 23-10

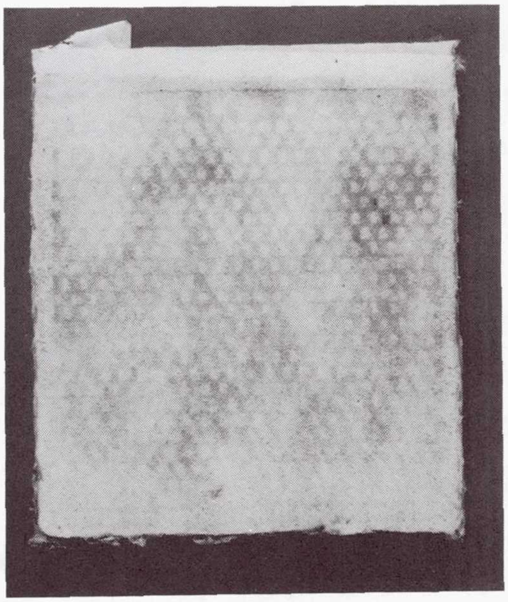


Figure 23-11

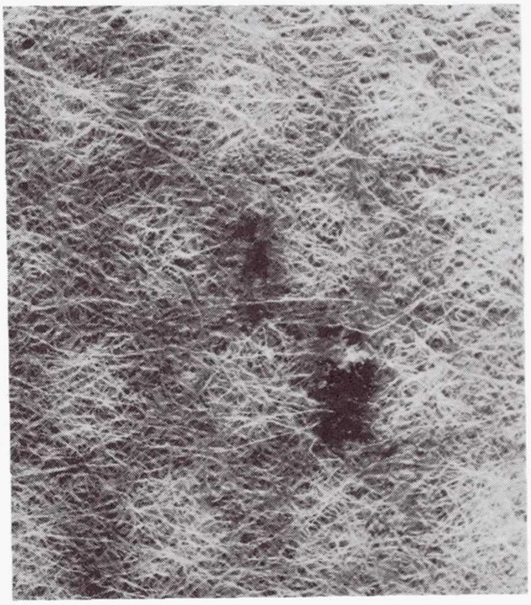


Figure 23-12

Figure 23-13

SESSION V

STATISTICAL ANALYSIS AND ACCELERATED TESTING

P. McDermott, Chairman
Coppin State College

ACCEPTANCE TESTS AND MANUFACTURER RELATIONSHIPS FROM THE 20A H STANDARD CELL DATA

H. Leibecki
NASA/Lewis

This talk will cover essentially multibearing non-parametric data analysis. We are looking at the acceptance test data acquired by Crane, because, with some information from them, we can start some more work on batteries without waiting for 16,000 - 30,000 cycles.

(Figure 24-1)

Goddard placed a group of standard cells on tests with four manufacturers to see if there was enough information from the acceptance test for separation. Figure 24-1 shows that the Yardney cells, the SAFT cells, the EP cells and the GE cells do contain enough information for separation from 17 test results on acceptance.

(Table 24-1)

This approach was then extended to a number of project cells in an attempt to classify them according to whether or not they fit into one of the four standard cell groups. It is obvious from Table 24-1 that some do fit, but that others do not. For example, the Landsat satellite cells do not fit the standard; the Teflonated negative electrode group of cells do fit; the stratospheric and aerocell gas experiment do not fit; and the tracking data relay satellite could not be classified as belonging to one of the four. This method required us to look at each cell and decide whether it is most like a GE, a SAFT, a Yardney or an EP cell?

(Table 24-2)

Table 24-2 shows a list of the 17 tests that were run. We have essentially capacity delivered values, end of charge voltage values and an internal short test (which was grouped with the capacity delivered because it is at the end of a discharge). The variance ratios listed in Table 24-2 indicate the ability of those tests to separate the project cells into various groups. Values of 1 would indicate no ability for separation. You can see almost all of the tests here have an ability for separation.

(Table 24-3)

In order to decrease the amount of data to look at from the tests, Karhunen-Loeve transformation was done on the data, in which we reduced them to four new variables that accounted for 91% of the information on separability. At the foot of Table 24-3 are listed the variables in the major eigenvector component for the test. In this case they are all the end-of-charge voltages.

(Figure 24-2)

The easiest way to look at that is by plots of the data. Figure 24-2 shows variables 1 and 2, and we can see the SAFT, the Yardney, the standard cell and Teflonated negative electrode groups, and the TIROS group, and then there is a large group of Eagle Picher and GP and the other project cells.

(Figure 24-3)

Figure 24-3 shows variables 1 and 3, and it may be seen that the Eagle Picher and the heat capacity mapping mission (HCMM) project cells break away from the rest of the group. We can therefore now separate out Eagle Picher, SAFT and Yardney, which leaves us with a big group of GE and project cells.

(Figure 24-4)

Figure 24-4 shows variables 2 and 3. Again the Eagle Picher cells separate out, and the SAFT and the Yardney cells group together. There is some splitting up of the project packs.

(Figure 24-5)

Figure 24-5 refers back to Figure 24-2. However, here I blanked out the Eagle Picher, the heat capacity mapping and the SAGE cells, because we knew we could separate out the Eagle Picher from the GE. We can now look at the GE cells in their grouping of project cells. You can see that they are close to the GOES cells and the DES cells. They have some correlation to the IUE and the TIRO.

(Figure 24-6)

Figure 24-6 shows the variables 1 and 3 (from Figure 24-3) with the SAFT, Yardney, Eagle Picher, and heat capacity mapping cells blanked out. This shows that GE is close to the IUE cells; the Landsat and the tracking data relay drop out into a group, the GOES, the TIROS cells, the DES, improved TIROS and the standard may all be formed into groups.

Now, we have only looked at variables 1, 2 and 3. However, when a decision was made from the original data, it was made by using all 17 variables. We did not want to show you 17 more slides, but I think this shows that we can separate out by project.

(Table 24-4)

Here Table 24-4 shows how we did it by just using a scaled set of data. Here again we ran the Karhunen-Loeve transformation. I should like to point out that we can only save 83% of the total variables. The first new variable has 35% of the separating information; the second 22%, the third 18%.

In this case, we see that the major eigenvector components of the first variable are discharge capacity tests, those of the second one are end-of-charge voltages and those of the third one are one discharge, and end-of-charge voltages.

(Figure 24-7)

Figure 24-7 shows a plot of these data; and we can see that the Yardney cells separate out by themselves with the SAFT also in a group. We again find EP and GE cells and project cells. Since we are not looking in this case for separation into project cell groups from the first standards, we could do that by using the other technique.

(Figure 24-8)

Figure 24-8 shows the data with the GE, EP, SAFT and the Yardney cells blanked out, so that we can view just the project cells. They are pretty well stretched out. It is rather interesting that we can find a line that goes up through this direction. I think these started out in 1974 and they went up by years, and stopped at 1980. Down in here we had a group that were 1978 and 1979, and the GE pack formed a bridge across from here to here. We can see the SAGE ones dropped off by themselves. This tells us that we can separate them out by differences. The other side of the coin is, what is similar about them?

(Figure 24-10)

We looked at similarities, using all 17 tests again as a composite. Figure 24-10 looks a little noisy at first. You can see that the first two blocks compose the GE standard pack project cells. There are two cells that are not much like these 28 GE cells.

There is a group of IUEs, one at 15 and one at 5. The GOES cells, the TIROS, the Landsat, which breaks down into a 6-cell group and a 2-cell group, and the tracking data relay (TDR), all form a group unto themselves. You can see that Eagle Picher cells form a group. One of the things that will be interesting would be to watch the top level, because the block filled in here is a composite of the differences of the similarities of the whole group. The Eagle Picher cells had a little more variation from cell to cell between the group. The high capacity mapping mission (HCMM) cell group was pretty close together, each one in their acceptance tests. We then find another three Eagle Picher cells that are quite different from the others. We would have to go all the way up to 74% similarily and back down to connect those three. The DES cells fall into a group by themselves. The Yardney and the SAFT form a group. They are connected, but they are really not that similar because they are only connected at the 76% level. Then we have the standard and Teflonated negative electrode group and the improved TIROS group here. The SAGE group is on its own at the end. In five cells they were only similar up to about the 50% level.

(Figure 24-11)

Now, if one looks at the data from which that composite was made: in Figure 24-11, two cell are a little higher than the other group. One I have no information on, the other was cell 4, pack 26, in its 30th month with no variation. We have another one, pack 26, cell 3, 30th month. We said there is an end-of-charge variation, although it does not show any difference here. The Landsat group is also shown here. We have one cell that is rather high and has a slightly lower output. The one next to it, which is also rather high compared with this group, has an end-of-charge voltage variation.

(Figure 24-12)

Figure 24-12 shows the TIROS cells, which form a small group. One of the DES cells sticks out, but it is in its 6th month. There is no listed variation. We ran into a problem here with the heat capacity mapping mission. They say there is an end-of-charge voltage variation, and yet the values are very low and very close together. Since I do not know what one would consider a variation, it may be that the voltages are not being measured to a low enough value. Acceptance tests have to be broken apart to get better information.

(Figure 24-13)

Figure 24-13 shows GOES cells. Two of these cells seem to be out from the others. One is in its third period, with no listed variation. This is not cycling, it is in storage. Below these cells are the SAGE cells. One seems to have entirely different cycling parametry, if the acceptance tests tell us anything at all about what the cells are like.

(Figure 24-14)

Figure 24-14 shows the standard and the Teflonated standard cells, the negative electrode cells. There is nothing of significance to report here. One is high; here again I do not have enough data available to say how far this has to be different from the other groups before it becomes significant. Ideally, one should have all the dots on the first line, meaning that all the tests had the same values for the acceptance tests. I think it is a little optimistic to expect that.

(Figure 24-15)

Figure 24-15 shows the IUE cells. One group was broken off from the five that we showed before. I should expect those to show somewhat different characteristics from the others.

We have got the results, but we still have some of work to do in understanding all there is to get the conclusive results for the experiments that were run. However, I think it does point out that there is enough information being gathered by acceptance tests to warrant further work.

DISCUSSION

FORD: You started off your statement that you were looking at the acceptance tests. This is the initial valuation tests that you are referring to?

LEIBECKI: Yes.

FORD: Later on in the discussion you implied that you were comparing cycle life?

LEIBECKI: No, I never look at cycle life.

FORD: Then all your charts are based on those initial 17 or 18 series of tests?

LEIBECKI: Yes. There are really eight tests, but when you take the capacity delivered, the end-of-voltage, you end up with 17 data points for each cell.

FORD: On Table 24-1, I do not understand the significance of the two right-hand columns. Could you explain those?

LEIBECKI: The first one is a classification of these cells as belonging to one of the four standard cell groups that Goddard ran. There are two methods of choosing: one is the K, nearest neighbor, which takes a cell and puts it in that group that it resembles most closely.

FORD: The Landsat D 50A h cell is a GE cell. Are you saying that the data indicate that it groups closely to the SAFT type cell?

LEIBECKI: These are all GE cells, except for the heat capacity mapping mission and the stratospheric aerosol and gas experiment. Yes, the Landsat D cell is most like the SAFT cell. The other column is a similarity-to principal-component model. This model only recognizes these four groups. It looks at the cell and decides, which one of these four it belongs to.

Now, when we looked at the plots of the Karhunen transformation of the data, which included all these pack data, we saw that the Landsat fell by the GE, but was nearer the bottom of the graph. If it put the Landsat cells near the SAFT cells, then the classification would have been SAFT, and not GE. If it would have fallen near the EP cells it had been classed as belonging to Eagle Picher. All the classification knows is that these four cell types exist.

THIERFELDER: Since there were no SAFT cells, how could it fall closer to the SAFT cells?

LIEBECKI: In order to find out why it classified some correctly and some incorrectly, the set was then incorporated into a standard set.

THIERFELDER: Where did you get the SAFT data?

HALPERT: I might be able to answer that. Several sets of cells were put on test at Crane; these were the standard cell program. That is, there were four packs from General Electric, four from Eagle Picher, four from SAFT and four from Yardney. All these data are being related back to what he saw on those four packs. Therefore, when he says that the Landsat cells look like SAFT, he is saying that if he compares them with the data that he got out of the SAFT cells in the initial evaluation test, they look most like those.

BOGNER: Generally the reason we go through these acceptance tests, I think, is to weed out bad cells. Now, have you been able to, or do you intend to use these data to try to correlate the acceptance test data with cells that fail early?

LEIBECKI: On the last part, where I showed similarities, I think there is enough to indicate further work there. You could then start to pick cells that are most similar to each other. It does not pick out bad cells from good cells, but just indicates that if one is way off, it is different.

If one was to build a balanced battery from cells, one would want them all to be as close as possible, and we should get enough information out of it to indicate that we can do that. At this point, I do not know.

FORD: I am intrigued by some of the data, by the fact that you mentioned the Hickeman SAGE. Battery designs for both of those spacecraft were discussed at previous workshops and they did fail prematurely. I am intrigued by what I see there after the fact.

LEIBECKI: I had no before-the-fact knowledge.

CLASSIFICATION OF PROJECT CELLS USING NASA'S STANDARD CELL PROGRAM

CELL TYPE		CLASSIFICATION	
		KNN (1)	SIMCA (2)
DYNAMIC EXPLORER SATELLITE	6.0 A-H	G.E.	G.E
GOES-D, E AND F SATELLITE	6.0 A-H	G.E.	G.E.
HEAT CAPACITY MAPPING MISSION*	9.0 A-H	E.P.	E.P.
IMPROVED TITROS OPERATIONAL	6.0 A-H	E.P.	SAFT
INTERNATIONAL ULTRA VIOLET EXP.	12.0 A-H	G.E.	G.E.
LANDSAT-D SATELLITE	50.0 A-H	SAFT	SAFT
STANDARD AND TEFLONATED NEG.	20.0 A-H	YARDNEY	SAFT
STRATOSPHERIC AER. & GAS EXP.*	9.0 A-H	E.P.	-
TIROS-N & NOAA-A SATELLITE	26.5 A-H	G.E.	G.E.
TRACKING DATA RELAY SATELLITE	40.0 A-H	E.P.	SAFT

*EAGLE PICHER
(1) K-NEAREST NEIGHBOR
(2) SIMILIARITY TO PRINCIPAL COMPONENT MODEL

Table 24-1

GEOMETRICAL AVERAGES OF THE VARIANCE RATIOS STANDARD CELL PROGRAM & PROJECT CELLS

ACCEPTANCE TEST	VARIANCE
CAPACITY DELIVERED	
CAPACITY TEST NO. 1	13.87
CAPACITY TEST NO. 2	19.62
CAPACITY TEST NO. 3	12.51
SPECIAL CHARGE RETENTION	12.04
CHARGE EFFICIENCY	9.64
OVERCHARGE TEST NO. 1 (0^{0}C)	9.52
OVERCHARGE TEST NO. 2 (35^{0}C)	11.14
INTERNAL SHORT TEST	12.96
END-OF-CHARGE VOLTAGE	
CAPACITY TEST NO. 1	7.11
CAPACITY TEST NO. 2	6.54
CAPACITY TEST NO. 3	4.16
SPECIAL CHARGE RETENTION AT	
END-OF-CHARGE	4.77
24 HOURS	17.95
1 WEEK	20.02
CHARGE EFFICIENCY	27.08
OVERCHARGE TEST NO. 1 (0^{0}C)	11.03
OVERCHARGE TEST NO. 2 (35^{0}C)	9.34

Table 24-2

KARHUNEN-LOEVE TRANSFORMATION OF VARIANCE RATIO WEIGHTED DATA

```
 EIGENVALUE  INFO PRESERVED *****************************************EIGENVECTORS*****************************************
               EACH  TOTAL
1  1.147E 03   36.4   36.4 -3.272E-01 -4.214E-01 -2.782E-01 -2.512E-01  1.681E-01 -2.569E-01 -1.292E-01  3.183E-01  8.232E-02
                            6.282E-02  3.395E-02  9.915E-03 -4.648E-02  1.562E-01  5.659E-01Ⓐ 1.708E-02  5.945E-02

2  1.043E 03   33.1   69.4 -1.835E-01 -3.509E-01 -1.917E-01 -1.682E-01  6.192E-03 -4.303E-02 -2.467E-01 -1.532E-01 -8.302E-04
                           -5.468E-03  1.343E-02  6.107E-02 -4.539E-01Ⓑ 5.229E-01Ⓒ 4.229E-01Ⓓ 1.678E-01 -3.926E-02

3  5.078E 02   16.1   85.5 -1.456E-01 -2.869E-01 -2.136E-01 -2.344E-01  2.203E-01 -2.709E-02Ⓔ 1.553E-01 -6.752E-03 -4.294E-02
                           -9.817E-03 -9.248E-02 -5.620E-02  4.227E-01  3.854E-01 -5.284E-01 -1.635E-01 -9.314E-02

4  1.866E 02    5.9   91.5  5.986E-02  8.713E-02  3.174E-02 -3.972E-02  5.857E-02 -8.718E-02 -2.861E-01Ⓕ 1.821E-01Ⓖ-3.466E-01
                           -3.039E-01 -1.827E-01 -2.218E-01 -1.159E-01 -9.661E-02  5.762E-02 -5.376E-01 -5.000E-01
```

KARHUNEN-LOEVE VARIABLE		MAJOR EIGENVECTOR COMPONENT
1	A	*END-OF-CHARGE CHARGE EFFICIENCY TEST*
2	B	END-OF-CHARGE SPECIAL CHARGE RETENTION TEST (1 WEEK)
	C	END-OF-CHARGE SPECIAL CHARGE RETENTION TEST (24 HOURS)
	D	END-OF-CHARGE CHARGE EFFICIENTY TEST
3	E	END-OF-CHARGE CHARGE EFFICIENCY TEST
4	F	END-OF-CHARGE OVERCHARGE TEST (0^{0}C)
	G	END-OF-CHARGE OVERCHARGE TEST (35^{0}C)

Table 24-3

KARHUNEN-LOEVE TRANSFORMATION OF SCALED DATA

```
 EIGENVALUE  INFO PRESERVED *****************************************EIGENVECTORS*****************************************
               EACH  TOTAL
1  6.003E 00   35.3   35.3 -3.716E-01 -3.722E-01 -3.674E-01 -3.430E-01  2.336E-01 -3.460E-01 -2.417E-01  2.181E-01  1.973E-01
                            1.777E-01  1.562E-01  1.497E-01 -1.527E-01 -4.056E-02  1.439E-01  1.409E-01  8.745E-02

2  3.795E 00   22.3   57.6 -6.784E-02 -4.047E-02 -9.429E-02 -1.446E-01  2.712E-01 -1.752E-01  1.457E-01  2.961E-01 -1.540E-01
                           -1.314E-01 -3.243E-01 -3.928E-01  3.254E-01  3.780E-01  1.351E-01 -4.064E-01 -1.352E-01

3  3.054E 00   18.0   75.6 -7.789E-02 -1.519E-01 -1.309E-01 -1.483E-01  1.054E-02 -9.826E-03 -3.240E-01 -1.969E-01 -3.690E-01
                           -3.569E-01 -2.816E-01 -1.296E-01 -2.932E-01 -3.345E-01 -3.078E-01 -5.916E-02 -3.634E-01

4  1.379E 00    8.1   83.7  6.548E-02  1.635E-01  1.896E-01  2.183E-01 -2.684E-01 -2.196E-01 -3.383E-01  3.551E-01 -1.174E-01
                           -2.064E-01  1.639E-01 -1.271E-01 -2.616E-01 -9.623E-02  5.803E-01 -7.504E-02 -7.170E-02
```

KARHUNEN-LOEVE VARIABLE	MAJOR EIGENVECTOR COMPONENT
1	DISCHARGE CAPACITY CAPACITY TEST #1 CAPACITY TEST #2 CAPACITY TEST #3 SPECIAL CHARGE RETENTION OVERCHARGE TEST #1 (0^{0}C)
2	END-OF-CHARGE VOLTAGE CAPACITY TEST #3 *SPECIAL CHARGE RETENTION* SPECIAL CHARGE RETENTION (24-HOURS) SPECIAL CHARGE RETENTION (1-WEEK) OVERCHARGE TEST #1 (0^{0}C)
3	DISCHARGE CAPACITY OVERCHARGE TEST #2 (35^{0}C) *END-OF-CHARGE VOLTAGE* CAPACITY TEST #1 CAPACITY TEST #2 CAPACITY TEST #3 SPECIAL CHARGE RETENTION (24-HOURS) SPECIAL CHARGE RETENTION (1-WEEK CHARGE EFFICIENCY OVERCHARGE TEST #2 (35^{0}C)

Table 24-4

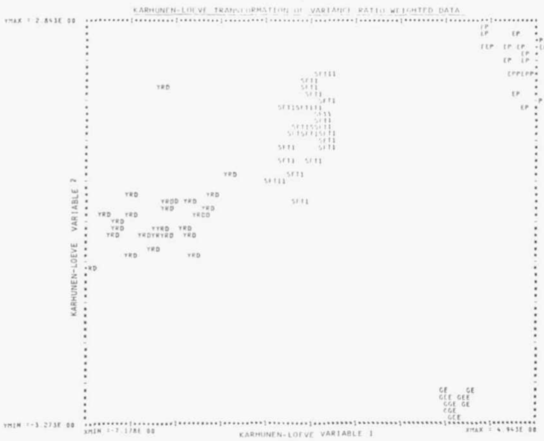
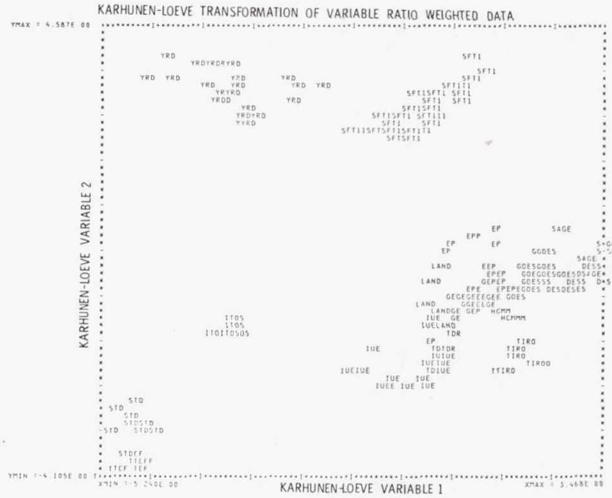


Figure 24-1



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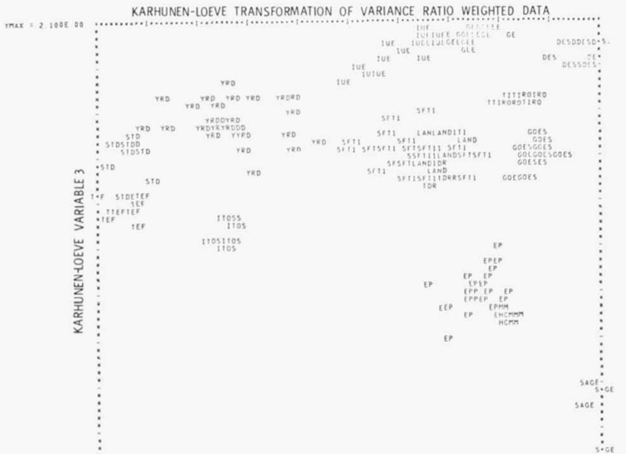

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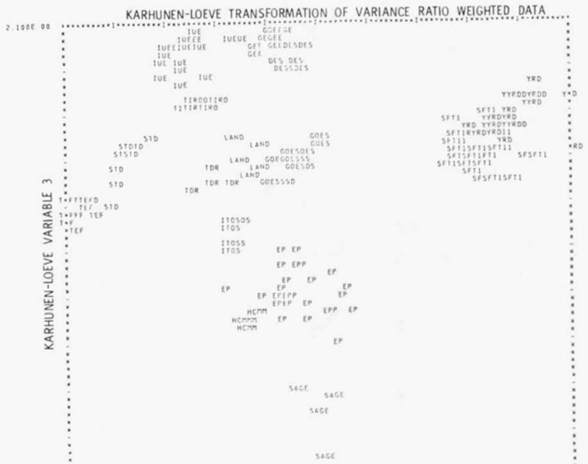

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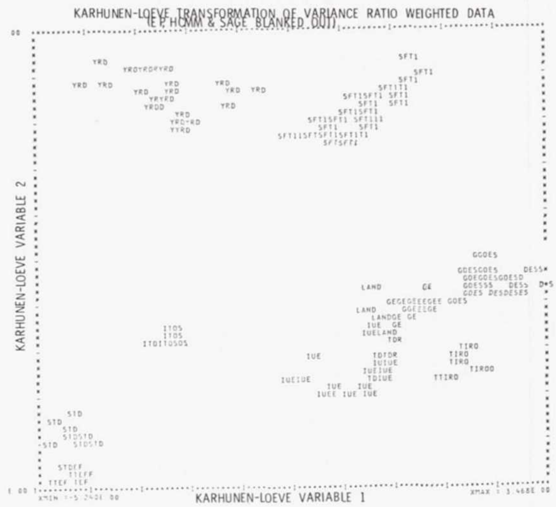

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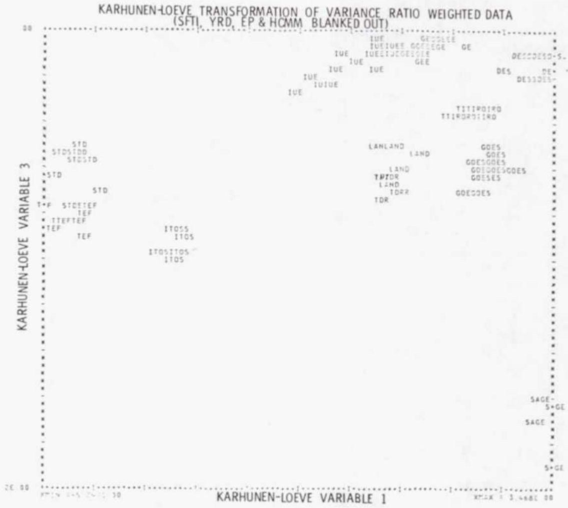

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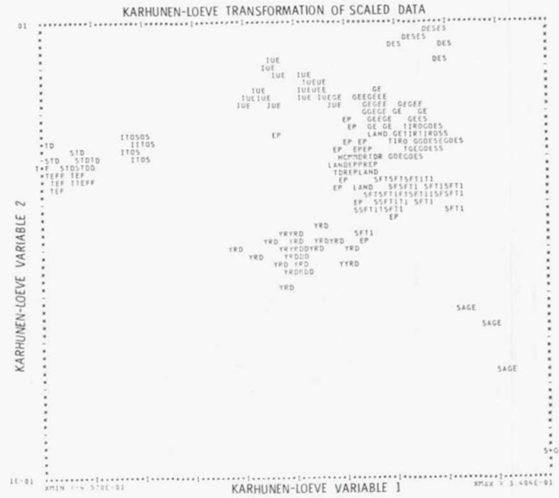

Figure 24-7

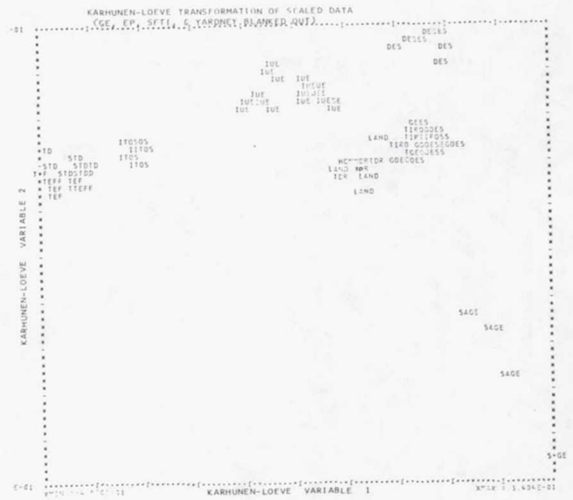

Figure 24-8

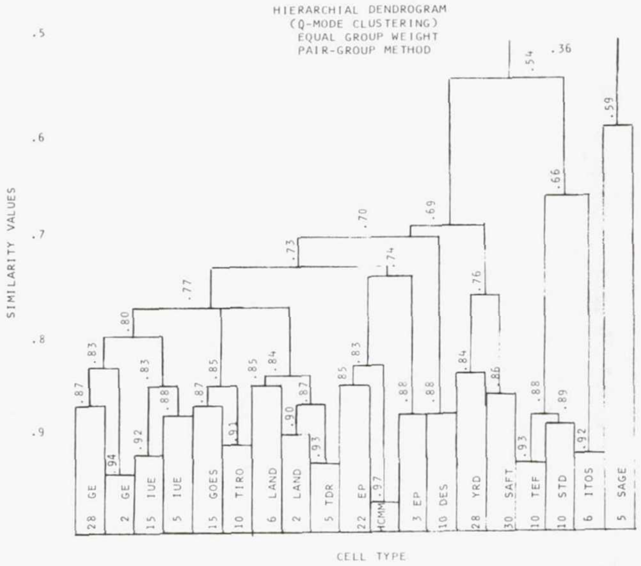

Figure 24-10

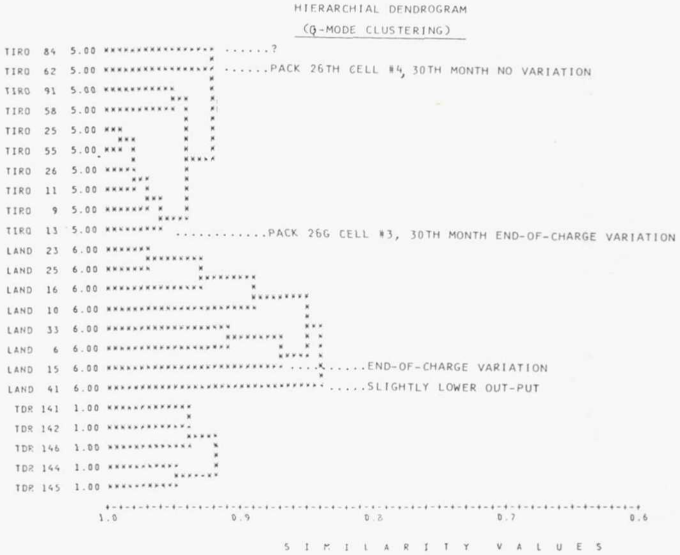

Figure 24-11

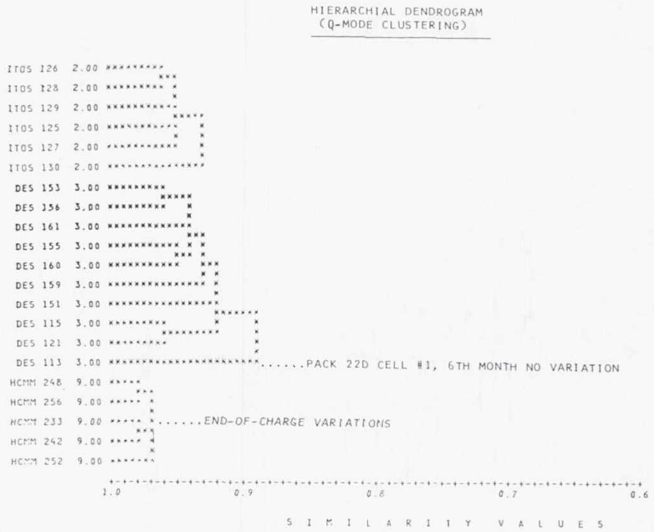

Figure 24-12

Figure 24-13

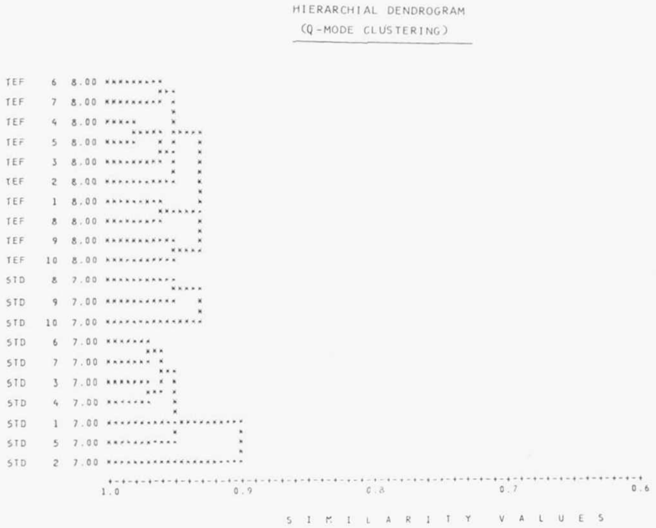

Figure 24-14

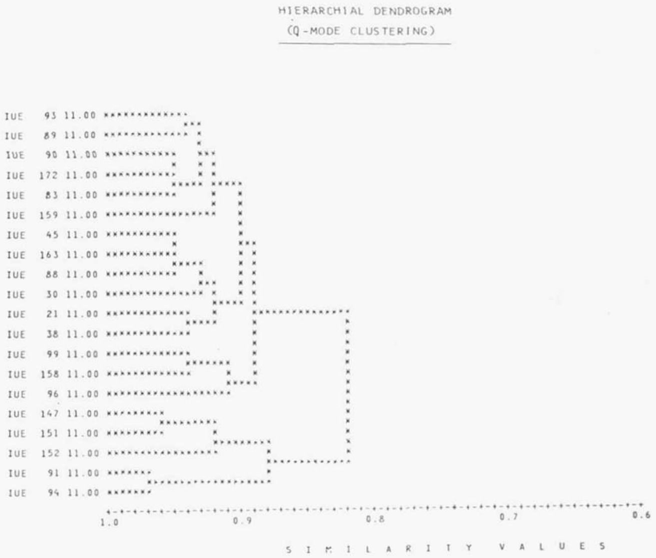

Figure 24-15

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BATTERY FAILURE MODEL DERIVED FROM FLAW THEORY

I. Schulman
Jet Propulsion Laboratory

At the fall meeting of the Electrochemical Society in Florida, Dr. Cizmecioglu of JPL presented a paper on a failure model for sealed nickel cadmium cells; this was based on work accomplished at the Jet Propulsion Laboratory. It is the purpose of this presentation to review the derivation of the failure model and, more important, to demonstrate the practical application of that model. I shall also present some of our latest findings which indicate the universality of this model.

It is not the intention of this review of the derivation to merely reiterate a very thorough paper delivered by Dr. Cizmecioglu, but to reexamine the basis for this failure model and to emphasize certain points pertaining to the derivation. For a full derivation, I recommend that you read the original paper to which I referred.

There are two ways to approach a predicted model for battery lifetime. The first method, and certainly the more popular, is to describe the data from various programs in terms of linear or non-linear mathematical functions. These functions may be empirical or based on the system reactions, but in either case, the fit of the data provides the numerical values of the coefficients appearing in the function. Once these coefficients are known, the function can be used to obtain interpolated values for the variables of interest. Excellent predictive models have evolved from the analyses performed by Dr. McDermott and others, and we are now attempting to compare these models with the JPL failure model to understand all the similarities and the differences.

The second approach is to develop a model that may be derived from either a detailed knowledge of the behavior of the system, or more commonly from intuitive arguments. The basis for our model is the assumption that a nickel cadmium cell fails because of the growth of a pre-existing flaw or defect to a critical value. In this treatment, the exact mechanism of failure need not be known. Thus, in this model developed for predicting cell lifetimes, the following assumptions are made: that flaws or defects exist in all the cells; and only one type of flaw exists.

The flaw characteristics, which we would like to describe because they are important are: the rate of growth of the flaw; the distribution of the flaw sizes; and the total number of the flaws present.

The first factor to be considered is the rate of growth of an individual flaw. It is reasonable to assume that the growth of the flaw is caused by its interaction with electron movement within the cell. Thus, for a cyclic charge/discharge test to failure as described in the various Crane reports, it is assumed that the rate change in the flaw size, c, with cycle n, is given by equation 1.

$$\frac{dc}{dn} = kf^{m} c^{s} \qquad (1)$$

where f is the number of faradays passing through the cell per cycle, k is the reaction rate constant, and m and s are constants.

This equation can be recast in the form of equation 2:

$$c_0^{(1-s)} \left[\frac{d\left(\frac{\Delta c}{c_0}\right)}{dn} \right] = kf^{m} \left(1+\frac{\Delta c}{c_0}\right)^{s} \qquad (2)$$

where $c = c - c_0$, c_0 is the initial flaw size when the cycle number is n_0 and c is the flaw size at cycle number n. If we integrate equation 2, we arrive at equation 3:

$$(n-n_0) = \Delta n = \frac{1}{kf^{m} c_0^{s-1}} \left[\frac{\Delta c}{c_0} - \frac{s}{2}\left(\frac{\Delta c}{c_0}\right)^{2} + \frac{s(s+1)}{6}\left(\frac{\Delta c}{c_0}\right)^{3} - - - \right] \qquad (3)$$

Another important assumption made in the derivation is that the reaction rate constant k depends only on temperature, and is given by an expression of the Arrhenius form, and that is shown in equation 4,

$$k = k_0 e^{\frac{-\Delta E}{RT}} \qquad (4)$$

where k_0 is a parameter independent of the temperature, whose value depends only on the nature of the reaction involving the growth of the flaw, and ΔE is the energy associated with the reaction or transformation.

A few other transformations are made, which are best explained in the original article. The equation shown here (equation 5) represents a general expression relating the growth of a single flaw of initial size c_0 to the cycle number.

$$\Delta n = \frac{e^{\frac{\Delta E}{RT}}}{k_0 (DOD)^m (2C_0 g)^m c_0^{\,s-1}} \left[\frac{\Delta c}{c_0} - \frac{s}{2}\left(\frac{\Delta c}{c_0}\right)^2 - \frac{s(s+1)}{6}\left(\frac{\Delta c}{c_0}\right)^3 --- \right] \qquad (5)$$

You will notice that f has disappeared; it is replaced by DOD, the depth of discharge. C_0 (which is a very unfortunate choice of terms; we have C_0, c_0 and g) is the intrinsic capacity of the cell, and g is a function related to the test conditions, temperature, rate, etc, and how it affects the capacity of the cell.

Since we have no way of estimating the value of s, we assume as a first estimation that its value is zero. This assumption means that the rate of growth of a flaw is independent of the flaw size. The eventual application of data proves the validity of this assumption.

The value of, s being zero cancels out all of the terms of the expansion except the first term, and leads to the simplified equation 6.

$$c_f - c_0 = n_f k_0 (DOD)^m (2C_0 g)^m e^{\frac{\Delta E}{RT}} \qquad (6)$$

where n_f is the number of cycles to failure and c_f is the size of the flaw at battery failure.

So far, we have been concerned with the growth of a single flaw of initial size c_0, and we must now deal with the remaining flaw characteristics, the distribution and the number of flaws within the cell. If we assume that in any given cell the largest initial flaw will determine the lifetime of the cell, then we are concerned with the distribution of the largest value of c_0 in a population n, which represents a large number of flaws within that cell. This type of problem can be treated by a branch of statistics called extreme value statistics. The limited power low probability density function is convenient to describe the distribution $h(c_o)$.

$$7) \qquad h(c_0) = (c_f - c_0)^{\beta - 1} \qquad \beta > 1, \quad c_0 < c_f \qquad (7)$$

where β is independent of the test conditions.

It has also been shown that for a large number of flaws per cell, the distribution of c_0 follows the Weibull distribution shown in equation 8.

$$\phi(c_0) = 1 - \exp\left[-\left(\frac{c_f - c_0}{c_f - c_0^*}\right)^{\beta}\right] \tag{8}$$

where c_0^* is the characteristic or most probable value of c_0; if the value of $c_f - c_0$ from a previous equation is substituted into the Weibull distribution, we arrive at the equation for a cumulative distribution of lifetimes as shown in equation 9a,

$$\text{a)}\quad \left|1 - \phi(n_f)\right| = \exp\left[-\left(\frac{n_{f,\,red}}{n^*_{f,\,red}}\right)^{\beta}\right] \tag{9a}$$

$$\text{b)}\quad n_{f,\,red} = n_f\, k_0\, (DOD)^m\, (2C_0 g)^m\, e^{\frac{-\Delta E}{RT}} \tag{9b}$$

If we substitute equation 9b into 9a, and take natural logs of both sides, we arrive at equation 10.

$$\ln\left[-\ln\left(1 - \phi\,(n_f)\right)\right] = \beta \ln n_f + \beta \ln k_0 + \beta \ln (DOD) + \beta m \ln (2C_0 g) - \beta \frac{\Delta E}{RT} - \beta \ln n^*_{f,\,red} \tag{10}$$

In equation 10 you have a log of a log. Unfortunately, when you are dealing with Weibull distributions, that is what you end up with.

With the data from the NASA accelerated test program, (n_f), m and E have been determined, and the method for doing this is explicitly described in the paper by Cizmecioglu. ΔE has been determined to have a value of 5.5kcal/mol, which is a rather low value for a chemical reaction, but of an appropriate magnitude for a physical or transport process. The constant m has been determined to be 1.5. The accelerated test program data were divided into four groups according to the charge/discharge rate imposed. Within each group the lifetime data were reduced to this final equation 11:

$$n_{f,\,norm} = n_f\, (DOD)^{1.5}\, e^{\frac{\Delta E}{RT}\left(\frac{1}{303} - \frac{1}{T}\right)} \tag{11}$$

Now, $n_{f,norm}$ is equal to the expected lifetime of a cell at 100% depth of discharge and 30 C. That is an arbitrary choice that we took.

Figure 25-1 shows a typical graph describing $n_{f,red}$ or $n_{f,norm}$ plotted against the probability of failure for data obtained from the NASA accelerated test program run at Crane.

(Figure 25-1)

These data are from the packs of cells cycled at the C charge rate and the C/2 discharge rate.

(Figure 25-2)

Figure 25-2 shows a practical application of these types of graphs. To illustrate, we have made up a little problem. In this problem we assume we have a mission requirement of 50,000 cycles at a cell temperature of 20 C and a DOD of 10%. We are trying to determine the probability of failure, or by subtracting that from 100, the probability of survival. Using the final equation as shown, and substituting the initial conditions, we get a reduced or a normalized cycle lifetime of 1160 cycles. Moving to the curve and dropping down to the abcissa gives us the result that the probability of failure is 42%. It is interesting to note that if we reduce the depth of discharge from 10% to 5%, the probability of failure would be also reduced from 42% to 7%.

In order to test the universality of the flaw theory, Dr. Fadus of JPL gathered all the Ni/Cd data he could find the Crane reports, and he plotted all these data en masse.

(Figure 25-3)

He used cycling data from eleven manufacturers, and some of the data, I am quite sure, are for flooded pocket types. I can not think what else NIFE makes. He also used cycling information from tests run at 20 to 40 C. Figure 25-3 depicts the normalized lifetime and probability of survival rather than probability of failure. There is at least an indication of some linear relationship between the probability of survival and the normalized lifetime. This implies a universality of the flaw theory as far as it pertains to the total nickel cadmium system. Of course, the term "universality" also implies that the theory should apply to other systems.

(Figure 25-4)

Because there are only a few data pertaining to silver systems, Dr. Fadus combined cycling data from both the silver cadmium and silver zinc cycling programs, and described the data as shown in Figure 25-4. Although this is by no means a perfect linear relationship , there is still a very strong implication that the flaw theory can be applied to the silver cells. This, in turn, supports the argument of universality of the theory.

We are continuing along this path at JPL. We intend to look at many other systems, such as the lead acid systems, to try to apply this theory there. In addition, we are proceeding with the diagnostic tests, which support the overall theory.

DISCUSSION

LEIBECKI: When you made the comment the size has no effect on a flaw, are you are saying that if it is a short in the surface areas it has no effect?

I should also like you to comment on why you picked the Weibull distribution. It is rather interesting. We ran some silver zinc cells at Crane and did an impeding failure mode analy- sis to determine the probability of failure by short or by capac- ity loss, and it also came out to be a Weibull distribution.

SCHULMAN: To answer your first question, the first assumption that s = 0 was a convenience, to simplify the equation,. We feel that the application validates that assumption. The explanation that when s = 0 the rate growth of the flaw is not equal to the original flaw size, because if you look at the first differential equation it would merely say $dc/dn = kf^m$. In fact, most of this could have been simplified if the authors did not try to generalize it and get into a series. They could have simplified it from the beginning by saying that s = 0.

As far as the Weibull distribution is concerned, it is used by other organizations. For instance, in their analysis for reliability on the HEO program, TRW applied Weibull distributions and found that they pertained.

LEIBECKI: The reason I asked is that we actually measured the distributions.

SCHULMAN: I see. Did they apply?

LEIBECKI: Yes, for silver zinc.

SCHULMAN: Yes, that is very good. That is all this is saying.

LEIBECKI: I just wondered if you had some other reasons.

SCHULMAN: No, we are only using the Weibull distribution in describing the distribution of flaws.

KUNIGAHALLI: You said that E has a value of 5.5kcal/mol which is a very low value for a chemical reaction. Do you think that it would vary depending upon the ampere average of the cell considered, of on the impurities added in the cell? That would also contribute to the type of reaction that may be going on there, in addition to the temperature.

SCHULMAN: No. We tried to measure E on the silver cells and we had a tremendous scatter. For this particular program we just assumed that it was the same for silver as it is for nickel cadmium. Probably the obtaining of E is the most difficult part of this program because there are not really many data to obtain it. However, in my judgment it has nothing to do with the additives or anything of that nature. It is a characteristic of the cell itself.

KUNIGAHALLI: Is it possible to experimentally verify the value that one can get by the theoretical prediction for E?

SCHULMAN: I do not know. It may be.

BATTERY FAILURE MODEL DERIVED FROM FLAW THEORY

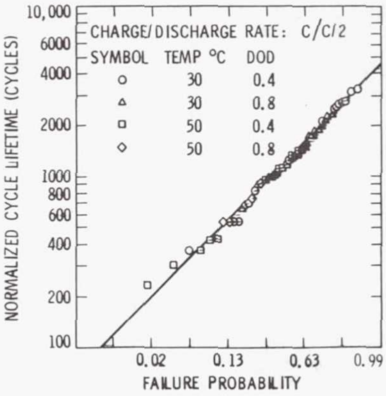


Figure 25-1

BATTERY FAILURE MODEL DERIVED FROM FLAW THEORY

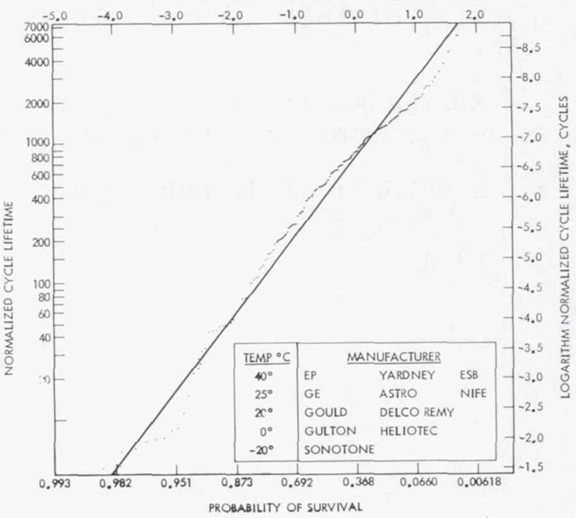


Figure 25-2

BATTERY FAILURE MODEL DERIVED FROM FLAW THEORY

EXAMPLE: MISSION REQTS: 50,000 CYCLES, BATTERY TEMP 20°C, DOD = 10%
DETERMINE: PROBABILITY OF SURVIVAL

1ST CALCULATE CYCLE LIFE PARAMETER
(NORMALIZED TO 30°C, 100% DOD)

$$n_f' = n_f\,(DOD)^{1.5}\, e^{\frac{\Delta E}{R}\left(\frac{1}{303} - \frac{1}{T}\right)}$$

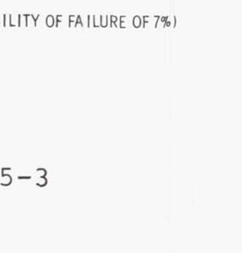
WHERE n_f = 50,000 CYCLES, DOD = 0.10

$$\frac{\Delta E}{R} = 2750 \qquad \left[\begin{array}{l}\Delta E = 5500 \text{ cal/mole}\\ R = 2\end{array}\right]$$

T = 293°K

n_f' = 1160 CYCLES

2ND ENTER GRAPH AT 1160 → TO CURVE: DOWN TO READ 42% PROBABILITY OF FAILURE



(NOTE: SAME EXAMPLE, BUT DOD 5%, GIVES PROBABILITY OF FAILURE OF 7%)

Figure 25-3

BATTERY FAILURE MODEL DERIVED FROM FLAW THEORY

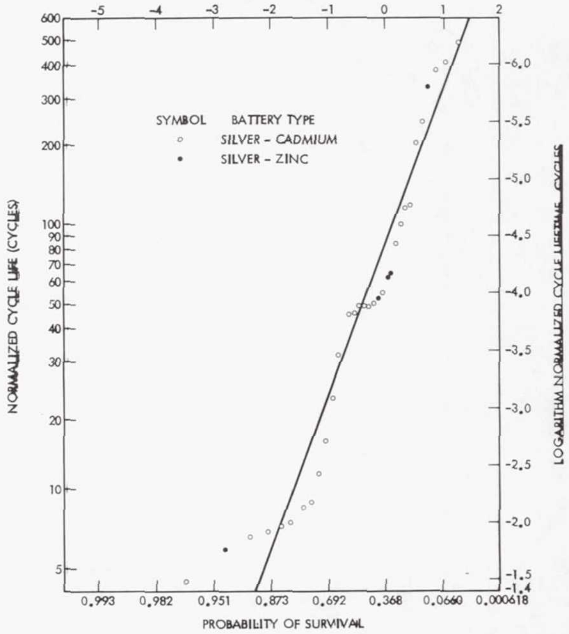


Figure 25-4

ACCELERATED TESTING FOR SYNCHRONOUS ORBITS

P. McDermott
Coppin State College

I should like to present an update of the work that I have been carrying out on the Crane acceleratd test program. For the last two workshops, the question has arisen as to whether the Crane data are really relevant to synchronous orbit. The equations that we were developing with the regression analysis were not really directly applicable, and so it was a very important question.

I tried to see if there was a new way that we could extract from the data some information that would be important for synchronous orbit. At the beginning I felt I might have been too optimistic in trying to generate a synchronous orbit test out of essentially near-Earth orbit data. However, when I looked into it, I saw that there might be a way of extracting some influences of variables that we had not seen before, for example, the influence of charge rate.

If we look at a synchronous orbit, there are really two modes of degradation present. One is degradation that is going on during the eclipse period when the cell is cycling at different levels of depth of discharge and then charging from of the next shadow period, the next day; I take that as one period in the life of that cell, as the period during eclipse, however many eclipses the cell has to undergo. Then there is the long period in overcharge during the light period when the cell is not cycling but is simply sitting on trickle charge. This period also has degradative effects. Up to now we really have not known the balance between the degradation due to that long life period and that due to the eclipse period.

We know that if we put simulated eclipse periods back to back, we can run many more eclipse periods than we would anticipate that a cell could take in real synchronous orbit. There must therefore be some degradation at least, and possibly a lot of degradation, during that overcharge period.

I was trying to see if there was a way of quantifying this. I tried to look at the Crane data and separate out, if possible, the degradation simply due to charge rate and temperature when the cell was in a state of equilibrium. I tried to find this in the period of the cycle. When we think of a cell cycling, there are really three periods or phases of the cycle: the first is a discharge period down to whatever depth of discharge the cell is going; then there is a charge up to 100% charge is taken out. This would be the charge period. Then there is the period in overcharge, where it is essentially sitting at a trickle charge or at some specific charge rate.

With the Crane data, every cell would have gone through one of those three phases, each of them at different rates, at different temperatures and different depth of discharge.

(Table 26-1)

Table 26-1 shows the matrix for the accelerated test program.

(Figure 26-1)

We tried to see what influence the various parameters had on degradation. Figure 26-1 shows the qualitative effect of the parameters on life, where the cycles are plotted on the ordinate, and the various parameters, temperature, depth of discharge, discharge rate and charge rate for these four are plotted on the abscissa. This is qualitative in the sense that there are only three packs involved in each of these graphs. Therefore I am not putting much quantitative weight to this.

We see that the temperature is roughly linear from 20 to 60 C for the Crane packs. There is quite a variation from 5000 cycles at 20 C down to very few cycles at 60 C, and it approaches a linear relationship.

In the depth of discharge, there is even more of a variation, from almost 14,000 cycles down to less than 1000 cycles, over the range (20 - 100%) that we were using for the Crane test. It turns out that this is an exponential function.

For discharge rate and charge rate, we found that the maximum occurred somewhere in the middle of the range that we were using for the accelerated test matrix for both discharge rate and charge rate. However, in later examinations, I think we have come to the conclusion that this failure for the charge rate at C/4 may be somewhat artificial, i.e. the cell simply was not charging up enough and therefore it showed itself as a failure for loss of capacity or at low voltage. In reality, for the temperatures involved, it just was not charging up. Therefore, that cell coming off of the test would be actually in very healthy condition and I should not consider it a real failure.

(Figure 26-2)

Figure 26-2 shows the variation with other parameters there. For the percentage of KOH, and amp hours of recharge,tThere is not too much variation, 1000 cycles over the range that we studied; and for the volume of KOH there is less variation. There was quite a bit of variation for percentage recharge, and it was again somewhat linear from 3000 down to 1000 cycles.

I wanted to look at this quantitatively to see what was the change in variation for each of these.

(Table 26-2)

If we look at the analysis of variance, which is a statistical technique, we can essentially divide the packs in the whole test matrix into two and consider all the cells that have the low level of temperature in one category and all that have high-level temperature in another category. There is quite a bit of variation for temperature, considering the classes (5000 versus 2000 cycles).

This confirms again that temperature is a definite degradative effect in the test matrix. The DOD varies from 6000 roughly down to 1300; here again is a very large effect.

The discharge rate does not vary so much, and nor does the charge rate. The percentage recharge has moderate variation. The percentage KOH and volume of KOH and precharge do not show very much variation at all. This was a quantitative confirmation of what we had suspected just by plotting a few of the packs of the individual parameters versus cycles to failure.

(Table 26-3)

If we look at the interaction of these parameters (Table 26-3), we see the more important combinations of these variables. By combinations I mean that if you take the packs with high temperature and high depth of discharge, and compare them with those packs having low temperature and low depth of discharge you see quite a variation. This is a way of saying which of the variables are interacting with each other to produce the greatest change of degradation with cycling. As we would anticipate, temperature and depth of discharge are the highest; all the temperatures and all the depths of discharge have a fairly large impact on the change of cycle. Notice that a combination of discharge rate and charge rate does not produce that variation.

(Table 26-4)

Discharge rate and charge rate and the other parameters are combined with each other in Table 26-4. The differences from column to column are much smaller, which again is a quantitative way of saying that the variations are not large.

I concluded last year that in terms of accelerated testing, the best accelerating parameters would be temperature and depth of discharge. Depth of discharge is probably the most important, because it can be mapped very well with an exponential function. Over the temperature range that we were studying the cycle life was linear. However, I suspect that it is not linear at the extremes of high temperature or very low temperature. However, at least in the range that we were talking about, it did seem to map in a linear fashion. The recharge rate is another useful parameter. As far as the discharge rate and the charge rate were concerned, there was some uncertainty.

(Figure 26-3)

Figure 26-3 is a graph showing the computation when you take the independent variables (in this case the temperature, depth of discharge and the other parameters where cycles to failure is a dependent variable) and go through a regression analysis; you will get regression coefficients, which will be used as the output to make a prediction on the normal packs.

(Figure 26-4)

For a nonlinear regression equation (which we have developed and talked about previously, and so I shall not go into too much detail here), we have put recharge in as a linear term, temperature as a linear term, and depth of discharge as an exponential term. We see in Figure 26-4 the addition into the program of the various parameters one at a time. In other words, for the dark circles, it shows that the program is taking a constant multiplier A1 with a temperature term here and with the depth of discharge, so that it is only considering three of the variables and not the other aids or the other three cycling parameters. It will calculate a constant for each of those, 1500, 70 and 0.38. Then, if you add in the recharge term (the triangles) as shown, A1 is being calculated, A2 and also A3 and A4. This now excludes discharge rate and charge rate, and we find different coefficients, 0.38 and 0.37, as expected. However, there is not much change. At the time I added discharge rate and charge rate as linear terms because I did not know their functional relationship. Notice that they had extremely low coefficients, which means that this is adding or subtracting very few cycles to the end product. This implied that either discharge rate and charge rate were not really affecting degradation much, or that I was putting it in the equation incorrectly. In other words, I did not have the proper functional relationship, and therefore in the regression analysis itself, it was not having a great impact.

(Table 26-5)

Table 26-5 shows the cycles times 1000. You see by the addition, this was only -- the dark circles were discharge, depth of discharge and temperature only. This was depth of discharge, temperature and recharge. And this was including discharge rate and charge rate. You see there is not that much change in the normal pack predictions.

(Table 26-6)

If we were going to go into a discussion of synchronous orbit and the effect of charge rate, we should then have to get a functional relationship for charge rate and degradation. This means that we had to look for a different type of interaction of charge rate with those other parameters. Table 26-6 shows the breakdown that I mentioned before, into the three phases of the cycle that the parameters used in the Crane accelerated test have meaning. In the discharge phase, the depth of discharge certainly has an impact, but the recharge, percentage recharge and charge rate do not, and the discharge rate has an effect. In the second phase, charge to 100%, DOD, temperature and charge rate have an impact, but the recharge and discharge rate do not. Finally in overcharge, depth of discharge, temperature, recharge and charge rate have an effect. However, discharge rate has no impact. If we could therefore find a way of separating out the effects of these, and just concentrate on the effects during each phase, then we might be able to pick up a dependency or a relationship to cycles to failure for charge rate. SOC stands for state of charge. This means that in the calculations with the regression analysis, the depth of discharge is really put in here as the maximum state of charge down to which the cell is cycled, and here the amount put back in. We are really calculating a limit of an integration of state of charge interacting with the other parameters. That integral is going to enter the regression equation.

(Table 26-7)

By going through a process of comparing the 140% packs with the 200% packs, all other variables being the same, I was able to extract a relationship of charge rate and degradation. I cannot go into much detail now, but the method I used to extract this relationship is documented in more detail at the ICEC meeting in Seattle. It is concerned with comparing packs that are the same in all respects except for the fact that one pack was cycling at 200% recharge, and the other at 140%. In every case, the 140% pack lasted longer, as expected. Therefore, by finding the reciprocal of the number of cycles that that particular pack went at 140% depth of discharge, I could say that the cycling up to that point had a fraction of life of the reciprocal. Then, considering the 200% recharge pack -- let us say that it went 2000 cycles -- if I multiply 2000 cycles by that fraction that was derived from the 140% pack, I can find out how much of the proportion of degradation for the 200% pack was due to cycling up to 140%, and how much was due to being in overcharge from 140% up to 200%.

Thus, what I was doing was putting the degradation of the overcharge period on to a clock time in the sense that if the cell had been put on tests only at a particular charge rate and temperature, it would theoretically last so long. Table 26-7 shows the data that came out of it: simulated, synchronous orbit with the Crane packs versus some Crane real time synchronous orbit tests.

I simulated the life in years at these various overcharge rates and temperatures. I am emphasizing that this is simulated and it is not a real time test. However, it is difficult to get a test of an overcharge at 2C at 30 C without the cell blowing up.

We are thus extracting the influence of charge rate and temperature only for that period when the cell is beyond 140% up to 200%, so that it does not have that much time in that interval in the Crane test to accelerate to outlandish temperatures and so on.

(Figure 26-5)

By plotting this (as shown in Figure 26-5) I found a dependence between time to failure in sychronous orbit and temperature. With different charge rates, 12A, 2C for these particular cells, 3A and 0.2A I found that there was a convergence up around 57 C, which means if you had put them on tests at 60 C, they would not have gone for any time at all.

From these data I was able to derive some relation between temperature and charge rate in overcharge only. The coefficients that came out of that particular calculation are 0.5 and 57, and 1.17 for this and the square root of charge rate. The life prediction equation for the three phases of cell degradation is as follows:

$$\text{Life} = K_1 f(T, e^{DOD}) + K_2 f(T, e^{DOD}, CR) + K_3 f(T, RC(DOD), e^{CR}).$$

I have not gone into this calculation yet, but the next phase of the work is to go back and take the different phases of the cycle and look at each one of them with a new additional function of charge rate, the square root, as an exponential term. This will be relevant to phase 2. Since the cell is undergoing a particular charge rate during phase 2 and phase 3, these functions will be relevant. In phase 1, phase 2 and phase 3, you will have depth of discharge. I put depth of discharge down here as an exponential function, and here because I feel that the depth of discharge is again a limit of an integral, and your integrated state of charge from zero down to whatever depth of discharge. In phase 3, depth of discharge is coming in simply as a calculation along with recharge rate to tell how long or how many faradays of electricity were actually going through the cell during the overcharge. The temperature will remain linear, and there will be constants for each of the three phases.

What I am searching for is the ability to separate variables by separating the different periods of the cycle to find the functional relationships for each phase for the various parameters, to try to link that to degradation. Therefore, the final nonlinear regression equation will contain three major terms for the three separate phases, and each of those will contain terms, some of which we have already derived, and others that we shall have to put in.

DISCUSSION

DUNLOP: Are your depth of discharge numbers rated or measured?

MC DERMOTT: They are rated. That has always troubled me. Some of the experts in the regression field said that it makes no difference whether depth of discharge is rated or not, that it comes out as a constant and will actually be a constant multiplier. Therefore, let us say the actual value was 9A h, the rated was 6. Let us say 8A h, that it becomes a constant multiplier throughout the equation.

DUNLOP: I would agree with that, except that the problem is when you try and compare other batteries. There has been a tendency in the last ten years to change the difference between the measured and rated capacity. Ten years ago there used to be roughly a 20% margin between measured and rated capacity if you ran a discharge at, say, 20 C. Today, if you look at the same manufacturer, you will probably find more like a 10% difference between rated and measured capacity. I think one of the reasons is that today's manufacturers are controlling the process a little better and they are pushing energy density a little harder. There is a tendency to squeeze down that ratio between measured and rated.

If you want to take any variability out of your -- and depth of discharge becomes an extremely important variable for synchronous operation. It is very important to be clear whether you are talking about 50% or 60% depth of discharge, in terms of your lifetime expection.

LURIE: Did you actually carry through the various analyses and and then make an estimate of the significance of the trend? Some of the trends look significant, and others, considering what is involved, really did not.

MC DERMOTT: I did not carry out that portion. That was done at JPL and I just took their results. Do you remember if they did that sort of thing, Mr. Bogner?

BOGNER: No more than what you showed on your graphs.

MC DERMOTT: I think one of the problems with that in the case of charge rate and discharge rate, is we were hitting the midrange. That is, if the range went from low cycles up to high cycles down to low cycles, and you cut that population in half, they might not show a great variation. However, the low ones, particularly for charge rate, might have been artificial failures. Therefore, I am not sure that the analysis of variance really gives you a clear quantification of that difference.

LURIE: If in fact there is no trend, but if normal variation dispersions account for a large part of those differences, what is the significance of the fact that it can be fit in some kind of an arbitrary equation?

MC DERMOTT: We put a number of different equations and different functions, and we looked at the standard estimate of the error for each. We found, as you added and removed functions, you could improve on the standard error estimate. We figured that was a confirmation, and that we were going in the right direction in terms of the fit. The nonlinear fit ended up with about an error of magnitude of about 10 over the linear fit in terms of the error estimate.

LEIBECKI: I should like to comment on the capacity in the DOD. When we ran the test on the silver zincs, we found it made a profound difference if you did measure the capacitance of the cell and adjust the depth of discharge in the equation for it. In our case it did change the equation entirely in some of the interactions.

MC DERMOTT: Did it change the equation or the coefficients?

LEIBECKI: It changed the equation.

MC DERMOTT: It changed the functional relationships?

LEIBECKI: Yes.

MC DERMOTT: You got outside of a log function?

LEIBECKI: Yes. What you are saying is true if you do not have any variation in the capacities from cell to cell.

MC DERMOTT: No, it does not. It says that there is going to be a distribution of capacities in the cell. That is assumed.

LEIBECKI: When you made the statement that it is just a multiplier, that can only be true if the capacity of the cells was constant. When you used a 6A h cell, it would not make that much difference if they were all 6.5A h. However, if you are talking about some that are 6, and maybe some that are 7.5, it does make a difference.

MC DERMOTT: It would change the coefficient. I am not saying it would not. However, it would not take you from an exponential function into another function. I am saying the functional relationship would stay the same.

LEIBECKI: It all depends which ones they come out to. If you have a low capacity on your high DODs, you have gone way beyond your parameter. It all depends on these things, where they fall in where you are doing the work.

TABLE 1

MATRIX OF TEST PARAMETERS FOR CELLS CYCLED IN THE ACCELERATED TEST

TEST PARAMETERS	LEVEL OF EACH PARAMETER				
	A	B	C	D	E
1. TEMPERATURE (°C)	20	30	40	50	60
2. DEPTH OF DISCHARGE (%)	20	40	60	80	100
3. CHARGE RATE	C/4	C/2	C	2C	4C
4. DISCHARGE RATE	C/2	C	2C	4C	8C
5. PERCENT RECHARGED (%)	110	140	140	200	200
6. CONCENTRATION OF KOH (%)	22	26	30	34	38
7. AMOUNT OF KOH (cc)	17.5	18.5	19.5	20.5	21.5
8. PRECHARGE (Ah)	2.20	2.50	2.80	3.00	3.30

Table 26-1

Mean Time to Failure (Cycles to 0.0 volts)
at Indicated Variable Level

Variable	Low Level	High Level
Temperature	5210	2122
DOD	5972	1360
Discharge Rate	3310	4022
Charge Rate	3456	3876
% Recharge	4286	3046
% KOH	3740	3592
KOH (cc)	3598	3734
Precharge	3622	3710

Table 26-2

Variable Combination	Mean Time to Failure (Cycles to 0.0 Volts) at Indicated Variable combination levels			
	High-High	High-Low	Low-High	Low-Low
T X DOD	657	3588	2063	8356
T X DR	2490	1755	5555	4864
T X CR	2713	1532	5040	5379
T X CHG	1558	2687	4534	5885
T X PKOH	2181	2064	5004	5416
T X AKOH	2200	2045	5268	5152
T X PC	2052	2193	5369	5050
DOD X DR	1392	1328	6653	5291
DOD X CR	1562	1158	6191	5753
DOD X CHG	1163	1557	4929	7013
DOD X PKOH	1354	1365	5830	6114
DOD X AKOH	1423	1297	6044	5900
DOD X PC	1387	1333	6034	5911
DR X CR	4736	3309	3017	3602

Table 26-3

Variable Combination	Mean Time to Failure (Cycles to 0.0 Volts) at Indicated Variable combination levels			
	High-High	High-Low	Low-High	Low-Low
DR X CHG	3116	4929	2976	3643
DR X PKOH	3981	4064	3204	3416
DR X AKOH	4321	3724	3146	3473
DR X PC	4172	3873	3249	3370
CR X CHG	2910	4893	3181	3730
CR X PKOH	3540	4213	3644	3267
CR X AKOH	3972	3781	3495	3416
CR X PC	3930	3823	3491	3420
CHG X PKOH	3184	2907	4000	4572
CHG X AKOH	3094	2998	4373	4159
CHG X PC	3174	2918	4247	4326
PKOH X AKOH	3618	3566	3849	3631
PKOH X PC	3476	3708	3945	3535
AKOH X PC	4078	3390	3343	[illegible]

Table 26-4

PREDICTION OF NORMAL PACKS

T	DOD	DCR	CR	CYCLES x 1000		
				●	▲	■
20C°	40%	C/1.2	C/4	15	15	14
0C°	40%	C/1.2	C/4	20	22	21
20C°	20%	C/2.4	C/2.4	34	34	35
0C°	20%	C/2.4	C/2.4	47	45	51

Table 26-5

IMPACT OF VARIABLES ON THREE PHASES OF CYCLE

	I DISCHARGE	II CHARGE → 100%	III OVER-CHARGE
DOD	✓*	✓*	✓
T	✓	✓	✓
RC			✓
CR		✓	✓
DCR	✓		

*50C — DOD = 50C AT LIMIT

Table 26-6

Pack Description	Depth of Discharge	Overcharge Rate	Temperature	Life in Years
Crane Real-Time Synchronous Orbit Tests	40%	C/30	25° C	10.0
	40%	C/30	30° C	7.8
	40%	C/30	40° C	5.0
Simulated Synchronous Orbits with Accelerated Test Packs	40%	C/2	30° C	1.65
	40%	C/2	50° C	0.25
	40%	2C	30° C	0.48
	40%	2C	50° C	0.05

Table 26-7

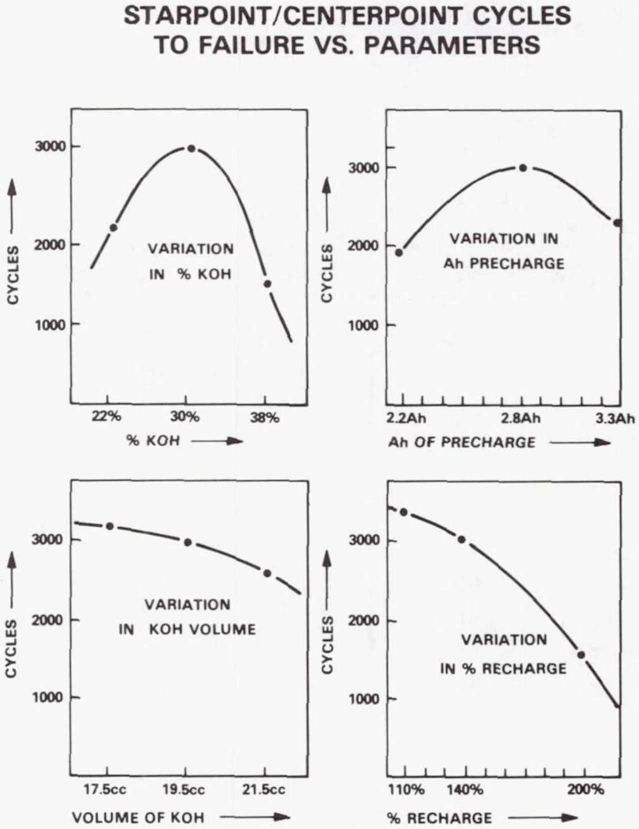

STARPOINT/CENTERPOINT CYCLES
TO FAILURE VS. PARAMETERS
3000
2000
1000
CYCLES
VARIATION
IN % KOH
22%
30%
38%
% KOH
3000
2000
1000
CYCLES
VARIATION IN
Ah PRECHARGE
2.2Ah
2.8Ah
3.3Ah
Ah OF PRECHARGE
3000
2000
1000
CYCLES
VARIATION
IN KOH VOLUME
17.5cc
19.5cc
21.5cc
VOLUME OF KOH
3000
2000
1000
CYCLES
VARIATION
IN % RECHARGE
110%
140%
200%
% RECHARGE

Figure 26-1

STARPOINT/CENTERPOINT
CYCLES TO FAILURE VS. PARAMETERS

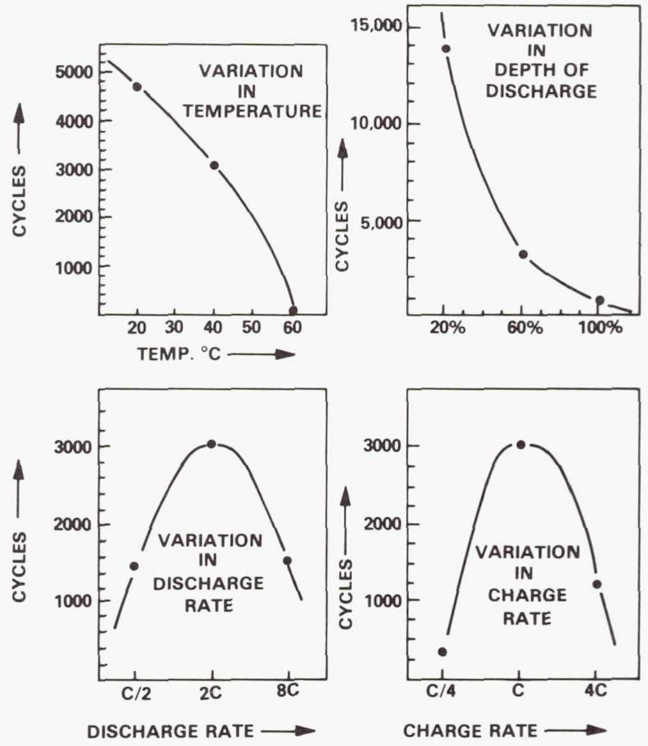
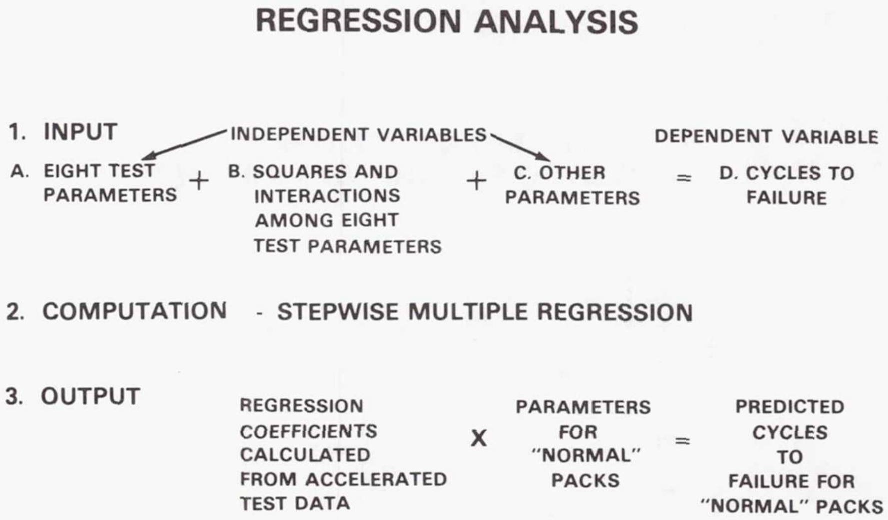


Figure 26-2



REGRESSION ANALYSIS

1. INPUT

INDEPENDENT VARIABLES — DEPENDENT VARIABLE

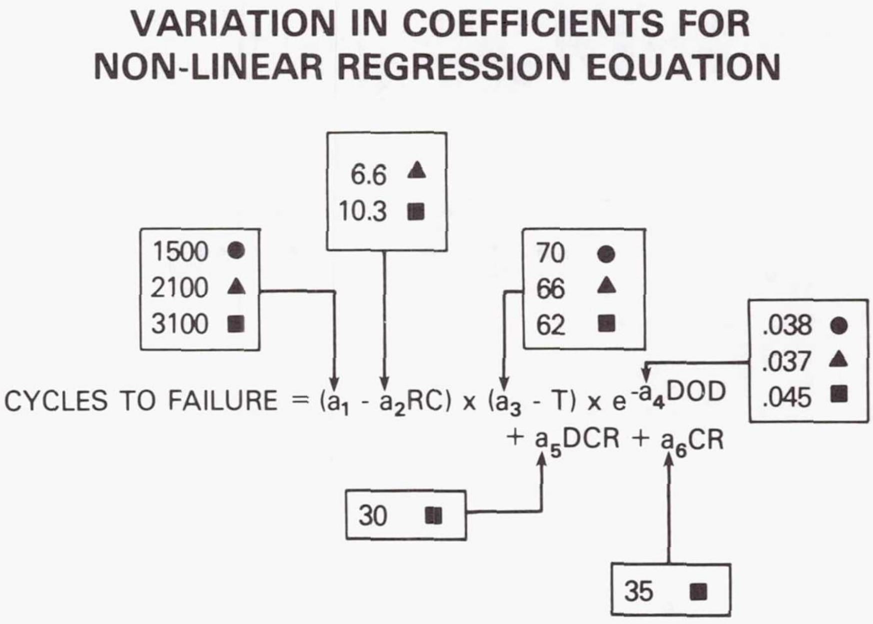
A. EIGHT TEST PARAMETERS + B. SQUARES AND INTERACTIONS AMONG EIGHT TEST PARAMETERS + C. OTHER PARAMETERS = D. CYCLES TO FAILURE

2. COMPUTATION - STEPWISE MULTIPLE REGRESSION

3. OUTPUT

REGRESSION COEFFICIENTS CALCULATED FROM ACCELERATED TEST DATA X PARAMETERS FOR "NORMAL" PACKS = PREDICTED CYCLES TO FAILURE FOR "NORMAL" PACKS

Figure 26-3



VARIATION IN COEFFICIENTS FOR NON-LINEAR REGRESSION EQUATION

$$\text{CYCLES TO FAILURE} = (a_1 - a_2 RC) \times (a_3 - T) \times e^{-a_4 DOD} + a_5 DCR + a_6 CR$$

Figure 26-4

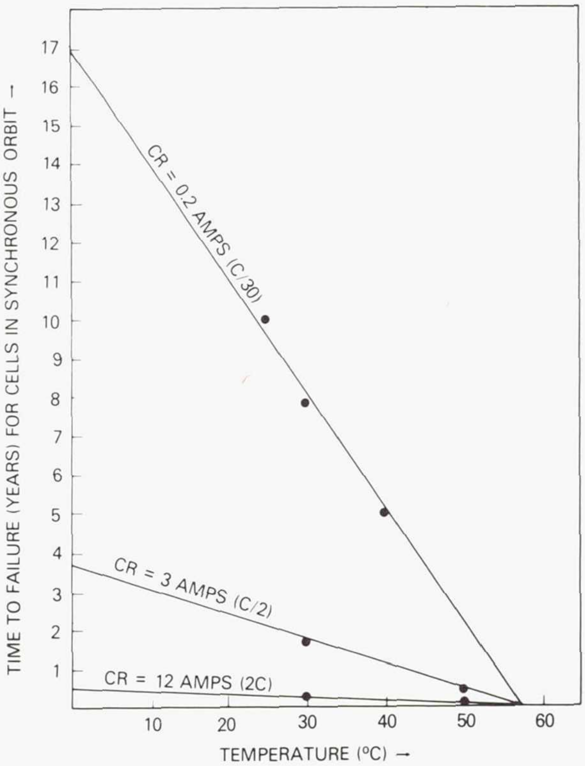


FIGURE 1. TIME TO FAILURE (IN YEARS) FOR CELLS IN SYNCHRONOUS ORBIT VERSUS TEMPERATURE

Figure 26-5

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PANEL DISCUSSION: SYNCHRONOUS ORBIT ACCELERATED TESTING

I. Schulman, Chairman
Jet Propulsion Laboratory

SCHULMAN: Let me first introduce the panel for this discussion. They are Pat McDermott of Coppin State College, Dean Maurer of Bell Labs, Sam Bogner of Hughes Aircraft, Helmut Thierfelder of General Electric, James Dunlop of Comsat, and Steve Gaston of RCA. I have known these people for a long time and I know that they represent firms with a definite interest in the geosynchronous orbit type of problem. That is the particular reason they were asked to join the panel.

I had written a letter to each one of them describing the topics and the problems with which we could start our panel discussion. I should like to read the relevant part of the letter to you, the audience, so that you will know the points from which we are starting.

"So that we are all considering the same problem, let us define the synchronous equatorial orbit as one in which during any year there are two seasons when eclipses will occur, each season being approximately 45 Earth days long. The eclipse seasons will be separated by solstice seasons that last for approximately 134 days.

"During the eclipse season, the actual eclipse periods for a 24 hour day varies between 5 and 72 minutes. We are interested in designing an accelerated test program that can be correlated to real time periods of 5 - 15 years in geosynchronous orbit, which can aid the battery engineer in making credible predictions concerning the life of a battery under particular operating conditions.

"Now the following problems may be of interest to the audience:

1. A large accelerated test program more applicable to low-Earth orbit than geosynchronous orbit has been conducted at the Crane Naval Weapons Support Center for the past six years. This program included 87 packs of cells and the cycling program has been completed except for a few packs which are still cycling under normal test conditions. The program design included eight factors; five environmental and three of a design nature; there were five stress factors. Is it necessary to conduct as large a program to obtaining meaningful results for the geosynchronous orbit? Which factors should be included in an accelerated test program and how many stress levels are really necessary? How could accelerated results be correlated with real time in real environment conditions?

2. The question of reconditioning is continuously reviewed -- deep, not so deep, single or multiple. All these methods of reconditioning have their advocates. Since it is reasonably apparent that some form of reconditioning will be included in a flight program, should reconditioning be included either as a variable or a fixed condition in an accelerated test program?

3. Many of the system organizations represented in the audience have conducted accelerated and real time geosynchronous orbit programs. As an example, TRW conducted an accelerated program in which there was no or a very small solstice period, the eclipse period was based on foreshortened days and the actual eclipse time of 5 to 72 minutes were actually followed, but the day was a 12 to 16 hour day rather than the conventional 24 hour day. This was done to obtain the charge/discharge cycles more quickly. They have reported over 40 eclipse seasons of successful charge/ discharge cycles at a depth of discharge of approximately 75%, with deep reconditioning being performed between each eclipse season. Can the results of a program that determines degradation only during solstice periods under similar operating conditions, for instance temperature, be integrated with the TRW results and correlate with real-time performance? Would such a program be considered credible?

4. Accelerated test programs generally increase the stress on the test samples and attempt to show relationships between increased stress, higher temperature, increased charging rates, etc., and decreased cycles, and in turn predict the increased life versus normal stress. What stress levels could be increased in an accelerated test program for geosynchronous orbits without introducing spurious failures that would only misdirect the predicted capability of any failure model based on this program? How does the DOD get into the program, if at all?

5. Will any accelerated test program ever have the necessary credibility with program managers?"

I have given the panel quite a lot to think about. I should like to call on them one at a time to give you their views on these various topics, after which we shall entertain comments and questions from the audience.

GASTON: I might not answer all of Dr. Schulman's questions point by point, but I shall try to add as much as I can. First, I should like to start out with my experience and my opinion, and then go into what I think we ought to do in the future.

I have always been concerned about accelerated testing, particularly in geosynchronous orbits. When I do run some tests, what do they really mean? As Dr. Schulman mentioned before, if you eliminate the solstice time and just have the eclipse seasons, and you obtain good results for 40 eclipse seasons, can you then draw the conclusion that a nickel cadmium cell is good for 20 years, because that is what 40 eclipse seasons means? We all know that we cannot use it for 20 years. So, what have I achieved? If I concluded that the cell could operate for 20 years, I should be dangerous, misleading and drawing the wrong conclusions. Therefore, one has to be very careful, before one sets up an accelerated test, to find out what it means in terms of, how it behaves in the real world.

When I have set up tests in different groups, I always make sure I have a control group. The control group is a real-time test, with no shortcuts. It will run simulated orbits on a real-time basis. For the accelerated testing, I did take some shortcuts, obviously. I reduced the solstice time from about 134 days, which is normal, to about 5 days. What I planned to do (I have not done this yet) is to periodically withdraw one cell from each group, take it apart and analyze as much as I can. There are certain degradation rates going on; I know the rate of degradation on nylon, I know the cadmium penetration rate. I should then be able to develop some degradation rates and correlate the two. That means that I have some confirmation, an electrochemical basis for what the electrical data show. That may give me a better tool, which I can eventually use. Eventually I might not have to run any real-time testing. Perhaps, if I have enough confidence in the data, I could just run a quick accelerated test on new cell designs, take a number of cells apart at specific intervals, and then look for the correlation and degradation rates. It is not an easy task, but I shall certainly make an attempt to do it and hope that somebody else will consider it. After all, if we are dealing with an electrochemical reaction, we always like to go back to the mechanisms. Once we understand the mechanisms, I think we are more able to make corrections. Also, the electrical data on which we get the statistics.

I should like to comment on the accelerated testing that was discussed before on low-Earth orbit. I do not have the answers. I have some suggestions. I said that before we do any planning on accelerated testing for geosynchronous orbit applications, I should like to re-review the data that we got in low-Earth orbit, and possibly we can take this cycle life, and turn it into operating lifetime. We can make the transition from cycle life to operating time. We take the orbit time out. Therefore, once I can do this, whether I have a 100 minute orbit, a 6 hour orbit, a 12 hour orbit, a 24 hour orbit, or geosynchronous orbit, I shall have some common factor. I bring this up because there was a paper several years ago by Peter Fono (published in the IECEC), which directly or indirectly implied that it appears to be a constant, or very close to that for same depth of discharge cycles times the number -- times the cycle time gives you a constant. If that could be separated out, we could make the low-Earth orbit data or the regression analysis work for us in geosynchronous applications; of course, to go one step further on the low-Earth orbit application, we have a function as a depth of discharge in cycle life, or we can convert to cycle time as a function of depth of discharge. If we extrapolate this information to zero depth of discharge, it may be equivalent to having a long-term trickle charge. If we can take that factor plus the other cycle life, we might be able to get some prediction for geosynchronous orbit. I do not know how well it works. How would I envision a geosynchronous accelerated test program? Again, it was brought out before, there are a minimum of three environmental factors that prove to be the best indicators in low-Earth orbit: depth of discharge, temperature and recharge.

As far as the design factors are concerned, I think we can use a design that we think is the best possible we have at present, so that we can reduce from three design factors for low-Earth orbit to one to simplify it.

On the question of reconditioning, I feel it should be done on an individual cell basis. This way you avoid reversal, and you have no stresses and other chemical effects due to reversal. It has been applied successfuly by all three, Satcom, F1 and F2, which are now operating close to five years. We had very good performance.

The question is, as Dr. Schulman raised, whether to apply it once or twice. I think he mentioned more than once during each solstice season. So far we only applied it once, and it seems to work. Perhaps that should be another variable, applying it twice might make it even better, because we do have some slight voltage degradation during the maximum depth of discharge from cycle to cycle, although it is very small.

The third thing I should recommend is a better knowledge of the basic cell chemistry; this means that the cell component degradation should be established for the life terminating factors. Towards that goal, periodic cell removal from both the control group and the test group should be done, followed by dissection or qualitative and quantitative analysis. I realize that with this approach we need a larger number of cells because we have to constantly remove some; it will not be an easy task to accomplish, to establish the degradation rates. However, I think ultimately we shall know a little more about the chemistry of failure and then, when we have a new component, be able to put that into effect and relatively quickly examine the value or the addition in life for the new component.

DUNLOP: I should like to describe what we have done at Comsat for our battery work at the labs, and how we work together with the control center in trying to make our satellites work for as long as possible in orbit.

There is a very important factor. Nickel cadmium batteries have been used in all the Intelsat spacecraft today and, as far as I know, in all the communication satellites today. For the Intelsat spacecraft, they are probably one of the major, if not the major, lifetime-limiting subsystems at present. That is certainly true for our Intelsat IV spacecraft. Intelsat IV spans about a decade. We started with the cell design and fabrication of the nickel cadmium cell in 1968. We put a battery of those cells on a real-time life test in 1968, 1969 at Comsat Labs. We ran that life test in real time for eight years, simulating as closely as possible the real-time in-orbit operation, including charge management, power conditioning and temperature profile. We did electrochemical and chemical analysis on a large number of those cells from a number of different lots before starting those tests. The cells in that test came from two or three labs, and we periodically removed cells from test once a year for electrochemical and chemical analysis. We presented the data and the results of that test at these meetings over a period of five or six years. What we saw in those tests and in the analysis has been reported in the literature many times.

I should like to show two figures that summarize the in-orbit performance of the F2 spacecraft, which was launched in 1971 and is still working.

(Figure 27-1)

The depth of discharge that I have listed in Figure 27-1 is based on measured capacity. If it were based on rated capacity, that depth of discharge would be about 60% or more at the beginning of life. There is a big difference between rated and measured capacities. The rated capacity was 15, the measured capacity was about 20.

We decided that the best way to present the data was on the basis of measured capacity. We can then look at batteries made now, made in 1968 and made in 1975, and measure the capacity. When we talk about depth of discharge we are talking about depth of discharge at the measured capacity.

This is a synchronous operation, and so that is the depth of discharge that occurred on the longest eclipse day. It was about 45% up to -- started dropping of a little. We actually had to reduce the load slightly from about the 12th eclipse season. By the time we reached the 14th eclipse season, we had dropped it to about 20%. We have been operating that battery at about 20% depth of discharge ever since. Dennis Cooper, from our control center, could probably tell you more about this battery than I can, because he watches it every day.

Figure 27-2, which is interesting, is the one that shows the voltage performance of that battery.

(Figure 27-2)

The cell voltage is plotted on the left-hand ordinate. The battery voltage is beside it. The cutoff point was simply an arbitrary cutoff point below which the battery was not supposed to go. The battery is operating at a temperature of approximately 17 C during the eclipse season; this temperature changes a little between the summer and winter solstice, but it remains between 10 and 20 C.

The battery is constant curve charged at about a C/12 rate, and the overcharge is minimized so that as soon as we put about 105% of what we take out back in on each eclipse day, we switch back to a trickle rate, which is about C/45, and we keep that on trickle charge during the storage mode. Initially we did not do this. We had it on open circuit stand between eclipse seasons, and we observed in our open circuit life tests at the lab (we had two life tests going: one that we were trickle charging and one on open circuit) that there was extremely large growth of cadmium hydroxide crystals. After two years we decided to switch all our batteries over to trickle charge to avoid that growth. By the way, the observation of these large cadmium hydroxide crystals was the result of a real-time life test. We would not have observed that kind of thing in an accelerated test mode. That happened to be the only variable we had in that program. We had two batteries; one was open-circuit charge, and one was trickle charge. Notice what happened when we got down to about the 14th eclipse season. The voltage really went down. That is why we cut the depth of discharge back: so that we could maintain the voltage above that cutoff value. Actually, the voltage has come back up. It is above that cutoff value now and so we have really come back up with that reduced depth of discharge.

I happen to have these data on here. We looked at what failed in these batteries. We looked at what failed and what was failing at the time. We saw carbonate buildup very much as you predicted based on the activation energy reported by Hughes and Bell Labs.

VOICE: Did you do any reconditioning?

DUNLOP: This battery is reconditioned to 1.15V per cell average, which we have now determined is totally a inadequate reconditioning. However, at that time, that is what we were doing. The point I was going to make is that in looking at the failure mechanisms we saw carbonate buildup and electrode swelling. The electrode swelling was as if it had been in there for three years. It only has 100 cycles a year, or 300 cycles, but the rate at which it is swelling is at least three or four times the rate at which it swells if you just take an electrode, do 300 cycles, take it out and look at it. Therefore, the rate of swelling of the electrodes, and hence the rate of movement or migration of the active material, is much greater for cells operating on a realtime basis than for cells operating in an accelerated continued cycling basis. We spend a lot of time now looking at micropore structure and change in the location of the active materials in the electrode. We are seeing the active materials compacting towards the surface, as well as expansion of the positive electrode; we have reported these data. We show, in other words, an expansion of electrodes, but also a large increase in the micropore structure with time. That micropore structure occurs near the surface of the electrode and is competing for the electrolyte, it is, in essence, causing the cell to dry out as you approach this point in time of 14 years.

The other problem we observed was that the carbonate buildup also reduces the overcharge protection. You could notice the cells beginning to swell towards the end of life with a buildup of some hydrogen pressure. Once they swell, this aggravates the tendency for the impedance to increase on discharge. By 14 eclipse seasons, the cell is tending to dry out quite badly. If you discharge it at a high rate the current density is very sensitive. If you discharge it at a C/2 rate, you get about 5 or 6A h out of it. If you discharge at a C/60 rate, you may still be able to get 15A h out of it. That is simply because of the high impedance generated in the cell on discharge as it tends to dry out.

Probably one of the most interesting things going on now is a life test we have on the IV-A battery, which was a follow-up to this. In the IV-A battery, we have added the silver cadmiums to the negative, in order to add more electrolyte to the cell to overcome this dryout problem. There is then roughly 15% more electrolyte in the IV-A cell: about $2.1cm^3$/A h compared with 1.7 - $1.8cm^3$/A h. We also put the IV-A cell on real-time test, again simulating the in-orbit operation again as closely as possible. However, we put in a couple of variables, 0V reconditioning and 0.9V reconditioning. The results after 11 eclipse seasons are shown in Figure 27-3.

(Figure 27-3)

For the first three eclipse seasons shown in Figure 27-3, we were running at 11.9A, a 51% depth of discharge based on measured capacity. That simulated the Comstar satellite with depth of discharge. We were doing this 1.15V reconditioning and the end of discharge voltage deteriorating very rapidly. We changed the depth of discharge after the third eclipse season to 9A h, the normal Intelsat IV-A, closer to what Comstar is now running, and during the first season we reconditioned one battery to 0V and did not recondition the other one at all. For the fifth through the eleventh season, one battery was discharged to 0V and one battery was discharged to an average of 0.9 per cell. The discharge to 0V is simply done by putting a resistor across the entire battery.

It is the reconditioning resistor thrown across the entire battery and we do indeed reverse the number of the cells. We watch that very closely.

I do not have the plots here today, but we watch when the first cell goes into reversal and then when the next two go. Usually they do that at a very low voltage, showing that the cells are still very well matched up through eleven eclipse seasons.

This is eleven eclipse seasons in real time, and so these cells were manufactured about six years ago. The first thing you notice is that there is no voltage degradation as before. This voltage performance is compared with the voltage performance we got out of the Intelsat IV spacecraft, and this is significantly better. What seems to show up here is that deep discharge reconditioning, whether you do it to 0V or whether to 0.9V average in essence has eliminated most of that voltage degradation that we observed on the Intelsat IV battery. There is not really much change between these two cell designs other than the silver cadmium; I think the major thing you are seeing here is the effect of reconditioning, and it really is quite impressive in terms of the voltage performance. That voltage performance, by the way, is the end of discharge voltage. If you are close to 1.19V at the end of a 42% depth of discharge, it is between 39 and 42, and that is really not a bad performance.

The question is, what will happen in the next couple of years, because we think that other mechanisms are going to come into play here within another year or two. These mechanisms are the effects of the expansion of the positive electrode, etc. We are waiting to see what is going to happen. We used these results to determine how we want to manage our Intelsat V spacecraft. That is our real reconditioner.

The other thing I should like to show you is that we have used this to try to predict the lifetime of batteries.

(Figure 27-4)

Figure 23-4 shows data from NASA. We just took the Crane data and converted them from rated capacity to measured capacity for depth of discharge. After about 7 years at 43.2% you start having problems; that is exactly what happened on the Intelsat IV data. The Crane data and the Intelsat IV data agreed well, as they should, because the data that they are using are basically from the same cell design.

There are also two other variables.

(Figure 27-5)

Figure 27-5 shows two other batteries in that life test, one with a Teflonated negative, and one with a Teflonated negative with lithium added to the electrolyte. At present, we are up to about nine eclipse seasons and we have not seen very much. However, it is not unlike anything you have already been hearing today. You are looking at the same things. You are looking at the carbonate, the expansion of both the positive and negative electrodes. Both electrodes expand with time. You are looking at electrolyte redistribution, and whatever other mechanisms might affect the lifetime of that battery.

Telsat, Canada, also have life tests in their laboratories going on their next spacecraft, and we work with them to analyze their cells periodically to look at the degradation mechanisms taking place there. We have worked with Bell Labs in the last few years, both with real-time and accelerated tests to look at the effects of carbonate degradation, high-temperature performance, etc.

Accelerated tests are very useful if you want to look at something like nylon degradation. We put accelerated tests into a category we call exploratory research. We do not use accelerated tests at present to predict the performance of the battery at the end of 7 or 8 years in operation. What we actually do of is to put a battery on life test. Usually we have about a two year lead. For example, the Intelsat V battery is supposed to be launched next month, and we have already had an Intelsat V battery on test in the laboratory for about eighteen months. We have completed three eclipse seasons. We have about a two year lead on everything, and so we are able to work closely with our control center and provide them with all these data to tell them what to expect at least two years ahead, which is very important in the commercial communications satellite, because we have to plan ahead. In your Intelsat system you have to plan your whole network to maintain your communication links with the world.

I should like to summarize this by saying that I do think it would be worthwhile to do an accelerated test. We simply have not. We have had a lot of accelerated tests run. There has not been one we have run yet that has helped us one bit in predicting what a battery is going to do at the end of seven years.

A lot of accelerated tests have been done to tell you whether one kind of separator material is better than another kind of separator material.

Once you have a battery made you have got two things to worry about: the charge and the operation. Frankly, the operation of your battery is every bit as important as the battery you are making. Based on our test data today, we are going to this Intelsat

V with a constant power discharge, which is something we have never done before. I am sure that constant power discharge is going to be a tough animal because you are talking about maximum current at the end of discharge, which is much harder than the constant current discharge that we have been looking at.

THIERFELDER: I should like to preface this by describing what the General Electric interest is in synchronous orbit satellites, because until about six years ago we were strictly interested in the near-Earth orbit type satellites. We did get involved, and we have built in orbit the BSC satellite for the Japanese. That was a three-year synchronous orbit mission. After two and a half years, all the TWTs have failed; at two and a half years they were still doing fine.

We are also the subcontractors on the global positioning system satellite to Rockwell International; they have six satellites in a 12 hour elliptical orbit, which is not exactly geosynchronous. However, it goes through four eclipse periods a year, and we have had to resort to some of the background and data on geosynchronous orbits to design them. Those six satellites have been up there for three years, and have been operating totally successfully, with no degradation in the batteries.

As well as that, we are currently designing and building the Defense Satellite Communications Systems satellites for the Air Force; these have a ten-year synchronous orbit mission. This is our big challenge. Therefore, we are now integrating the satellite and have a life test going. However, with that preface, I have to say that I cannot generate very much enthusiasm about the accelerated test. I should like to mention some of the reasons.

In the actual operation of satellites, reliability factors are the design and quality of nickel cadmium cells (I think everybody agrees on that) the battery charge control system, a thermal control system, and the battery reconditioning system.

Now, where we begin to differ is that from our point of view all the factors are equally important. Looking over the history of the batteries, not only ours but others, there have been very few -- probably less than 25% -- failures in battery cells. Most of the failures have been in the other categories, basically battery charge control system and battery thermal control system. Therefore, on both the GPS and in the DISCUS program we have gone to extremes to optimize these. In the accelerated test program, as I see it, we could accelerate the testing of the nickel cadmium cells, and so could have high confidence in them. We have already had high confidence in the cells for ten years. However, we do not see how we could accelerate the battery charge control system variables or the battery thermal control system variables, which are the ones giving the problems. In the battery reconditioning system, we have decided on a total reconditioning to 1V per battery on DISCUS. Tomorrow I shall present some DISCUS life test data on these.

To item no. 5 in Dr. Schulman's letter: "Will any accelerated test program ever have the necessary credibility with project managers?" I should definitely answer, no. This is because I deal directly with each of our program managers , and they want to see real tests, or else they will be satisfied with analysis. They go from one extreme to the other with the accelerated test program.

Everything we do, for example, on DISCUS, is different from what they do in Intelsat: the charge is different, the temperature control is different, and all the reconditioning is different. Therefore, I do not believe that these tests would have much credibility with the project managers.

BOGNER: At Hughes, we are vitally interested in synchronous orbit application and are involved in many programs.

(Figure 27-6)

Figure 27-6 shows a schematic of Hughes' approach to accelerated testing. We have parametric acceleration factors, temperatures, DOD, and of course the cycle rates. We feel that the temperature and DOD are the primary factors, and the cycle rates, the discharge rates etc., are secondary factors.

Therefore, we must be careful when we integrate those into your test program, because, as we found out on the NASA accelerated tests, you are testing at high temperatures and you use low charge rates, you might as well forget that test, because you cannot charge your batteries up. You must therefore be judicious in selecting your rates and temperatures.

We have a two-pronged approach. Hong Lim has done some work in accelerated testing on nylon separators, and I think most people agree with that work. He is now starting to do some work on the swelling of electrodes. We are therefore identifying life-limiting mechanisms in the components, and at the same time we are running real-time tests and accelerated tests on cells. We periodically take those cells apart to do analysis and make comparisons between some of the component tests and accelerated tests and cell accelerated tests, and the real-time tests. We are beginning to find some correlations. We are not yet able really estimate the exact life under the spacecraft operating conditions, but we think we are getting there.

Some of the life-limiting mechanisms, not necessarily in order, are nickel electrode expansion, active material morphology changes, core structure crystalline growth, cadmium migration, and what causes the electrode capacity to decrease, and separator degradation. While we studied the separator degradation, we are now looking at the electrode expansion.

The primary conditions we have settled on in the accelerated tests are: temperature up to 50 C (if we go much above that, particularly at the cell level, we are getting into other failure mechanisms that would not occur in real-time conditions); depth of discharge cycling around 60%; and rates up to 1.5C for both charge and discharge. We also believe in preconditioning; the level to which you go may be in question.

MAURER: First, I am a believer in accelerated testing, with two factors that you have to consider. One is that you always have to match the failure modes in accelerated testing with the actually observed failure modes in real practice.

That becomes difficult in geosynchronous orbit use. The amount of experience that we have had in that mode is quite limited. Cell designs have changed from the time the oldest ones have been put into service. Therefore, we are in a pinch in comparing with real-time orbit. However, the other thing you can do, which is not entirely a substitute, is not to look at the cell as a black box the way you normally would in an accelerated test, but to actually take it apart as Mr. Dunlop was describing, look at all of the failure mechanisms in progress at any one time, and try to extrapolate each one of those to its failure point. In one set of conditions, one failure mode will dominate. In another set, another will dominate.

Accelerated testing also has some use in comparing one design with another to see whether we are on the right track in improving things. As I have said in the last couple of years here about geosynchronization, I like to divide it up into two modes; the solstice aging, and the aging that occurs in the eclipse period. I think these two things are separable, but they do have their linkages. I said the rate of solstice aging is a function of temperature. It is also a function of other things such as the charge rate. However, the major thing going on in the solstice period is nylon degradation. Nylon degradation can give rise to two types of failure modes: one is that the act of degrading the nylon causes the negative electrode to become fully charged, to generate hydrogen and to vent uncontrollably; and the other is that the degradation product of nylon is carbonate, which has some effects on the cell. Another thing going on in the cell is that some factor is giving rise to capacity loss with time. If you look at data on long time overcharge of cells with, for example, a polypropylene separator where you do not have to worry about nylon confusing the issue, you see a capacity loss.

Looking at how you would accelerate that, I presented a paper here in 1971 on accelerated aging of batteries for terrestrial use.

(Figure 27-7)

If you do a high-temperature overcharge, a plot of a normalizing function, which accounts for different currents, versus 1/T gives a good straight line (Figure 27-7). This has an activation energy of about 15k cal. Above 80 F, this line breaks and there is an activation of about 19kcal, and above or below 110 F, or room temperature, roughly, there is another break. This is about 6kcal. I think both of these are nylon degradation, and this one capacity loss. You get this activation by looking at the Crane data, for example.

Let us look at the things going on in the eclipse part. The rate of degradation is as you have seen, a function of the depth of discharge, temperature, cycle numbers, etc. Some of the things going on are the thickening of the positive electrode, which may lead to shorts, and corrosion resulting from various impurities such as carbonate in the cell. Corrosion will increase the capacity of the positive electrode to the point where hydrogen is generated on the negative electrode, and so it will be the hydrogen problem. And, of course, there is cadmium migration, which will lead to shorts.

The real problem is that the carbonate, accumulated owing to the solstice aging, affects the rates of all these other reactions. We know that carbonate increases the solubility of cadmium and increases cadmium migration.

Data that we presented here last year on thickening rates show that carbonate had a disastrous effect on the rate of thickening of the nickel electrodes, especially at elevated temperatures. It also affects the corrosion rate. Therefore, all these rates are a function of time as well as all the other variables, and so you cannot ignore one, aging, with respect to the others. That is why you can get 40 eclipse seasons if you ignore solstice, which is obviously an error. You therefore have to include the solstice as well in these things.

In our accelerated aging program, we would allow the cell to spend a certain amount of time in solstice aging and a certain amount of time in eclipse aging back and forth to accumulate an equivalent of ten years. Our first shot of that gives us failures where you expect failures to occur. However, it is too early to talk about that now. We shall probably talk about it next year, and at the same time introduce things that would eliminate some of those failure modes, such as electrochemically made positive electrodes and polypropylene separators.

However, we have now changed the mechanisms, and so the accelerated aging mechanisms we use for a nylon cell will not be directly applicable to the one we have with the polypropylene cell.

McDERMOTT: I should almost like to question the panel myself --does it

The idea would be to run two tests simultaneously. Accelerated testing attempts to reduce the whole time that a test takes, otherwise you are in a whole cycle of ten years. You cannot make improvements and see if those improvements are going to make sense unless you run a life test. You are then in an eight-year or a ten-year cycle.

We are into a "Catch-22" situation in that the better you build the batteries, the longer they are going to run on life tests, and it is going to take longer to find out what improvements should be made, and so you must top it off at some point.

BOWERS: What is the correlation between the accelerated aging and the real world?

McDERMOTT: I think the only way you can tell is if you can find in the accelerated mode some functional relationships that can extrapolate back to the real mode. It is difficult, but it seems that this is the only way. In other words, if you find that you can isolate out one of the factors like depth of discharge or temperature at different levels, then you can extrapolate back to real life. The only way you can confirm it is to actually have a real-life test going on. That was the idea behind the Crane program. I suspect that you could do it for other acceleratd parameters.

SCHULMAN: I might add that the acceleratd programs generally have, or can have, two functions. One is to provide a data base so that we can perform some modeling and make predictive models for the use of the battery engineer. The second is to provide a screening medium so that we can determine, in a very short time, what is worth putting into a vehicle. At present it is a very difficult thing to determine.

DUNLOP: One of the things that is interesting about this discussion is that we are talking about nickel cadmium. You may be looking at the wrong battery system for the synchronous operation, because we are probably going to switch to nickel hydrogen in communication satellites very shortly. I think that from the middle of 1981, we intend to switch all our satellites (Intelsat V, Intelsat V-A, Intelsat VI) to nickel hydrogen.

SCHULMAN: I think you must remember that the same problem is going to exist with nickel hydrogen.

DUNLOP: The same problem will not exist.

SCHULMAN: The project office is putting out the same information. Your are going to have the same answers.

SCOTT: I was going to raise the same question. You know we are spending a lot of time and energy here debating about how to produce a credible life test that a program manager will believe. I want to ask Mr. Dunlop how he is getting his program manager to go along with nickel hydrogen with no life test.

DUNLOP: The Intelsat V battery is very similar to the NTS II battery. The battery is a much-improved version of the NTS II in terms of battery weight. However, the cells are very similar, and in accelerated cycling we really have a real-time test going on. The NTS II battery has completed eleven eclipse seasons in real time. The test started in 1975. The battery was built by TRW using NTS II cells.

The other thing is, we have run accelerated tests on those cells that have been cycled for over 10,000 cycles. The accelerated tests are like three hour cycle tests and six hour cycle tests and a lot of other variables. However, they are up to about 10,000 cycles.

The other thing that you get into, by the way, with any system -- and I think this was alluded to a number of times this morning and during the course of the panel discussion -- is that when you try and evaluate a cell design, you have to use more than just test data. You have to look at what has gone into the cell. If you take a nickel hydrogen cell and look at the degradation mechanisms that exist for nickel hydrogen systems, you have actually eliminated most of the degradation mechanisms that have been discussed this morning in terms of separators. In terms of positive electrodes, we have gone to the electrochemically impregnated positive electrodes with much lower loading levels, which have been shown in accelerated test programs to expand significantly less. This is where an accelerated test program really pays off. You can compare different types of electrodes in a similar test mode and really evaluate how they behave under accelerated testing to get a figure of merit between the two.

SCHULMAN: Are you saying that you are in favor of accelerated tests on components rather than on the total systems?

DUNLOP: Yes, that is basically what I have said.

MAURER: On accelerated testing for either nickel cadmium or nickel hydrogen, some of the problems that have surfaced in recent years in nickel cadmium, which I expect will also occur in nickel hydrogen, are some of the low activation energy processes. One of the problems in any kind of accelerated test is just these low-activation energy processes. If you take a 15kcal activation, you can get many years of real time or real operating condition in a fairly short period. However, if you lower the activation energy just down to 5kcal, this is an activation energy for a lot of diffusion processes. Some of the problems going on in the nickel electrode could be dehydration of the active material (giving rise to capacity loss), or creep of the Teflon in the hydrogen electrode, giving rise to wettability problems. Processes in that activation energy range could take two to three years at 80 C to be equivalent to ten years. Therefore, even if you accelerate them to very high levels, it takes a very long time before you can see whether they will give you trouble in the objective time of your designs.

All you have really done in the usual kind of accelerated testing is to eliminate the high activation energy processes, but you have to be careful of the load.

ROGERS: If, as has been discussed, you eliminate the chemically-impregnated positives as we do in nickel hydrogen by putting in elecrochemicals, and if you change the separator material to a longer-life material, and if you trickle-charge the cadmium electrodes, should you not have a long-life nickel cadmium cell as well?

DUNLOP: What you have said is correct. I think the major point of interest, though, is that even if you did all those thing for nickel cadmium, nickel cadmium systems would still inherently have the cadmium migration problems as discussed by Dr. Scott today, and they do not have the same overall life expectancy as nickel hydrogen.

THIERFELDER: Intelsat may be switching to the nickel hydrogen. However, there are a lot of programs. We have just made a product-improvement study on DISCUS, and we are starting a new design on GPS. On both of these programs we traded off nickel cadmium versus nickel hydrogen. Both of these programs will continue with nickel cadmium for at least another ten or fifteen years. However, at General Electric we have considered the use of nickel hydrogen for the near-Earth orbits.

SCHULMAN: I should like to thank the panel for their cooperation.

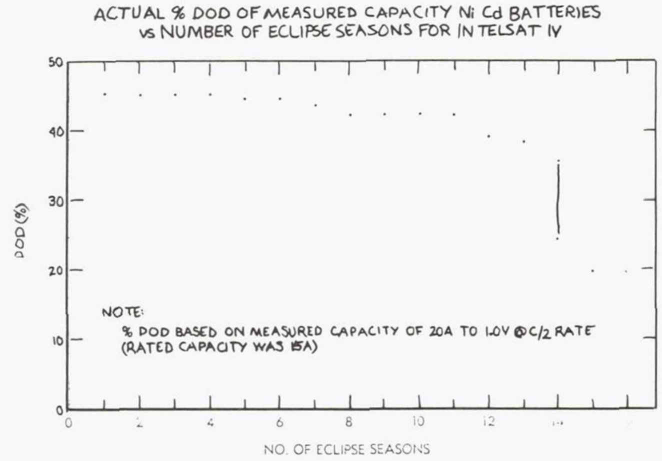


Figure 27-1

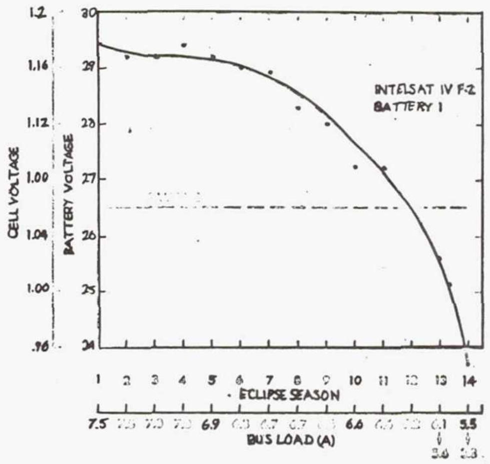


Figure 27-2

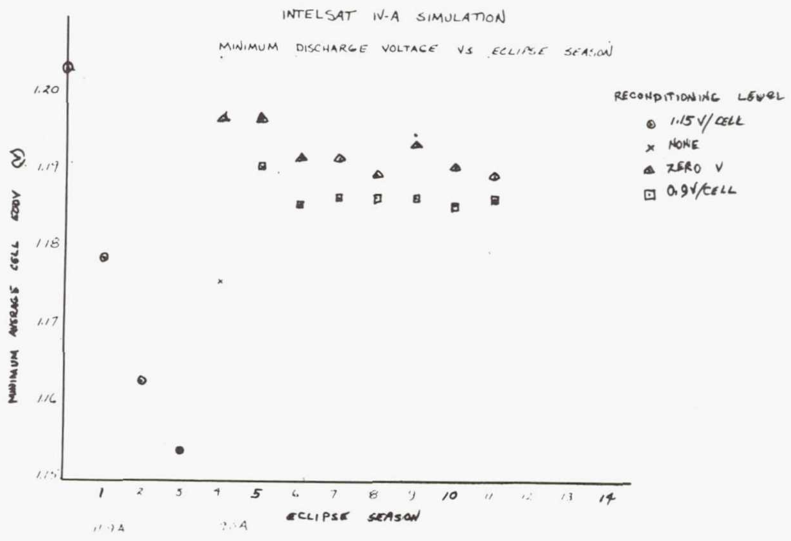


Figure 27-3

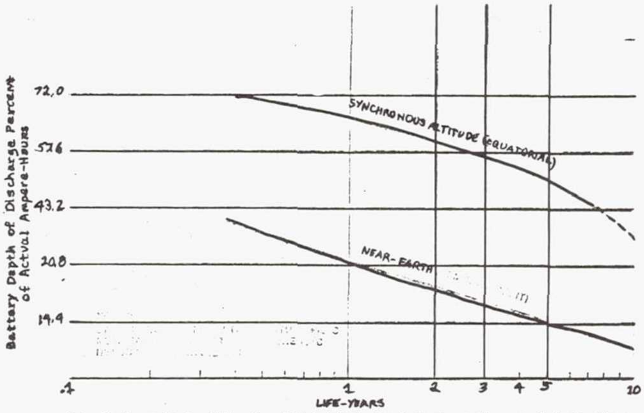


Figure 27-4

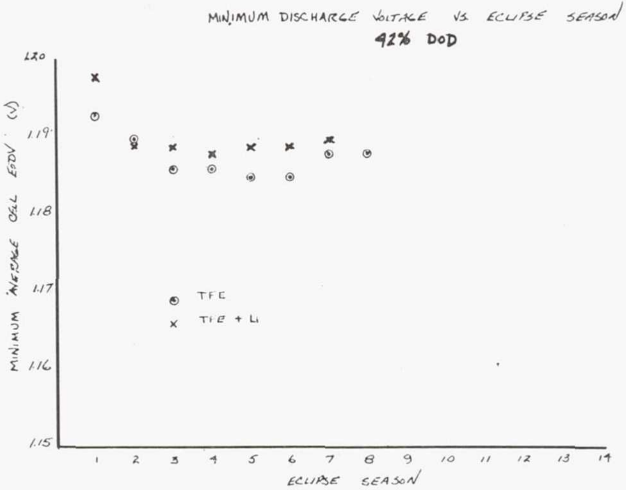
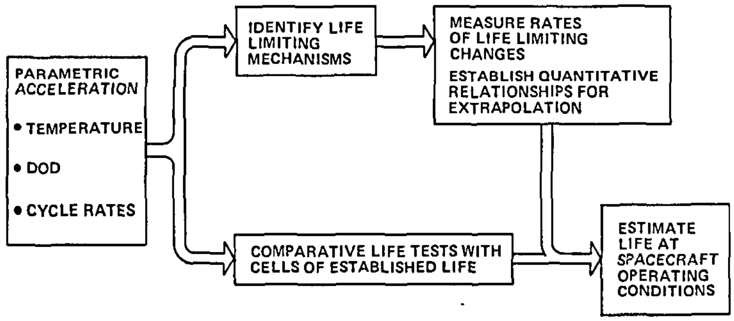


Figure 27-5

ACCELERATED LIFE TEST
HUGHES APPROACH



PARAMETRIC ACCELERATION
- TEMPERATURE
- DOD
- CYCLE RATES

IDENTIFY LIFE LIMITING MECHANISMS

MEASURE RATES OF LIFE LIMITING CHANGES

ESTABLISH QUANTITATIVE RELATIONSHIPS FOR EXTRAPOLATION

COMPARATIVE LIFE TESTS WITH CELLS OF ESTABLISHED LIFE

ESTIMATE LIFE AT SPACECRAFT OPERATING CONDITIONS

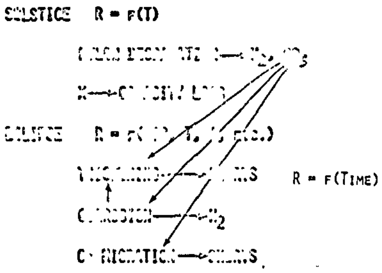


Figure 27-6

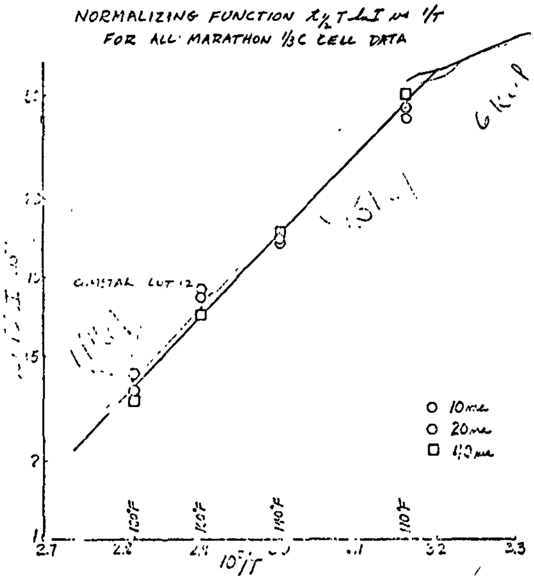


Figure 27-7

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SESSION VI

NICKEL CADMIUM PERFORMANCE AND TESTING

D. BAER, Chairman
Goddard Space Flight Center

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APPEARANCE OF SECOND PLATEAU VOLTAGE

G. Halpert
Goddard Space Flight Center

I should like to talk about the second plateau voltage, from the experience that we have gained at Crane in our testing of two different kinds of cells -- those that are used in TIROS N and NOAA A spacecraft, and then follow that with some life experience on the standard cells.

The TIROS N cells were originally called 30A h cells as designated by the manufacturer. However, we made some changes. First, we lowered the loading in the positive plates and the negative plates by some 10%, consistent with standard cell loadings. That has been reported in the Crane initial evaluation tests, and also here at the Workshop in the past years. An obvious reason for lowering the loading is to decrease the expansion of the positive and hence increase life. It also permitted us to put more electrolyte in these cells, and we have somewhere between 3.5 and $4cm^3$/A h. As a result of lowering the loading, we requested the manufacturer to change the name on the cell, because it was not consistent with the loading and nominal capacity designations in the previous cells. We agreed, between RCA and GE and ourselves, to call it a 26.5A h cell. By virtue of that, all the tests are done on the basis of 26.5A h, the nominal capacity. The cells actually had about 30A h in capacity.

(Table 28-1)

Table 28-1 slide indicates that we had two 5-cell packs at Crane, entitled 26G and 26H. The orbit period was typically 90-100 minutes. The temperature for both tests was 10 C. The only new difference between the packs was that one was 25% depth of discharge and one was 20%. These were from the same lot of cells that was flown on TIROS N and NOAA A. The charge currents were on the low side for what we normally run, but were typical of what RCA was running at the time, 5.3 and 6.62A in two cases. We ran them at that level for about 6400 cycles and then raised the current to 7.5A charge on each one, which is consistent with the C/4 rate. We charge at that current until it reaches a voltage level of 1.457 per cell (Table 28-2).

(Table 28-2)

I shall show you another curve which indicates the RCA voltage limits and the NASA standard voltage limits.

The levels are shown in Figure 28-1. The RCA level 3 is the same as Goddard level 6 in both cases. The resistor and the signal electrode circuit was 300 ohms, and so essentially they are the same, except for a bit of the charge rate and the depth of discharge.

(Figure 28-1)

Figure 28-1 shows the voltage limits that NASA has essentially written into its standard battery document. There is now a new issue of that, Revision B. The solid lines, 1 to 8, are the eight levels that we have recommended and are in the Solar Maximum Mission (SMM) spacecraft.

The dotted lines show the voltage levels that RCA is using in its TIROS N and NOAA A spacecraft.

(Figure 28-2)

Just to give you an idea that everything seems to be going well, Figure 28-2 shows some 11,000 cycles of history on 26G; this is a 20% depth of discharge cell.

The dots, which are the significant ones that are dropping, represent the end of discharge voltage; this drop was the reason why it ran 6000 cycles, and one of the reasons why, at about 6400 cycles, we raised the charge current to 7.5A. What it did raise is the charge-to-discharge ratio (represented by the Xs); they are all quite low, and we find that in most of our operations now the charge-to-discharge ratios are between 103 and 105. At one point it went up to about 107, and somewhat stabilized the end of discharge voltage. However, the purpose of showing this is to indicate that everything is doing well, and you would never know anything about a second plateau based on this.

(Figure 28-3)

Figure 28-3 shows a similar situation for the 26H cells. We do see that the end of discharge voltage started to drop again, at about 6000 or 6400 cycles. Again, this is the reason we raised the charge current a little; it did not have much effect. Finally, I am not sure what would have happened in this area, but it did level out. It did start dropping again, and actually as we got toward the end of about 1000 cycles we did raise the voltage level from 1.457 to 1.477V per cell. That did raise the C/D from about 103 to about 106. Again, everything is doing well, and you would never know there is any second plateau.

(Figure 28-4)

Figure 28-4 shows, for pack 26G, the typical six-month capacity test, which we run each time on each pack. One cell (cell no. 1) is removed from the circuit on the first test at the end of six months. At the end of twelve months, cells 1 and 2 are removed.

At the end of eighteen months, cells 1, 2 and 3 are removed, and so on. These are the individual cells you see after six months, cell no. 2 after twelve, 3 after eighteen months, and cell no. 4 at the end of twenty-six months.

You see the capacity has changed relatively little. However, the voltage is low, down to about 105V per cell. Within a very short time after we have taken out our 20% depth of discharge, we are down on the lower level.

(Figure 28-5)

Pack 26H shows a similar effect. We see the voltage lowered after six months, and then twelve. It stays pretty constant over the 24, 26 months that we did the test. Again, the voltage level is lowered, but the capacity is still there.

From that, I decided to try a different approach in looking at this kind of data.

(Figure 28-6)

I plotted it in a different way. Figure 28-6 has ampere hours on the ordinate versus the number of cycles in thousands on the abscissa. This indicates the change in ampere hours to certain voltage levels. If we look at the bottom curve, we see that is the number of ampere hours to 1.2V. Therefore, within a period of less than six months, we are down to a little over 8A h to 1.2 V. After one year, roughly 5000 cycles, we are down to a 6A h cell, and it is pretty level from there on.

At the 1.1V level the capacity is a little higher. The significance, kind of important significance because we have been talking about reconditioning, remember that cell no. 1, for example, was taken down every six months, where the other ones are taken down in the sequence over longer periods. We can see that, if we take it down every six months and then put it back in the circuit, this really is the effect of reconditioning, i.e. the increase in the ampere hours to a given voltage. In this particular case it is more significant than I have seen in others. If you go up to 1V, the capacity stays pretty high; at 0.9V it also stays pretty high.

The reconditioning here is not an absolute reconditioning, but a discharge to 0.75V. The cell is then put back in the circuit and testing is continued.

(Figure 28-7)

Figure 28-7 shows 26H, the 25% depth of discharge cell; the voltage has reduced significantly, or more rapidly than in the 20% depth of discharge cell. There is hardly any capacity at

10A h, even to 1.1V, and there is hardly any effect of reconditioning. The fact that we took it out every six months did not change very much there at all. Of course, the capacity is there to 1V. Those TIROS N cells are continuing, and we are making some decisions with what we want to do at present.

I shall now move on to the next subject: some of our data from Crane on the standard cells. I appreciate the help of Jim Harkness at Crane in preparing these figures.

(Table 28-3)

Table 28-3 shows a summary of our testing at Crane. If you remember, the standard cell program had four different manufacturers. There were four packs for each manufacturer: one at 10 C and 40% depth of discharge, the second at 20 C and 25% depth of discharge, a third at 20 C and 40% depth of discharge, and finally a fourth pack at 30 C and 40% depth of discharge.

The table shows the number of cycles and the current status. This is our third year now on the GE tests and we are continuing those because they are quite similar to the cells in the SMM spacecraft, and are considered the standard cells. We are discontinuing the others after two years because they are no longer available, and we are not using them. The Yardney cells have not reached the two-year point, and so we are continuing with that test for the time being.

You will notice that all the cells in the 40% depth of discharge, 30 C, regime have failed for one reason or another, except the Yardney ones, which are approaching a two year point. We shall have to see what we can do with these if they continue to work in the same fashion. One point I might make is that the Yardney cells have electrochemical positive and negative in their cells.

I shall now show you the same kind of a curve I did with the TIROS N; that is, the effect of change in capacity with time.

(Figure 28-8)

In Figure 28-8 (the GE cells, 10 C, 40% DOD), the abscissa represents the voltage, the life in months and the charge-discharge ratio, and the ordinate represents the ampere hours. These are nominal 20A h cells. The manufacturers were required to have the capacity of 24 ± 2A h. We see here that again we have a slightly higher capacity to the 1V limit than we did previously. You can also see that to this point there was not much effect in taking the cells out or not taking them out. In this case, cell no. 4 was taken out each time. You can see that they are fairly consistent with the others. Therefore, reconditioning, so to speak, the way we did it, was not much help in this case.

(Figure 28-9)

The Eagle Picher cell data shown in Figure 28-9 indicate also that for 1.2V there is not much capacity, but a little higher than the other, and it is a lot more random.

(Figure 28-10)

Figure 28-10 shows data for the SAFT cells. They show the same kind of behavior. Again, the capacity drops off with regard to time to the individual voltage levels. The capacity is significantly decreased even to 1V: 10A h, 50% of capacity in 18 months.

(Figure 28-11)

For the Yardney cells, which are not as far along, we also see the same thing (Figure 28-11). However, to 1V the capacity is still somewhat higher here, and to 0.9V, you see it is even increasing a little.

(Figure 28-12)

Figure 28-12 shows data from the Yardney pack at 30 C and 40% depth of discharge, after 18 months. The voltages have all been suppressed here but not as drastically as we have seen in some of the others.

I shall show one more curve, which deals with a GE pack that is part of the standard cell program on synchronous orbital test at 60% depth of discharge.

(Figure 28-13)

Figure 28-13 is the same kind of plot, showing that the ampere hours to the voltage level are remaining still -- the voltage cutoffs are remaining fairly high. We are running at 60% depth of discharge and 20 C.

In conclusion I am pointing out that these cells, which appear to have good characteristics in terms of their operational orbital parameters, are obviously suffering on the voltage side. The spacecraft people will have to look at the possibility, if they are going to need more energy during the night period, of operating between 1 and 1.1V for significant periods. However, there is not much danger of falling off the edge, because there is obviously quite a bit of capacity left even at that lower level.

DISCUSSION

GASTON: I know the 26.5A h cells have Teflonated negatives. Do the standard cells also have Teflonated negatives?

HALPERT: The GE cells do have Teflonated negatives. They are the only ones out of the four manufacturers.

ALLEN: I notice you had a reference electrode on the cells. What do you use those for?

HALPERT: We are not using them for cutoff. We are just using them for a signal to tell us whether there are any pressure increases, what level of pressure increases we can expect, and whether there are any changes. Certainly, in the GE tests, which at present we are most interested in because they are related to the two spacecraft programs, there is very little pressure at the end of charge. We are getting just a few (20-40) millivolts charge. We are just using them for monitoring.

ALLEN: You are not using them for charge control or anything?

HALPERT: We are not using them for charge control. Our charge control is charge at constant currents over the voltage limit which we selected, and then taper.

ROGERS: Do you know what causes the drop in voltage?

HALPERT: I have some ideas. In a brief discussion yesterday we disagreed on which electrodes occur. And I think there is some general disagreement whether it is positive or negative. It may even be both. I am not really sure, but I am looking at that at present

Table 1
Cell Serial Numbers

Pack Position	Cell Serial Numbers Pack 26G	 Pack 26H
1	9	26
2	11	55
3	13	58
4	25	62
5	84*	91*

*Signal electrode cell.

Table 28-1

TABLE 2
Operating Parameters

Pack Number	26G	26H
Orbit Period (h)	1.68	1.68
Temperature (°C)	10.0	10.0
ECLIPSE		
Period (min)	31.0	31.0
Depth of Discharge (%)	20.0	25.0
Current (A)	9.3	11.5
DAYLIGHT		
Period (min)	67.0	67.0
Charge Current (A)	5.30* to V_L	6.62* to V_L
Voltage limit (V_L) (volts/cell)	1.457	1.457**
RCA Level	3.0	3.0
GSFC Level	6.0	6.0
Auxiliary Electrode Resistor (ohm)	300.0	300.0

* Changed to 7.50 A orbit 6453 (26G) and 6473 (26H)
** Increased to 1.477 V/cell (GSFC Level 7, RCA Level 2) on orbit 10,134.

Table 28-2

NASA STANDARD CELL

NEAR EARTH ORBIT TEST
AT
NWSC CRANE

TEST REGIME: 40% DOD, 10°C

CELL	CYCLES GE	 SAFT	 EP	 YD
1 to 4	18275	11696-D*	11684-D*	10831

TEST REGIME: 25% DOD, 20°C

CELL	GE	SAFT	EP	YD
1 to 4	18443	11738-D*	11619-D*	10937

TEST REGIME: 40% DOD, 20°C

CELL	GE	SAFT	EP	YD
1	11703-F	11697-D* (all cells)	4570-F	11022 (all cells)
2	11794-D		4080-F	
3	11897-D		4523-F	
4	11794-D		4687-F	

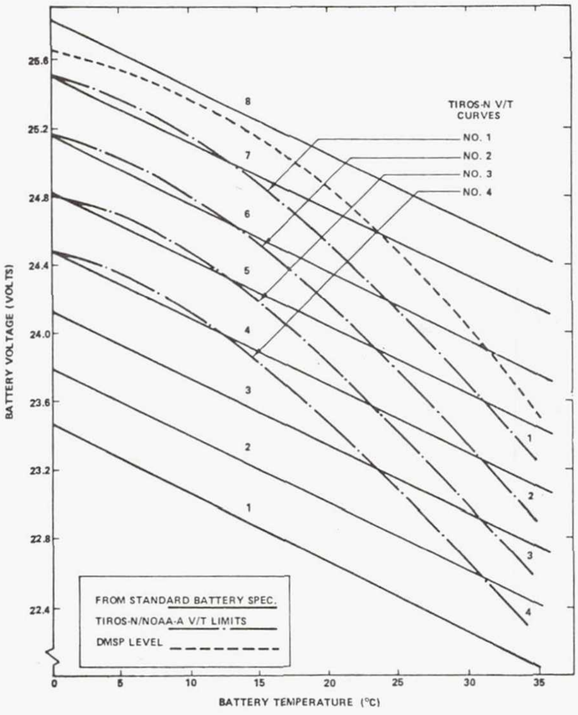
TEST REGIME: 40% DOD, 30°C

CELL	GE	SAFT	EP	YD
1	9266-F	11445-F	677-D	10919 (all cells)
2	8124-F	7114-F	679-D	
3	9012-F	11004-F	679-D	
4	8933-F	9058-F	626-F	

F - Failed
D - Discontinued
D* - Discontinued at 2 years cycle life

NOTE: Test status as of 14 November 1980

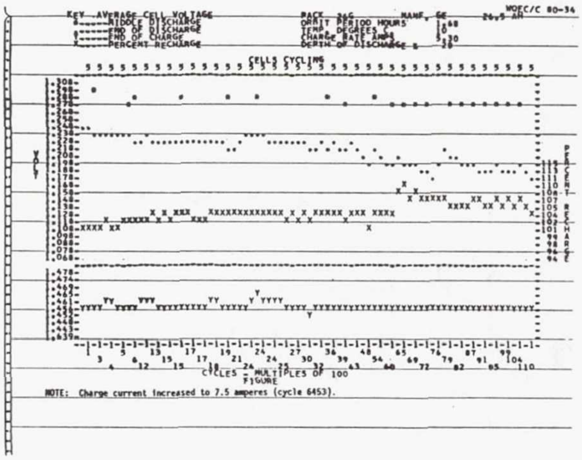
Table 28-3



* 17 CELLS

Figure 1. Nominal Battery Voltage Limits

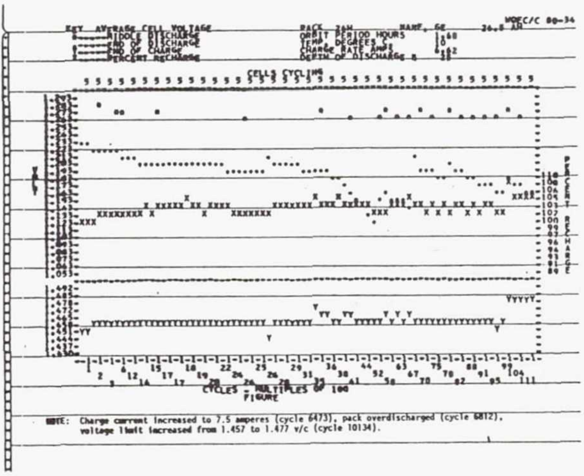
Figure 28-1



NOTE: Charge current increased to 7.5 amperes (cycle 6453).

NWSC/Crane Pack 26G Cycle Parameters

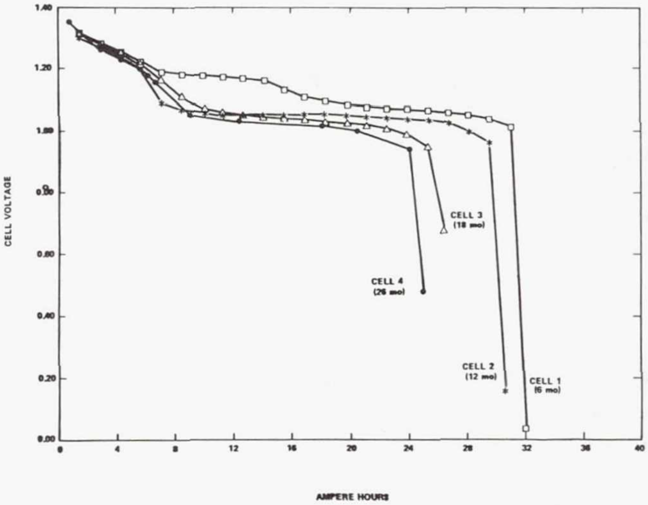
Figure 28-2



NOTE: Charge current increased to 7.5 amperes (cycle 6473), pack overdischarged (cycle 6812), voltage limit increased from 1.457 to 1.477 v/c (cycle 10134).

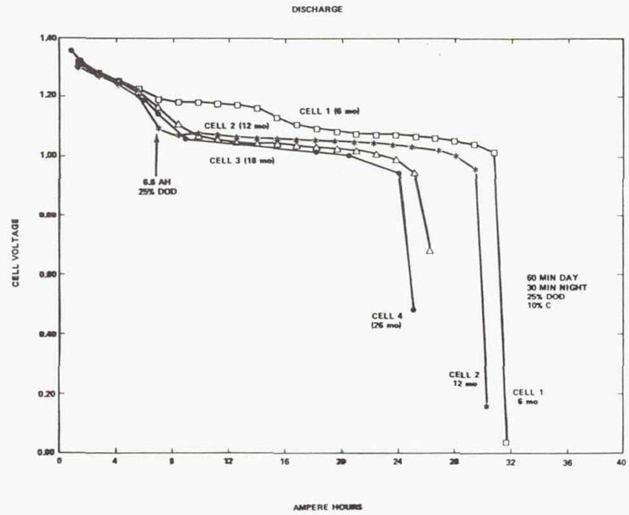
NWSC/Crane Pack 26H Cycle Parameters

Figure 28-3



Six-Month Capacity Test for Pack 26G

Figure 28-4



Six-Month Capacity Test for Pack 26H

Figure 28-5

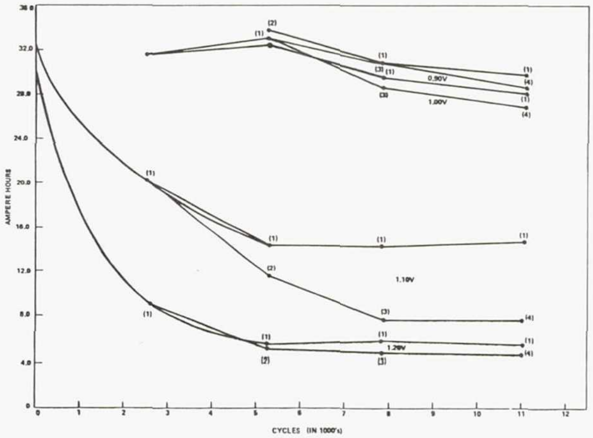


Figure 4. Ampere-Hours to 1.2,1.1, 1.0, and 0.9 V as a Function of Cycle for Pack 26G

Figure 28-6

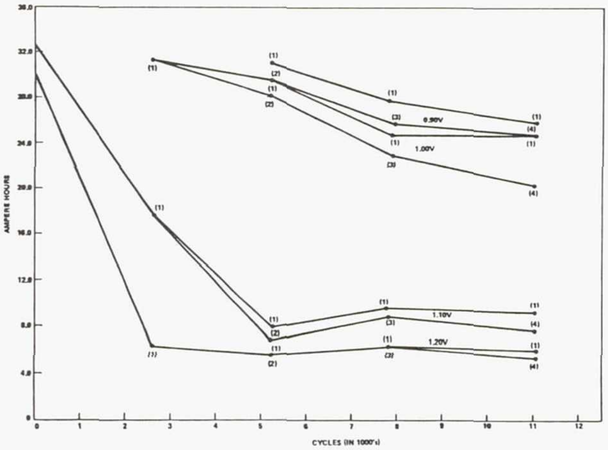


Figure 5. Ampere-Hours to 1.2,1.1,1.0 and 0.9 V as a Function of Cycles for Pack 26H

Figure 28-7

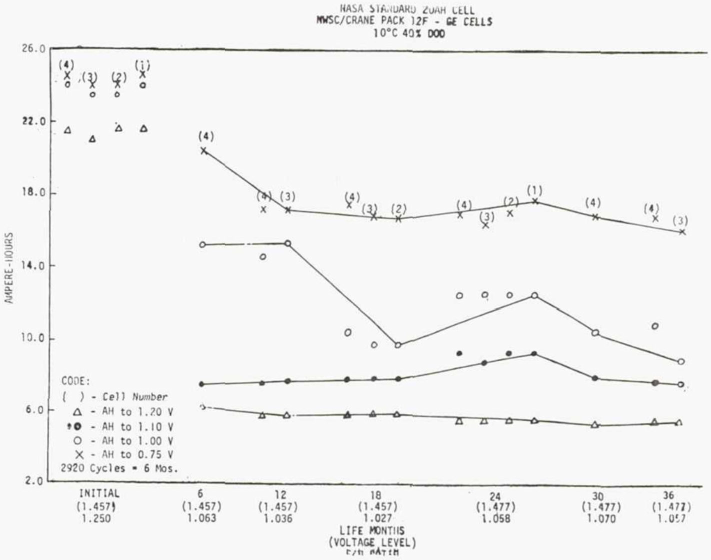


Figure 28-8

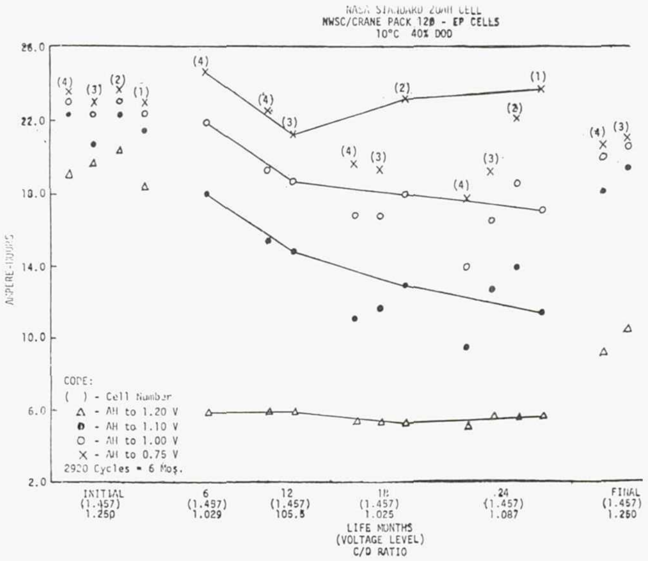


Figure 28-9

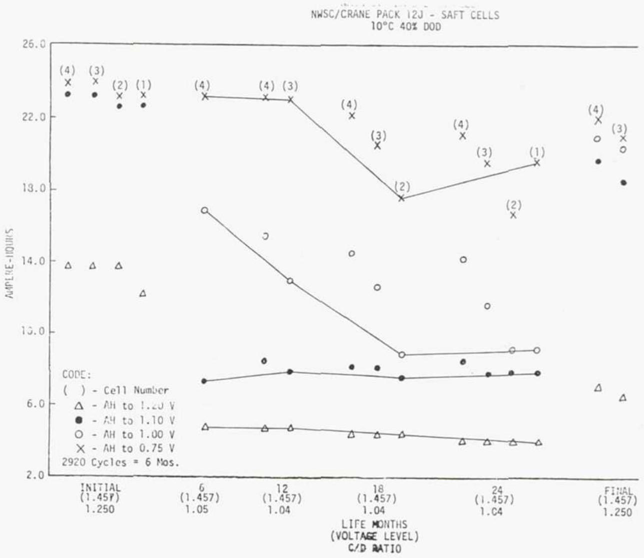


Figure 28-10

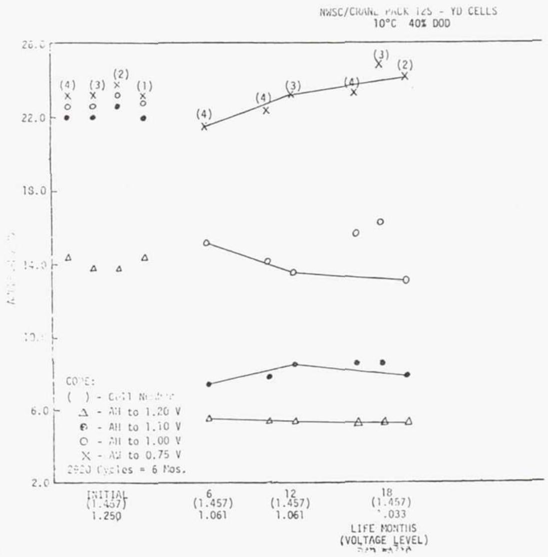


Figure 28-11

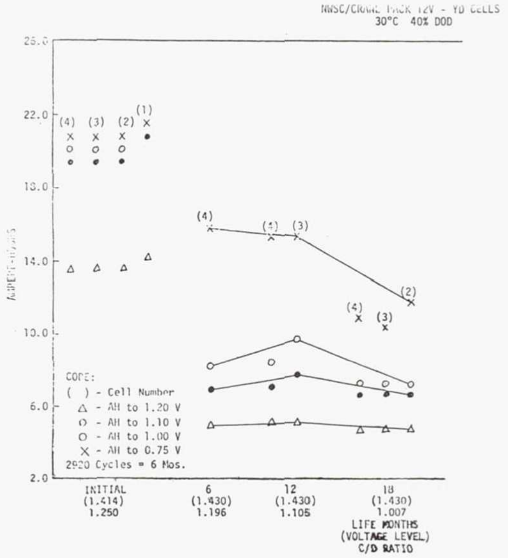


Figure 28-12

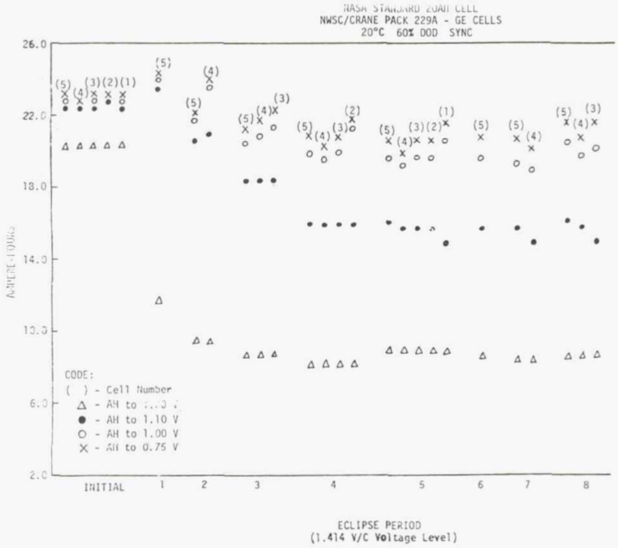


Figure 28-13

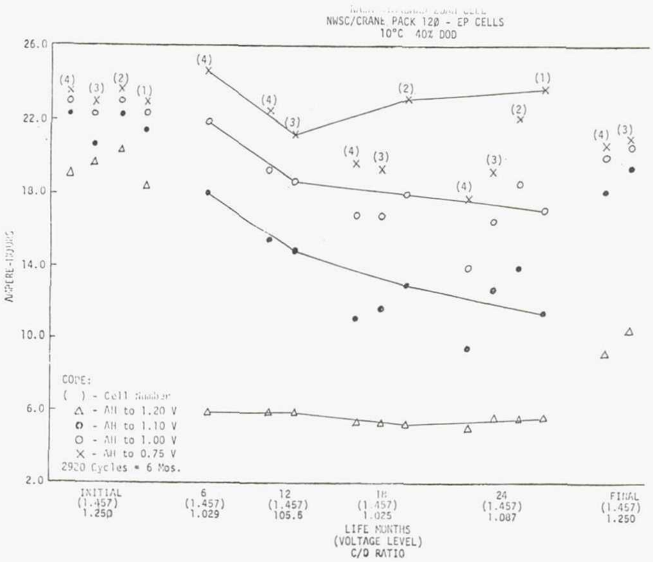


Figure 28-14

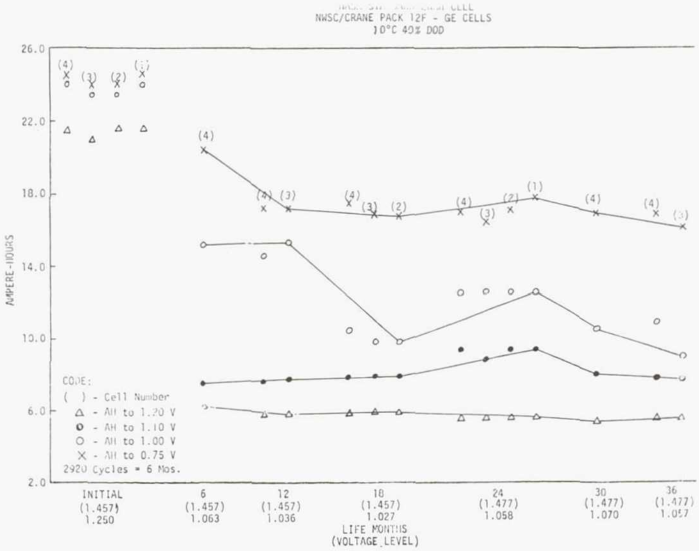


Figure 28-15

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DSCS III BATTERY TESTS

H. Thierfelder

General Electric Company

The General Electric Company is involved in the Defense Satellite Communications Systems (DSCS) program; we are building the batteries, which are 35A h batteries. In fact, all the flight batteries have now been built. What I am going to discuss is actually the life test (of which we are only in the 30-plus period) we are now running, after the fact of all the batteries being designed and built.

(Figure 29-1)

Figure 29-1 is a photograph of a flight battery. Actually, this is during the acceptance test, and the life-test battery is not a flight configuration as that. However, it is very similar. The 16 cells are stacked in configurations the same as that, and it is wired up the same way.

We do not have the heaters as we see on here, and the thermostats. We do have the thermistors on the top in the same locations as in the flight batteries. The other difference between the life-test battery is that we have four cells with both pressure gauges and pressure transducers on them. They are not the first four cells in the configuration. However, on the electrical data they are the first four cells.

(Figure 29-2)

The life tests that we are running are very mission-oriented. Figure 29-2 shows a plan of what we are doing. In the 45-day eclipse period, the line is the nominal time of eclipse going from zero to 72 minutes to zero. We have made an approximation of that with the heavy, square lines. For the first 8 days we operate a 40 minute eclipse period, for the next 8 days a 63 minute eclipse period, for the next 13 days, 72 minutes, back to 63, and then back to 8. In addition to these steps, we are planning to run 20 eclipse periods, but not all the eclipse periods are the same.

As shown on the figure, the even number eclipse periods of 40 minutes have a 31% depth of discharge, and the odd periods have a depth of discharge. In the odd number 72 minute eclipse periods, the depth of discharge is 62% and in, even number periods it is 55%. All these things are mission oriented, depending on the power requirements of the spacecraft.

(Table 29-1)

To actually show what we are doing now, eclipse periods number 1 and 20 are performed as shown in Table 29-1. During days 1 - 8 we operated for the first 28 minutes at 18.4A discharge, and for the next 12 minutes, at 16.1A discharge. We then recharged for 1400 minutes, which is the balance of the 24 hours at 1.4A.

I should just like to comment on the 1.4A. This is not the normal charge rate, but it is what we have analyzed to be the lowest charge current available at the end of ten years. This is a ten-year mission. At the end of the mission the power will be array-limited, and the power left to charge the batteries will be equivalent to 1.4A. This is then the worst case for the lowest charge rate. The schedule calls for eclipse period 1 and eclipse period 20 to operate with this low charge current.

Then it shows that we increased from 28 minutes to 51 minutes during the second eight days, and to 60 minutes for days 17-29. That has been run, no. 1 eclipse period.

(Table 29-2)

Table 29-2 shows eclipse periods 2, 4, 6, etc. (the even-number eclipse periods). We have completed eclipse period 2, and I shall show data on this.

We have gone to what is the nominal power requirements of the spacecraft, that is 16.1A. Again, this is actually the worst case for normal conditions, for the expected loads. The 18.4A was an additional load that they added on later. Therefore, at this time, it is actually broken down into two events, although the currents are the same for event 1 and event 2.

We have now gone up to the 2.8A charge, which is the normal charge current expected during the ten-year mission, except for the very last one or two eclipse periods.

(Table 29-3)

The odd number eclipse periods are, I consider, the worst cases, because here we are starting with the discharges with 12 minutes at 16A, and the last portion at 18.4A. These would then go up to the 63% depth of discharge. We have just completed no. 3 eclipse period; the values are shown in Table 29-3.

(Figure 29-3)

Eclipse period no. 2, which was completed some weeks ago, is summarized in Figure 29-3. We have a rather good temperature control. The top line shows (and this is per day, 45 days in real time) that during discharge the battery will warm up; and, although we control it on a heat sink, the temperature that we are trying to hold is 10 C. The end of discharge temperatures are somewhat above 10 C, and the end of charge temperatures are slightly below.

We have a voltage-limited taper charge; the next curve therefore shows the end of charge current. This actually increases from the beginning, about a 200mA rate, to about 400mA. It was a 35A h cell, and so at 400mA you are around a C/80 rate. At the beginning you are around a C/160 rate. Thus, as the eclipse period progresses, the battery will require more current and the voltage is held constant. The charge current at the end of the 24 hours is then increasing during the eclipse period.

The end of discharge voltages are shown below for the different periods. The worst time of the eclipse period, of course, is day 29, which is the 13th day of the 72 minute eclipse period. We have only run one eclipse period of this type, and so I have no comparison as yet. Each of the three eclipse periods we have run has been different. However, as I hope to report over the next few years, we should like to show a trend of what these are doing from one eclipse period to the next.

(Figure 29-4)

Figure 29-4 shows the actual data for day 29, which I mentioned as being the worst day of the eclipse period. For eclipse period 2, run in August 1980, the discharge currents is automatically held at 16A. The voltage, of course, is shown coming down. The numbers I have added, which do not come out on the computer printouts, are the final values. I obtained those with digital data. I have indicated both the current, and the end of discharge voltage. This is the 60-minute period, 120. As for the pressure, we actually have only two of the transducers working. The transducers are less reliable than the cells. Of the original four tranducers on here, only two are working. Fortunately, one is on the highest pressure cell, and since we still have the pressure gauges on there, we can read those manually. We only print out two transducers automatically, and this is the average of the two. The pressure is decreasing during the discharge. The temperature is being held quite close to 10 C. The 72 minutes are broken up into the two periods here. The second 12 minutes, of course, is still at 16A, and the discharge is continuing. I have summarized the ampere hours out. This was exactly 16A h. Togehter with the 3.13A h hours, this gives a total of 19.13A h out with the 72 minutes on the 35A h battery.

I shall show the charge back on the other Figure 29-5.

(Figure 29-5)

So, you had two discharge, three discharge, and then it immediately goes into the recharge of the battery. As I mentioned, this is a voltage-limited system. We have four voltage limits, but the standard limit is what we call voltage limit no. 2. At 10 C, this turns out to be 1.42 or 1.43V per cell. The battery reaches the voltage limit here. It is about 90% charged. The current stayed constant at 2.8A. When it reaches the limit the current goes into taper. Now, we feel the fact, of course, the battery is not 100% charged here, we are really getting no overcharge in any appreciable current. The current drops off very rapidly.

At the point where the voltage limit is reached the temperature is just starting to increase a little. It does not increase very far because the current is then immediately dropping off. Also, the pressure, of course, is starting to increase at that point. This is 720 minutes, or 12h. So, at around 12 h we reach a state of equilibrium between all the parameters. The voltage, the pressure, the temperature and the charge current are all constant.

The 0.420A is the number we had plotted before, showing the end of charge current values. In this particular case we have put 26.45A h (1.38 C/D ratio). This is quite low for a synchronous orbit. We normally expect a figure of 1.5 or 2 for a C/D ratio.

(Table 29-4)

I wanted to show the digital data that I have been showing with the computer curve printouts. Table 29-4 shows the individual cell data or the individual readings. At the top there are the actual time of day and the elapsed time in minutes. This particular chart is the 60 minute discharge. It is programmed to read out and record every seven minutes, and so you have each of the cell voltages for every seven minutes during the 60 minutes. Then you have the computer-calculated average cell voltage. You have the current. The current actually shows a big jump from 0 to 7, but this automatically corrects itself in less than 30s. However, there is no reading in between there, and so it goes from 15.75 to 16s. The accumulated ampere hours are shown. A total of 16A h hours is taken out during that hour. We have three thermistors on there, and the two pressure transducers. The readings are shown. The average pressure, average temperature and battery voltages are also given. All the data are recorded on magnetic tape. The curves and this is then run offline on a computer from the magnetic tape.

(Figure 29-6)

One other thing that has been discussed quite a bit lately is reconditioning. In this test program we are reconditioning between each of the eclipse periods. Figure 29-6 shows the reconditioning discharge after eclipse period no. 2. The '5th' in the figure legend refers to the fact that on these cells this is the fifth time that we reconditioned it this way. We did it twice during the engineering development test, once before the start of the life test, once after the first eclipse period, and now after the second eclipse period. In our reconditioning system we have a resistor across the entire battery. We reconditioned the battery to 1V per battery, not 1V per cell.

However, the thing that is probably unique about our system is that we start off with a resistor that will give us a current of about 350mA, or about a C/100 rate. However, when the battery voltage drops to 18V, this automatically switches in another resistor which drops the current to about one-third of that C/300 rate, 120mA here. In other words, at 18V, the current, which has been decreasing because the voltage is decreasing, then takes a step function.

We are also recording the pressure, both manually from all four pressure gauges and from the transducers. Figure 29-6 includes a plot of the highest cell pressure. One of the things that we were concerned about was developing pressures with reverse cells. I have marked the point at which the first cell reversed. The first cell reversed where the current was already quite low, and then the pressure just stayed there. I think that on one of the early ones we had a slight pressure rise.

On this discharge, the current drops to a very low value; we have 7mA at the end of 20 days when the battery voltage is 1V. On this particular reconditioning system, 13 of the 16 cells were reversed, and 3 cells still had positive voltage. On one of the early ones, all the cells but one were reversed. None of the reversals is greater than 0.15 V, and they are only at 0.15V when the current is still appreciably high. When the current gets lower, they fall, usually down below 100mV.

(Figure 29-7)

Following that reconditioning, which is about a ten day (240 h) process, we charged the battery back up with the normal charging system (see Figure 29-7). We had arbitrarily programmed four days for it.

It turned out that that is about the right time for charging the battery back. We had taken (Figure 29-6) about 40A h out on the reconditioning discharge, and I have shown on Figure 29-7 what the ampere hours return were. As is normal, it took about 6 - 6.5 h at the full current, 2.8A, before the battery went into taper. It actually took 70h to get 41A h back. Finally, after the four days (96 hours), we had returned 44A h to the battery. The absolute pressures, and not the gauge pressures, are shown; 31 pounds is actually about 15 gauge.

As of this week we are completing eclipse period no. 3. We shall then go into this reconditioning cycle, and continue. We plan to run the 20 eclipse periods, which will take us to the end of 1982, and report our results annually here.

DISCUSSION

HORNBUCKLE: What is the life of the battery?

THIERFELDER:

HORNBUCKLE: What was the peak depth of discharge at the 72 minutes?

THIERFELDER: It was 63%.

HORNBUCKLE: Generally, for synchronous orbit, I know we do not allow the battery to support the load during non-eclipse portions of the orbit. Sometimes it happens. I was wondering whether this occurs on DSCS III at any time?

THIERFELDER: Yes. We have discharge during the sunlight period when they turn on some of the special loads.

HORNBUCKLE: How do you take that into account in your prediction of life and in your life testing?

THIERFELDER: We have made the assumption that these discharges during the sunlight period will have no significant effect. It is arbitrary.

HORNBUCKLE: Depending on the depth of discharge, that is every orbit. It could be every orbit, and it could be significant. I do not know the depth of discharge during the sunlit portions.

THIERFELDER: I do not think we have ever analyzed this in detail. It has been discussed at the meetings with the Air Force. However, I do not think that the amount taken out would be more than 2 or 3% of the capacity of the batteries. It would not be a high percentage.

GASTON: I do not know how many batteries you have on the spacecraft, but you mentioned that it takes about 10 days to recondition. If you have two it would take you 20 days, and for three it would take 30 days.

THIERFELDER: We have 134 days.

GASTON: How many batteries do you have in the spacecraft?

THIERFELDER: We have three.

GASTON: That means you have to start your reconditioning at least 30 days before. Are you not concerned that by the time you go into eclipse season you might have lost some of the effect of reconditioning?

THIERFELDER: No, we are not.

ROGERS: Do you have a specific reason for changing from C/100 to C/300 discharge rate on reconditioning?

THIERFELDER: Yes, we are very specific about the reversal of the cells. We do not want to have any high reversal currents. A paper has been presented to safely reverse at a C/100 rate, but just to make sure we have gone to a C/300 rate.

RISEBOROUGH: You have not proved that C/100 is hazardous?

THIERFELDER: No, we are just being conservative.

FOUGERE: When you get the first reversal, have you noticed the pressure evolution until the end of discharge of the battery, and what was the level of this pressure, if any?

THIERFELDER: We do not see a pressure rise when that cell reverses.

ELIASON: You show on Figure 29-7 that you charge up from a fully discharged cell, and then reconditioning occurs in 6h? Is that correct?

THIERFELDER: It goes into taper at 6h. At that time it is not fully charged. You only have 30A h back in.

ELIASON: What is your charge rate?

THIERFELDER: It is 2.8.

ELIASON: 2.8 times 6h only gets you about halfway there. You want to be up to about 30A if it is a 34A h cell.

THIERFELDER: When it is down here you can put 34A h back. Therefore, at that point you put less back. I did not have the number annotated for up there.

ELIASON: However, if you are charging at C/12, it is going to take you at least ten hours to get up to your 34A h.

THIERFELDER: It takes about 24 hours.

HORNBUCKLE: Do you recondition on the spacecraft?

THIERFELDER: Yes. This circuit we are using to run this reconditioning is the same circuit that was used on the spacecraft.

TABLE I

ECLIPSE PERIODS 1 AND 20

TEMPERATURE 15 ± 5°C

Programmed Event No.	Mode		Day 1-8	Day 9-16	Day 17-29	Day 30-37	Day 38-45
Event 2	Discharge	Amperes	18.4	18.4	18.4	18.4	18.4
		Minutes	28	51	60	51	28
Event 3	Discharge	Amperes	16.1	16.1	16.1	16.1	16.1
		Minutes	12	12	12	12	12
Event 4	Charge	Amperes	1.4	1.4	1.4	1.4	1.4
		Minutes	1400	1377	1368	1377	1400

Table 29-1

TABLE II

ECLIPSE PERIODS 2, 4, 6, 8, 10, 12, 14, 16, 18

TEMPERATURE 10 ± 5°C

Programmed Event No.	Mode		Day 1-8	Day 9-16	Day 17-29	Day 30-37	Day 38-45
Event 2	Discharge	Amperes	16.1	16.1	16.1	16.1	16.1
		Minutes	28	51	60	51	28
Event 3	Discharge	Amperes	16.1	16.1	16.1	16.1	16.1
		Minutes	12	12	12	12	12
Event 4	Charge	Amperes	2.8	2.8	2.8	2.8	2.8
		Minutes	1400	1377	1368	1377	1400

Table 29-2

TABLE III

ECLIPSE PERIODS 3, 5, 7, 9, 11, 13, 15, 17, 19

TEMPERATURE 10 ± 5°C

Programmed Event No.	Mode		Day 1-8	Day 9-16	Day 17-29	Day 30-37	Day 38-45
Event 2	Discharge	Amperes	16.1	16.1	16.1	16.1	16.1
		Minutes	12	12	12	12	12
Event 3	Discharge	Amperes	18.4	18.4	18.4	18.4	18.4
		Minutes	28	51	60	51	28
Event 4	Charge	Amperes	2.8	2.8	2.8	2.8	2.8
		Minutes	1400	1377	1368	1377	1400

Table 29-3

```
PROGRAM  DSCS III LIFE TEST
TEST-ECLIPSE PD 2 DAY 29
RACK NO       1
CONTROLLER NO      1
DATE OF TEST  AUG 18 1980

TIME              16 22    16 29    16 36    16 43    16 50    16 57    17  4    17 11    17 18    17 22
MIN                 0        7       14       21       28       35       42       49       56       60

       CELL
     POSITION
         1        1 3981   1 2841   1 2586   1 2473   1 2408   1 2349   1 2277   1 2193   1 2088   1 2020
         2        1 3906   1 2796   1 2546   1 2431   1 2365   1 2309   1 2241   1 2157   1 2052   1 1986
         3        1 3848   1 2784   1 2534   1 2427   1 2362   1 2305   1 2236   1 2152   1 2046   1 1979
         4        1 3813   1 2785   1 2536   1 2429   1 2366   1 2311   1 2245   1 2161   1 2056   1 1987
         5        1 3707   1 2866   1 2631   1 2525   1 2460   1 2398   1 2325   1 2231   1 2120   1 2049
         6        1 3539   1 2653   1 2414   1 2311   1 2250   1 2191   1 2123   1 2038   1 1932   1 1864
         7        1 3806   1 2843   1 2600   1 2489   1 2425   1 2364   1 2296   1 2210   1 2102   1 2033
         8        1 3760   1 2820   1 2574   1 2460   1 2397   1 2335   1 2266   1 2179   1 2071   1 2002
         9        1 3754   1 2795   1 2548   1 2438   1 2374   1 2316   1 2248   1 2164   1 2060   1 1992
        10        1 3702   1 2776   1 2532   1 2422   1 2359   1 2299   1 2227   1 2136   1 2027   1 1958
        11        1 3739   1 2843   1 2601   1 2494   1 2429   1 2369   1 2299   1 2211   1 2105   1 2037
        12        1 3724   1 2806   1 2566   1 2462   1 2398   1 2341   1 2271   1 2182   1 2075   1 2006
        13        1 3677   1 2787   1 2551   1 2449   1 2386   1 2327   1 2257   1 2168   1 2059   1 1989
        14        1 3641   1 2778   1 2537   1 2429   1 2367   1 2304   1 2237   1 2146   1 2041   1 1970
        15        1 3687   1 2851   1 2620   1 2515   1 2451   1 2389   1 2315   1 2227   1 2117   1 2047
        16        1 3658   1 2888   1 2653   1 2549   1 2486   1 2428   1 2363   1 2275   1 2170   1 2102

AVG CELL VOLTS    1 3746   1 2807   1 2564   1 2456   1 2393   1 2333   1 2264   1 2177   1 2070   1 2001

CURR             15 7520  16 0490  16 0900  16 0900  16 0800  16 0800  16 0900  16 0900  16 0900  16 0900

ACCUMULATED
 AHRS             0        1 9010   3 7770   5 6530   7 5290   9 4060  11 2830  13 1600  15 0370  16 0030

TEMP 1            8 2500   8 3300   8 4500   8 5500   8 6200   8 6800   8 7100   8 7300   8 7300   8 7400
TEMP 2            9 7100  10 0100  10 2500  10 4400  10 5900  10 7000  10 7900  10 8400  10 8800  10 9000
TEMP 3           10 2700  10 5300  10 7700  10 9600  11 1400  11 2900  11 4100  11 5000  11 5600  11 6000

AVG  TEMP         9 4100   9 6200   9 8200   9 9800  10 1200  10 2300  10 3000  10 3500  10 3900  10 4100
PRES 1           54 1600  51 9000  49 3900  46 9900  44 8500  42 9900  41 3100  39 8100  38 4400  37 7400
PRES 2           57 2300  54 9000  52 2000  49 6200  47 3400  45 3000  43 4900  41 8900  40 4600  39 7200

AVG  PRES        55 6900  53 4000  50 7900  48 3100  46 0900  44 1400  42 4000  40 8500  39 4500  38 7300

BATTERY
VOLTS            22 2580  20 5050  20 1170  19 9440  19 8410  19 7470  19 6350  19 4960  19 3250  19 2150
```

Table 29-4

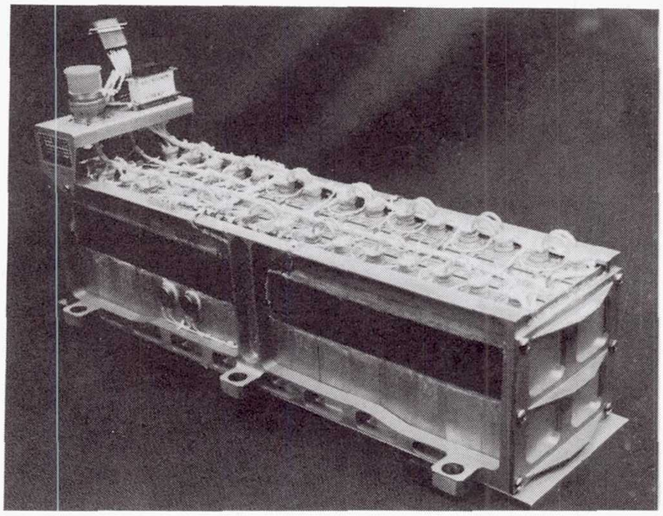

Figure 29-1

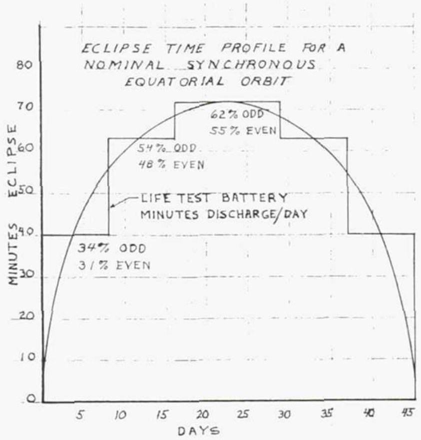

Figure 29-2

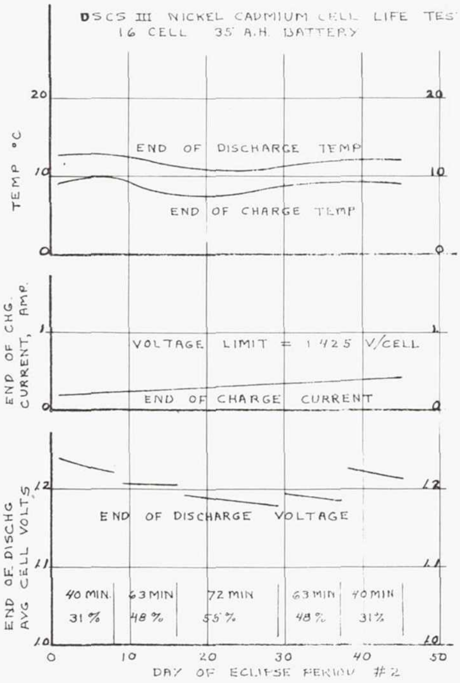

Figure 29-3

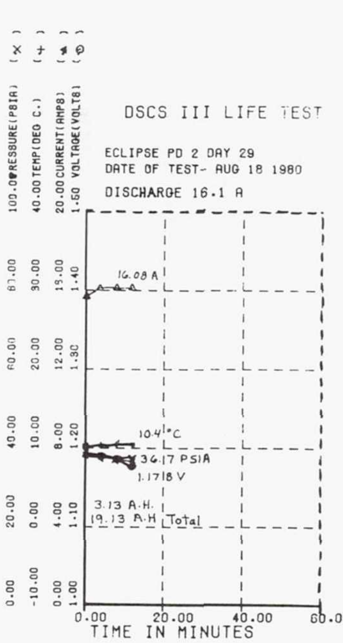

Figure 29-4

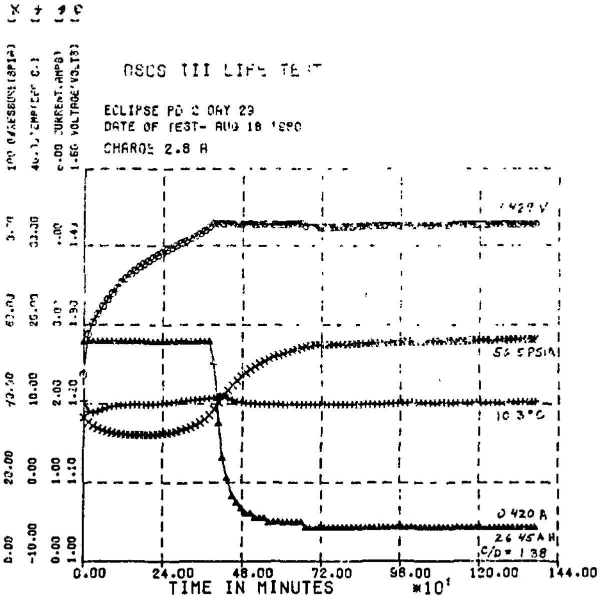

Figure 29-5

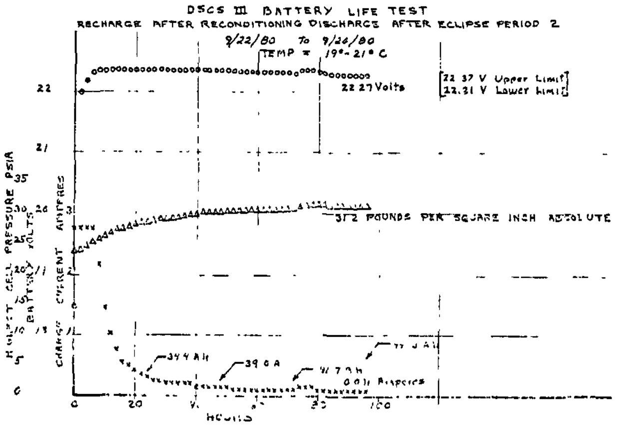

Figure 29-6

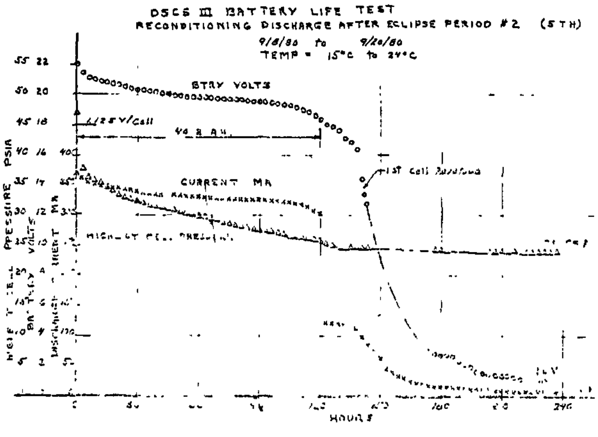

Figure 29-7

FIG 6

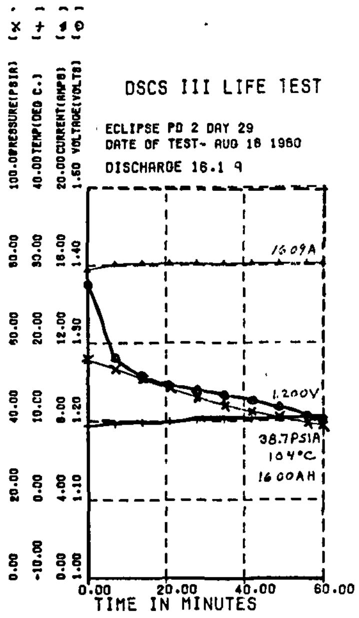

Figure 29-8

NICKEL CADMIUM CELL OPTIMIZATION PROGRAM

D. Hafen
Lockheed

My objective today is to give a short presentation on a test program. The data will come out of the pipeline around next November at the ICEC. The objective of this program is to test six cells. The design of these cells involved taking a baseline cell and making minor changes to it, keeping the same battery package. The way we conducted it is much like our standard Lockheed test, to go through an acceptance test, a parameteric test to determine optimum operating parameters, and a life test. I shall go more into that at the end of this presentation.

(Table 30-1)

The way that we changed the designs of these cells was based on a few considerations (See Table 30-1). One was precharge: we lowered the precharge value to 30%, so that we would have a little more overcharge protection. We examined the electrochemical method of impregnating the positive in a couple of these designs. This was to reduce growth, thereby lengthening the life, and also to have a more stable electrode in general. There are a couple of things in Table 30-1 that are nonexplanatory. One of these is the separator compression. The way we arrived at that was first to construct a graph of the pellon separator void volume versus milliliters or millimeters allocated. For each of these designs we just took the two void volumes and divided them to get an idea of which one is compressed the most.

The 55-3 (first column) is our baseline design. Most of these have lower compressions. High compression in the separator has been hypothesized as leading to failure.

(Figure 30-1)

Figure 30-1 shows a diagram of how the cells are related to each other. We have a 55-5 cell, which is much like cells that other aerospace people besides ourselves have tested. The only difference here was that they were hydrogen-vented instead of oxygen-vented. The other four are new designs using various combinations. One of them reduces the loadings to the level used in the old RSN 45 cell, which had an excellent cycle life.

During the manufacture of these cells by Eagle Picher, we made several observations of the manufacturer's process. When we started out, we noticed in the Fleischer process that the negatives end up out of the polarization process in a charged state, which if continued, could lead to undesirable species of cadmium oxide etc. Someone suggested that we discharge the negatives so that they would not react so fast. We tried that, but it was not good for the solutions or the electrodes. There were heavy deposits of cadmium hydroxide on the surface.

We also made the observation that we had great grouping of the positive pickup weights; they all went the same number of impregnation cycles. However, looking at a given impregnation cycle, some of the negatives were out of range, and some of them were not. Therefore, some of them had to go one more cycle, which should not really be a critical thing as long as you have a right weight. However, it would be desirable if somehow they all had the same level to begin with.

As for the formation process, Eagle Picher normally does one formation cycle only, but for our program they agreed to do three. For most of their electrodes, however, the discharge is incomplete. One of the reasons is a premature time limit on the positives, and for both the positives and negatives it is a case of first-cell-to-one-volt. Since there is a series string those cells that did not reach 1V are incompletely discharged. The vendor added a couple of new holding tanks before he started manufacturing our cells.

The conditioning process was performed a little differently from his standard by addition of a power discharge, which was to assure that the negative would reach full state of charge, which was said to be a problem. Then, instead of using a constant value of the overcharge protection, it was calculated from the capacities that were found in the NASA-type elecrode evaluation test, the flooded test. Finally, a rigorous overcharge test was performed at the end. It was about C/10 for 24 hours, getting a large percentage of recharge into them, and looking at the pressure to determine if the electrolyte was right. By the way, the electrolyte was calculated from the void volume of the separator and the plates.

(Table 30-2)

Going into the plate data briefly, there are two loading levels for each type of electrode. They are shown in Table 30-2. I do not think there is anything unexpected in this table. The utilization of the EDs are greater.

(Figure 30-2)

Figure 30-2 shows a picture of these cells in our test setup, showing the pressure transducers and so on.

(Figure 30-3)

Figure 30-3 shows a diagram of the program. Going into these tests a little, the acceptance test is a standard thing: weights, capacities, overcharge capability at three different temperatures (I think at 25 C we go for C/10 for a long time, at 0 C we try C/20 and at -20 C we go for C/100). As for charge retention, we charge it up and let it stand for a week and then do the capacity dump to see if there is any self discharge in AC and DC impedances. There is then a split, off into five cells going into parametric tests and two cells going to an accelerated test. This accelerated test is not like the normal accelerated test; it involves completely charging the cell and discharging it every cycle. Usually we do it at a C/2 rate, so that it really stresses the cell. You may not get the cycles going so fast, but you are stressing the cell more quickly. These cells should rank themselves in the same order of best to worst. You could not, however, predict the life in the satellite from this. I have the parametric test shown as 15% DOD and 30% DOD matrix. Actually, we have decided to change that to a standard value of 25% DOD at a couple of temperatures, which will allow us to run more cutoff levels at each matrix element. The life test will be at a worst-case condition, 25% at 25 C.

I have shown here that we shall select the best cell after 6 months. This simply shows that, by then, enough data will come out of this rigorous test to probably say which is best. Of course, the cells will continue after this for however long they want.

NICKEL – CADMIUM OPTIMIZATION CELL CHARACTERISTICS

		RSN 55-3A	RSN 55-5A	RSN 55-7A	RSN 55-9A	RSN 55-11A	RSN 55-13A
NEGATIVE LOADING (G/IN.^{2})		1.07	1.07	1.07	1.07	1.07	0.85
POSITIVE LOADING (G/IN.^{2})		0.69	0.60	0.69	0.65	0.59	0.60
IMPREGNATION OF POSITIVE PLATE C = CHEMICAL EC = ELECTRO-CHEMICAL		C	C	C	EC	EC	C
SEPARATOR STYLE (PELLON)		2506	2505	2505	2506	2505	2505
CALCULATED SEPARATOR COMPRESSION (PERCENT)		54	70	58	52	58	58
CAPACITY (Ah) (VENDOR TEST)	0° C	60.9	59.9	65.0	56.6	48.4	61.5
	25° C	55.5	49.7	56.5	54.8	48.2	49.7
	35° C	38.0	45.2	48.4	32.5	32.8	47.0
ELECTROLYTE WEIGHT (g)		250	255	256	250	277	263
WEIGHT (g)		1982	1838	1928	1981	1902	1848

Table 30-1

NICKEL-CADMIUM OPTIMIZATION CELL PLATE PROCESSING DATA

PLAQUE TYPE	LOADING (g/in.^{2})	ELECTROCHEM CAPACITY (Ah/in.^{2})	UTILIZATION (%)	ENERGY DENSITY (Ah/g)
LIGHTLY LOADED NEGATIVES	0.85	0.210	67.0	0.245
HEAVILY LOADED NEGATIVES	1.07	0.240	60.9	0.223
LIGHTLY LOADED CHEM POSITIVES	0.60	0.169	98.0	0.283
HEAVILY LOADED CHEM POSITIVES	0.69	0.187	93.7	0.271
LIGHTLY LOADED ED POSITIVES	0.59	0.210	112.3	0.325
HEAVILY LOADED ED POSITIVES	0.65	0.228	103.6	0.299

Table 30-2

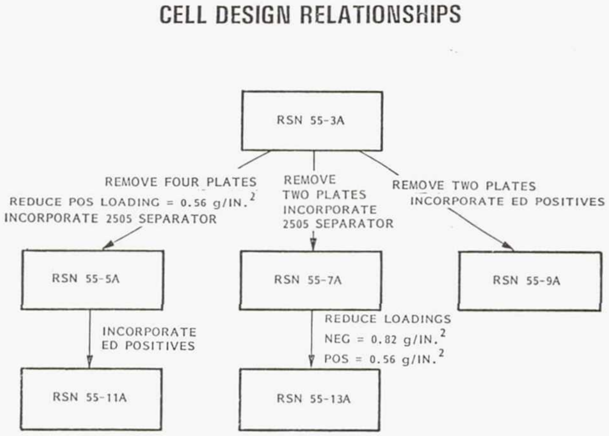

Figure 30-1

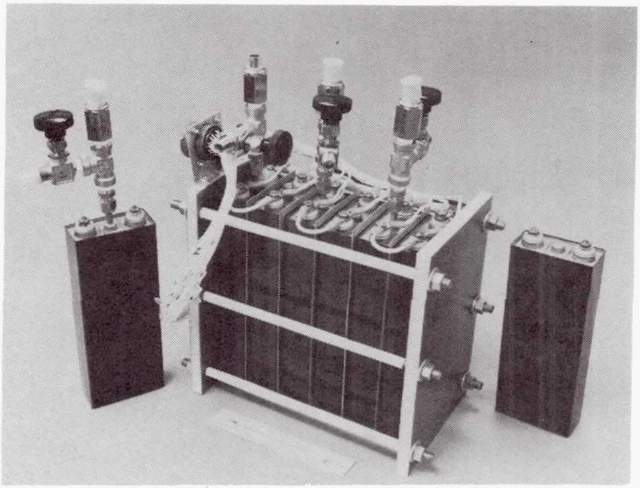

Figure 30-2

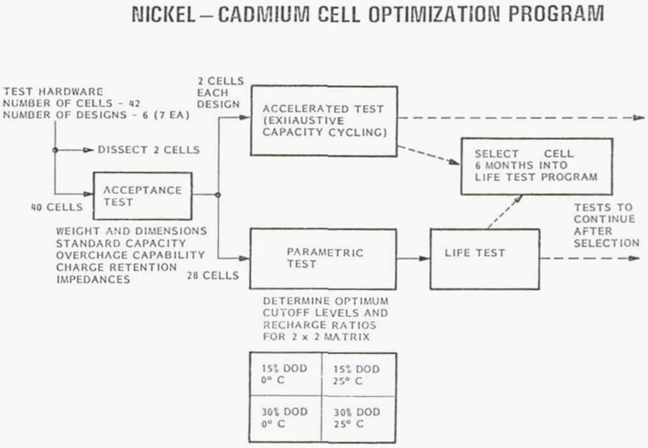

Figure 30-3

MULTIMISSION MODULAR SPACECRAFT PARALLEL BATTERY TESTS

M. Tasevoli
Goddard Space Flight Center

A battery test program was undertaken about three years ago at Goddard to study the effect, performance and operation of parallel battery operation as it affects both abnormal and normal flight conditions, and to recognize significant trends in battery operating characteristics during each simulation.

The test program was an attempt to build on our operational experience on the OAO missions earlier in the 1970s, and also supported the design concept and studies for the multimission modular spacecraft (MMS). Its objectives were the evaluation of charger voltage levels with respect to temperature, temperature imbalance between batteries, impedance mismatch of power cables, a shorted cell is one battery and transient effects when enabling battery to charger bus.

Several simulations were of interest to us and have been reported in past workshops; they will be the subject of a forthcoming NASA technical manual.

I should like to talk about the results of the battery acceptance tests that were repeated at the end of life for both batteries, and attempt to characterize battery degradation that occurred during the test program. The simulations were performed on two 12A h batteries and the acceptance test program included three capacity measurements at 0, 10 and 20 C. Additionally, there was interest in studying the effect of an individual cell case to battery negative short on both cell and battery performance on single battery both in continuous overcharge and in a near-Earth orbit cycling mode.

(Figure 31-1)

I shall now say a little about the batteries. The batteries were life cycled for approximately 2.5 years at 25% nominal depth of discharge at 10 C. The cell is a typical GE design. There are two ceramic feedthroughs, a pellon separator, a polypropylene cell stack liner, generally lighter loading than the NASA standard.

Of particular interest in comparing the acceptance test data was to look at the change in voltage profiles both on charge and discharge, the pressure increase or decrease in cells, and the response of the third elecrode cell. There were several things of interest: the softening of the voltage profile on charge; the generally more gradual discharge plateau; an approximately 7% loss in battery capacity to the final end point; and a loss of 1A h (the initial capacity being approximately 15 and the final capacity 14A h). The cell pressures have doubled, and while the output of the third electrode is nearly identical, the shape or response of the third electrode cell is different.

I am presenting data on one battery here, a battery at 20 C and C/10. I shall simply state that the response of the second battery at the same temperature was nearly identical. At the other two temperatures, 0 and 10 C, there was very little difference in either the shape of the voltage plateau, or the third electrode response. There was, however, a slight decrease in the capacity. Here, at 20 C, it was approximately 7%, and at 0 and 10 C, it was approximately 10% of the initial value.

(Figure 31-2)

The next series of tests was a simulation of a cell case to battery negative short. Figure 31-2 is a simplified schematic diagram of the test assembly, showing the 22 series connected cells, the power supply feeding constant current either in continuous orbit charge or in the near-Earth orbit cycling mode, a resistive shunt hardwired to the negative end of the battery, and connected at the other end to a movable probe so that we can go up and down in the cell stack and record both the initial current and also the taper current.

(Figure 31-3)

The test data presented in Figure 31-3 are on Battery B at ambient temperature at C/20 continuous overcharge. The battery had been in this condition for several days before the start of the evaluation. The initial and final currents through the shunt were first measured on all the non-third electrode cells; and, except for two cells, the initial and the final currents appeared to be well grouped. You will notice that the final currents, marked X are approximately one-twentieth or one-thirtieth of the initial currents.

The probe was then moved to the third electrode cells, specifically four on the most positive end of the battery. During the simulation the initial currents were quite high (about 15 - 20A), but were soon to taper within two or three minutes to approximately 1 or 2A. On one particular cell, no. 2 the short was fixed to the cell for a longer period (approximately nine minutes). This resulted in a cell short between the positive and negative terminals. In order to continue with the program, a shorting wire was placed across the terminals of that cell.

(Figure 31-4)

The next test was identical to the previous simulation, except that the short would remain on a cell for approximately four days. The cell in question was cell no. 12, which is approximately in the center of the stack. That cell had a pressure transducer affixed to it. The short was applied at 18 hours, and at least initially the pressure in the cell did not rise (see Figure 31-4). However, there was an increase in the cell pressure, which appeared to taper off at approximately 65 psi, increasing from the initial value of 45 psi.

The pressure on cell 22, another cell in the string, is also presented to give an idea of the pressure in some of the other typical cells in the string. The voltage on cell no. 12 did not increase or decrease appreciably during the period.

(Figure 31-5)

In the last case of the simulation, the battery was placed on a low-Earth orbit cycling regime at ambient temperature at a nominal depth of discharge at 103%. The battery had been cycling for approximately a week before its evaluation, to allow the battery to stabilize. Again, data are presented for cell no. 12 with the pressure transducer (see Figure 31-5). The short was applied at orbit 14, and at least initially there is no increase in the pressure. Then, for a period of approximately six or seven orbits, the pressure in the cell did, in fact, vary, but eventually stabilized to some stable operating point.

The data on cell no. 22, another cell in the battery, are shown here. During that period of five or six orbits, its pressure did, in fact, change. You will notice that the C/D ratio during the stabilized period remained constant.

In summary then, repeating and comparing the battery acceptance test data revealed a softening of the voltage profile, a lowering of the discharge profile and a loss of approximately 10% of battery capacity over a 0 - 20 C. For the case-to-battery negative short, the short-circuit current appears to be independent of cell position in the case of the continuous overcharge simulation. Repeating the same test with the signal electrode resulted in cell failure, which may be a function of both cell position in the string and the resistance path.

DISCUSSION

SCOTT: In those cells that had auxiliary electrodes, were the auxiliary electrodes connected to the case?

TASEVOLI: Yes.

SCOTT: Then when you connected the cases of those cells to ground to the shunt, I believe that essentially all the current that you measured was probably flowing through the auxiliary electrode?

TASEVOLI: That is correct.

SCOTT: Did you observe in general that the behavior of those auxiliary electrodes was essentially the same after that treatment as before?

TASEVOLI: Yes. For the three signal electrodes that were probed, the probe was only placed on for three or four minutes. On the one cell that I did single out, the short was placed on for an extended period, approximately nine or ten minutes, at which time there was a considerable drop in the cell voltage. In fact, the voltage decayed to less than 1V within a few hours.

SCOTT: Did the performance of that test, except possibly in that one cell, alter the behavior of the auxiliary electrodes in any way that you could see?

TASEVOLI: No, it did not. The cell voltages, both on the non-signal electrodes and the signal electrode cells, did, in fact, recover once the short was removed.

RITTERMAN: When you shorted your negative to the case, did you actually get an increase in current in the cell? On your pressure curves, the suggestion is that there is an increase in oxygen evolution. From your voltage, it has to be oxygen because the voltage is about 1.45.

TASEVOLI: For the non-signal electrode cell, the potential at this point here is positive with respect to this potential. If that is the case, and based on the electrochemical reaction on continuous overcharge, the increase in cell pressure is due to hydrogen.

RITTERMAN: It can not be hydrogen at the voltages you have. The cell voltage is 1.45, even when you apply the short. The hydrogen has to be manufactured within the cell.

TASEVOLI: That is right, it is being manufactured on the inside of the case of the cell.

RITTERMAN: Did you check that?

TASEVOLI: I did not measure the cell species during the extended period of overcharge. However, again based on the flow of current to the shunt and the chemical reaction within all the cells during continuous overcharge, the gas was hydrogen.

RITTERMAN: If that is so, why, when you continue to overcharge, do you get pressure equilibrium? The pressures just continue to rise.

TASEVOLI: That is what I do not understand. Again, the test was only performed for four or five days. Really, what you are looking at is the short-term effect of the short.

DOTY: How many cycles had that battery been subjected to by the time you ran the short-circuit test? Did you attempt to recondition the battery before the short-circuit test or did you just continue right from the normal 100 minute orbital regimes when you ran this test?

TASEVOLI: The test sequence was as follows: after the life-cycling test the batteries were let down through 1 ohm resistors for approximately one week, at which time we went into the acceptance test. After that test, we went straight into the case-to-battery-negative short simulations.

DOTY: It might help to give a brief idea as to how many cycles that battery had been subjected to before running these tests over that four-year period.

TASEVOLI: Both batteries were charged and discharged for a period of about 2.5 years at 10 C at 25% depth of discharge. During that period, the batteries shared the load quite equally even after the simulations that were performed.

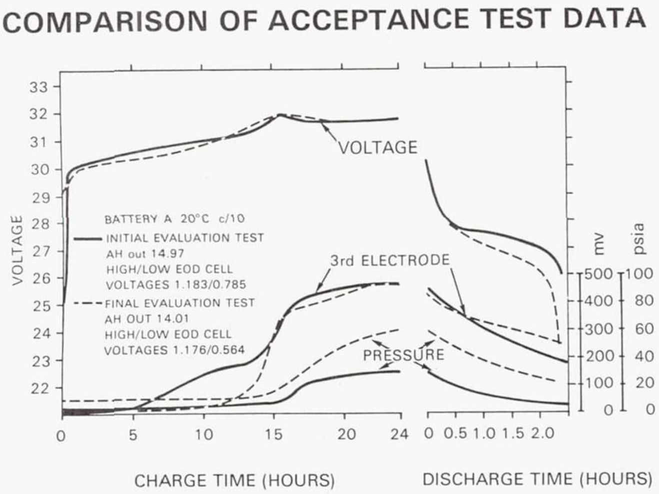
COMPARISON OF ACCEPTANCE TEST DATA

Figure 31-1

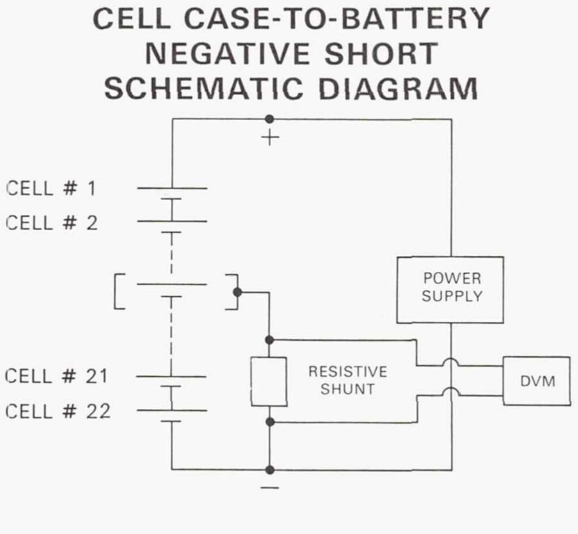
CELL CASE-TO-BATTERY NEGATIVE SHORT SCHEMATIC DIAGRAM

Figure 31-2

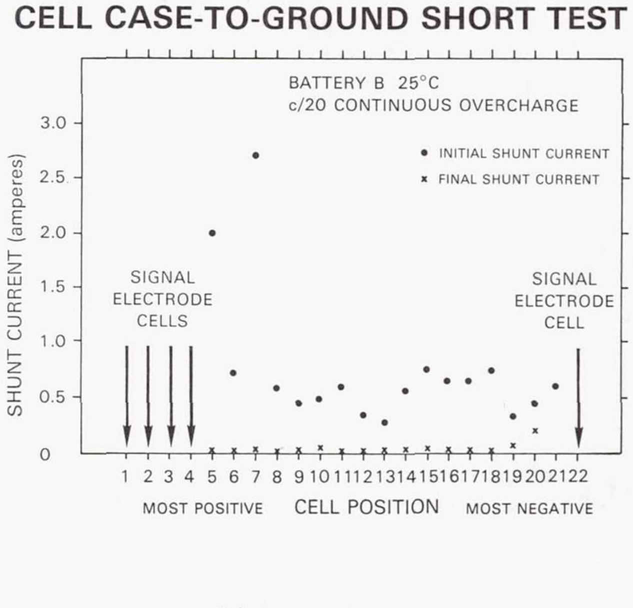
CELL CASE-TO-GROUND SHORT TEST

Figure 31-3

CELL CASE-TO-GROUND SHORT TEST
C/20 CONTINUOUS OVERCHARGE 25°C

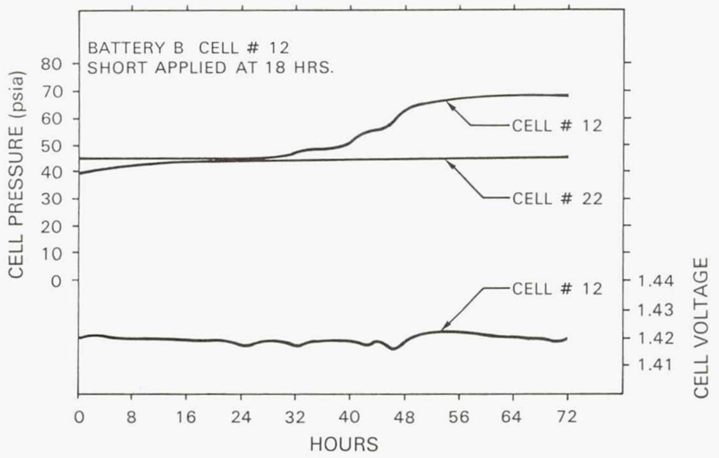

Figure 31-4

CELL # 12 CASE-TO-GROUND SHORT TEST
BATTERY B 25°C VL 5
100 MINUTE ORBIT, 36 MINUTE SHADOW
CASE-TO-GROUND SHORT APPLIED AT ORBIT 14

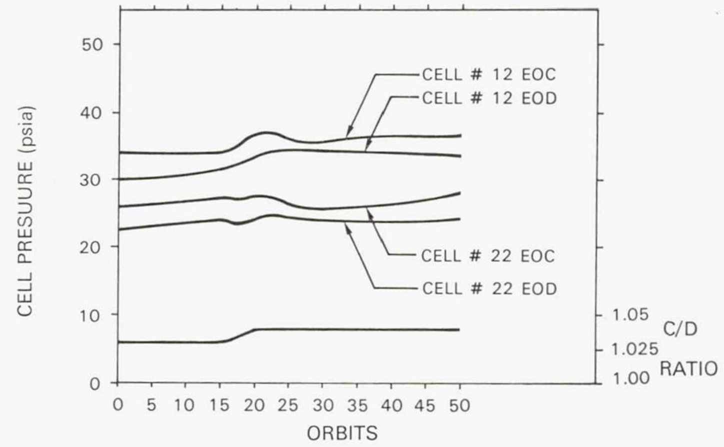

Figure 31-5

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PREDELIVERY CELL AND BATTERY SUMMARY FOR SMM 20 A H BATTERIES

D. Webb
McDonnell Douglas

As Mr. Halpert mentioned earlier, the SMM batteries are standard NASA nickel cadmium 20A h batteries. This is the first application of the standard battery; the data I shall present are from some of the cell testing, the battery testing and the process of building those batteries. With the life-test data that Mr. Halpert presented on the cells, and the presentation to follow, this should give you a complete picture of the NASA standard.

(Figure 32-1)

Figure 32-1 shows a schematic of the MMS power system module. You will see that the batteries are required to charge and discharge in parallel. There is a single regulator unit, another NASA standard component that is part of the system. That regulator has two modes of operation on SMM; the first mode is a peak power tracking mode where the regulator utilizes all array available power for supplying the load demand, and then whatever residue is available will charge the batteries with that available power. Once the batteries have reached a selected voltage limit, that voltage limit will then become the controlling factor and the current will taper for the rest of the charge period.

The batteries on the spacecraft are serial numbers 3, 4 and 5, and they are in positions 1, 2 and 3 on the spacecraft. That will give you a point of reference when Mr. Broderick talks about the performance on the SMM.

(Figure 32-2)

I am sure you are all familiar with the curves shown in Figure 32-2. These are the eight selectable voltage limit curves. The voltage varies with the temperature detected by the regulator, and they are selectable by ground command. In our testing, where we do simulated orbit testing in vacuum conditions, we have been using level 6.

(Figure 32-3)

Figure 32-3 gives some idea of the detail of battery design. The cells are standard cells, and are fabricated in accordance with a NASA approved MCD at GE. The battery dimensions are: height, 9.83 in max; length, 13.73in max; width, 7.83in max; and the battery weight is 52.2 pounds. We have a lightweight construction, a tension rod end plate construction. The cells are individually bonded, and then they are bonded into four packs or two packs, and the total battery is bonded at one time. There are ten thermal fins. They are between each set of cells and provide a heat path from the cells to the baseplate, which is the normal plane of heat rejection on the battery. In the SMM it is a passive system with louver thermal control.

The cell matching is in accordance with Revision B of the battery specification issued by Goddard. We match within ±3% of the average capacity at two temperatures, 0 and 24 C, and we also match within ±8mV on end of charge voltage at those same conditions.

The objective of the NASA standard cell program is to build in enough control and quality that the vendor's data can be used for cell matching. The data that will follow should show that this is feasible.

As I said, the cells are GE cells, and they were procured by McDonnell to the MCD that had been approved by Goddard. The plate loading is the lighter plate loading as Mr. Halpert mentioned (11.6±0.6g/dm^2 for the positive, 14.92±0.6g/dm^2 for the negative). They are chemically impregnated plates. The negative-to-positive ratio is in the range 1.65 - 1.75, and the total plate areas are 10.44dm^2 (positive) and 11.39 dm^2 (negative). The required capacity is 24±2A h at 24 C, and the average cell weight is 891.4g. There are additional plate treatments. The negatives are Teflonated, and there is cobalt hydroxide and some cadmium in the positive.

(Table 32-1)

The data shown in Table 32-1 are taken from the capacity cycles performed by the vendor, GE. If you are familiar with their procedure, they group their cells up to 25 cells in a series string.

There was no active coolant in the room temperature conditions other than convection on these tests. You can see the results in Table 32-1. I have given maxima and minia for the various groups. It is split up a little differently in the 35 C and 0 C test because of a Tinney chamber, which is capable of handling more than can be worked in one series string. They had two series strings in at one time. Groups 2 and 3 ran at one time, 4 and 5 at another.

(Table 32-2)

Table 32-2 shows capacity cycling that we performed at McDonnell after the battery was fabricated. The acceptance test is about a six-week test, and there is considerable charging and discharging going on other than what is shown here. Therefore, between the first and the second 24 C capacity test, there are approximately four weeks of testing.

The cell vendor data is the results, that the matching should indicate what we should expect in both the 24 C and the 0 C cases. You can see that the results match rather well. There is no 10 C test performed at the vendor. The third electrode on the batteries is loaded with 200 ohms at the vendor when he does his testing, and that 200 ohm resistor has been incorporated into the battery design.

(Table 32-3)

I mentioned the simulated orbit testing that we do. This is done in vacuum, and our control of the battery temperature is by means of an active cold plate. In this particular case the cold plate temperature is maintained, while on the other tests we attempted to hold a top-of-cell temperature. Here we hold the baseplate at the test temperature and conduct consecutive 90 minute simulated orbits going to a 25% depth and a 10A constant current charge until we hit voltage limit. This is not exactly as in flight, but it is the arrangement in this particular test.

I have shown here the voltage between the cells at the end of discharge and at the end of charge; also, the C/D ratios, the amp-hours-in, amp-hours-out ratio are averaged over the last three cycles of each condition. These are the three batteries that are currently flying in SMM. The C/D ratios are slightly below the goal levels specified in the S711 16. This has been consistent, not only here, but in the 50A h batteries.

Based on what we see, we feel that the material and process controls that have been imposed are effective and that the data base is suitable for selection. The battery acceptance performance substantiates that the predictions based on the cell match are legitimate. The proof of the pudding is in the eating. Mr. Broderick will talk about flight performance. However, from what I hear, I think that you will see the compatibility of the cells continues in the mission.

CAPACITY CYCLE PERFORMANCE
SMM FLIGHT BATTERY CELLS

	EOC PRESSURE		EOC VOLTAGE		CAPACITY		
	MIN	MAX	MIN	MAX	MIN	AVG	MAX
24°C CELLS							
TEST GRP 1	10 PSIG	30 PSIG	1.432 v	1.444 v	1339 AM	1386 AM	1428 AH
2	10 PSIG	28 PSIG	1.426 v	1.436 v	1386 AM	1426.5 AM	1477 AM
3	4 PSIG	26 PSIG	1.441 v	1.452 v	1335 AM	1391.5 AM	1443 AM
4	12 PSIG	39 PSIG	1.448 v	1.450 v	1359 AM	1385.7 AM	1408 AM
35°C CELLS							
TEST GRP 1	-12 PSIG	0 PSIG	1.391 v	1.404 v	1244 AM	1298.5 AM	1369 AM
2	- 7 PSIG	4 PSIG	1.393 v	1.397 v	1199 AM	1247.2 AM	1289 AM
3	-10 PSIG	1 PSIG	1.387 v	1.405 v	1180 AM	1260.9 AM	1348 AM
4	- 5 PSIG	2 PSIG	1.393 v	1.399 v	1255 AM	1322 AM	1363 AM
5	0 PSIG	7 PSIG	1.395 v	1.400 v	1310 AM	1339.3 AM	1368 AM
0°C CELLS							
TEST GRP 1	26 PSIG	49 PSIG	1.486 v	1.491 v	1257 AM	1310.7 AM	1389 AM
2	27 PSIG	38 PSIG	1.482 v	1.489 v	1301 AM	1337.5 AM	1365 AM
3	28 PSIG	55 PSIG	1.481 v	1.489 v	1270 AM	1337 AM	1447 AM
4	27 PSIG	55 PSIG	1.483 v	1.489 v	1240 AM	1303.4 AM	1407 AM
5	30 PSIG	66 PSIG	1.486 v	1.488 v	1254 AM	1304.5 AM	1370 AM
24°C CELLS							
TEST GRP 1	10 PSIG	30 PSIG	1.428 v	1.441 v	1426 AM	1464.4 AM	1487 AM
2	8 PSIG	28 PSIG	1.431 v	1.444 v	1451 AM	1490.8 AM	1515 AM
3	16 PSIG	41 PSIG	1.441 v	1.455 v	1447 AM	1478.7 AM	1504 AM
4	9 PSIG	34 PSIG	1.432 v	1.439 v	1477 AM	1494.5 AM	1520 AM

Table 32-1

CAPACITY CYCLE PERFORMANCE
SMM FLIGHT BATTERIES

	CELL VENDOR 24°C TEST	1ST 24°C TEST BATTERY	2ND 24°C TEST BATTERY	CELL VENDOR 0°C TEST	0°C BTRY TEST	10°C BTRY TEST
A.H. CAPACITY						
BTRY A003	24.56 AH	22.68 AH	24.19 AH	22.35 AH	22.10 AH	22.44 AH
A004	24.38 AH	24.23 AH	23.82 AH	21.69 AH	21.58 AH	22.33 AH
A005	24.16 AH	24.01 AH	23.33 AH	21.15 AH	21.12 AH	21.96 AH
EOC VOLTAGE						
BTRY A003	31.59 v	32.21 v	32.29 v	32.76 v	32.98 v	32.39 v
A004	31.57 v	32.29 v	32.15 v	32.74 v	33.02 v	32.45 v
A005	31.55 v	32.27 v	32.16 v	32.73 v	33.00 v	32.43 v
EOC CELL △ VOLTS						
BTRY A003	12 mv	11 mv	11.3 mv	6 mv	7.6 mv	6.5 mv
A004	13 mv	10.9 mv	11.6 mv	6 mv	7.5 mv	7.6 mv
A005	10 mv	11.8 mv	13.8 mv	6 mv	6.4 mv	8.4 mv
EOC SIGNAL ELECTRODE VOLTS						
BTRY A003	370 mv	442 mv	394 mv	338 mv	350 mv	316 mv
A004	388 mv	478 mv	418 mv	314 mv	293 mv	319 mv
A005	466 mv	552 mv	475 mv	356 mv	368 mv	385 mv

NOTES: 1 24°C CHARGE CURRENT IS 2 AMP, CHARGE DURATION 24 HOURS
2 0°C CHARGE CURRENT IS 1 AMP, CHARGE DURATION 72 HOURS
3 10°C CHARGE CURRENT IS 1 AMP, CHARGE DURATION 48 HOURS
4 SIGNAL ELECTRODE LOADED WITH 200 OHMS

MCDONNELL DO.

Table 32-2

SIMULATED ORBIT PERFORMANCE
SMM FLIGHT BATTERIES

	EOD VOLTAGE	EOD CELL △ V	EOC VOLTAGE	EOC SIG VOLTAGE	EOC CELL △ V	C/D RATIO (AVG)
0°C BATTERY						
A003	27.25 v	2 mv	32.59 v	152 mv	5.8 mv	1.025
A004	27.19 v	2.1 mv	32.59 v	195 mv	5 mv	1.020
A005	27.19 v	2.1 mv	32.59 v	215 mv	3.9 mv	1.024
10°C BATTERY						
A003	27.28 v	1.8 mv	32.07 v	124 mv	6.2 mv	1.045
A004	27.26 v	1.9 mv	32.08 v	201 mv	4.5 mv	1.036
A005	27.26 v	2 mv	32.08 v	215 mv	6.6 mv	1.041
20°C BATTERY						
A003	27.24 v	2.1 mv	31.55 v	134 mv	6.8 mv	1.084
A004	27.22 v	1.7 mv	31.55 v	157 mv	7.3 mv	1.075
A005	27.22 v	1.9 mv	31.54 v	197 mv	7.7 mv	1.076

NOTES: 1 DEPTH OF DISCHARGE 25%
2 RECHARGE VOLTAGE LEVEL LIMIT 6
3 SIGNAL ELECTRODE LOADED WITH 200 OHMS
4 10 AMP CHARGE CURRENT TO VOLTAGE LIMIT AND THEN TAPER
5 SIMULATED ORBIT 90 MINUTES 30 MINUTE DISCHARGE 60 MINUTE CHARGE.

Table 32-3

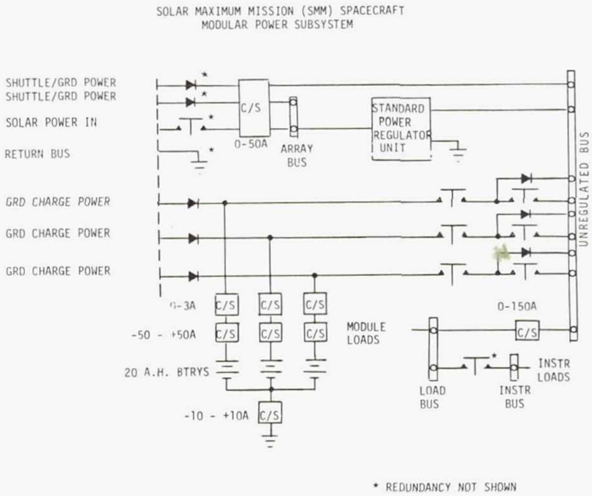
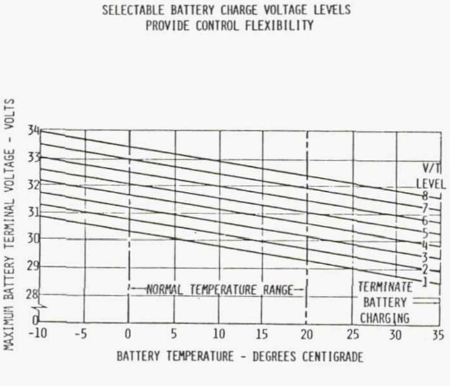


Figure 32-1



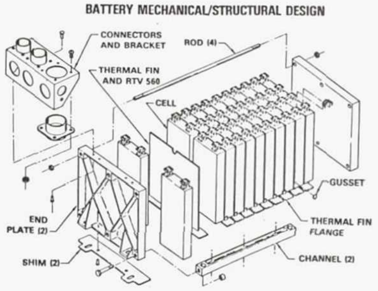


Figure 32-2

Figure 32-3

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SOLAR MAXIMUM MISSION (SMM) IN-FLIGHT PERFORMANCE

R. Broderick
Goddard Space Flight Center

I should like to begin by trying to indicate the importance of this mission, referred to in earlier presentations by Dr. Tasevoli, in design testing that went into this system, and by Dr. Webb from McDonnell Douglas in battery design. This is the first standard battery flown, and it is the first application of the modular power system. The modular power system design will be implemented on the Landsat prime spacecraft. It could very well become a workhorse power system for the 1980s.

I shall try to not repeat what has already been said this morning. I shall go into a brief system description, a summary of the first nine months, typical orbit data, some a typical orbit data and a comparison with some life-test data.

We integrated the flight batteries last November, and so they actually have near one year life. However, the mission launch was not until February. Currently up around 4100 orbits, a near-Earth spacecraft, with a 96 minute orbit period, fluctuating between 28 and 35 minutes eclipse period. We started off with a two-year design life and because of slippages in the shuttle, (SMM is the first retrievable spacecraft) its lifetime has been spread out to about four years.

(Figure 33-1)

Figure 33-1 shows a picture of the modular power system. As Dr. Webb said,the positioning of the batteries is, from left to right, battery 1, battery 2, battery 3. There are some strip heaters along the edges of the module for thermal control of the batteries, and the thermostats that control those heaters are located on the bottom of this module.

(Figure 33-2)

Briefly, back to the system description that Dr. Webb went into: the only thing I think he did not mention was that there are control relays on the battery, and there is circuitry for automatically removing them in case of overheating (See Figure 33-2). They can be manually disconnected.

(Figure 33-3)

Some of the general systems overview of it (Figure 33-3). Orbit number is shown along the abscissa. We are now up to around 4100 orbits. Volts are on the ordinate. We are typically getting about 1.43V per cell end of charge, and 1.21V per cell end of discharge. Voltage level 4 was selected at orbit no. 271, and replaced by level 5 at orbit no. 1428.

(Figure 33-4)

Figure 33-4 shows the charge-to-discharge ratio plotted against the orbit number. The on-board computer (OBC) has an algorithm for summing ampere minutes in and out of the batteries, and we dump that once per orbit for all three batteries, which we then use as the state of charge indicator. There are some inaccuracies associated with that, such that we do not really believe that the indicated C/Ds are actually that high. I think there is about a 6% error. We are getting an indication of an average of about 1.20 C/D; we think it is a little lower, probably around 1.15.

(Figure 33-5)

Depth of discharge (Figure 33-5) has generally been in the range of about 14 to 16% over the 4000 orbits.

(Figure 33-6)

There is a circuit in the modular power system for monitoring the top and lower portions of each battery, and we have that in there to indicate if we start seeing any cell shorts or degradations throughout the mission (Figure 33-6). Since we went back to voltage level 5, battery no. 1 has started to creep slightly above the others, but we are really down in a millivolt range of difference.

(Figure 33-7)

For an early orbit, no. 17, on day 2 of the mission, Figure 33-7 shows the battery voltage total load current and the three battery currents plotted on top of each other. You can hardly detect a difference in the three battery currents, but it does indicate the initial surge on sunrise that we get into the battery peak power tracking, which amounts to about 22 - 24A per battery, quickly going into a taper, and tapering down to somewhere in the range of a C/30 end of charge current.

(Figure 33-8)

Figure 33-7 was included to provide a comparison. Figure 33-8 shows orbit 3200, a typical orbit. There are similar data, 0.6A, C/30. During discharge you can see a slight variation in the load current sharing of the three batteries during discharge. We are discharging at about 6A C/3 rate. Again, the peak charge currents on sunrise are 22, 24A. Peak power tracking for about four minutes before hitting the voltage limit.

(Figure 33-9)

As Dr. Webb or Mr. Halpert said, we do have a third electrode in the battery. It is not an active control but we do use it as a state-of-charge indicator (Figure 33-9). During the first minute of Sun, we get some oxygen generation, which exceeds the recombination. As we go into the taper charge, the pressure will decrease. We are getting a definite indication of an increase midway in the orbit, towards the end of the orbit, which we take as an indication that we are indeed reaching a full state of charge, or an overcharge condition.

(Figure 33-10)

As I mentioned, the batteries are thermostatically controlled to the baseplate thermostats. Typically, under thermostatic control, we have been operating in the range 10 - 12 C. The difference between the cold and hot battery has been a maxiumu of about 1 C over the orbit. Many times they are exactly right. Figure 33-10 shows how the heater of the center battery actually got turned off before this. The other two batteries are cooling off. The center battery, not having side radiators, tends to have a slower thermal cooldown than the outer batteries, and we cycle around wherever that third battery reaches an equilibrium.

(Figure 33-11)

That was a typical orbit. We have had a couple of a typical orbits (Figure 33-11). We have not been as fortunate in the other areas of the module's multimission satellite as the modular power system. The attitude control system has suffered a couple of hardware failures. When that happens, we do have some software in the OBC for disconnecting non-essential loads. In essence, the battery heaters got turned off during one of those hardware failures, and for a period of about 11h, we had no thermostat control. Without the heaters there to control the baseplate, the batteries will drop down and diverge. We had about a 4 divergence between the two operating temperatures.

We saw these data during integration and tests as well. From that, and from what we are seeing here, we determined that we can possibly increase mission lifetime by, instead of operating in a range 10 - 12 C, letting these batteries cool down to where they might go, and then trying to control to a much lower temperature range. This week we have initiated that turning off of the heaters. We shall go to a manual control over the heaters, rather than a thermostat control.

Currently, we are down to around 5 C on the third battery, and nos. 1 and 2 are at zero. We do not really want to operate there on a long-term basis with that much temperature difference. We should like to get into a cycling: wherever this battery no. 3 reaches equilibrium, we shall try to oscillate around it.

(Figure 33-12)

Around orbit 3000, when we lost attitude for a couple of orbits and were in essentially a random tumble mode, we got very little Sun for these two orbits. In fact, the batteries were still on discharge for about a 4-hour period. The bus voltage ran down to about 24.5V, 1.11V per cell (Figure 33-12). We took 36A h out of the three batteries, which is a 60 A h rated total, somewhere in the range of 57% DOD. You can see that as we got down in state of charge, we did start to get some divergence of the three battery currents sharing. However, it was not very significant. It was perhaps 0.8A.

(Figure 33-13)

We had a series of orbits during the autumn equinox, a period of about two weeks when the heaters were on continuously. During that time we reached an unstable equilibrium, such that the baseplate did not quite reach the 7.4 C cutoff point (Figure 33-13). As a result, the heater stayed on continuously. If you remember, the strip heaters are along the edges of the module, and so the two outer batteries in direct line to that radiation heated up. We got about a 2 C difference across the battery packs. However, they did stabilize at about 14 C peak. Therefore, even in a simulated heater-on failure, we had some control of the battery temperatures. We were able to determine that this happened as a result of autumn equinox and Earth albedo effects, such that we were getting a much more efficient radiation off the baseplate than we normally do throughout the year.

(Figure 33-14)

Last year Mr. Halpert presented some of the data on the Crane tests, and he went over that again today. There are a couple of packs, GE cells, that are currently being cycled at 20 C, 25% DOD, which is not identical to our orbit, but it brackets it (see Figure 33-14).

(Figure 33-15)

The other pack that brackets our operation is 10 C, 40% DOD (See Figure 33-15). We are actually more in the range of 10 C, 15% DOD. Therefore, it is not an exact comparison. However, I make comparisons where I can.

(Figure 33-16)

We ran an in-module conditioning cycle back in November before integrating the batteries at the launch site. Because of these deep depths of discharge, which I went into, we have some data as to the ratio of ampere hours at the voltage.

Comparing Figures 33-14 and 33-16, you can see that we are slightly better than in the 20 C, 25% DOD regime that we would expect, and comparing Figures 33-15 and 33-16, better than a 10 C, 40% DOD regime that we would expect.

In summary, we have been rather fortunate in the power system. We have achieved performance as predicted. It appears that although we cannot say that we are doing better than the Crane life test data, we are not doing worse. So far, we have had a good mission, and we hope that it will continue.

DISCUSSIONS

COLBURN: On Figure 33-4 you had some recharge fraction numbers that were, I believe, up to 1.28, and some were lower. You said that you did not quite believe that they were that high in reality, and that there was about a 6% error associated with those numbers. I am wondering how you arrived at how to determine the confidence of a recharge fraction number, and how you did that error analysis?

BRODERICK: In a way I stepped through the system components. The accuracy of the current sensor itself, 1% of full scale. Full scale for us is -50 to +50A, and so we have a 1A error associated with the current sensor. Current sensor accuracy is a function of temperature and load voltage.

The remote interface unit, which samples the telemetry, has digitation errors of 0.4A. We have done hand integrations to correlate, and these hand integrations just give us what the computer gave us. Therefore, it was really just the accuracies of the current sensors themselves that give us that large error.

COLBURN: You just did the errors by each individual components and added them together?

BRODERICK: That is correct.

HALPERT: I might just add that these are comparable to the Crane data, and there we are running between 105 and 106% for the same cells and those two different orbits that you were looking at there. Therefore, obviously, if we are running 105 and 106% in one case, and 115 - 120% in another, we know we have some concern there. The current sensors will give us that kind of an error.

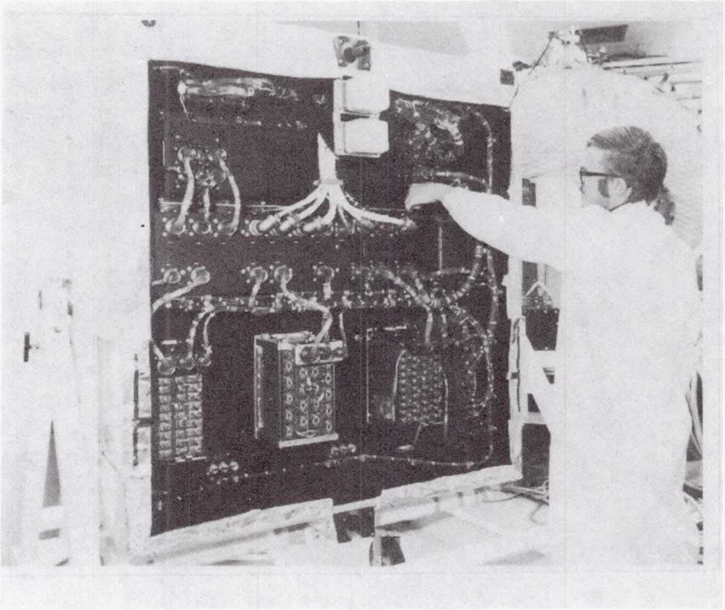
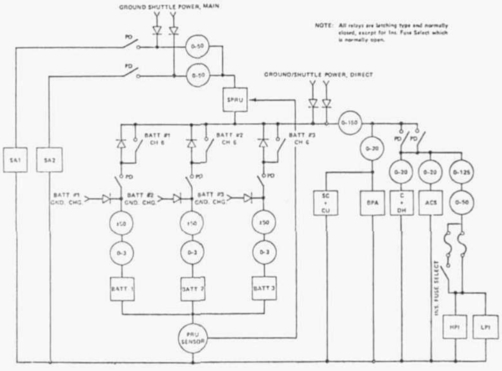


Figure 33-1



MPS block diagram

Figure 33-2

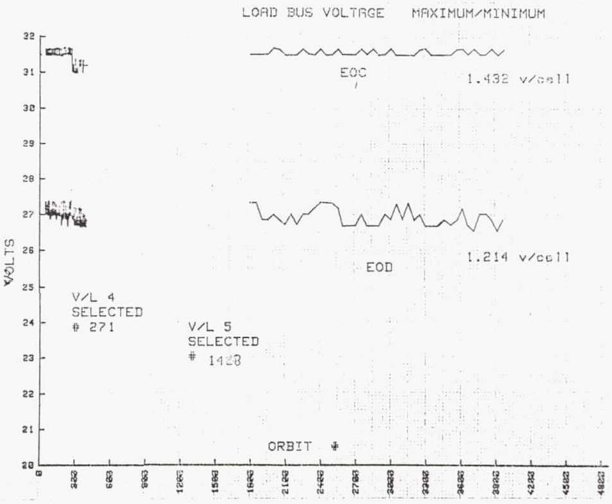


Figure 33-3

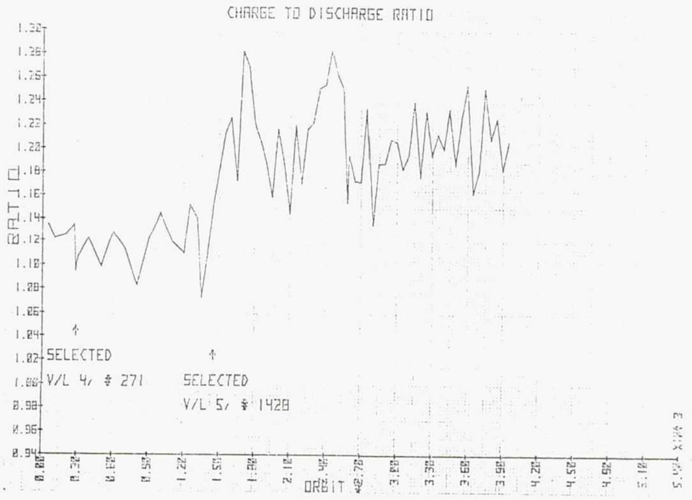
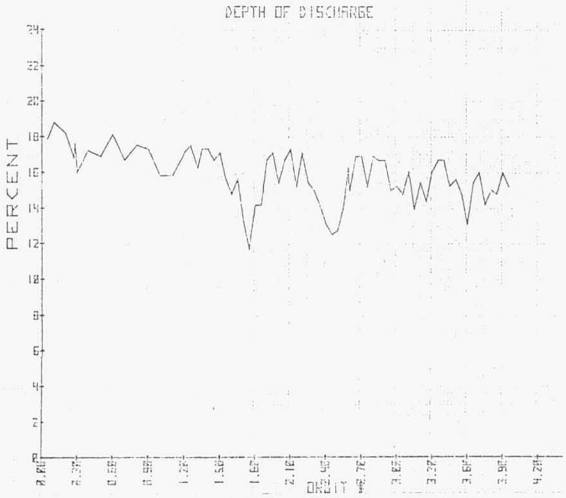


Figure 33-4



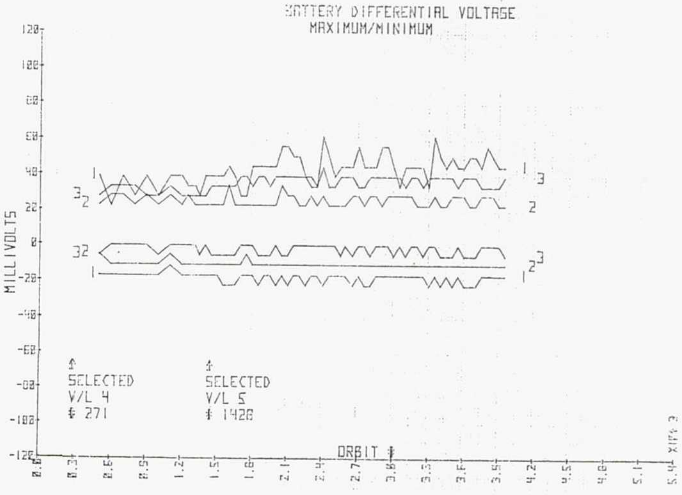


Figure 33-5

Figure 33-6

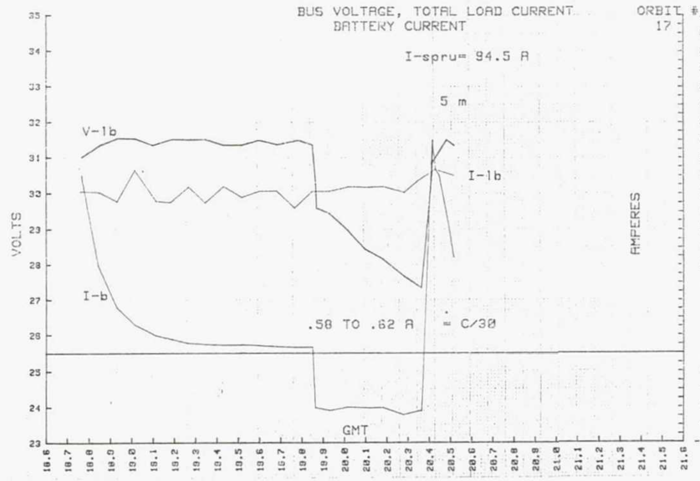


Figure 33-7

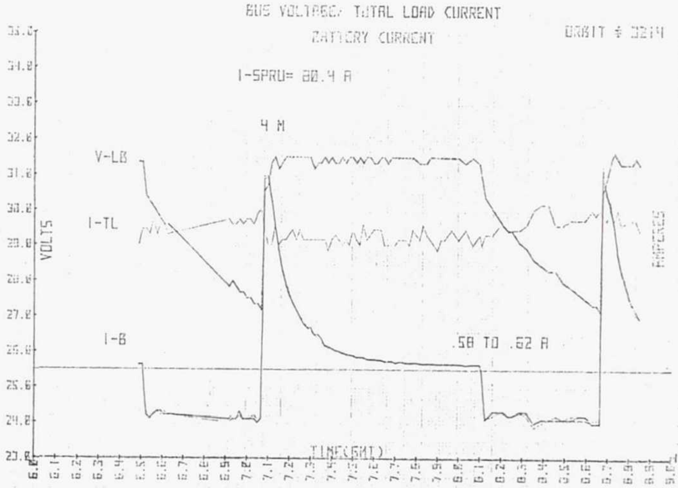


Figure 33-8

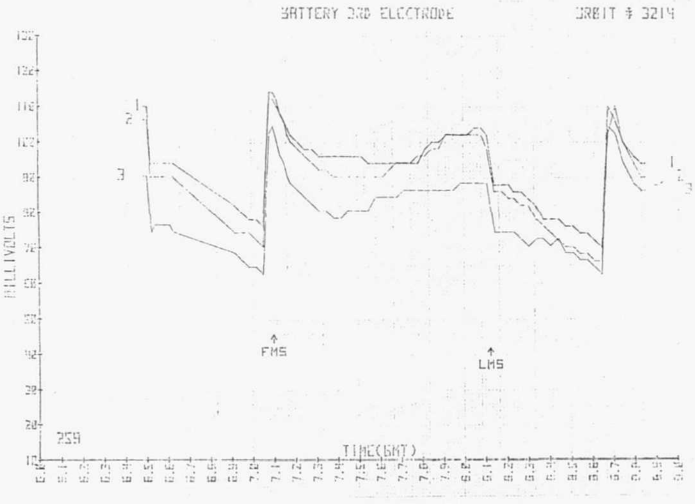


Figure 33-9

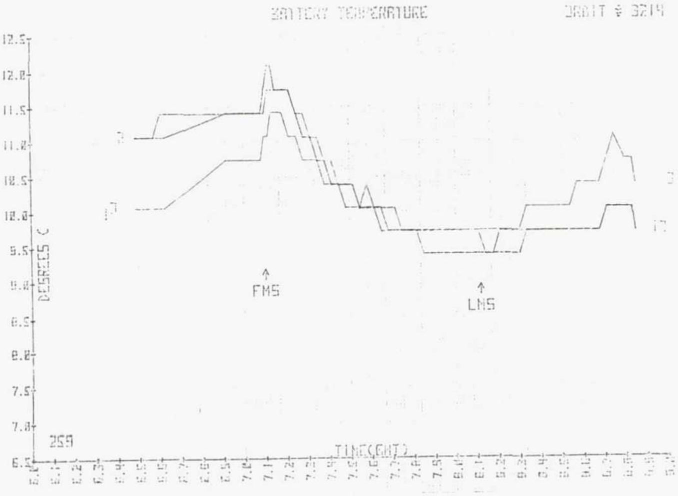
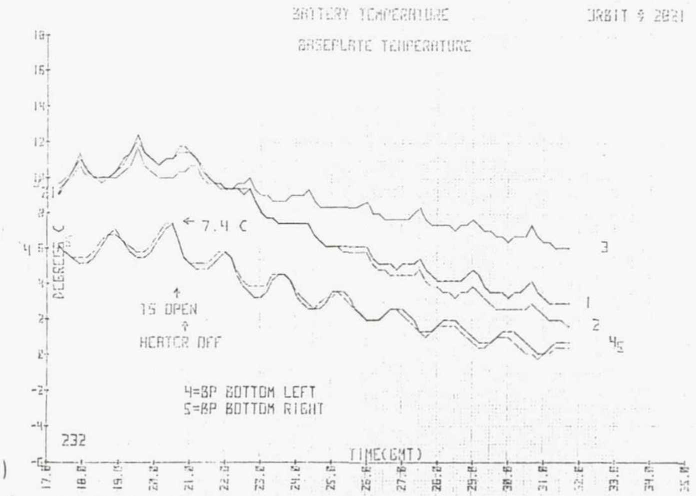


Figure 33-10

Figure 33-11



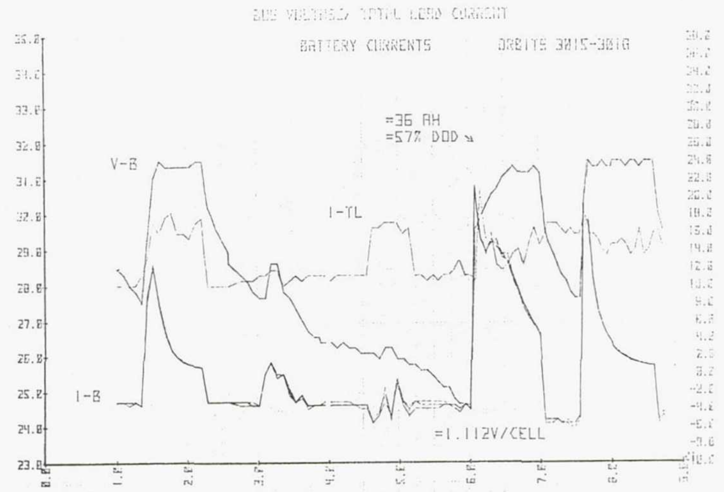


Figure 33-12

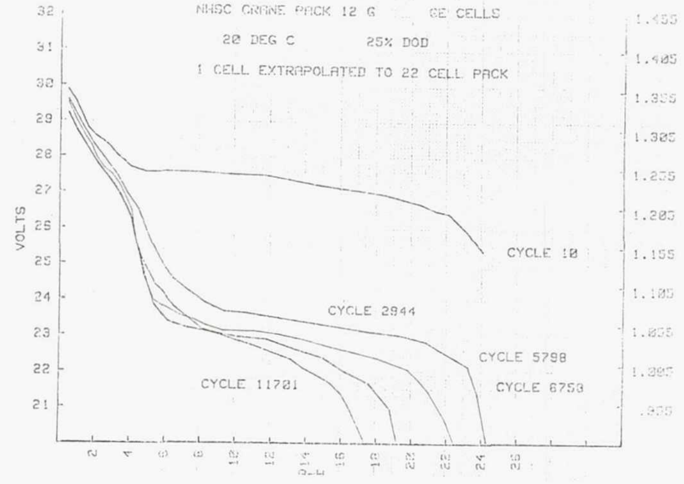


Figure 33-13

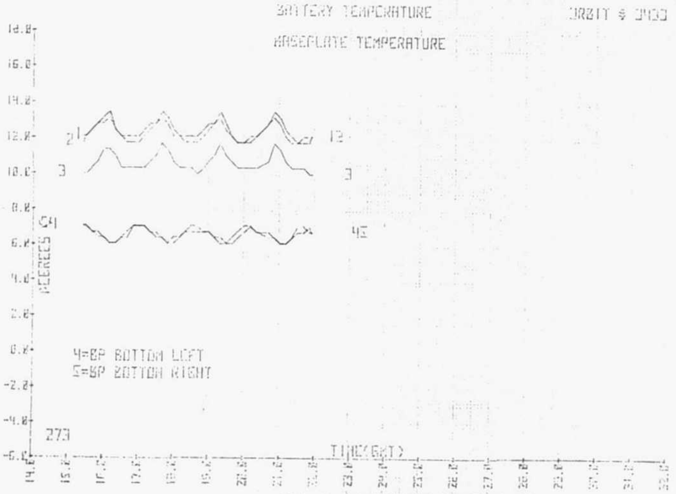


Figure 33-14

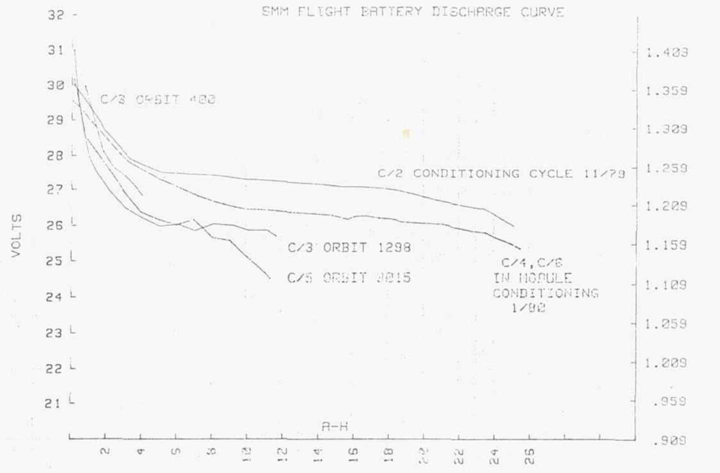


Figure 33-15

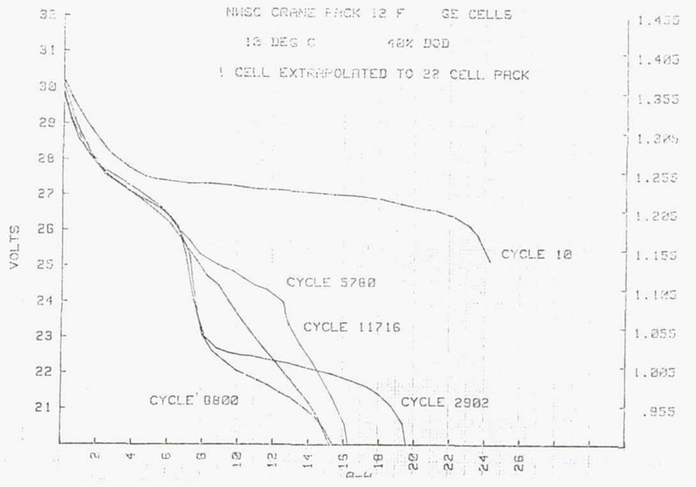


Figure 33-16

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VIKING LANDER FIVE YEAR SUMMARY

A. Britting
Martin Marietta

(Figure 34-1)

I shall be talking about the Viking landers, built by Martin Marietta, that were launched in 1975, cruised eleven months to Mars, and landed in July and September of 1976 (Figure 34-1). Their planned mission was 90 days of scientific investigation and search for life. We are currently in the 1600th day of our landed operations on one of the two Landers. The mission of the other one has been terminated.

(Figure 34-2)

The battery assemblies in the Lander (Figure 34-2) are located as temperature and battery voltage monitoring. On Earth we did have individual cell monitoring for initial tests.

I should mention that the cell construction was pellon FT21, non-woven polypropylene separator material. The cells were manufactured by GE.

(Table 34-1)

Table 34-1 identifies the total number of cycles on the Lander 1 and Lander 2 batteries that exceeded 5%. To date, on Lander 1 we are approaching 10,000 cycles, the majority of which are between zero and 5% depth of discharge.

Our charging scheme is such that during the 4h period we have one battery on charge for 1h, and the other three on the equipment bus. After 1h, that battery is taken off and the next battery is put on the bus; the battery gets charged until such time as the voltage temperature compensator scheme senses a high on the voltage on the battery to terminate the charge. The greatest depth of discharge encountered during the mission was during the descent portion of the mission. We had 50 and 55% depth of discharge on Lander 1, 46 and 29% depth of discharge on Lander 2. The majority of the cycles that have any significant discharge hardly exceed 20%.

(Figure 34-4)

As shown in Figure 34-4, last year at this time we had identified that the Lander 1 batteries were performing normally; in fact, a little better than expectation, having degraded probably

10 - 15% from the cruise conditioning tests we had performed. We were still in the area of 7A h. Lander 2, however, had experienced an anomaly that caused the Lander to operate in excess of 80 F (27 C) Fahrenheit for 137 days. During that time we had no communication with the Lander and no way of running any tests of the impact on the batteries. Also, during this time we did not discharge the batteries significantly. The majority of those discharge cycles were in the 0 - 5% range. We were still doing the 1h charge, 3h off charge cycles. Once we recovered and regained communication with the Lander, we found initially that one battery was down by 4.5A h. Subsequently to, the other batteries were found to be in the area of 2 - 2.5A h from the initial 8A h end of 90-day mission design requirement.

We then embarked on a scheme to recharge or condition-charge the batteries by discharging them to 27.3 V through the 19.3 ohm resistor, about C/5, and then recharging at roughly a C rate to charge cutoff. It appeared that we were well on our way to recovering a good portion of the capacity of the batteries. We were doomed, however, soon to reduce communication with Lander 2, because our main method of communication was with an orbiter that was fast losing its attitude control system. Therefore, we did not get the batteries all completely conditioned. I do not have all the information I should have liked at this time to report on that particular set of batteries on Lander 2.

(Table 34-2)

I did report last year that our scheme of discharging at 27.3 V at C/5 and then recharging at the C rate, picking battery C there from Lander 2, was able to recover. Table 34-2 shows the 90-day timeframe. We measured 2.12A h out of the battery at this time. 90 days later, after having performed a conditioning cycle, we had recovered about 50% of the cycle. A week later we did one more test, and recovered another 40% of the capacity.

At this time, knowing that we were going to lose the Lander, I was a little curious to see what would happen if we discharged a battery below 1.1 or 0.8 V per cell, knowing full well I would probably end up reversing cells, and we might find that we permanently damaged the battery. We did, in fact, reverse cells. However, having a fixed resistance across the battery during the discharge tests, and having the voltage decay, and the current discharge current was naturally decaying. As a result, even though we did reverse the cells, it was not permanent and we were able to recharge the battery and use it. I noticed additional improvement in the capacity of the battery.

We then embarked on doing this to all the batteries on the Lander. However, the mission ended. We simply ran out of time and could not get enough additional information for me to report anything significant other than the fact that it looked as if discharging and taking the cells all the way down, as was mentioned in an earlier paper here, does significantly improve the batteries.

(Figure 34-5)

Figure 34-5 shows a typical charge/discharge scheme that we are now using on Lander 1. On Lander 1 we have not been doing any conditioning for the last two years. We saw that the open-circuit terminal voltage was about 32 - 33V, as it had been right at touchdown. We saw no reason to do anything with regard to conditioning there. However, having seen the weakened batteries on Lander 2, we chose to play with those.

Figure 34-5 is the curve showing the discharge voltage, a cutoff at our 27.3V, a recovery during which time the battery voltage did rise, the recharge at C/8 to the voltage temperature compensator charge cutoff. On the scale on the right ordinate, is a discharge current curve. The bottom of the scale is the temperature scale from 50 to 64 F. The typical diagonal temperature variation on the Lander ranges as shown on the chart here. During the discharge, because it is exothermic, you can see the impact it had. Since the recharge was somewhat endothermic, you see a time lag before the normal temperature rise starts taking effect. These are typical cycles we are performing now on each of the Lander batteries, 37, 38 days apart, repeating once every five months.

(Figure 34-6)

The reason for doing that is displayed in the Lander 1 battery performance chart (Figure 34-6). The A, B, C and D on the graph identify the four batteries on the Lander. Batteries A and B are the two in the very corner of the Lander, and tend to operate 5 or 7 cooler. Batteries C and D, until the beginning of Martian summer, a little over six months ago, were operating well. At that time we discovered that the batteries were increasing in temperature and were operating at about 10 - 15 higher than batteries A and B.

At that same time I began to notice the battery terminal voltage depressing to 30 - 31V. We determined at this time that we should run some conditioning tests, if for no other reason than to find out the difference in ampere hour capacity reached in the four batteries and to see if we could find a scheme to cool the two currently depressed voltage batteries. We ran our discharge tests. We found that batteries A and B were roughly 30% degraded since their initial pre-sterilization test, or about 15% degraded since cruise. Batteries C and D, however, were down to 3.6A h, or hardly 50% of their initial specification capacity, and down to 67% of their initial cruise capacity.

Our power system is designed such that all excess power is first supplied for battery charging. If the battery charge cutoff has occurred, the power is dumped through shunt regulators in the Lander legs and radiator. If battery charge cutoff does not occur, any excess power not being used on the equipment bus is channeled into whatever battery is on the charge bus. These two weaker batteries, having a lowered terminal voltage, and the temperature not being high enough for the temperature compensation portions to cut off the batteries, accepted all the excess unused power on the equipment bus for charging, and through an I^2R heating, began rising in temperature. I proved this by putting some additional loads on the equipment bus, sucking some of the extra power from the radioisotope thermoelectric generators (RTGs); I put about a 1A load on the equipment bus for a short time and noticed a significant drop in the battery temperatures. I could not leave that on for ever because the RTGs are decaying at 4W per year and will not be able to handle that additional load.

We decided to do our conditioning test on all four batteries on this five-month cycle; once every 38 days, take a battery, discharge at 7.23V, C/5, and then recharge at C/8. Until such time as we determine that we need to command the Lander not to do that any more -- if we find we are not having any significant gains -- that will happen ad nauseum, or until the Lander decides to shut down. I say that because we do have undervoltage sensors on board, which we can trip.

From a performance standpoint, Lander 1 has, on a once-a-week to once-a-month cycle, been going through a normal 1A discharge cycle (C/8 for 1h at 12% DOD) because of the normal communication it makes with Earth. We had, in the past, found that we had no problems with terminal voltages on that Lander, and thought no additional conditioning would be necessary on those batteries. We were discharging to roughly peak discharges to 15%, and recharging at C/8.

We have since found little degradation on two batteries, as I recorded earlier. Two batteries had greater degradation, having depressed terminal voltages. We are seeing unequal load sharing between the battery pairs, i.e. the two good batteries are monopolizing the equipment bus load when there are heavy loads on the equipment bus. We are seeing the 10 - 15 F higher operating temperatures on these batteries.

In summary, we have had a five-year operation with no failures. We have had no opens (to our knowledge) and no shorts (to our knowledge) with regard to battery performance. As far as the 90 day mission, obviously we are well past that, being at the 1600 days that I reported earlier. The Lander 2 mission has been terminated. For the Lander 1 mission we found, as I did report earlier, that the weekly maintenance, if I can call it that, just powering up the Lander for communication link, was not sufficient to keep the batteries in any good condition. We have determined to go ahead and do the reconditioning. One of the reasons we want to keep the reconditioning scheme going is that the Galileo program is planning on using the Mars gravity assist to save some of the trajectory correction fuel of its Delta V to get on to Jupiter. The best way to determine Mars's ephemeris is to locate Mars exactly. We have the equipment on Mars to locate Mars exactly, and to locate the Galileo spacecraft exactly. The plan is, in June or July 1984, to have the Galileo spacecraft pass within 200km of Mars by using the Mars gravity assist, and then doing a Delta V burn and going on to Jupiter. Thus we now have an added incentive to keep our 90 day mission going until 1984.

DISCUSSION

GEORGE: You said the anomaly would recharge at the C rate?

BRITTING: C/8.

GEORGE: What did you determine was the maximum safeguarding rate for those batteries?

BRITTING: We did not really have that problem. We were limited by the amount of power we could get out of the RTGs.

GEORGE: When you did your reconditioning, you did an experiment to drop the cell voltage to 0.8V average?

BRITTING: In fact, even below 0.8V. We actually discharged the battery for seven hours with a 19.3 ohm load across it. On the particular battery that I showed, we discharged it to a level of 9.88 V the first time. A subsequent discharge some time later only took it down to 18.04V. However, during the discharge we did see cell reversals. You could actually see, if you plotted the curve, little dips as the cells were reversing. I did not have indvidual cell monitoring, and so I had no way to say that a certain cell reversed.

GEORGE: You said you had two 24-cell groupings?

BRITTING: Yes.

GEORGE: So you took that to 9.8V?

BRITTING: Yes.

GEORGE: If you were able to detect soft shorts -- you indicated you had no shorts -- were you able to see any of those dips in other than your discharge during reconditioning?

BRITTING: The only dips were in the voltage curve, and the resolution of the transducers was not such that I could honestly identify the occurrence of a dip.

VOICE: Were the cells matched?

BRITTING: Initally, the cells were matched. If Mr. Mason is here, perhaps he could identify the tolerance. I do not recall.

VOICE: If the cells were matched, what do you think caused the cell reversal?

MASON: The cells were matched initially, but of course this is several years into the mission. I do not know exactly where you started seeing the reversals, but I believe they were matched to within 2% of initial capacity after burning prior to battery assembly. It may have been even closer than that. Whatever mismatching you are seeing at this point is divergence due to aging.

BOWERS: Were there any periods during this mission when the batteries were on open circuit, between the end of charge and the start of discharge?

BRITTING: For short periods, yes. For instance, during a charge cycle, if when we hooked the battery to the charge bus, the battery immediately showed a high enough voltage to cause our charge control logic to terminate charge for the rest of that 1h charge period, the battery would be just sitting there on open circuit. However, as far as any prolonged period during the mission, we were always under once an hour on the charge bus, 3h off, 1h on, six times a day on each battery.

GEORGE: I am counting 48 cells that you have for a given battery.

BRITTING: For a given battery assembly. In each battery assembly there are two 24-cell batteries, and there are two batteries per spacecraft.

GEORGE: You discharged this to about 10V?

BRITTING: Yes.

GEORGE: That comes out to less than 0.8V per cell.

BRITTING: I said that I was going to discharge the batteries for 7h, not to 0.8V per cell. If I did not get that across, I am sorry. I knew full well I would reverse some cells when I did this, and as the mission was going to terminate in the near future anyway, we just wanted to see what would happen.

FORD: Would you clarify a point you made during the presentation concerning the charge characteristic? Did I understand that you got to a condition on two of the batteries where you were not hitting the voltage limit and initiating the logic to terminate charge?

BRITTING: That is correct.

FORD: Do you understand the phenomena there? Was it a lack of adequacy in the design of the VT system? I am assuming it is a voltage-temperature compensation. Or, are you attributing that to an aging phenomena associated with those two batteries?

BRITTING: It is not anticipating the aging phenomena of the batteries. We designed for a 90-day mission. We felt we had fully characterized the batteries for the 90-day mission and did not, if I may, skip a beat for charge cutoffs during the 90-day mission. In fact, for the first several years, we did not. However, as time went on, the voltage did become depressed. We do not have the capability to change the values on the charge control logic electronics, and so now we are stuck with what we have got up there.

FORD: Could you comment on approximately how old were the batteries, or how long into the missiion before you saw this?

BRITTING: On Lander 2 it did not occur until roughly 600 days after landing. On Lander 1 it was more like 900, 950 days after landing.

FORD: If I remember past presentations on these batteries, they were not used in the spacecraft during integration and testing. Is that correct?

BRITTING: That is correct. I might also identify the fact that possibly the reason for the 600 days on Lander 2 versus 950 on Lander 1 was that Lander 2 operated significantly hotter throughout its entire mission. That might have had some contribution.

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 10-20% Typ	61 Nov 76	29% Max 10-20% Typ
Thru Conjunction	Nov 76	65	20% Max 13-20% Typ	8	5% Max 5% Typ
Thru Extended Mission	Jun 78	308	40% Max 10-20% Typ	211	42% Max 10-20% Typ
Thru Nov 78		32	15% Max 5-10% Typ	8	20% Max 10-20% Max
Thru Continuation Mission	Mar 79	32	15% Max 5-10% Typ	2	22% Max 12-20% Typ
Thru Survey Mission	Oct 80	51	15% Max 5-10% Typ	10	20% Max 12-18% Typ
Total		540 Cycles		310 Cycles	

Table 34-1

PERIOD	UTC DATE	DISCHARGE DURATION (HRS)	AVERAGE DISCHARGE VOLTAGE (VOLTS)	DISCHARGE AMPERE-HOURS (AH)	DISCHARGE TEMPERATURE (°F)
CRUISE	138/139-76	6.3	30.2	9.13	83.0° - 91.1°
SOL 547	078/079-78	5.6	29.4	8.15	55.1° - 59.2°
SOL 777	315/316-78	1.5	28.7	2.12	57.5° - 58.3°
SOL 858	033 - 79	2.0	28.9	2.95	40.2° - 43.5°
SOL 865	041 - 79	3.42 7.0	29.95* 24.78**	5.11* 8.74**	41.9° - 50.1°
SOL 953	131 - 79	4.35 7.0	29.37* 27.66***	6.50* 9.84***	46.8° - 54.2°

* To 27.3 V nominal PCDA charge control logic cutoff level

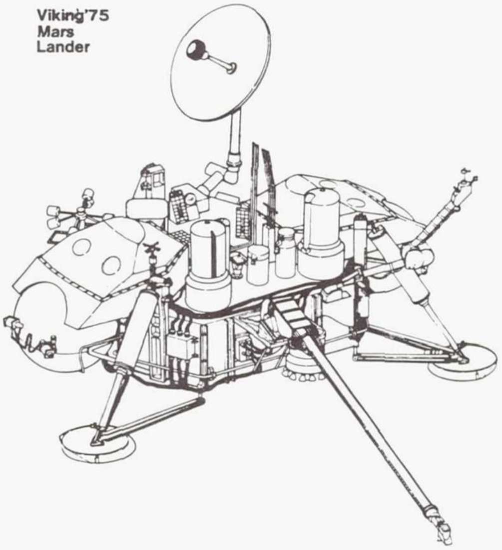
**

** To 7 hour timed discharge. Battery terminal voltage at this time was 9.88 volts.

*** To 7 hour timed discharge. Battery terminal voltage at this time was 18.04 volts.

VL-2 RECONDITIONING HISTORY

Table 34-2



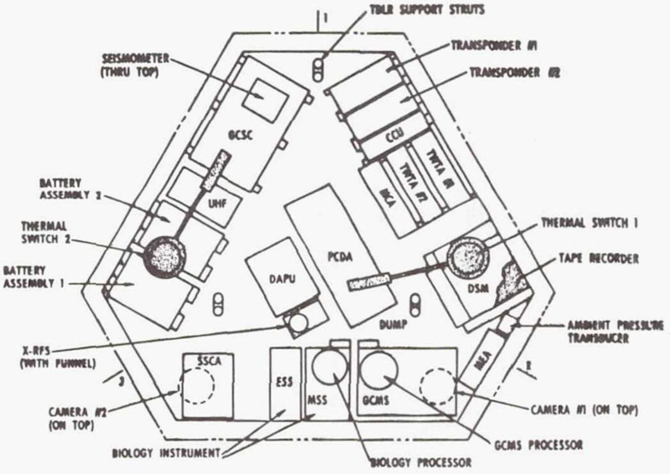
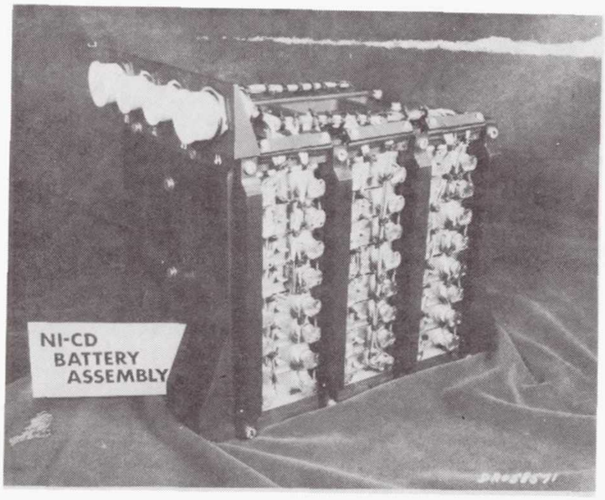


Figure 34-1

Figure 34-2



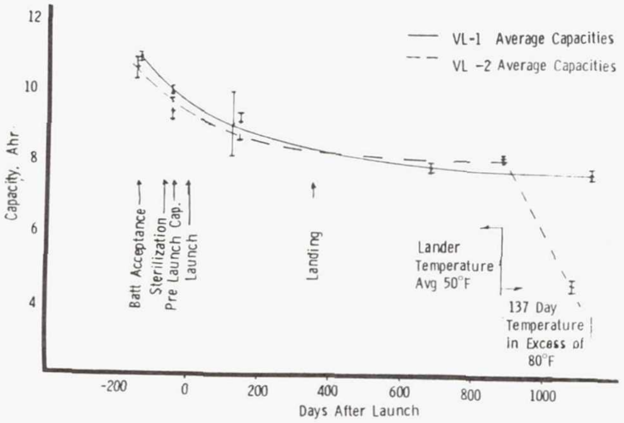


Figure 34-3

Figure 34-4

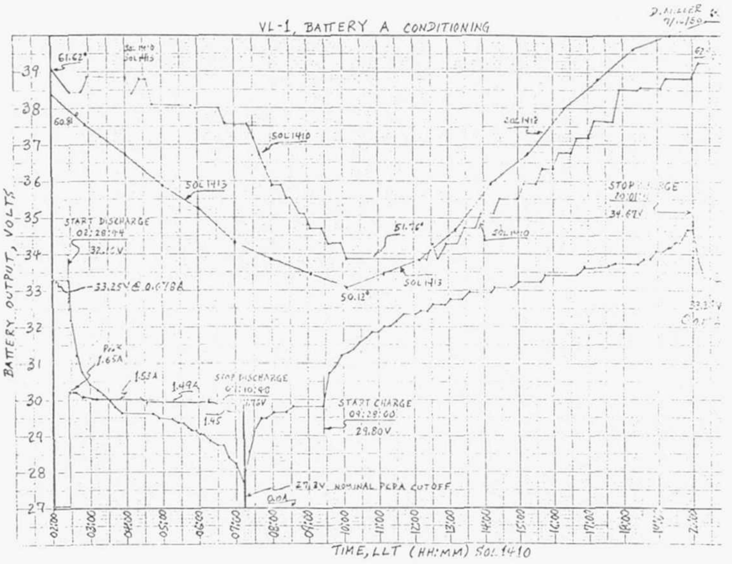


Figure 34-5

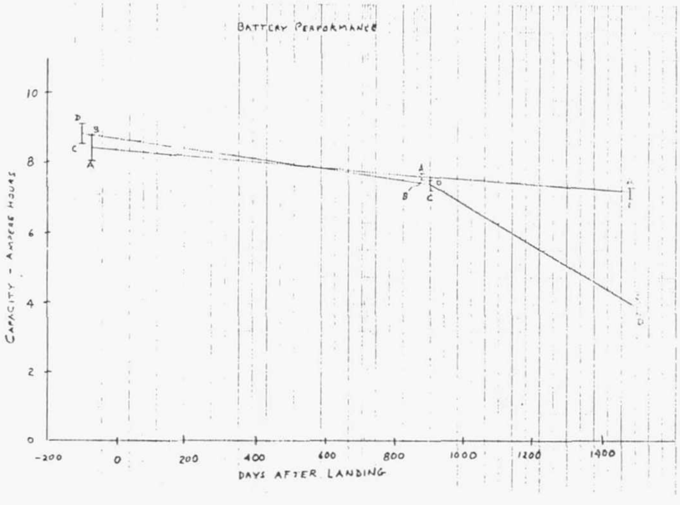


Figure 34-6

COMPARISON OF DIFFERENT PLATE TREATMENTS AND DESIGNS, AN UPDATE

D. Baer
Goddard Space Flight Center

Nine packs of cells of different designs were put on test at Crane. First, they were run through their initial evaluation tests, and then they were put into a cycling test. These were GE 12A h cells. The temperature was 20 C., the orbit was 90 minutes, the depth of discharge was 40%, the discharge rate was 9.6A and the initial charge rate was 9.6A to a voltage limit where it went into a taper. The goal was to get 100% return. The voltage limit was 1.453V through most of the testing, although recently we had to lower some packs and raise some to hold 115% return.

After one year, one cell from each pack was removed and the initial evaluation tests was repeated.

(Table 35-1)

In Table 35-1 we show a comparison of the 25 C. voltages and ampere hour capacity. I shall not go into the details of design. It was presented in a paper co-authored by Floyd Ford and myself, and Mr. Ford presented it at the Fall 1978 Electrochemical Society Meeting. It was also presented in this Workshop in 1978 and 1979. Table 35-1 contains a list of the variables. The control group was essentially GE's basic plate designs, which they have been using since about 1970. That included deep heat treated positive, which I do not think is a secret any longer. There is a little cadmium in the positive plate. The second group was cells with Teflonated negatives; the third had a silver treat; the fourth were quite lightly loaded plates; the fifth did not have a PQ treat; the sixth group had polypropylene separators; and the seventh and eighth groups were the old plate designs from about the late 1960s. The seventh group had the old Aerospace processes of treating the plates, and the eighth group had the present processes, such as taking the negatives all the way down to 0.5V, and incremental oxygen venting with precharge.

The first column shows the Crane pack number and the serial number of the cell.

The next column shows the removal cycle. As you can see, most of them are removed after about one year, although group 8 had cells removed at 2459 cycles and 2008 cycles. The reason for that removal was that they were having trouble controlling the amount of overcharge because of voltage convergence, and so we had to remove two cells at that point to keep the remainder of the cells on test. These are 5-cell packs, incidentally.

The next two columns compare the end of charge voltages (C/10 charge for 24 hours). As you can see, for the first six groups, there is not much difference in comparing the after-test with the before-test voltages. For the AK plate old processes, however, the end of charge voltage is down to 1.419V. These dip peak to about 1.46 V, and then they just came down. I am not sure of the reason. The AK plate present processes had end of charge voltages that were substantially increased. That indicates why we are having trouble with the percentage return.

The next two columns show a comparison of the ampere hour capacity, the initial evaluation test, and evaluation after one year of test, with the last column showing percentage change in the one year. As you can see, the cells without the PQ treatment are performing the best. They had lost about 5.6%. Disregard the AK plate present processes, since those cells were removed with less than six months of test. The next best are the Teflon and the AK plate old processes. I might add that the AK plate did not have the PQ treat either. The cells that were doing the worst were the ones with the polypropylene separator. These cells also had the highest internal resistance, about 4.2 milliohms. This was measured after one hour of discharge. The other cells range from 3 to 3.7 milliohms. It looks as though there is a problem with drying out in the polypropylene cells, although they did contain more electrolyte than was usually put in the polypropylene cells.

(Table 35-2)

Table 35-2 shows a comparison of the 0 C. overcharge voltages. The only cells that ran for the whole 60h of test were the control, Teflon and silver. The other cells were either terminated owing to high voltage (the criterion was that if they exceeded 1.56V for a 2h period, they would be removed) or to high pressure, (the pressure criterion was 100 psia). I might add that the only cells that had pressure gauges on them were the last three cells, the AK plate cells. There are pressure gauges on some of the other cells, except they were not removed from the test at this point.

(Figure 35-1)

On Figure 35-1 the bottom axis shows time in months. A capacity test is run at the six month, one year and eighteen month points. That is what the data points are. These discharges were done at 9.6A rate, and this graph shows discharge of 1V. The Y axis shows the percentage of initial capacity. In all the packs, either cell no. 1 was the limiting cell, or else all the cells were coming down together, except for the AK plate old processes. That probably explains this increase of capacity. I think, if that were the limiting cell in the initial case, this graph would not have the top curve, and then you would probably break and come down to there.

You might also note that these numbers are the cell number that was removed from the pack. The cell that was removed after a year was usually the no. 1 cell in the pack, in most cases. Therefore, at the one year capacity check, there are two data points. You can see that in most cases they fall close together because there was a switch in the cell in which the capacity check was being run, except for the PQ or the non-PQ. There is quite a bit of difference there, although this point falls pretty much in line. There is also another pack added. This was the ninth pack, GE electrochemical impregnated plate. In fairness, this is one of GE's earlier attempts at making that type of plate. The cell did not have much initial ampere hour capacity, something of the order of 11A h. That is not doing well at the six month test, although it does look as if it has improved after the one-year capacity test. That is lighter than the other packs by about six months. As you can see, the light-loaded plates are not doing well during this capacity test either. Here again the polypropylene is the worst.

I think probably the most significant conclusion from these data is that the plates without the PQ have a much better capacity down to 1V than the plates that have the PQ treatment. That may also be a reason for the need to recondition now, where in the past there was not quite as big a stress on it.

The other item of interest is that the capacity down to 0.7V at the one year point, even at the higher rate and even though it is coming right off of cycling, compares favorably with the one year capacity test that was shown on the previous chart.

I do not think there is a difference of more than about 0.8A h between the two tests.

DISCUSSION

KUNIGAHALLI: Could you comment on the amount of the electrolyte? I see that there is a variation in the amount of electrolyte from one group to another. Does it have any influence on the performance, based on their difference in volume?

BAER: I should say that the ones that have more electrolyte usually have a different treatment associated with them, like Teflon and silver. For the controls, the Teflon and the silver-treated cells, there does not seem to be much difference. I think you could get that much difference in a normal distribution of the performance of the cells.

KUNIGAHALLI: Do you mean to say that there is no difference between a Teflonated and a non-Teflonated cell?

BAER: It is so slight that I hate to draw any conclusions at this stage. That might show up a little later.

FORD: I should like to add a couple of comments to the presentation. As most of you know, this area of cell evolution, which is what we are talking about here, has been of some concern to us at Goddard for a number of years. That is what prompted this test matrix that we have been following for the better part of three years.

What is interesting is that in the evolution process, a lot of trends have developed, all of which are true for a given cell design. For instance, there are still people who say that the trend in degradation of cell is for the overcharge voltage to increase. That is true for certain designs. There is also a trend for the overcharge voltage to decrease, which is true in certain designs, as the data presented.

As for the area of reconditioning -- I have been working at cell data since 1966. One of my first assignments when I came to Goddard was to follow the Crane program and to do some analysis. In the course of those years, I have accumulated many graphs, charts, data, statistical analyses. One thing that always bothered me, from about 1975, was that I began to detect, intuitively at best, that something was different in the cells we were testing at about 1970 from those we were testing before. Certainly, the main characteristic was the overcharge characteristic of the cell. We thought we had learned to make better cells because we could now pass a low-temperature overcharge test and see cells maintain a fairly stable characteristic, without increasing. However, another thing that came out is that if you go back and compare the degradation in capacity of some of the older cells, I think one thing is very clear: The cells made by General Electric during the 1960s did perform quite well when you could cycle them without high pressure with high voltage. They maintained capacity quite well. If you look at cells made since 1970, particularly with the evolution of PQ and the other variables that have been put in the cell since that time -- all of which, incidentally, were an attempt to solve some type of problem that manifested itself for reasons that were not always clear to the user -- you see a heritage of cells, a plural heritage, not single cells.

The challenge today is to get back to the basics. From the data and from this test, I have concluded one thing: a pure, unadulterated nickel cadmium cell seems to be the best thing we can build. I think it is time that we seriously looked at all these things we have been doing to cells, and looked at the ramifications, not only for the short term, but also for the long term, as we are talking about here.

I think we have done things that have compromised the life of the cell, and in doing that, we have come up with fixes that have further compromised cell designs. Therefore, I challenge the manufacturers of nickel cadmium cells to really take a hard look at what we have done in the 1970s and see if we have not learned something that may, with all these improvements, turn us around to the period of the 1960s and see what we were doing right as against what we are doing wrong today. I think that if we do that, we are going to find a cell in the 1980s that outperforms anything you are flying today, and probably outperforms things we were flying in the 1960s, too.

LACKNER: What kind of polypropylene did you use, and did you have any particular treatment for it before your characterization?

BAER: I think I shall have to refer that to Guy Rampel. I think it is a GAF polypropylene. When I said polypropylene up here, I recalled that I am not sure exactly what it was. I believe it was a GAF.

RAMPEL: Yes, it was a GAF.

BAER: Were there any special treats?

RAMPEL: Not that I know.

LACKNER: There is great variability in polypropylene depending upon the air permeability, the wetting agents you have, etc, so that you can get disastrous results in one day, or you can run it for ten years, like some of the Alouette cells.

BAER: I think this was some material that was left over from another program where the cells did seem to do very well. I am not sure of all the treatments.

LACKNER: You would have to say that polypropylene is a good material if it is used properly?

BAER: Yes.

HELLFRITZSCH: After Mr. Ford's comment there, one thing that has been running through my mind, too, is whether one could go back to the way, say, that Junger made nickel cadmium batteries? Did they have all these troubles in cycle life? They always had the reputation of being used for ever, and any time you wanted to use them, if they had been dead, you just charged them up again and you had a good battery.

It could well be, though, that those are all very bulky and very heavy, and the thing you have forced the industry to do is to make them very light, especially when you go into space. Therefore, you inherit a lot of problems that Junger, I am sure, did not have. You may be asking for something that is going to be very difficult to untangle by saying that we should get away from the problems that we are inheriting as we go on.

FORD: We are always asking for lighter weight. However, the ultimate is reliability: something that will work and something that will do the mission. I was intrigued yesterday with the accelerated test discussion. In every case, when you talk about reliability you are talking about a cell in a battery that, relatively speaking, is a fairly small cost of the whole mission, and yet it is usually one of the weakest elements in the mission in terms of being able to fully complete the mission objectives. I think we have a challenge before us to get both reliability and light weight. However, I recognize that they are not always compatible.

I hope that in the past decade, we have learned something from all this, and that with this background we can now take a hard look at the fundamentals. There is nothing wrong with sintered plate nickel cadmium cells. It is what we are doing to them after we make the plates that appears to be where the problems are.

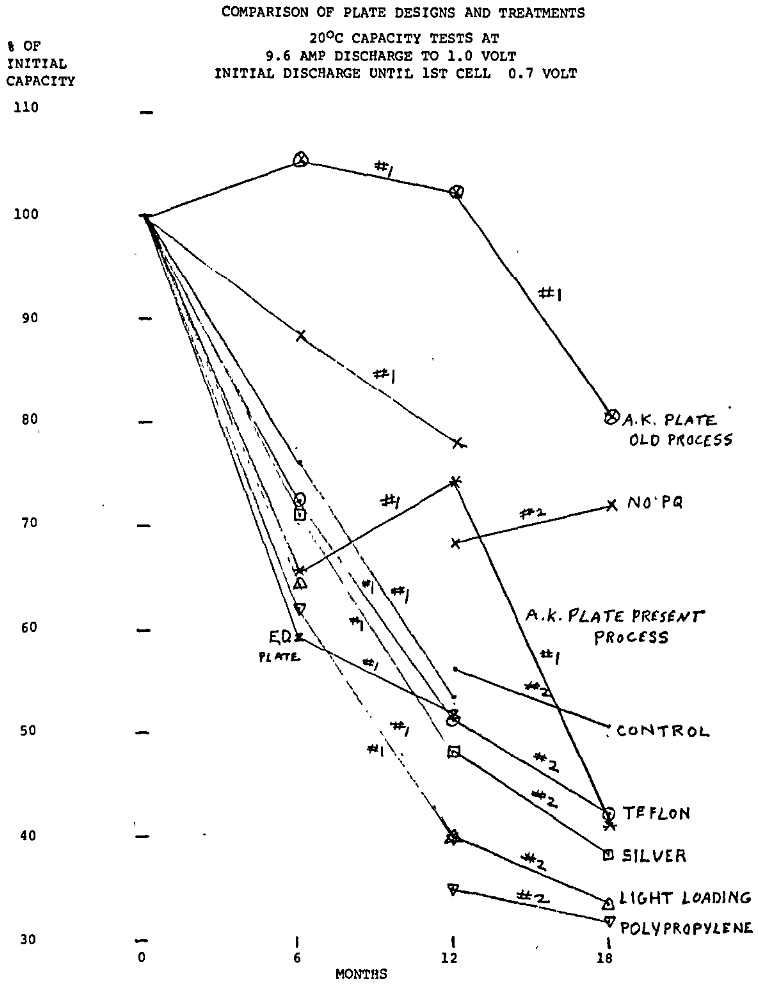
HENDEE: I have had an increasing feeling over the last few years that maybe we should not be blaming the cell manufacturers for decreasing performance, life, etc; that perhaps it is due to the requirements that we are putting on them for beginning of life performance. I can think of at least two things that we do not need at the beginning of life. If we want to end up ten years later with an adequate cell, we should stop designing for beginning of life performance where we do not need it. I can think of a variety of things. If we are going to go along with nylon separators, we do not really need all the precharge in the cell at the beginning of life. We are going to get it at the end of life anyway, more than we want. Why are we putting the cadmium in the positive at the beginning of life? It is going to get there when we need it, more than we want. Several other factors that we are imposing upon the cell manufacturers are decreasing the life of the cells.

HALPERT: I should like to believe that, but I should have to say that in my dealings with manufacturers, we are told what is going into the plates, not what we can have in the plates, in general, because it meets the manufacturer's program or requirement. It is very difficult to work with them to make that kind of a change. I can understand their feeling in that regard. They are doing it for a whole process. They are not doing it just for us. To turn around their whole manufacturing operation is maybe quite difficult for them. Therefore, in a lot of cases where we do not want PQ, we do not have any choice. In other cases where we should like to leave some things out, we do not have any choice either. I am not so sure that we have much control, unless we have enough data to be able to tell them to keep material out.

HENDEE: I tend to agree with you, with the exception that the manufacturer does have to go to PQ because of the beginning of life requirements that we are imposing upon them. There are other ways of looking at this. I think you could just as easily set up other requirements. As opposed to electrochemical testing, you could do a greater chemical analysis. I have found that the manufacturers generally give us what we ask for.

FORD: I agree wholeheartedly with the point that you are making in principle. For instance, it is my understanding that PQ was brought about indeed to improve the performance of the cell at high temperature, namely to capacity at 35. If you go back and look at the initial evaluation data, it indeed does accomplish that. However, this evolution process that we have gone through is very intriguing. For once we are getting data recorded in history books and workshops, such that we can reexamine what we have been doing to our cells. I did not stand up to point a finger at the manufacturer per se. I think we are all equally guilty of this crime to the nickel cadmium cell.

HENDEE: I am not disagreeing with you, but let me make one other observation. Going hand in hand with cell design is management. We need proper design of the cell, and I am not talking about beginning of life design, but end of life design. If there are some shortcomings at the beginning, we had better create the proper environment. That is part of cell lifetime, and we had better create the management techniques to handle them correctly.



COMPARISON OF PLATE DESIGNS AND TREATMENTS

20°C CAPACITY TESTS AT
9.6 AMP DISCHARGE TO 1.0 VOLT
INITIAL DISCHARGE UNTIL 1ST CELL 0.7 VOLT

Figure 35-1

EVALUATION TEST RESULTS

	VARIABLE	VOLTAGE C/20 CHARGE FOR 60 HRS @ 0°C INITIAL EOC	AFTER TEST EOC	 PEAK	
1	CONTROL	1.496	1.508	1.552	
2	TEFLON	1.486	1.496	1.529	
3	SILVER	1.494	1.494	1.546	
4	LIGHT LOADING	1.492	1.576	1.577	(1)
5	NO PQ	1.508	1.599	1.600	(1)
6	POLY PROPYLENE SEPARATOR	1.497	1.573	1.583	(1)
7	A.K. PLATE OLD PROCESSES	1.575	1.585	1.583	(2)
8	A.K. PLATE PRESENT PROCESSES	1.578	1.572	1.585	(2)
		1.577	1.638	.638	(1)

NOTES: (1) TERMINATED DUE TO HIGH VOLTAGE; VOLTAGE EXCEEDED 1.56V FOR 2 HRS.

(2) TERMINATED DUE TO HIGH PRESSURE; PRESSURE REACHED 100PSIA

Table 35-1

EVALUATION TEST RESULTS

	VARIABLE	PACK#/S/N	Removal Cycle	EOC VOLTAGE C/10 CHARGE FOR 24 HRS @ 25°C INITIAL	 AFTER TEST	25°C CAPACITY C/2 DISCHARGE INITIAL	 AFTER TEST	 % CHANGE
1	CONTROL	3D/01	5833	1.462	1.465	15.3	12.1	-20.9
2	TEFLON	3E/01	5841	1.455	1.457	14.7	12.5	-15
3	SILVER	3F/01	5844	1.456	1.458	15.2	12.1	-20.4
4	LIGHT LOADING	3G/02	5844	1.458	1.477	13.9	11.6	-16.5
5	NO PQ	3H/02	5840	1.454	1.452	16.0	15.1	-5.6
6	POLY PROPYLENE SEPARATOR	3I/01	5833	1.459	1.457	15.6	9.5	-39.1
7	A.K. PLATE OLD PROCESSES	3J/06	5834	1.459	1.419	17.7	14.9	-15.6
8	A.K. PLATE PRESENT PROCESSES	3K/05	2459	1.458	1.520*	17.4	18.0	+3.4
		3K/06	2008	1.460	1.520*	17.4	17.8	+2.3

*TEST TERMINATED AT 23.4AH IN, DUE TO HIGH VOLTAGE

Table 35-2

RCA SATCOM IN-ORBIT EXPERIENCE

D. Stewart
RCA

I should like to provide a brief update on RCA Satcom in-flight battery performance. We have made presentations of this sort in the past, and not much has really happened since the last year. However, I feel it is important that we do this for two reasons: one is that we have reached five years for both spacecraft, and five years and six years have been critical in many other space programs; and the other is that we have made presentations over the last four years, and if we were to stop, some people might get the idea that our batteries have taken a turn for the worse.

I should like to point out some aspects of the battery design and history. Our F1 spacecraft was launched in 1975, which means we have had about five years. F2 was launched in March 1976, which means that we have had almost four and three-quarter years.

I was hoping to have data from an F3 spacecraft here, but we seem to have misplaced our spacecraft. If we ever find it, I shall give you an update. For F1 and F2, the battery systems were the same design. We have three batteries of parallel connected, diode connected. All three are essential for supporting the mission. There are 22 nickel cadmium GE cells in each battery, 12A h rated (measured capacity), initial capacity is 14A h, and they are in 10A h cases. We have three charge rates. There is a C/20 charge rate, which we use for eclipse seasons, and for recharging after plane change maneuvers during the solstice period. We have a high C/10 charge rate, which we use for battery reconditioning and emergency situations. During the solstice periods when the batteries are in storage, we have a C/60 trickle rate. We also have a voltage temperature taper curve, which is used for the C/10 charge rate. The yearly average temperature is about 12 C. We do see peak temperatures over 30 C in the summer for very brief periods for just two days, and we do get down to about 1 or 2 C. However, on average, we stay between 2 and 15 C. For reconditioning, we have individual 1 ohm resistors on each cell, and we recondition down to 0.1V per cell.

(Figure 36-1)

While on the subject of reconditioning, Figure 36-1 shows the history of our battery reconditioning, and it is best for showing trends. The first curve shows the first reconditioning cycle; it is interesting to note the high voltage for the first reconditioning. For the fifth and tenth reconditioning, the voltages remained about the same. You do see effects of aging here, and we are seeing a flattening on the near curve. However, for the portion of the battery we are using, which will correspond to about eight hours of discharge, voltages seem to remain pretty flat.

For completeness, I have data for our F2 spacecraft.

(Figure 36-2)

Figure 36-2 shows curves from battery no. 1 on the F2 spacecraft. The other batteries are quite similar. I have only shown the seventh and ninth reconditioning cycles here because on F2 for the first three years of life, we had a daily 28% depth of discharge and we would do our discharge and start reconditioning from there. This 28% daily depth of discharge was due to a problem we had with our solar array. We had blockage, which prevented it from rotating 360 every day. It is a Sun-tracking array, and so we had to reverse it. For this period when we reversed the solar arrays, we had to go on batteries. We have since stopped doing that rewind procedure; the problem has corrected itself. Now we start from full charge on the batteries before reconditioning. Those curves show trends and are more qualitative than quantitative.

(Table 36-1)

Table 36-1 shows the RCA Satcom minimum average battery voltages during eclipse. This minimum does not always occur on the equinox (the 21st of the month); it may occur several days afterwards. The fourth column shows the average voltage, which is the average of the three batteries. What we have done differently from past years is to take the voltages seen on both our telemetry units and to average them. In the past, in one year we might take it from one telemetry unit, and the next year the other telemetry unit. Then we had quite a bit of variation and a lot of scatter in the data. We have done some averaging and we get much better curves. There is a big jump in the voltage after the sixth eclipse season. I have shown that graphically in Figure 36-3.

(Figure 36-3)

We have cell voltages on the ordinate. We have taken the battery voltages, divided by 22 for 22 cells, and if you look at the line for F1, it seems to be pretty consistent. It is decreasing slowly, but the data seem to be pretty smooth. For F2, as I mentioned, we had daily 28% depth of discharge and we may not have been fully charging it before each of the depths. Also, after the sixth eclipse season we lost two transponders, which accounts for about 5% of our load. We also performed the double reconditioning after the sixth eclipse season. Thus, several things were going on there. The high voltage may be due to the double reconditioning. We shall have to get some more data before we make any more conclusions.

Our prediction here was based on Crane data, and it is based on packs 209A (at 20 C) and 207A (at 0 C), which had 60% depth of discharge. I have also shown our minimum voltage cutoff and, unless we see anything catastrophic here, we have got a long way to go before we reach that.

(Figure 36-4)

Another measure we have of battery performance is current sharing. Figure 36-4 shows a plot of several things. We have discharge current near the end of discharge. The current sharing seems to be pretty close; it is within 1.5% of the average. If I had to do this over again, I should plot them on one voltage here. We also have a plot of the temperature.

For completeness, I have the same data for the F2 spacecraft, which shows even better current sharing.

(Figure 36-5)

DISCUSSION

HALPERT: Can you give us the approximate age or time when these cells were manufactured?

STEWART: Mr. Gaston?

GASTON: They were flown in December 1975, and I think they were built in Summer 1974. The depth of discharge is about 50 - 55%.

RCA SATCOM MINIMUM AVERAGE BATTERY VOLTAGE DURING ECLIPSE

(ALL VALUES ARE IN VOLTS)

ECLIPSE SEASON	SATCOM F1					SATCOM F2				
	V BATT. 1	V BATT. 2	V_{B3} BATT. 3	V_{AVG}	$V_{AVG/CELL}$ (V_{AVG} ÷ 22)	V BATT. 1	V BATT. 2	V_{B3} BATT. 3	V_{AVG}	$V_{AVG/CELL}$
1	26.56	26.71	26.45	26.57	1.208	26.61	26.48	26.42	26.50	1.205
2	26.27	26.35	26.47	26.36	1.199	26.36	26.18	26.11	26.22	1.192
3	26.26	26.42	26.27	26.32	1.196	25.97	25.99	25.90	25.95	1.180
4	26.26	26.42	26.27	26.31	1.196	25.97	25.93	25.90	25.93	1.179
5	26.20	26.40	26.25	26.29	1.195	25.81	25.78	25.75	25.78	1.172
6	26.13	26.29	26.11	26.18	1.190	25.81	25.75	25.75	25.77	1.171
7	26.05	26.23	26.18	26.16	1.189	26.46	25.38	26.31	26.38	1.199
8	26.04	26.23	26.08	26.12	1.187	26.36	26.22	26.11	26.23	1.192
9	26.09	26.29	26.17	26.19	1.191	26.24	25.99	26.10	26.11	1.187
10	25.92	26.13	26.13	26.06	1.184					

Table 36-1

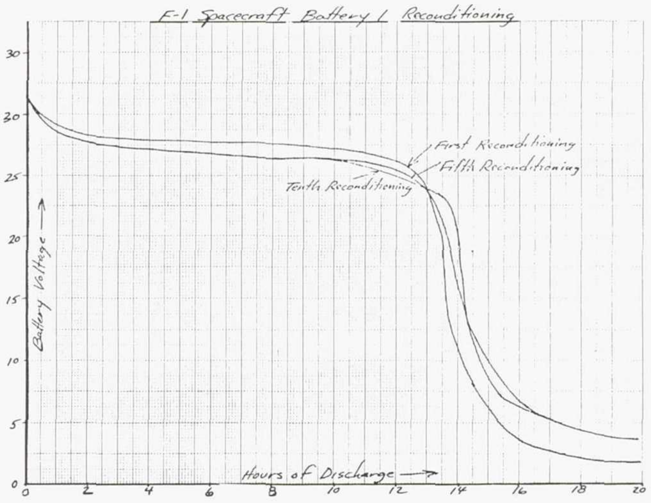


Figure 36-1

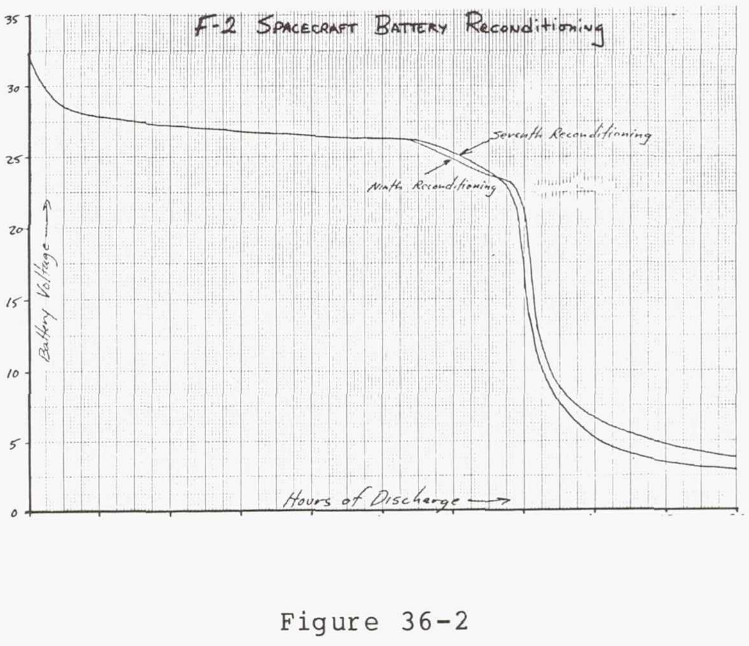


Figure 36-2

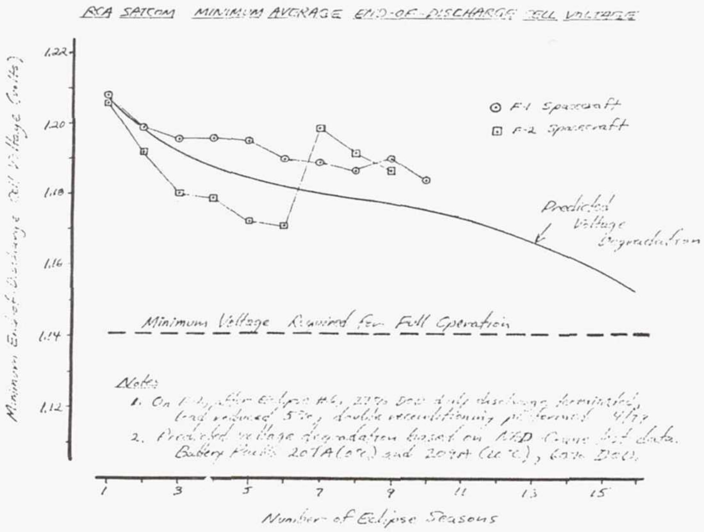
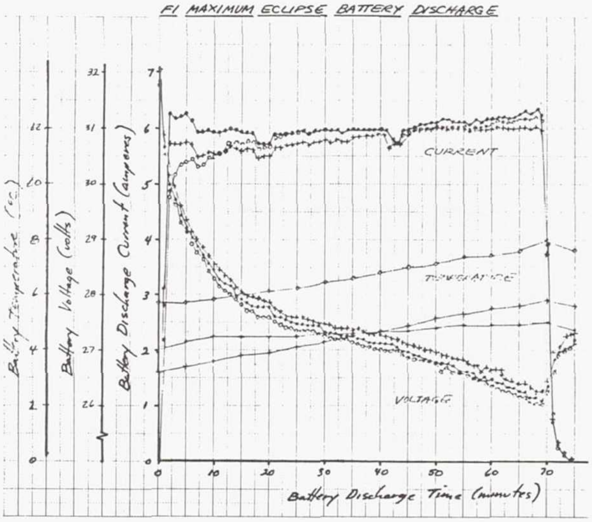


Figure 36-3



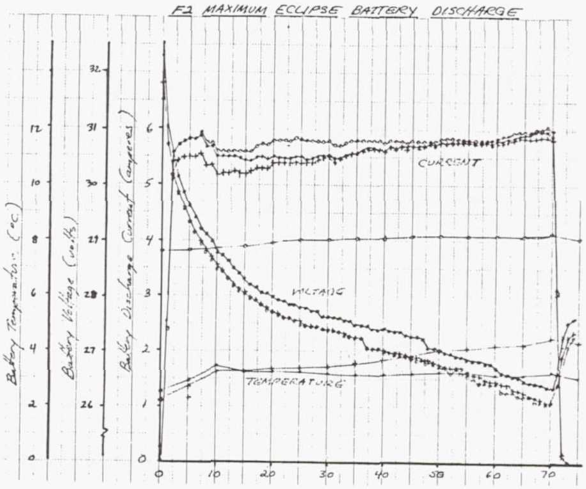


Figure 36-4

Figure 36-5

SESSION VII: NICKEL HYDROGEN CELLS/BATTERIES

M. Tasevoli, Chairman
Goddard Space Flight Center

AIR FORCE NICKEL HYDROGEN CELLS

D. Warnock

Air Force Aeropropulsion Laboratory

I should like to show Figure 37-1, which gives an overall picture of the Air Force nickel hydrogen development program from its origins in 1972 to the present, and indicate some of the things that we are looking to in the future.

(Figure 37-1)

We started work in 1972 with exploratory development, which went through about 1976. All that effort has been devoted to the development of a 3.5in diameter, nominal 15A h cell, which went into advanced development in 1976 and is still in advanced development. The program will be winding down next year. It was done by Hughes Aircraft. Up to the present, practically all our efforts have been devoted towards this one cell design.

We are now in a transition period where we shall be branching in about three different directions. The first thing is manufacturing technology. That program will be aimed mainly at assessing the design of the present 3.5in diameter cell to improve its manufacture and reduce costs. Of all of the programs that the Air Force has been doing, that is the only one that will not be done by the propulsion lab. Manufacturing technology programs are run by the Air Force Materials Lab, which is also at Wright Patterson. This program will be no exception. The evaluation has been done. I expect the contract to be let before the end of the year.

About a year ago, we also went into exploratory development on common pressure vessel nickel hydrogen modules. This is a two year program, and we are a little over halfway through. The concept is to put a number of nickel hydrogen cells into one pressure vessel. There is a very modest advantage in terms of weight energy density, but a substantial advantage in both volume energy density and cost. I shall not dwell on that too much now, because Dr. Holleck of EIC Corporation will be giving a presentation on the status of his work on that program later this afternoon.

The third thing that we are looking at is a 4.5in individual pressure vessel, a larger diameter cell. We call that a large capacity cell program. Figure 37-1 shows a scaleup of this design to a larger diameter to give us a wider range of capacity. The capacity range on the larger diameter cell should extend up to about 150A h. The status of that work at present is that we issued a draft RFP this summer, and obtained responses from a number of companies. We had hoped to come out with a formal RFP this fall, but the program has been held up. The space division that funds our advanced development programs has had a number of questions about the impact of large capacity cells in terms of cost and reliability and weight, and they have kept us busy doing studies, and answering questions related to the impact of large capacity cells. We are hoping to finish that later this calendar year. We expect to have a formal RFP out some time after the first of the year.

The last thing shown in Figure 37-1 is not actually a planned program. That is why it is dashed. It simply indicates that if you have done the large capacity program and if you have successfully done the common pressure vessel program, those two programs taken together imply that you could build a large capacity common pressure vessel. I think we are getting a little ahead of ourselves now, because this feasibility study has not been completed yet. However, it does indicate a possibility, but is not one that we are planning on.

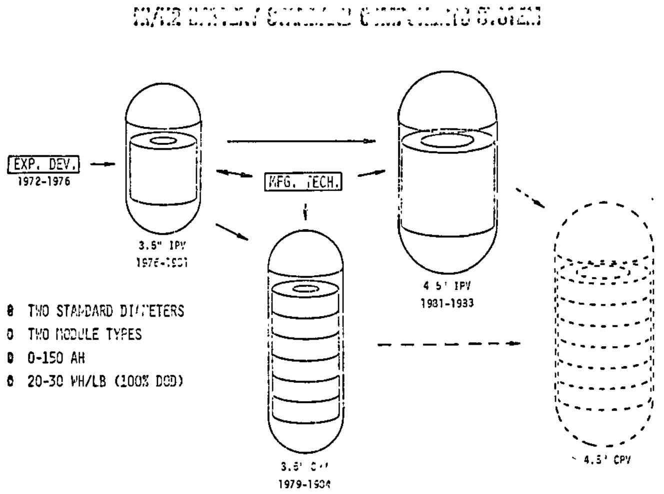

EXP. DEV.
1972-1976
3.5" IPV
1976-1981
MFG. TECH.
4.5" IPV
1981-1983
3.5" CPV
1979-1984
~ 4.5" CPV
● TWO STANDARD DIAMETERS
● TWO MODULE TYPES
● 0-150 AH
● 20-30 WH/LB (100% DOD)

Figure 37-1

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NICKEL HYDROGEN CELLS, AN HISTORIC OVERVIEW

L. Miller
Eagle Picher

The year 1980 marks an approximate decade of activity associated with the development of nickel hydrogen battery systems primarily for replacement of the nickel cadmium battery and space power systems. During the last ten years, an intensive effort was conducted, involving many different organizations, to move rapidly from the basic conceptual design stage to the present status of a flightworthy battery system suitable for the multiple high reliability space application. It is the purpose of this presentation to briefly review and summarize the major events and milestones associated with this successful effort.

With respect to the basic system electrochemistry, several references to nickel hydrogen work pre-dating the subject renascence may be found. However, the origin of the initial work leading to the space type designs we know today may be attributed to two sources who share jointly in this distinction. Around 1970, while under contract to Comsat Laboratories, Clarksburg, representing the International Telecommunications Satellite Organization (Intelsat), Tico Laboratories, Waltham, experienced difficulty during the development of a regenerative or rechargeable hydrogen-oxygen fuel cell, the purpose of which was to replace nickel cadmium systems on Intelsat communication satellites. This difficulty resulted in the consideration of two related alternative systems, the oxygen-cadmium couple and the hydrogen-nickel couple. The oxygen-cadmium couple was soon eliminated for technical reasons. On the other hand, the immediate success of the hydrogen-nickel couple resulted in that subsequent rapid development. Therefore, history may take note of this accomplishment, and in consideration of this contribution, we believe the responsible personnel should be recognized. At Comsat Laboratories we have Jim Dunlop, Gert Van Ommering and Joe Stockel. At Tico Laboratories, we have Jose Giner, John Perry and Larry Swette.

As mentioned, many organizations have made significant contributions to the development of the nickel hydrogen battery system. However, for the purpose of brevity this presentation will be keyed off the activities of the two major sources of support and funds for system development. The first, of course, is Intelsat, via Comsat Laboratories, and the second is the Air Force Aeropropulsion Laboratory (under the direction of Don Warnock), located of course at Wright Patterson Air Force Base, Ohio.

A chronological review of the major events and milestones leading up to the current system status may be summarized as follows.

In the 1970-71 period, Intelsat, both in house and at Comsat, and Tico labs initiated the nickel hydrogen space systems development. In 1972, the Air Force became involved with their own in-house system development.

In the 1973-74 period, Intelsat awarded a dual contract to both Eagle Picher Industries in Joplin, Mo, and to the Energy Research Corporation, Danbury, Conn, to develop and produce lightweight flight configuration nickel hydrogen cells. Testing in this program produced up to 6000 cycles, at 60% depth of discharge with what we call a cylindrical cell configuration. There were other cell configurations produced during this period: one shaped like a flat pancake, another like a prism with radius edges on it. However, owing to technical reasons and manufacturing problems, the cylindrical cell was the design tht was carried on from this point.

Again, in 1973, the Air Force awarded the nickel hydrogen regenerative fuel cell program to Tico Labs. This program consisted of boilerplate cell construction to study the basic system components. Also in 1973, the Air Force awarded the nickel hydrogen satellite energy storage program to Hughes Aircraft Company, Los Angeles, Ca. From this award, subcontracts were awarded to Eagle Picher, Energy Research and Tico Labs. Again, the effort consisted of boilerplate cell construction for basic system study. Approximately 3000 cycles at 80% DOD were accumulated during this period.

1974 was a rather significant year, as it has bearing on the successful evolution of the nickel hydrogen system. Under contract to Western Electric Company, Eagle Picher established a production facility in Joplin for the manufacture of electrochemically impregnated (EI) nickel and cadmium electrodes. This, of course, was based on the Bell process.

In 1975 Intelsat awarded the nickel hydrogen system study program to Marcoussis Laboratories in France. Problems and constraints associated with the electrical parameters were studied and design solutions evolved.

Again in 1975, Intelsat awarded the nickel hydrogen cell and battery mechanical and thermal design study program to TRW, Redondo Beach, Ca. A 10-cell battery using Eagle Picher RNH-35-1 (which is basically our NTS-2 designs), was manufactured and subject to flight level electrical and dynamic testing. This battery has accumulated approximately 4.5 years of real time geosynchronous cycling at 60% DOD.

Again in 1975, a busy year for the nickel hydrogen effort, the Air Force awarded the nickel hydrogen failure mechanism program to Hughes Aircraft. Subcontracts were awarded to EIC Corporation in Newton, Mass, for development of an improved catalytic negative electrode. Problems and constraints associated with both electrical and mechanical parameters were studied and design solutions evolved. I think one significant milestone here was that the negative electrode was involved, which offered superior polarization voltage and oxygen recombination characteristics.

Still in 1975, Intelsat and the Naval Research Laboratory, Washington D.C., joined to launch a 14-cell battery consisting of two 7-cell modules as the primary battery in the Navy NTS-2 satellite. The 35A h nickel hydrogen cells, which we designated RNH-35-1 cells, were manufactured by Eagle Picher using Joplin EI positive electrodes, and Bell processed nickel hydrogen batteries. There were subject to full space type qualification program. Launched in June 1977, the batteries are still successfully performing in mission in the polar, 12 hour orbit. The depth of discharge has varied a little (40-60%) because some of the loads in the satellite have degraded and required some variation in the depth of discharge.

Still in 1975, the Air Force awarded the nickel hydrogen flight experiment program to Eagle Picher. Lockheed Missiles and Space Company, Sunnyvale, Ca, served as a system integration contractor. Actually their role in the program was much more important than that. I believe their contribution to the battery design integration was essential to the program success. This 21-cell, 50A h battery was manufactured by Eagle Picher, the prime contractor. Joplin EI positive electrodes were used and the system was qualified and launched on classified Air Force lowEarth orbit mission. It was launched about a similar timeframe as the NTS-2, around June 1977, and accumulated approximately 2000 cycles, both shallow and deep DODs (some were 100% depth of discharge cycles) over about an eight-month period before the mission was terminated as planned.

One thing that came out of this program, which was very encouraging, was that the program flew as an experiment, and we could only use power as power became available. Therefore, it got just a little power recharged every few orbits, which led to the position that the program management had no idea of what the state of charge of the system was. However, the cells were equipped with pressure transducers, which give very good indication of the state of charge in nickel hydrogen, and allowed them to maintain good program control even under these circumstances. Several batteries were made under these programs. One of them was shipped to Lockheed, and I understand that the life testing on that, which we shall hear more about today, is approaching 8000 real time cycles in the low-Earth orbit cycle regime, about 50% DOD.

In 1976-77, the Air Force awarded a manufacturing technology program to Eagle Picher to establish production facility to manufacture EI (Air Force process) nickel and cadmium electrodes. This facility was set up in our Colorado Springs plant.

In 1976, the Air Force awarded the nickel hydrogen advanced development program to Hughes Aircraft to develop and qualify a design and establish manufacturing sources for nickel hydrogen systems suitable for both LEO and GEO space missions. Subcontracts were awarded to Yardney Electric Division, Pawcatuck, Conn, and Eagle Picher, Joplin, for cell manufacturing; and Eagle Picher, Colorado Springs, was awarded a contract for EI positive electrode improvements. Two manufacturing sources were eventually selected from this effort. One was Hughes Aircraft itself, and the other was Eagle Picher, Joplin. Eagle Picher, Colorado Springs, will supply EI positive electrodes for both sources. Testing under this effort included space level qualification and real time LEO cycling approaching 8000 cycles at about 80% DOD.

In 1977, Intelsat awarded a cell design variable (elecrolyte management) program to EIC. Testing in this program included allowed accumulation of approximately 4000 cycles at around 80% DOD.

In 1978, Intelsat awarded a catalytic negative electrode improvement program, which was primarily concerned with assessing whether the design should allow reduction in platinum, to EIC.

In 1978, Intelsat awarded a positive electrode improvement program to Yardney Electric. I believe the intention here was to assess the impact of various loading levels on the performance of the electrode.

In 1978, Eagle Picher, Joplin, established the new aerospace electrode process facility with dedicated equipment for EI, space type, positive electrode production. Previously, Eagle Picher, as well as most battery manufacturers, depended on the screening of commercial type electrodes for the space systems.

In 1979, Intelsat awarded a high-pressure, high-energy density nickel hydrogen battery development program to Yardney Electric. I believe this program as constituted was reducing the free volume of the cells, thus saving weight but operating at higher pressures, which is possible in nickel hydrogen because of the extreme safety margin we had in the pressure vessel designs. We operated on levels up to four or five greater than the actual operating pressure of the cell.

Also in 1979, the Air Force awarded the common pressure vessel nickel hydrogen battery program to EIC for feasibility study. I believe we shall hear something on this program today.

Getting close to the present, in 1979 Intelsat allowed Ford Aerospace and Communications Corporation, Palo Alto, Ca, to prepare for replacement of nickel cadmium with nickel hydrogen on flights 5 - 9 on the Intelsat V program. FACC designed the

27-cell 30A h battery, which has now successfully undergone extensive electrical and space qualification testing, and in its final form offers a mass savings of potential mission extension. The cells used are designated the RNH-30-1; they are the NTS-2 design. They are manufactured by Eagle Picher (to date we have delivered approximately 300 units), and use the Joplin EI positive electrodes. One point of interest in special testing under the program is that one of the old NTS-2 batteries (I believe it was the integration battery) was put on test in a real time GEO type cycle regime in series, or against the new I-5 nickel cadmium battery, of approximately the same capacity, and under identical conditions. The last report we had on this after about 1.5 years of testing, showed that the nickel hydrogen system is still demonstrating superior performance.

Also in 1979, the Air Force in a similar undertaking, allowed Hughes Aircraft Company to prepare for replacement of nickel cadmium with nickel hydrogen on the Air Force satellite data system (SDS) program. Hughes has designed the 18-cell, 25A h battery, which is intended to support a long-term, low-Earth orbit mission with a launch in the early 1980s. Nickel hydrogen cells with an advanced development design will be manufactured by Hughes using Eagle Picher, Colorado Springs, EI positive electrodes.

That brings us up to date with respect to the major events.

Another area that might be of interest at present is that approximately a year ago we conducted a survey to see just how much test data had been accumulated on nickel hydrogen. Facility A has two test series going. The first test series is reported at four years real time, geosynchronous orbit, cycling at 60% DOD. The second series is reported 6000 cycles at 60% DOD. Facility B had one series going. They reported 7000 cycles real time low-Earth orbit at 50% DOD. Facility C had one series under way at that time: 3500 cycles real time low Earth orbit cycling at 50% DOD. Facility D had three test series under way. They have reported on the first series, 26 eclipse seasons, geosynchronous at 80% DOD; 32 eclipse seasons, geosynchronous, 80% DOD; and 45 eclipse seasons, geosynchronous at 80% DOD. One thing that might be of interest to note at this point is that with 45 eclipse seasons, these cells will really be the first generation nickel hydrogen cells ever produced from a time standpoint. That means they incorporated the old chemically impregnated positives and the pellon 2505 separator, both of which we know are definitely life-limiting designs in the system. However, we still achieved this type of cycle data even with those very early designs. Finally, facility E has two test series going. They report 7000 cycles real time low-Earth orbit and 80% DOD, and two years real time geosynchronous orbit at 80% DOD.

I should like to comment on the status of nickel hydrogen today; I can only speak from the standpoint, of course, of Eagle

Picher. Dedicated facilities at Eagle Picher include positive electrode area, about 4400 square feet, with a capacity of around 540 electrodes per 8 hour production shift. At the Colorado Springs production facility, we have around 5000 square feet dedicated to the system. The capacity is around 720 electrodes for an 8 hour shift. There is an analytical chemistry laboratory to support both of these operations, 440 square feet. The negative electrode production area capacity is about 150 electrodes per 8-hour production shift per station; there are two stations in operation. 500 square feet are consumed there. The cell and battery assembly test area is around 2100 square feet. The cell and battery test area has 2800 square feet. For general support, engineering and storage area and others we have 1500 square feet. This is a total of around 16,750 square feet of really directly related production facilities available for nickel hydrogen production.

The present production capability of this area is around 120 50A h cells per month. The limiting production line or area now is the negative electrode production. The test capability is around 100 cells per month, and the limits there are simply the test stations to hook the cells up when they go into about a month conditioning and acceptance testing.

(Figure 38-1)

Figure 38-1 gives an indication of the amount of paperwork associated with the production of the cells alone. Nickel hydrogen is probably one of the best documented cells we have ever produced. The paperwork is sufficient, I think, that if we did not have to go through all this we could probably sell the cells to you for about half price. However, it is not going to happen in this type of business. It just gives you a kind of quick overview of the amount of documentation that has to be followed along and carried through in the production of these systems.

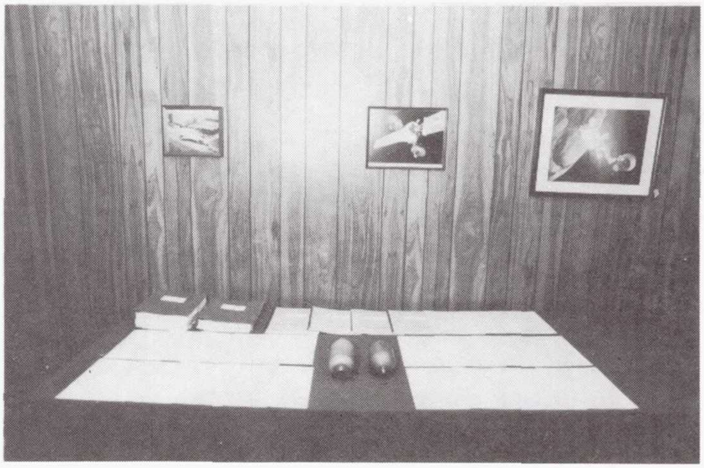

Figure 38-1

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NICKEL HYDROGEN LIFE CYCLE TEST RESULTS

M. Gandel

Lockheed

(Figure 39-1)

Figure 39-1 shows a photograph of the battery that Eagle Picher built for the Air Force and flew on an Air Force flight experiment in 1977. This is the unit that Lee Miller just reported as having 8000 cycles on it. It now has 11,040 cycles (LEO) to 50% DOD, and testing is continuing.

(Figure 39-2)

Figure 39-2 shows the general characteristics of the cycle. The sawtooth on the temperature curve is a reflection of the heat dissipation design on this battery. All the heat is taken out through the cold plate (Figure 39-1), through which we circulate a water glycol coolant at -5 to -7 C. The base of the battery will be at about 0 C, and the top of the cells will be between 10 and 20 C. Even with the severe temperature gradients, it has not seemed to impair the operation of the battery.

(Figure 39-3)

I hope that Figure 39-3 is not too difficult to follow, but I have tried to depict, from zero to over 10,000 cycles, that there is a decay at the end of discharge voltage with time as seen in the first slope. It is repeated through the operation. To compensate for that, we periodically increase the end of charge cutoff voltage. And tying it together, the end first. We did find out at about 5800 cycles, that we were electrolyte-starved, and by turning the battery on its side fully discharged and not operating for five days, we were able to get electrolyte back to the stack. We righted the battery and proceeded operating again. However, that progressive drawing out with time, I think, is what accounts for this increasing internal resistance with time. As Figure 39-3 shows, at about 4800 cycles we did the first full reconditioning, which gave us added life of another 1000 cycles. Out at the 11,000 cycle mark we are finding that the end of charge voltage is approaching where we were at about 5800 cycles. However, the capacity on discharge seems to be there pretty well. I think we shall get a few thousand more cycles before we have to turn it on its side and let the stack get wet again. One cell shorted at about 7200 cycles, and that cell is in the string. We have never touched it. It sees about -2V on the discharge and 0.3 - 0.6V on charge. This suggests that having redundant series cells in the nickel hydrogen battery is not the worst approach.

(Figure 39-4)

I should now like to mention the Air Force advanced development cells, which were manufactured by Hughes (Figure 39-4). We have the cells set in a cooling fixture. We use the mounting flange resting on the cold plate arrangement where we have the circulating coolant going through channels. This is pretty effective in controlling the cell temperature.

(Figure 39-5)

Figure 39-5 is a temperature profile of what we see at the end of discharge and the end of charge. At the worst extremes we see something like 7 C from the coolant itself out through the top of the cell. The hottest part of the cell is at the terminals.

(Figure 39-6)

Summarizing the results with these cells (see Figure 39-6): because we were able to have a very good means of heat removal, we decided to operate the cells at 80% DOD on a low-Earth orbit regime. The 80% DOD, seemed to be very severe cycle. It was really more like a 45A h cell rather than a 50, which meant that my 80% DOD might have been closer to 85 - to 90%. In any case, we operated these cells in that regime for nearly 1000 cycles. At that time one of the cells failed in a shorted mode. The failure was preceded by a cycle with a high percentage recharge. In the preceding cycle we had an early termination of the discharge because we had reached our end of discharge voltage of 1V, and so in the subsequent cycle we got about 138% recharge. I think that contributed to the problem. In nine minutes we dropped 550 psi, which I translated to about a 400A short.

We then put the remaining two cells on a 60% DOD regime, and continued out to 3500 cycles. At that point the second cell developed a short. On dissection, however, Dr. Adler at Hughes found that we had rotated the negative terminal about 90 . Our technician did not pull the restraining nut properly and the bottom or negative terminal was rotated about 90 , which took up the stress relief in the negative leaks. That, I am sure, closed the negative-to-negative distance and precipitated that short. So we shall take that responsibility. I understand that the same thing occurred at TRW. I think the Ziegler seal did hold. Then we operated the remaining cell to 4800 cycles, at which time we took it off test. It was unable to sustain the end of discharge voltage. We did check on that cell and had not rotated the negative terminal.

(Figure 39-7)

Going on to another test, Figure 39-7 shows three 23A h nickel hydrogen cells. They were manufactured by SAFT, France. These cells were placed on tests in summer 1978 and they are on an accelerated synchronous regime. We initiated the test by trying different depths of discharge and different charge rates as shown in Figure 39-8. After the fifth eclipse season, we decided on a C/15 charge in an 85% DOD, which we have been on ever since. About 12 December, we shall begin the 22nd 42-day eclipse season. There has only been one reconditioning. That happened after we had to shut the test down because of a test setup problem. The end of discharge voltage did show some improvement following that reconditioning.

(Figure 39-9)

The regime is described in Figure 39-9. The data in the earlier cycles, although I have not reproduced them here, are virtually the same as in this case, and so there is no reason to expect that we should not see the 46th eclipse season that Mr. Miller mentioned.

I do not know how to get around the use of the term accelerated, and it bothers me after yesterday's session. I wish that we had a comparable real-time test going on in parallel. However, as I say, this has given us the system design criteria that we are looking for, and we shall continue operation until we see some departure from the norm.

DISCUSSION

RITTERMAN: What kind of positive electrodes were there in the SAFT cells? Were they electrochemical or chemical?

FOUGERE: They were electrochemically impregnated.

RITTERMAN: I should like to point out that those cells you showed in your battery are the old Air Force design. Otherwise, we should not have to turn them on their sides. Is that correct?

GANDEL: I think they are a 1979 design.

RITTERMAN: As far as the TRW mistake goes, that happened about a year and a half before yours.

STOCKEL: What was the separator in the SAFT cell?

FOUGERE: It was polyamide. Nylon.

LAMB: How should you assess the 80% depth of discharge cycling regime used in the 50A h cells, the Air Force design? There were three failures for three different reasons. One was the first short that you said failed and you did not describe what happened; the second was attributed to mechanical stress at the terminals; and the third was failure to maintain the voltage at the end of discharge. What was the cause of the first failure, and what did you do to the third one, if anything, to see if you could rejuvenate the cell?

GANDEL: On the first failure, we dissected the cell and found rather severe burning. There was too much damage for us to be able to really assess what had occurred. We are unable to positively state that we did not rotate that negative terminal. I had not checked that, and so I have to carry that as an unknown. It looked as if the locus of the short was on the negative side where the negative leads were collected. On the second one, the cause was a straight rotation of the terminal. On the third one, I do not know conclusively whether the 80% DOD that it saw during the first 1000 cycles might have caused some damage. As far as doing anything to reconstitute performance or to help it, conditioning did not seem to rejuvenate it at this point.

LAMB: How did it compare with the older Air Force design, with the non-wettable internal surfaces. You ran that at 50%? It is now over 10,000 cycles with one failed cell.

GANDEL: To begin with, there were really two reasons for not operating at a higher DOD than 50%. The first was the thermal design. We see high T with 50% depth of discharge. To go to a higher DOD with higher rates may have driven it to excessive temperature. I do not think it should have sustained an 80% DOD regime. I think that we should have been unable to hold that capcity. In other words, all the way through at 50% DOD, you know we are seeing a need, each cycle; and I do not know whether to say that is just rate limited or what. However, I do not feel I can make a head-to-head comparison between those two cells.

RITTERMAN: The third cell that failed, did you tear it down or do you plan to tear it down?

GANDEL: We plan to tear it down.

RITTERMAN: And what was the final capacity of that cell? You said it started out at 45A h. What was it finally at C/2 when you stopped testing?

GANDEL: I cannot remember exactly.

RITTERMAN: Did you do a reconditioning before you measured that, or is this after your ordinary Earth-orbit cycling down to 1 V?

GANDEL: If I remember correctly, it was 27A h before reconditioning at the C/2. It was about 31 after reconditioning. We then did a 16 hour C/10 charge followed by a C/2 discharge, which gave us about 40A h.

RITTERMAN: That is all to 1V?

GANDEL: Yes.

DUNLOP: On that comment about 80% depth of discharge, I should like to note one thing. Last year, Gerhart Holleck gave a paper on the work he did in the Intelsat program that was referred to earlier by Lee Miller, in which he ran nickel hydrogen boilerplate cells with and without wall wicks. All the testing was done to 80% depth of discharge. It was done up to 4000 cycles. None of the cells failed at the end of 4000 cycles. Periodically, we looked for loss of electrolyte. There was a funnel at the bottom of those cells and any electrolyte that was lost would, by gravity force, collect in the bottom of the cells. Every 500 cycles we checked to see if any electrolyte came out. There was no loss of electrolyte in those boilerplate cells after the initial activation in the cells from cycle 50 to cycle 4000 at 80% depth of discharge. The temperature difference between the stack and the wall never exceeded about 8 C. That was, by the way, 80% in 1.2 hours. We charged in 1.8 hours with about a 5% overcharge.

GANDEL: We are taking out the 80% in 0.6 hours.

DUNLOP: If you ever deal with this thing you might want to deal with it on an energy-density basis some time. If you have to make 50% heavier in order to sustain electrolyte in your stack, it is not necessarily clear that you are talking about the same energy density. If you make a cell that has an energy density of, say, 60W h/kg, and a cell with an energy density of 40W h/kg, and you want to talk about usable energy density, then to have the same usable energy density, one cell may have to be discharged at 80%, and the other one at 50%. You are talking about the same usable energy density.

STOCKEL: I am curious to know what the composition of the negative electrode is in the cell.

ANTOINE: Charcoal with platinum as catalysts.

MUELLER: On the second cell that failed, was the failed condition also a short?

GANDEL: Yes.

MUELLER: That was also induced by twisting the terminal?

GANDEL: Yes. That was quite undramatic. It occurred about two minutes before the end of discharge. There was not much capacity remaining.

MILLER: I think I could say something that might help clarify. You mentioned you had to turn your cells over. We rewet them to get them to work. Since those days when we made those earlier cells, we have learned a lot more about how to activate these cells initially. I think the problem that you reported, and Martin Ritterman also saw these same problems on the earlier cells, would not show up as quickly on the newer cells that are activated in a proper manner.

GANDEL: They would not show up in zero G either.

DUNLOP: I think that, if you are going to try to do an 80% depth of discharge in a 30, 60 minute orbit, it might well be worthwhile having a wall wick. That is basically what your data would indicate. Probably when you try to put that into a spacecraft, with the thermal situation you describe, it is difficult to control that temperature throughout that whole can so that you do not have some fairly large temperature differences. Therefore, when you get to an 80% depth of discharge in 30 minutes, that is a pretty high rate, and you get into a fairly high rate of overcharge. You probably need a wall wick.

GANDEL: We have one in that cell. We have a zirconium liner.

DUNLOP: Did you have a wall wick in the can that dried out?

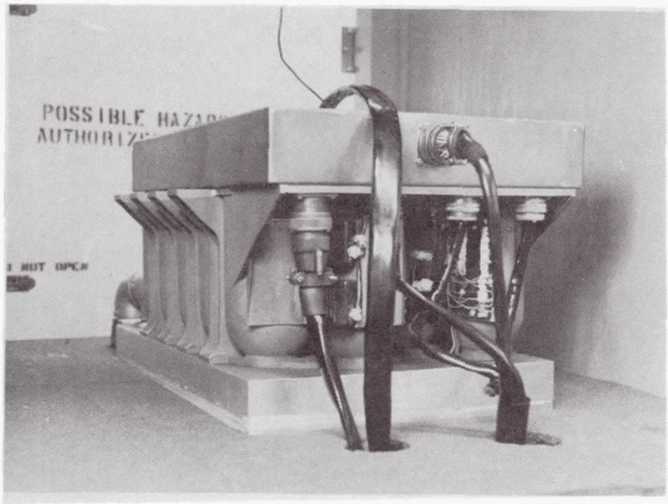
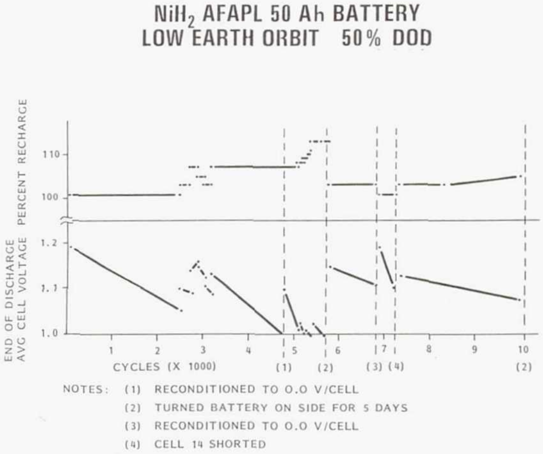


Figure 39-1



NiH$_2$ AFAPL 50 Ah BATTERY
LOW EARTH ORBIT 50% DOD

NOTES: (1) RECONDITIONED TO 0.0 V/CELL
(2) TURNED BATTERY ON SIDE FOR 5 DAYS
(3) RECONDITIONED TO 0.0 V/CELL
(4) CELL 14 SHORTED

Figure 39-2

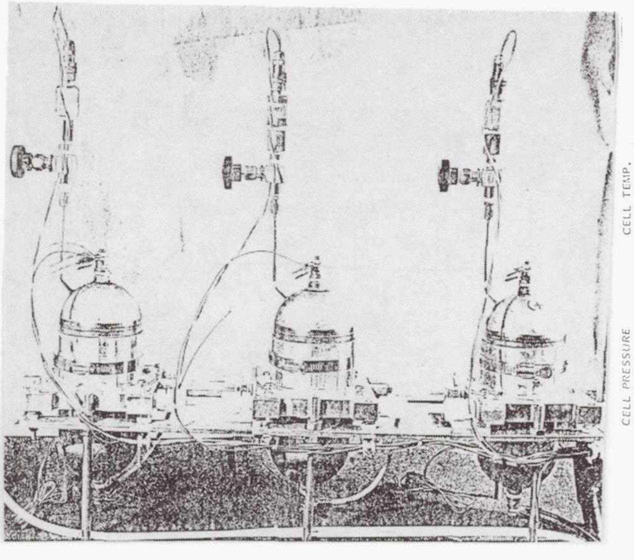
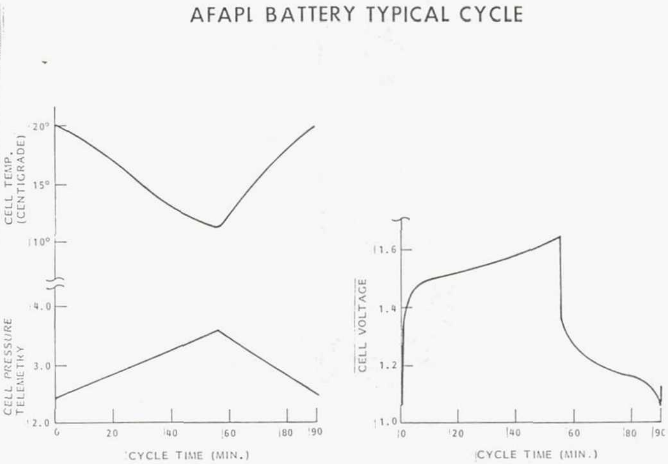


Figure 39-3



AFAPL BATTERY TYPICAL CYCLE

Figure 39-4

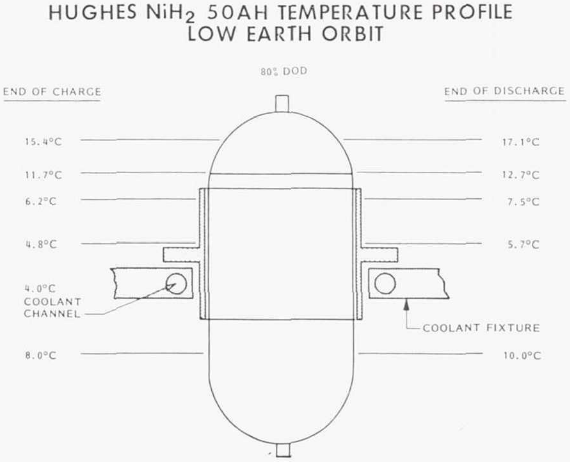
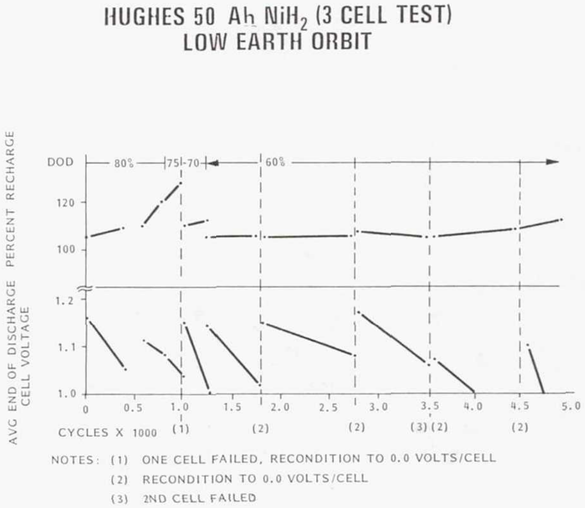

HUGHES NiH_2 50AH TEMPERATURE PROFILE LOW EARTH ORBIT

Figure 39-5


HUGHES 50 Ah NiH_2 (3 CELL TEST) LOW EARTH ORBIT

NOTES: (1) ONE CELL FAILED, RECONDITION TO 0.0 VOLTS/CELL
(2) RECONDITION TO 0.0 VOLTS/CELL
(3) 2ND CELL FAILED

Figure 39-6

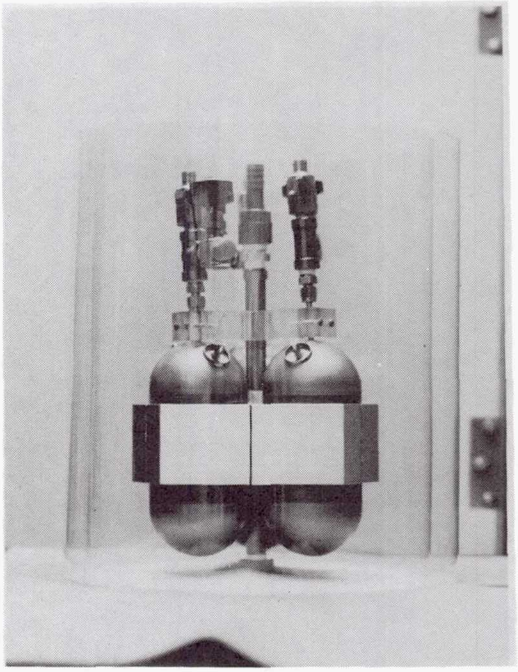


Figure 39-7

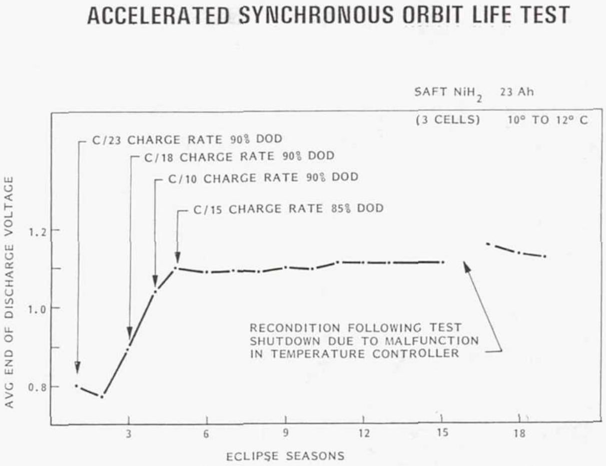

ACCELERATED SYNCHRONOUS ORBIT LIFE TEST

Figure 39-8

1979 SAFT 23AH NiH_2

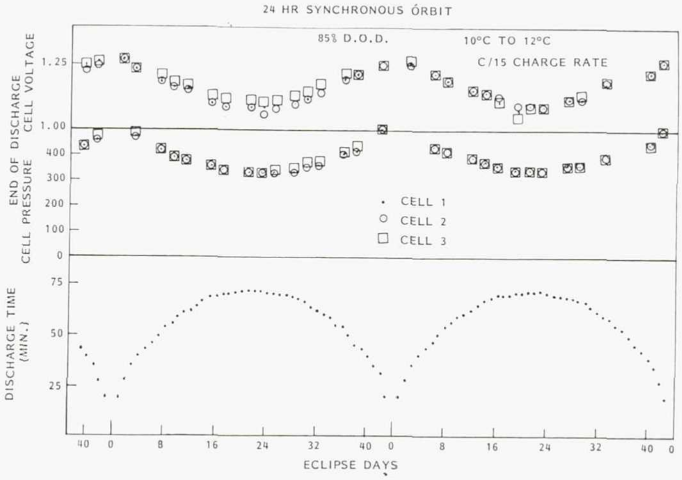


Figure 39-9

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NICKEL HYDROGEN CELL TESTS

V. Mueller
McDonnell Douglas

We have three of the Hughes Aircraft cells, the prototype 50A h cells that were provided to us by Don Warnock of the Air Force. We have essentially done some parametric tests followed by some cycling tests, and we are running the three cells as two packs; essentially, one cell independently at 50% depth of discharge in a 90 minute orbit, and the other two cells in series at 80% depth of discharge in 90-minute orbit. I shall only talk about the cyclic test.

We have three cells automatically cycled in simulated low-Earth orbit in 35 minute discharge, 55 minute charge, with charging voltage limited, temperature compensated. We have the cells mounted in a fixture that conducts heat to an aluminum baseplate. The baseplate in turn, is bounded in a temperature controlled bath to remove the heat from the mounted fixture. We had one cell with a zircar separator, which failed after 2473 cycles. That one was in the 80% depth of discharge cycling regime. We have two cells continuing to cycle. One has a zircar separator, one has asbestos. They are now at about 4000 cycles.

(Figure 40-1)

The failed cell was removed from the setup, and we do intend to dissect that. However, we have not done so yet. Figure 40-1 shows a picture of the test fixture; the cell that failed was mounted in the center. These are the fixtures, the clamp around the cell body, and the material is 60 mil thick aluminum. It is mounted on a baseplate that is just a lin thick plate of aluminum. The cells are very well instrumented with thermocouples. One of the tests we did before we started the cyclic test was a thermal characterization test. While we were cycling, until the second cell failed we used the middle thermocouple right at the flange for control. In other words, the temperature control system tries to maintain that point at some constant level and the other two just have to ride along. Since that one failed, we went to cell no. 3, which is still continuing to operate at high depth of discharge, and we are using that as control. Of course, they came with valves installed, and each cell has pressure telemetry.

One other thing I should point out: this is mounted inside a plywood box, and so there is no convection cooling. We packed it with Fiberglass, which underneath the cells and all around them, and then the whole thing is in a styrofoam box to provide an environment in which there is no introduction of external heat.

(Figure 40-2)

Figure 40-2 shows the cycling arrangement, with the three-quarter inch plywood box in which the cells are mounted (we had to do this for the safety people who, when they hear the word "hydrogen", immediately think of explosions). It is vented and we have a hydrogen detector to give an alarm if we should detect any hydrogen. So far we have not seen any. The coolant underneath provides the temperature control fluids that we circulated around the mounting baseplate, and our cycling consoles are shown. They cycle automatically. We take data on magnetic tape at roughly one-week intervals, at one-minute intervals during charge and discharge; during intermediate cycles we take data at ten-minute intervals, just in case there is a problem so that we can reconstruct the anomaly. We also have some alarm circuits, which will cut the cell off if there is an overdischarge and the voltage gets down below 0.5V per cell, or if we have overcurrents, the current exceeds 75A, or if we have an over undertemperature, overpressure or we lose facility power.

(Figure 40-3)

One of the things we wanted to do in this test was to determine whether we could use the same charging scheme as currently used on a modular power subsystem charging voltage-limited temperature compensator (see Figure 40-3). However, the levels per call that are used in the MPS are too low to actively charge a nickel hydrogen battery, and so levels 5 - 8 correspond to the levels currently in that MPS standard power regulator unit. Levels 9, 10 and 11 are our inventions and they are strictly just separated by 200mV with the same slope as the lower levels. We do not have an automatically controlled charger. The technician determines the average temperature as measured by the thermocouples, and sets the voltage on one of these to whichever level corresponds to the measured temperature.

One other thing I ought to mention is that we do have a limitation with our thermal control system in the amount of heat that we could take out of those cells. We cannot operate below about 8 C on average, and 23 C maximum. Therefore, those are the two temperatures we picked because we did want to get as wide a temperature range as possible.

(Figure 40-4)

Figure 40-4 shows the location of thermocouples. Thermodynamists are notorious for wanting a lot of thermocouples; they have got plenty of them there. We arbitrarily defined cell temperature as being the middle thermocouple on the right-hand side in each case. This one, as I said before, started as a control, and this cell failed. We are now using this for control.

(Figure 40-5)

I shall just show you a few data plots from the early part of the cycling. Figure 40-5 shows cell no. 1, a zircar-separator cell, 50% depth of discharge. We plotted the temperature. We are trying to operate at 8 C average nominal temperature on the middle cell. This cell is further removed from the control thermocouple, and because of the reduced depth of discharge you see very flat temperature excursion and fairly low temperature. The pressure, the voltage plot, we are charging here at 50A constant current until we reach the voltage limit. You can see the current taper.

(Figure 40-6)

We have the same kind of plot for cell no. 2 (Figure 40-6) and cell 3 (Figure 40-7). Cells no. 2 and 3 are hooked in series and they charge and discharge in series. One thing we saw rather early in cell no. 2 is that trying to operate at 80% depth of discharge led to some very low voltages. This one is not bad, down to about 1.1V, but rather early in our cycling we found we had to back off in the depth of discharge we were taking on almost as much capacity as was stored in the cell.

(Figure 40-7)

Figure 40-7 shows cell no. 3 in series with cell no. 2, has much the same characteristics. Cell no. 3 has the asbestos separator, and it seems to have a little more voltage. It seems to perform somewhat better than the zircar did.

(Figure 40-8)

Figure 40-8 shows a plot of end-of-discharge voltage in selected cycles. We started the cycling as shown, with cells no. 2 and 3, at the voltage temperature limit 9. Cell no. 1 was at a voltage temperature limit of 8, and completed almost all of its cycling at level 8. When we had completed some 1500 cycles, we decided that we needed some data at 25% depth, and so we reduced the depth of discharge to 25%, and you can see the response in the end-of-discharge voltage. At the same time, we reduced the temperature limit level from 7 to 6, and we found that the return factor, the charge-to-discharge ratio, was rather high. Therefore, we cut it back some more, at about 1900 cycles, to level 6. On cells no. 2 and 3 we started at level 9, and after 190 cycles, we were seeing voltages below 1V per cell on cell no. 2. We then went to level 10, and got a slightly better response in the discharge voltage, although it still continues to decay. Again, near 600 cycles, we had a problem with cell no. 2. We had a low voltage alarm, and the test shut down. At that time, we talked to Don Warnock of the Air Force, and he mentioned his problem with decay of capacity on some of the early cells, due to the popping phenomemon, and suggested we do a capacity discharge and check how much capacity we have, and possibly back off on the discharge. We did that. We measured about 42A h. We were taking 40A h out on each cycle, and so we backed off to 70%, or 35A h, and continued that for the balance of the 2000 cycles that you see in Figure 40-8.

(Figure 40-9)

Figure 40-9 shows a plot of the ampere hour return factor, the charge and discharge ratio corresponding to those same plots, again at a nominal temperature of 8 C. You can see the response of cells no. 2 and 3. You can see something of an increase in the return factor when it went from level 9 to level 10 at 190 cycles; there is another increase when we backed off on the depth of discharge, but we left the voltage on the same, and it levels out at 1.08 - 1.1. When we reached a point at 1500 cycles, we went back to 25% depth of discharge for cell no. 1. We got a significant increase in return factor, even though we backed off one level in the voltage limit. We then backed off again, and got it down to about 1.08. It seemed to us that a return factor about 1.08 is about what you need at this temperature to maintain a good end-of-discharge voltage.

(Figure 40-10)

As I said, we have completed 4000 cycles (see Figure 40-10). I do not have all the data with me, I have data through about 3000 cycles. We changed the temperature at 2000 cycles, because they wanted some data at 23 C nominal temperature. Again, we are at 50% depth of discharge for cell no. 1, and the voltage temperature limit is at level 9 throughout that.

For cells no. 2 and 3, we again encountered a problem at about 2050 cycles, and we ran another capacity discharge. We are still having problems. The voltage is getting too low, and so we backed off then to 60% depth of discharge, or 30A h, out in the cycle. We continued the cycle and, as you can see in Figure 40-10, these voltages are dropping off the graph. Finally, we got a cell cutoff at cycle 2473. We did a capacity discharge on cell no. 2 there, and I shall show you the profile in a monent. The discharge profile seemed normal enough; however, when we went to charge it after we had done that capacity discharge, it would not recharge. It had an internal short.

(Figure 40-11)

Figure 40-11 shows the return factor conditions for those same cycles. Cell no. 1 is relatively uniform, about 1.13, 1.14. After we took cell no. 2 out of the setup, we are running rather high return factors on cell no. 3, and we have since cut back on the voltage limit, and we are able to get that number down to about 1.1 - 1.3.

(Figure 40-12)

Figure 40-12 shows a plot of cell no. 2 capacity discharge for cycle 2473. It seems rather normal to about 60 minutes.

We got out 27A h to 1V per cell, and we got 40A h out to 0.5V per cell. The scales are offset as shown. Since cells no. 2 and 3 were in series, we just continued to discharge cell no. 2 until cell no. 3 reached 0.5V, and we reversed it for 14 minutes. The voltage dropped to 60mV during that 14 minute interval, when we stopped the discharge and recovered to 0V; and as I say, when we tried to charge it after that, it would not accept a charge at all.

(Figure 40-13)

Figure 40-13 shows some of the capacity data that we have so far. When the cells were received initially, they all showed right at 50A h. Cell no. 1 has stayed relatively constant at that value. There's some scatter, of course, but it seems to be holding 50A h rather well. Cells no. 2 and 3 dropped rather precipitously; cell no. 2, on cycle 2473, as we mentioned earlier, got 27A h out before it failed. Capacity checks, which we have run on cell no. 3 after we took cell no. 2 out of the test, have shown some recovery. We are now running about 46, 47A h.

In summary, we had three cells operating. One cell has shorted, and we have not yet dissected it. The other two cells continue to cycle; we are now at 4000 cycles, and the operation seems to be normal.

DISCUSSION

ROGERS: I have a couple of comments, rather than questions, to clear up a few things. The popping phenomenon does not affect the capacity of the cell, because it is at the negative electrode, and you have a positive limited cell. Therefore, unless it became severe enough to cause very large voltage drops in the negative -- which it does not, at least under any normal conditions -- you will not see it reflected very easily in the cell curves.

Secondly, your loss of capacity is generally caused by positive plate degradation in the cells. The asbestos, which performs better, tends to restrict migration material out of the positive plate, so that you retain your capacity better. The wall wick in the cell keeps the asbestos operating, so that the performance is similar to that of the zircar under normal conditions.

MUELLER: I see. I was under the impression the popping phenomenon was associated with capacity. Thank you.

DUNLOP: Why is it that you can take a positive electrode and put separator material like nylon adjacent to it in a nickel cadmium cell, and you do not lose capacity, although you do when you put zirconium oxide next to it?

ROGERS: These particular positives had a problem with extrusion in the type of material. It is not normally so.

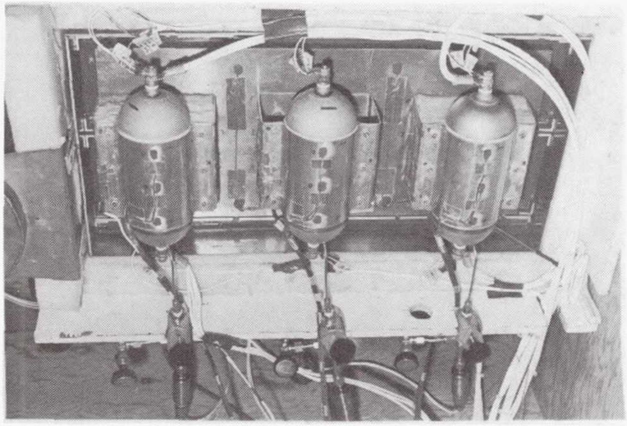


Figure 40-1

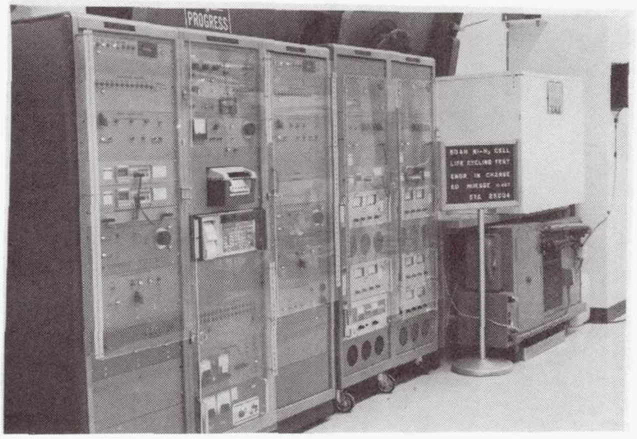


Figure 40-2

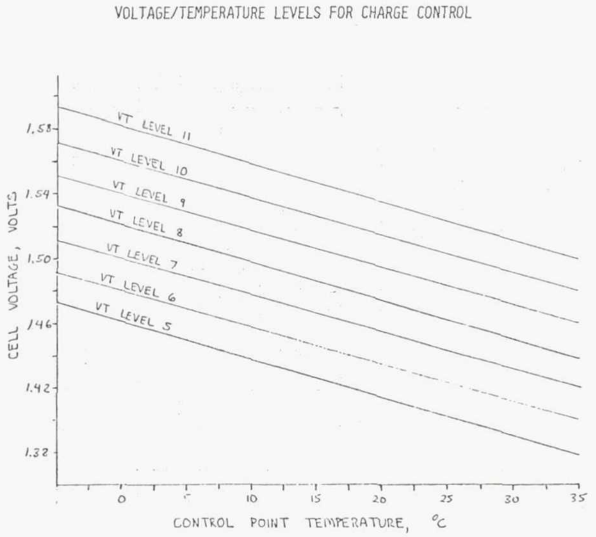


Figure 40-3

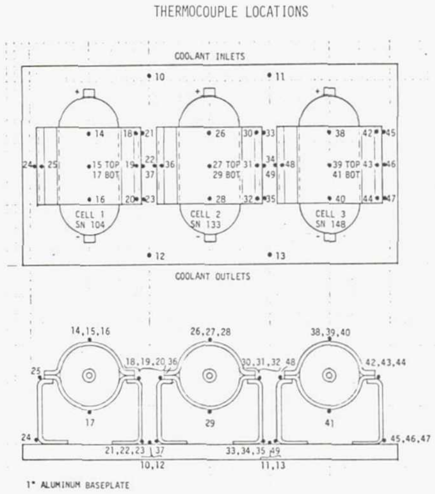


Figure 40-4

TYPICAL PERFORMANCE DATA - CELL 1

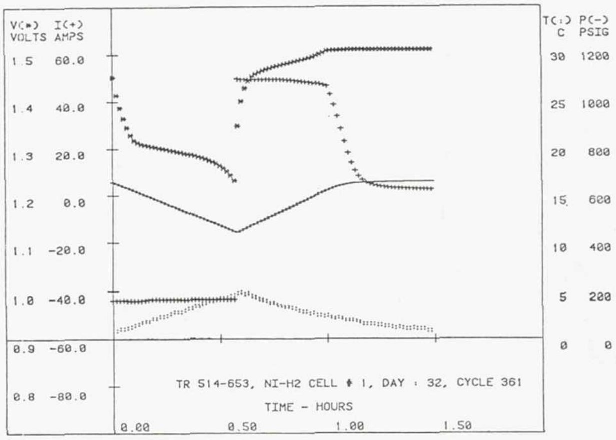


Figure 40-5

TYPICAL PERFORMANCE DATA - CELL 2

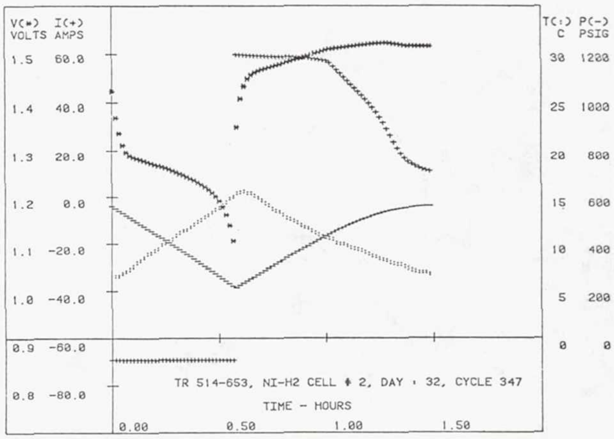


Figure 40-6

TYPICAL PERFORMANCE DATA - CELL 3

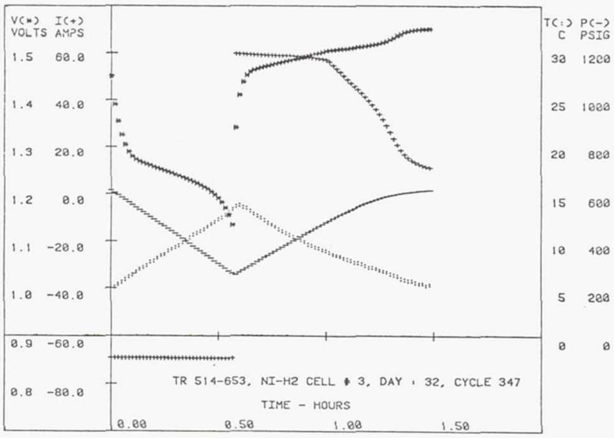


Figure 40-7

END OF DISCHARGE VOLTAGE VS CYCLES

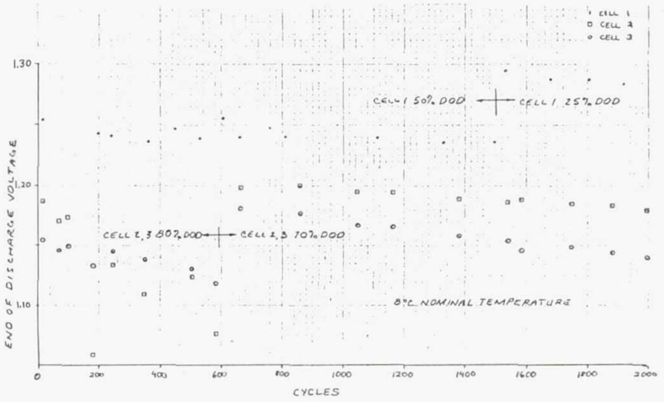


Figure 40-8

AMPERE-HOUR RETURN FACTOR VS CYCLES

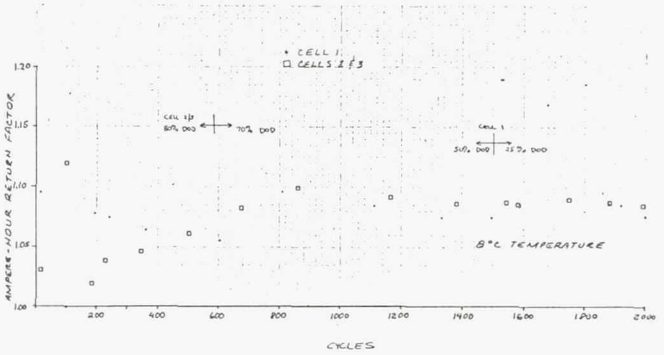


Figure 40-9

END OF DISCHARGE VOLTAGE VS CYCLES

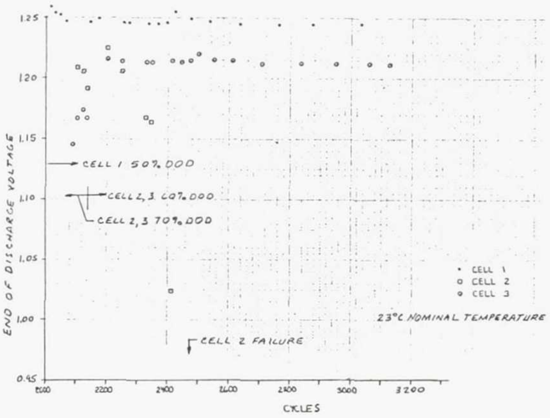


Figure 40-10

AMPERE-HOUR RETURN FACTOR VS CYCLES

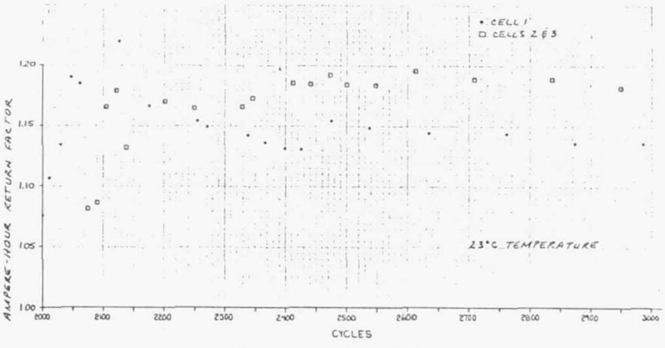


Figure 40-11

CELL 2 CAPACITY DISCHARGE - CYCLE 2473

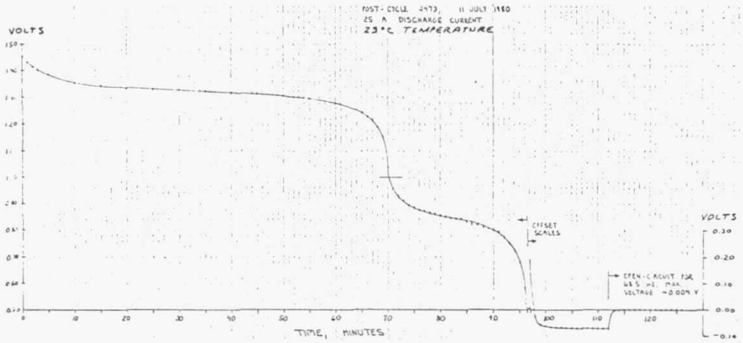


Figure 40-12

CELL CAPACITY VS CYCLES

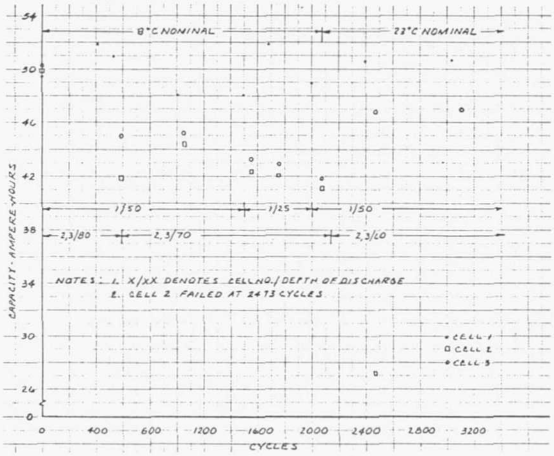


Figure 40-13

COMMON PRESSURE VESSEL DEVELOPMENT FOR THE NICKEL HYDROGEN TEDHNOLOGY

G. Holleck
EIC

As you have heard already, we have been active in the development and investigation of the nickel hydrogen system for many years, and today I shall present another nickel hydrogen battery design which involves a number of steps, within a common pressure vessel.

The nickel hydrogen power system is, like most other systems, generally not used on a cell level, but at a battery higher voltage. This can be achieved for nickel hydrogen cells in two ways: by taking individual cells and using them in series; or by arranging a varying number of stacks in series within a common pressure vessel.

A common pressure vessel approach has several advantages: in particular, a high volumetric and to some degree gravimetric energy density and various benefits with respect to construction and costs. These benefits are most obvious for lower capacity batteries, but may ultimately be equally attractive for larger battery modules. For the successful realization of common pressure vessel nickel hydrogen batteries, one needs to consider all the requirements for individual pressure vessel cells, and there are some extra requirements beyond this. The design considerations are: performance parameters, electrolyte management, oxygen management, thermal management, which are the three major areas; other considerations are the hardware aspects of a suitable cell, which is common to all nickel hydrogen cells.

Some specific problems must be addressed with common pressure vessel nickel hydrogen battery designs. First, there is the problem of electrolyte bridges. Electrolyte bridging in a cell stack must be avoided, and if such electrolyte shunts do occur, one problem is a loss of efficiency, because current is passed through these. This, however, is not really the main problem. The main problem is that whenever such a shunt due to transference of ions occurs, potassium hydroxide is transferred from one stack element into another, electrolyte in one is diluted, and is concentrated into the other. This is a unidirectional process and therefore is detrimental to long-term cell life. Interstack electrolyte distribution is important. Thermal balance must be considered, because now there is not only the problem of losing electrolyte from the whole stack to the vessel, but also the problem of transferring electrolytes from one stack into the neighboring stack. A practical way of stack interconnections must be found, and there is a potentially increased chemical stress, which comes from the high voltage between some parts in the cell, possibly causing electrolysis at high current densities, which can lead to hydrogen embrittlement, for example -- problems that do not occur to that extent in individual pressure vessels.

(Figure 41-1)

We have developed a nickel hydrogen cell design that addresses all these potential problem areas and has much in common with components of present individual pressure vessel nickel hydrogen cells. Let me describe this concept. It consists of individual nickel hydrogen cell stacks enclosed in thin-wall Teflon cups that sit on top of each other, and then there is a series interconnection in the cell stack. We have here chosen further elliptical domes instead of the hemispherical domes. One advantage of these is a smaller common hydrogen gas space, and a better stacking of batteries. The individual pressure vessels have opposite terminals on opposites sides, which enhances the symmetry of the battery and also reduces the heat generation due to the connections.

(Figure 41-2)

Figure 41-2 shows an individual stack with the interlocking Teflon cups; and the narrow spaces between the two cups and between the Teflon wall and the vessel prohibit or inhibit the formation of electrolyte shunts. The stack itself is in the configuration of a single electrode arrangement, and solves the oxygen management aspect where oxygen is evolved from the nickel electrode and recombined at the following hydrogen electrode. We then have reservoir components and a wick.

Naturally, in a series arrangement, you have to solve the problem of electrolyte management separately for each stack. Therefore, the successful method of a common wall wick, which would return electrolyte from the bottom of the pressure vessel, cannot be used in a common pressure vessel arrangement. You therefore have to solve the electrolyte management within each stack individually. This is done by these reservoir components and the wick structure, which helps to equilibrate the electrolyte and keep it equilibrated throughout the stack. The mechanical interconnection is done by such pin connectors; this allows the use of the standard pineapple-slice shaped electrodes without any restrictions with regard to the size of the stack or the number of stacks put in series.

I have mentioned the electrolyte management aspect. Let me mention a few other benefits of this cup arrangement. It minimizes electrolyte loss. We have operation and condensation mechanisms within the electrode stack. It provides good heat dissipation, since it does not compromise the heat dissipation compared with individual pressure vessels. The reason is that you replace half of the gas gap between the electrodes and the pressure vessel with a thin level of Teflon. However, the thermal conductivity of the Teflon is a little better than hydrogen gas.

Now let me mention a few of our experimental results. We have taken this concept and have built actual laboratory hardware. That is, the electrode size and dimensions are the same as are used today in individual pressure vessels, but we have housed them in boilerplate containers. We have built such cells with about 10A h capacity and up to 5 cells in series, not because this is a limit, but because we think it is a convenient size to test and prove the concept.

(Figure 41-3)

Figure 41-3 shows a charge/discharge curve from such a 5-cell series battery. It looks exactly the same as an individual pressure vessel cycle, except for the voltage scale. The test cycling regime that we used is the accelerated near-Earth orbit regime. You see a 35-minute discharge, one-hour charge. We generally used between 80 and 100% depth of discharge. In most of the measurements the depth of discharge is almost 100% of actual capacity.

(Figure 41-4)

Figure 41-4 gives you an idea of some routine cycling of such cells. They are discharged almost to the cutoff, very close to the 100% limit.

(Figure 41-5)

To determine the capacity we completely discharge the cell periodically. We would typically discharge it at the high rate to 1V per cell stack, and then continue discharge down to 0V at about a C/5 rate. In addition to the total battery voltage, we measure individual stack voltages. Figure 41-5 shows such a discharge at the high rate, followed by at the low rate. This is a battery with four cell stacks in series.

(Table 41-1)

Table 41-1 gives a short summary of some test results. As you can see, this is a 5-cell battery that has gone over 1300 cycles; the high-rate capacity and the follow-on capacity are shown. In the last column is the total capacity at the rate discharge with no significant changes.

Table 41-2 gives results from another battery that we are cycling.

(Table 41-2)

This is a 4-cell battery, which has gone nearly 2500 cycles and is also doing well, continuing on cycle.

In summary, this common pressure vessel nickel hydrogen cell design has the following key features: it eliminates electrolyte bridging; it provides for independent electrolyte management for each unit stack; it provides for independent oxygen management for each unit stack; it has good heat dissipation; it has a mechanically sound and practical interconnection; it has the maximum in common with state of the art individual pressure vessel technology. And, last but not least, it actually works.

Let me acknowledge the support of the Air Force for this work.

DISCUSSION

RITTERMAN: Have you done any calculations with regard to the specific energy and the energy density that an X cell number would have as opposed to a single cell?

HOLLECK: No, we have not done any detailed calculations at this time. Basically, most of these calculations have been done by Don Warnock. It has been determined that if you can achieve such a battery without having to accept an undue number of complications and inefficiencies, it would be a desirable step to take. Thus the objective of this program was to determine the feasibility of such an approach, and to determine what type of compromises you have to make, if any.

Coming back to your question, without having done actual calculations, the gravimetric energy density of this design as we have it in the cell stack is identical to what you have in individual pressure vessels. There are some weight savings due to using one pressure vessel, one set of terminals and so on. Therefore, in the common hardware, if you want the same capacity, the pressure vessel is naturally somewhat larger than in an individual. Exactly how much these savings are I cannot tell you in quantitative terms at that point.

STOCKEL: How did you put the electrolyte in that cell?

HOLLECK: We have looked at two ways. One way is just to do it in the same way as you do in normal cells: you put vacuum impregnator. Since you have narrow hydrophobic channels, the electrolyte connection will break up. It will not be stable. However, I think that a better way to do it is to actually put a predetermined amount of electrolyte into each stack, rather than to do it the common way. In most of our laboratory work, we meter into each stack a certain predetermined amount of electrolyte. We vacuum and equilibrate it under vacuum. Naturally, we do not just have the cells with the cups open to the top. They have to work in every direction, and we do turn them upside down with the cups down. The cups are really just an insulation of the stack to prevent electrolyte bridging. However, it is not a cup in the sense that it contains liquid. All electrolyte is absorbed, as it is in normal nickel hydrogen cells, in the porous medium of the electrode or the separator.

STOCKEL: So, in a lightweight cell, presumably you have to do the welding after the electrolyte loading?

HOLLECK: Yes.

GASTON: Did you ever measure the self-discharge rate? If you did, how does it compare with that of a single cell?

HOLLECK: We measured the self-discharge rate, and it compares exactly with that of a single or individual cell. We used this technique, because it is a very sensitive measure, for any electrolyte shunts. If you have, say, 5-cell stacks in series, and if there is a shunt between three of them, for example, and you let them sit there and then after 72 hours discharge the rest of the capacity, you see a big imbalance. In fact, we see no change at all, which is proof that there is no leakage current.

LEAR: Did you measure any temperatures on the case of the cells? Was it different from just a single cell?

HOLLECK: We measured temperatures, and the measurements we have are the same as for single cells.

DYER: Each individual stack has its own wall wick. What do you make this wall wick from? It is attached to the Teflon. Is it a permanent wall wick?

HOLLECK: In these cell stacks it is just a piece of nylon, Pellon. Ultimately you do not want the nylon in there. However, anything porous works. There is no magic about the wick.

DYER: It is pretty static, it does not shift around?

HOLLECK: Once you put it in it is wedged between the Teflon wall and the electrode package. It will not move anywhere.

STADNACK: Have you had any cell shorts in these stacks? Usually when we have seen a cell shorting, generally it is all kinds of noxious compounds of unidentifiable descriptions. Have you had any short, and does it affect the performance of the remaining stacks?

HOLLECK: We had a short in one case, and it did not affect the other cases. It was a real short, and we cycled this battery with the one shorted stack for a long time afterwards. I do not remember the exact number of cycles.

STADNACK: Did it short when it had a short on it, or did it fortuitously short, such as at the end of discharge?

HOLLECK: I cannot tell you exactly when it shorted.

STADNACK: Did you disassemble it?

HOLLECK: Yes.

STADNACK: Then you could tell.

HOLLECK: From the disassembly I think it did not short with full charge, because it did not look too bad.

STOCKEL: Did I understand you to say that the rate constants for the self discharge are the same in your high voltage cell as they were in the cells with electrodes in parallel?

HOLLECK: Yes. If you measure the rate of self discharge, you have to somehow normalize it, say, per capacity, and on that basis, it is the same. When I say capacity, if I have five 10A h stacks, that cell would self discharge, the pressure would go down the same way as a 50A h individual cell. The self discharge is a reaction of hydrogen with the nickel electrode. Basically it does not care how the nickel electrode is interconnected in the cell.

RITTERMAN: It is the surface area?

HOLLECK: I do not exactly know what it is. With normal, more or less standard electrodes that everybody uses, around 30-mil thickness and so on, it is either proportional to capacity or to surface area, or whatever. The reason that I cannot tell exactly is because all these electrodes have about the same ratio of surface area to capacity. If I really wanted to differentiate, I should have to have some electrodes with the same surface area, but vastly different capacity, or the other way around.

WARNOCK: I think I can answer Paul Ritterman's question about the energy density. We did the computer studies on energy density and common pressure vessel modules in preparation for the procurement for Dr. Holleck's contract. It turns out that the increase in weight energy density is not very dramatic. For a six-cell module it is, I think, around a 17 or 18% gain for a single cell. The biggest gain comes when you go from one cell to two cells; there is a smaller gain when you go to three cells, a smaller gain to four cells and so on. There is always an increase in energy density on going to higher numbers of cells, but that increase with each additional cell gets very small very soon. By the time you have, say, four to six cells in series in one pressure vessel, you have most of your energy density gain, and at about a six-cell module it will be a 15-18% improvement in energy density. The improvement with the common pressure vessel comes in volume energy density and in cost.

RITTERMAN: Once the volume energy density goes, there is a certain number of moles of hydrogen that you have to consume, whether you consume that in five separate cells or in five cells in a common pressure vessel. Therefore, I think that unless you are willing to go to higher pressures, I do not see the volume gain in that.

HOLLECK: I think the really big difference is not if you look at the internal volume of a cell, but if you look at the actual volume of a battery, say, the space you need to package a battery into. If you want a 10A h battery with 28V, for example, you have a lot of these little round things which do not pack very well and you have to put --

FOUGERE: Have you tested your design according to mechanical environmental specifications?

HOLLECK: We have not yet tested this in any vibrational or other mode.

FOUGERE: So you do not know the behavior, being an interconnecting system?

HOLLECK: I do not think there will be, but there may be some engineering that is necessary to accommodate whatever G forces and so on you might want to have.

Let me just mention that these individual stacks are set on top of each other, and at the end of the whole stack you have the same type of restraining plate that you would have in an individual stack here. Therefore, holding the whole package in the cell is no different in the series arrangement from in the individual arrangement. The pins do not hold it.

MILLER: From our manufacturing experience, we think that it is probably better not to have electrolyte in the same room as you are performing the cell closure operation. Have you, on this program, actually welded up preactivated cells in a lightweight, flight-type design?

HOLLECK: We have not welded up cells yet. The cells that we use are boilerplate vessels.

MILLER: Do you anticipate a special problem in this area?

HOLLECK: You encounter special problems everywhere. Comparatively, I should say that the main issue, and that is the issue we are addressing, is whether such cells are feasible, and whether they are sound from the chemistry and from the basic construction. We have not even tried to solve all the detailed engineering problems, but I feel quite confident that we can find a method of welding these cells without any difficulty. You certainly do not want to vacuum-weld them in an electron beam welder. However, I do not think that is the only possibility.

CPV Ni/H_2 BATTERY NO. 5 - CYCLE HISTORY

CYCLE NO.	DISCHARGE CHARACTERISTICS			TOTAL CAPACITY AH
	CURRENT A	CAPACITY AH	MDV V	
46	13.5	9.1	5.85	10.5
204	13.5	8.8	6.1	10.28
420	13.5	8.37	6.1	9.31
656	11.7	8.89	6.05	9.87
836	11.85	9.05	6.1	10.31
1311	12.25	9.07	6.1	10.17

*DISCHARGE CONTINUED AT 2A.

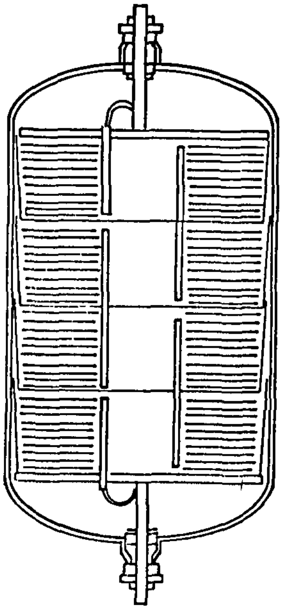
Table 41-1

CPV Ni/H_2 BATTERY NO. 3 - CYCLE HISTORY

CYCLE NO.	DISCHARGE CHARACTERISTICS			TOTAL CAPACITY AH
	CURRENT A	CAPACITY AH	MDV V	
65	14.33	8.76	4.8	9.65
689	12.8	7.4	4.88	9.5
1000	12.5	6.85	4.77	8.45
1162	13.5	9.2 ~~4.87~~	4.87 ~~9.24~~	9.24
1720	11.7	8.73	4.76	9.95
2410	11.5	7.80	4.8	9.78

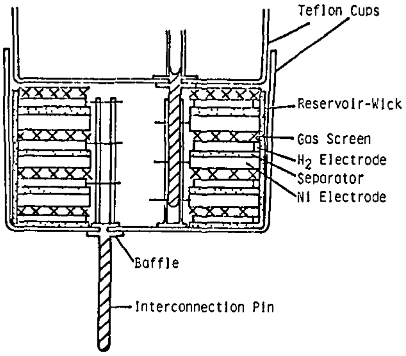
*DISCHARGE CONTINUED AT 2A.

Table 41-2



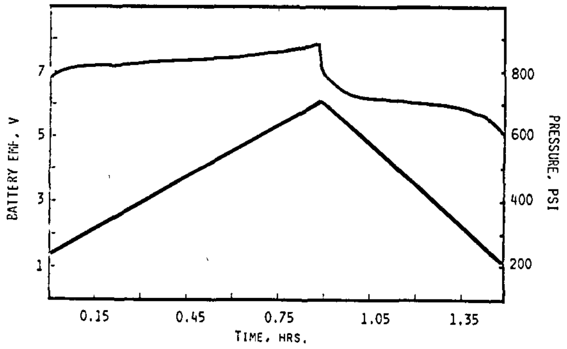
Schematic of the EIC CPV Ni/H_2 module concept using insulating cups and plug-in interconnections.

Figure 41-1



Unit stack detail of the EIC CPV Ni/H_2 battery module.

Figure 41-2



TYPICAL VOLTAGE AND PRESSURE PROFILES DURING A CHARGE-DISCHARGE OF CPV Ni/H_2 BATTERY.

Figure 41-3

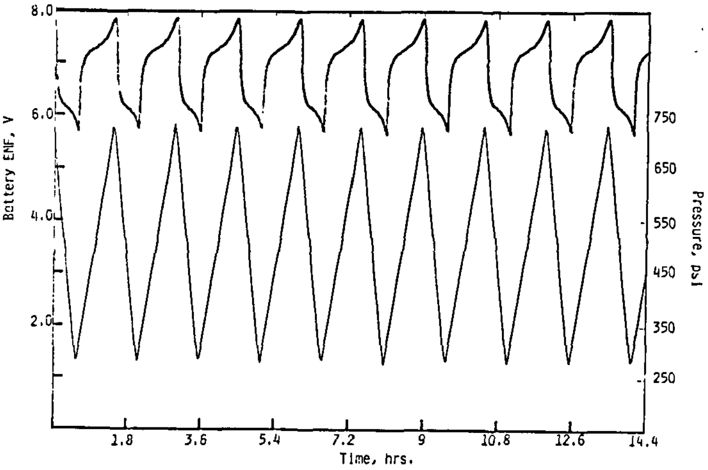
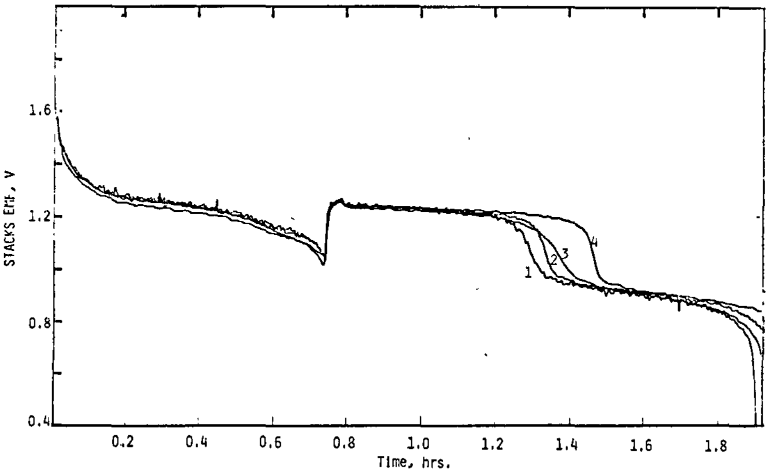


Figure 41-4



STACK VOLTAGE PROFILES DURING CAPACITY TEST. CYCLE 779, BATTERY NO. 3R (INVERTED POSITION).

Figure 41-5

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CAPACITY OF A NICKEL HYDROGEN BOILERPLATE CELL AS A FUNCTION OF TEMPERATURE

H. H. Rodgers, P. J. Dalton and L. A. Tinker
Hughes Aircraft

The program I shall talk about has been sponsored by Bell Telephone Labs, with Chris Dyer acting as the program coordinator for Bell Telephone. The objective of this particular study is primarily an evaluation of components, in this case, positive electrodes.

(Figure 42-1)

Figure 42-1 shows a boilerplate cell which we used for this program. We have used it for many others. One of the basic features of its design is a very low volume for hydrogen, so that you get the same kind of pressure profile in this cell, which is designed as a 6-electrode cell using full-sized pineapple-slice electrodes. We therefore see a pressure profile and behavior essentially the same as in a flight type cell, the major difference being that, because it is different thermally, we do have a wall wick in the cell so that we get a similar electrolyte distribution.

The design of this cell is the Air Force and Hughes recirculating design you have seen before. We use electrochemically impregnated positive electrodes, which are made on a slurry plaque by using a perforated steel substrate as manufactured by General Electric.

The thickness of the electrodes is about 27, 28 mils. The area is $48cm^2$ and the plates were actually made for another purpose, and so they were not coined. However, this gave us no particular problems. The weight gain ($7.6g/dm^2$) is what GE measured when they made the electrodes by difference measurement. The $8g/dm^2$ is what they obtained by analysis, and on which my calculations are based. These plates had about 10% cobalt; the negatives are conventional design with, in this case, 9mg platinum per square centimeter. The substrate is the etched nickel foil substrate. The separator was two layers of ZYK 15, a knit-weave zircar, which we use in other cells and which is chosen to give more uniformity because the weave is more uniform than the square weaves we used to use. The gas screen is a 12.5 mesh/cm woven polypropylene, 0.6mm thick, and is a relatively strong material since the fibers in that polypropylene are made and are stretched as they are made. The wall wick is plasma-sprayed yttrium-stabilized zirconium oxide.

The cell was prepared by evacuation and filling with 31% KOH. We normally use a minimum 16 hour soak overnight. The activation consisted of a 5 minute C-rate charge. That takes a little explanation. We use this to blow the excess electrolyte out of the polypropylene gas diffusion screens because we do not want to block the negative electrodes. We then gave it eight 100% depth of discharge conditioning cycles with a maximum time of 72 minutes. We then gave it 34 80% depth of discharge cycles in low-Earth orbit with a 1.05:1 C/D ratio. The end of discharge voltage at the end of that time was 1.071V. I might point out that that voltage is perhaps slightly lower than we usually get. However, these electrodes were made with the perforated foil substrate, which at one time we thought might give trouble at high rate discharge. If it does, it is very slight.

(Table 42-1)

The data shown in Table 42-1 are the capacity we obtained initially at 20 C We had our equipment run a little cold at one point here, and so it ended up at 17 C, which made a difference. You will see, in Figure 42-2, what effect this has. We then ran 35 C, went back to 20 C, then to 0 C, and finally back to 20 C. If you notice, there is very little change between the first and last 20 C cycling.

The cell was based on a 6.6A h capacity, nominal 1.1A h per electrode. This was based on a 16 hour C/10 charge, usual synchronous orbit cycle.

(Figure 42-2)

In Figure 42-2, the dots are the results we obtained. They are normalized to 6.6A h. The Air Force data I mention here are typical Air Force plate data. They have been normalized to a 6-plate cell. At 35 C we had basically the same capacity, and increasing to within experimental error, the same at 0 C. The 17 C point comes out about where it should. What you are seeing is the effect of the 10% cobalt even though the plates were made by GE, essentially similar to the Bell Telephone process, whereas the Air Force used Dave Pickette's process.

The capacity of this cell was consistent with the loading level I presented, and I calculated 103% utilization. As I mentioned, the temperature effect on capacity seems to depend on the cobalt level.

DISCUSSION

HENDEE: Were these positive plates electrochemically impregnated at GE?

ROGERS: Yes.

HENDEE: When were they built?

ROGERS: Only a few months ago.

HENDEE: Was that 10% cobalt added electrochemically or was it added chemically afterwards?

ROGERS: It is in the electrochemical bath; it goes in with the nickel.

HENDEE: So they had the sodium nitrite in it at that point?

ROGERS: Yes.

THIERFELDER: I just have one Figure here that was very interesting to me and I thought it might be of interest to a number of people here.

(Figure 43-1)

We are also testing nickel hydrogen cells, the Air Force 50A h cells from Don Warnock. We have done some cycling tests in 1979, performance tests. However, in 1980, they are running a program of comparing nickel hydrogen and nickel cadmium cells. We have three nickel hydrogen Air Force cells, and three 50A h nickel cadmium cells, such as being tested at Crane. These are the standard 50 A h cells.

On the lower graph we have the low-rate capacities. For the nickel hydrogen at 20 C, this is the average of three cells, 47A h, which is the same as has been reported by some of our other contractors. They have 45-50A h. At 30 C it drops off, and at 0 C it goes up. When we ran the nickel cadmium cells we got dramatically higher values. The 61A h checks with the data at Crane; they also got about the same data here.

The variation in temperature was interesting. However, the really big thing about it was when we went to the high rate (which was the same test as that run by Hughes; we have run it last year and this year), which is a 50A charge and a 70A discharge, things looked completely different. The nickel hydrogen cells are up at 40A h with the temperature dependence as shown, and the nickel cadmium cells were as shown. For what it is worth, I thought this was rather interesting and I thought I would show it today.

LACKNER: Did those nickel cadmium batteries have the same capacity as the nickel hydrogen?

THIERFELDER: They are rated the same, 50A h each, but those are the capacities that were found.

LACKNER: As you are well aware, nickel cadmium batteries are used for aircraft cranking applications, where you are taking out anywhere from 10 to 30C. At 10 C, which is not a cold temperature, you should get a lot more capacity than what you are getting here. You are saying 40%.

THIERFELDER: These 50A h nickel cadmium cells are not really built for such high rates, and so the terminals and the tabs may show higher losses. They are not built for that. However, these are the standard 50A h cells. You have to take it for what it is.

LACKNER: You are comparing two systems, one to the disadvantage of the other.

THIERFELDER: In one area we are, but in the other area we are not.

LACKNER: It is well known in the aircraft application that it can be used for high rate.

RITTERMAN: Do you find on the relative surface area you use positive electrodes in nickel hydrogen versus cadmium?

THIERFELDER: No. As I mentioned yesterday, we are constantly doing the tradeoff. This is part of our tradeoff study. It just consists of substituting the nickel hydrogen 50A h and seeing what the results would be.

SEIGER: Could you tell us something about positive electrochemically impregnated positive?

THIERFELDER: The nickel cadmium cells are standard NASA 50A h nickel cadmium; I cannot tell you about the Air Force cells.

STADNACK: As a general comment, those specific nickel hydrogen electrodes that you saw in there had an atypical temperature characteristic for nickel hydrogen at high temperatures and low charge rates. Both the Bell process and the Air Force process electrodes showing much less temperature dependence, as was illustrated by Dr. Rogers a moment ago.

DUNLOP: I think one of the things that you might consider, if you are going to try this kind of comparison, is that probably you are comparing positive electrodes, and not nickel cadmium versus nickel hydrogen. This is because, if you look at nickel hydrogen cells, for example, the hydrogen electrode does not really contribute much to the polarization loss in itself, independent of which of those temperatures you are talking about. I think the data really show the difference in positive electrodes more than they do the difference between the two systems.

THIERFELDER: That is true. Both systems are positive-limited.

CAPACITY OF NICKEL-HYDROGEN BOILERPLATE CELL, A-HR

CYCLE	20°C	35°C	20°C	0°C	20°C
1	6.84	5.36	7.04	8.07	6.95
2	6.84	5.20	6.99	8.06	6.92
3	7.36*	4.98	6.76	8.09	6.82

*RUN AT 17°C

16 HR C/10 CHARGE (C = 6.6 A-HR)
C/2 DISCHARGE TO 1.00 V

Table 42-1

NICKEL-HYDROGEN BOILERPLATE CELL

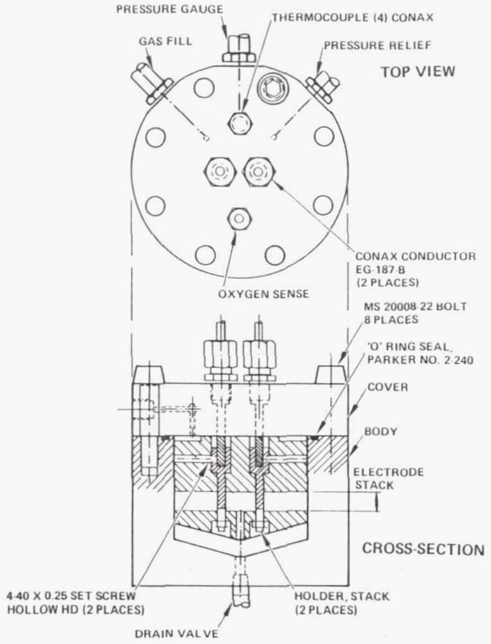

Figure 42-1

CELL CAPACITY AS FUNCTION OF TEMPERATURE

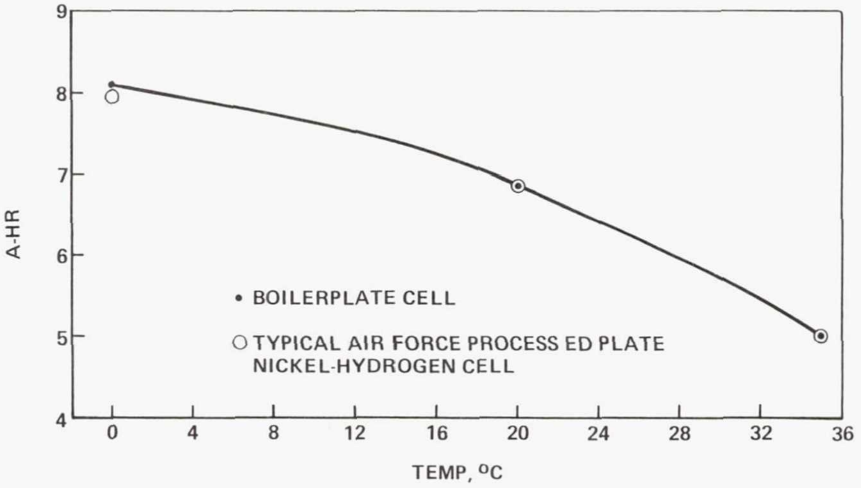

Figure 42-2

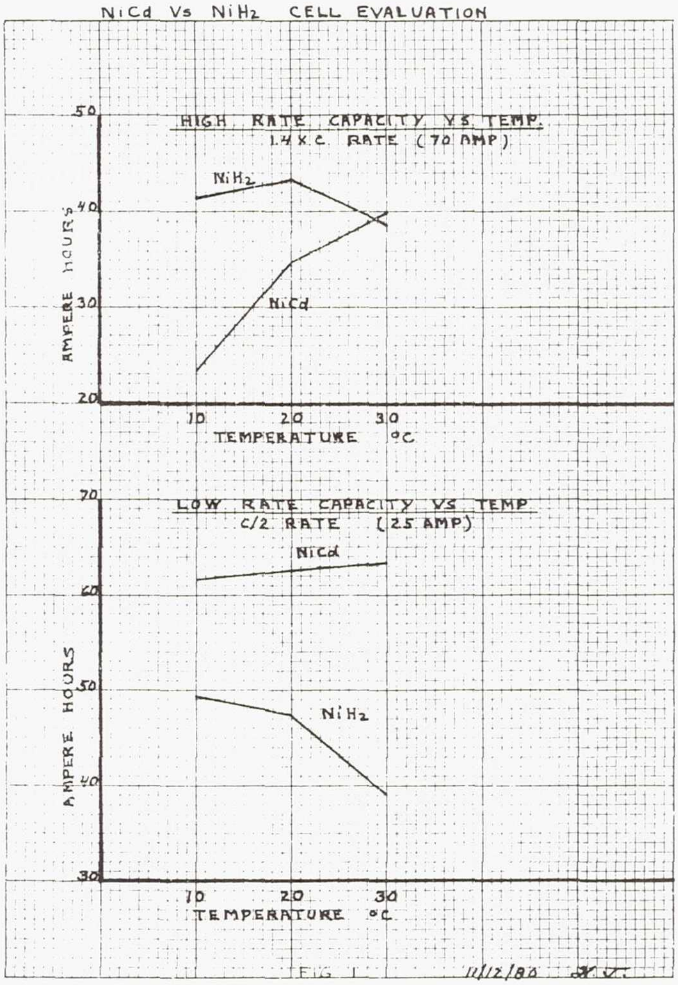
NiCd Vs NiH2 CELL EVALUATION
HIGH RATE CAPACITY VS TEMP.
1.4 X C RATE (70 AMP)
NiH2
NiCd
AMPERE HOURS
50
40
30
20
10
20
30
TEMPERATURE °C
LOW RATE CAPACITY VS TEMP
C/2 RATE (25 AMP)
NiCd
NiH2
AMPERE HOURS
70
60
50
40
30
10
20
30
TEMPERATURE °C
FIG 1
11/12/80

Figure 43-1

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1980 GSFC BATTERY WORKSHOP

LIST OF ATTENDEES

Philip Akers
FAA Headquarters AWS-130
800 Independence Ave., S.W.
Washington, DC 20591
(202) 426-8395

Maksim Aleksandrov
Code 663
NASA/GSFC
Greenbelt, MD 20771
(301) 344-6549

Albert C. Alfaro, 2nd Lt. USAF
USAF
20939 Anza Ave., #163
Torrance, CA 90503
(213) 542-2507

Gale O. Allen
Aerospace Corp.
P. O. Box 92960; SD-YRE
Los Angeles, CA 90009
(213) 648-5464

F. Alliegro
Exide
Yardley, PA 19067
(215) 493-7057

Walter Alsbach
INTELSAT
490 L'Enfant Plaza, S.W.
Washington, DC 20024
(202) 488-2638

Judith H. Ambrus
NASA Headquarters
RTS-6
Washington, DC 20546
(202) 755-2387

Arthur E. Anderson
Code 205
NASA/GSFC
Greenbelt, MD 20771
(301) 344-7443

Melvin M. Anderson
Bedford Engineering Corp.
3805 Mt. Vernon Ave.
Alexandria, VA
(703) 549-3930

Phillip Antoine
SAFT
156 Av de Metz
Romainville, France 93230
843-9361

Jon D. Armantrout
Lockheed Missiles & Space Co.
D/62-16, B/151, P. O. Box 504
Sunnyvale, CA 94086
(408) 742-4371

James D. Austin
Ball Aerospace Systems
P. O. Box 1062
Boulder, CO 80306
(303) 441-4574

Charles Badcock
The Aerospace Corporation
P. O. Box 92957/ MS A6/2657
Los Angeles, CA 90009
(213) 648-5180

Dave Baer
Code 711.2
Building 11, Room E208
NASA/GSFC
Greenbelt, MD 20771
(301) 344-5541

Dr. G. E. H. Ballard
Ballard Research Inc.
1155 15th Street West
N. Vancouver, BC
CANADA, V7P 1M8
(604) 986-5411

Wilbert L. Barnes
Naval Research Laboratory
4555 Overlook Ave., S.W.
Washington, DC 20375
(202) 545-6700

Philip W. Barnhart
JHU/APL
Johns Hopkins Road
Laurel, MD 20810
(301) 953-7100

Richard L. Beauchamp
Johnson Controls, Inc.
Post Office Box 591
Milwaukee, WI 53201
(414) 228-2361

John R. Beck
Canadian Astronautics Ltd.
1024 Morrison Dr.
Ottawa, Ontario
CANADA, K2H 8K7
(613) 820-8280

Louis Belove
Marathon Battery Co.
8301 Imperial Drive
Waco, TX 76710
(817) 776-0650

Jim Bene
NASA-Langley Res. Center
Langley Station
Hampton, VA 23665
(804) 827-3541

Charles W. Bennett
General Electric Re-entry
Systems Division
3198 Chestnut St.
Philadelphia, PA 19101
(215) 823-4345

Peter Benson
Gould Inc.
931 No. Vandalia St.
St. Paul, MN
(612) 645-8531

M. P. Bernhardt
Bell Labs, Room 1E-203
Mountain Ave.
Murray Hill, NJ 07974
(201) 582-3000

Fred Betz
Code 7048
Naval Research Lab.
Washington, DC 20375
(202) 767-2635

T. A. Bierman
Honeywell Power Sources Center
104 Rock Road
Horsham, PA 19044
(215) 674-3800

Samuel Birken
Aerospace Corporation
P. O. Box 92957
Los Angeles, CA 90009
(213) 648-6080

Frank Bis
R-33
NSWC, White Oak
Silver Spring, MD 20910
(301) 545-6700

L. J. Blagdon
Honeywell Power Sources Center
104 Rock Road
Horsham, PA 19044
(215) 674-3800

R. S. Bogner
S-12, V330
Hughes Aircraft
Airport Station
Los Angeles, CA
(213) 615-7200

F. M. Bowers
11817 Indigo Road
Silver Spring, MD 20906
(301) 946-9361

Alfred Britting
JPL
4800 Oak Grove Dr.
Pasadena, CA 91103
(213) 354-7998
354-7826

Dr. P. Bro
Southwestern Electrochemical Co.
P. O. Box 2031
Santa Fe, NM 87501
(505) 982-1286

Richard J. Broderick
NASA/GSFC
Code 711.1
Greenbelt, MD 20771
(301) 344-5073

Harry Brown
Naval Weapons Support Center
Bldg. 34, Code 3054
Crane, IN 47522
(812) 854-1599

Ernest Busboso
NASA/GSFC
Code 743.4
Greenbelt, MD 20771
(301) 344-5802

Don Bush
Sandia Laboratories
Division 2525
Albuquerque, NM 87185
(505) 844-6432

Robert B. Byrnes
U.S. Army
4316 San Carlos Dr.
Fairfax, VA 22030
(703) 273-9583

Stewart M. Chodosh
Power Conversion, Inc.
70 MacQuesten Pkwy. So.
Mt. Vernon, NY 10550
(914) 699-7333

John A. Christopolous
USA ERADCOM
DELET-PB ET & DL
Fort Monmouth, NJ 07703
(201) 544-4246

Virgil Cleveland
NASA/GSFC
Code 420
Greenbelt, MD 20771
(301) 344-5560

Jack Clifford
Battelle Laboratories
505 King Ave.
Columbus, OH 43201
(614) 424-5351

James S. Cloyd
U.S. Air Force
AFWAL/POOC-1
Wright-Patterson AFB, OH 45433
(513) 255-6235

Joseph Colbourn
NASA/GSFC
Code 513
Greenbelt, MD 20771
(301) 344-7154

Dennis Cooper
INTELSAT
490 L'Enfant Plaza, S.W.
Washington, DC 20024
(202) 488-0176

F. S. Cushing
Exide Corporation
19 W. College Ave.
Yardley, PA 19067
(215) 493-7189

Dr. Chester Dacres
Electrochemistry Branch - R33
Naval Surface Weapons Center
White Oak, Silver Spring, MD 20910
(301) 545-6700

Steven Dallek
NSWC/White Oak
R33
Silver Spring, MD 20910
(301) 545-6700

W. H. Dempsey, Jr.
Naval Sea Systems Command
Washington, DC 20362
(202) 692-2080

Robert A. DePaul
MPD Technology Corp.
681 Lawlins Road
Wyckoff, NJ 07481
(201) 891-7911

Gabriel J. DiMasi
USA Electronics Technology
and Devices Lab (ERADCOM)
Power Sources Div.
DELET-PB
Fort Monmouth, NJ 07703
(201) 544-4281

Sal DiStefano
JPL
4800 Oak Grove Dr., 67-201
Pasadena, CA 91103
(213) 354-4321

Dick Doty
Motorola Inc.
8000 W. Sunrise Blvd.
Ft. Lauderdale, FL 33322
(305) 475-6102

Sharon Draper
COMSAT Labs
22300 Comsat Drive
Clarksburg, MD 20734
(301) 428-4546

James D. Dunlop
COMSAT Laboratories
Clarksburg, MD 20734
(301) 428-4546

David Dwyer
Sanders Associates
NCA 1-3004/95 Canal Street
Nashua, NH 03061
(603) 885-3361

C. K. Dyer
Bell Labs
600 Mountain Avenue
Murray Hill, NJ 07974
(201) 582-3000

Marty Earl
COMSAT Labs
22300 Comsat Drive
Clarksburg, MD 20734
(301) 428-4503

Robert R. Eliason
Lockheed Missiles & Space Co.
1184 N. Mathilda Avenue
Sunnyvale, CA 94086
(408) 742-4470

Bob Eslaire
USAF/Space Division
21872 Seaside Lane
Huntington Beach, CA 92646
(213) 643-0709

Bob Estes
Consumer Product Safety Comm.
Washington, DC 20207
(202) 634-7700

Joseph O. Faweuf
GTE Products Corp.
189 B Street
Needham Hgts., MA 02194
(617) 449-2000

Vladimir Feiman
EIC Laboratories Inc.
55 Chapel Street
Newton, MA 02158
(617) 965-2710 X39

Ralph Feldhake
Ray-O-Vac
630 Forward Drive
Madison, WI 53711
(608) 252-7400

Dr. W. A. Ferrando
NSWC/White Oak
Bldg. 24-9, New Hampshire Ave.
Silver Spring, MD 20910
(301) 394-2730

Harold Field
Motorola Inc.
8000 W. Sunrise Blvd.
Ft. Lauderdale, FL 33322
(305) 475-5562

John E. Finnegan
Bell Laboratories
Murray Hills, NJ 07974
(201) 582-3000

John A. Flyzik
RCA Service Company
P. O. Box 666
Bellevue, NE 68005
(402) 291-3745

Floyd Ford
Code 711
Building 11, Room E214
NASA/GSFC
Greenbelt, MD 20771
(301) 344-5845

P. G. Fougere
SAFT
156 Av De Metz
Romainville, France 93230
843-9361

Harvey A. Frank
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, CA 91103
(213) 354-4157

Jay Frank
Naval Ocean Systems Center
Code 8105
271 Catalina Blvd.
San Diego, CA 92152
(714) 225-7072

Carol Freeman
NSWC/White Oak
R-33
Silver Spring, MD 20910
(301) 394-1146

David H. Fritts
USAF-AFAPL/POCC-1
Wright-Patterson AFB, OH 45433
(513) 255-2372

Edward M. Gaddy
Code 711
NASA/GSFC
Greenbelt, MD 20771
(301) 344-6202

Anthony K. Galassi
Hughes Aircraft Company
P. O. Box 339
Springfield, VA 22150
(703) 664-9606

Martin G. Gandel
Lockheed Missiles & Space Co.
Dept. 62-16, Bldg. 151
Sunnyvale, CA 95070
(408) 742-8301

Stanley J. Garlock
LearSiegler Instrument Division
4141 Eastern Ave., S.E.
Grand Rapids, MI 49508
(616) 241-7447

S. Gaston
RCA Astro-Electronics
P. O. Box 800, Mail Stop 113
Princeton, NJ 60850
(609) 448-3400 X2559

Franz Goebel
GTE Sylvania
520 Winter Street
Waltham, MA 02154
(617) 890-9200

Olga Gonzalez
NASA/Lewis Research Center
MS 309-1, 21000 Brook Pk. Rd.
Cleveland, OH 44135
(216) 433-4000

H. R. Grady
Foote Mineral Company
Route 100
Exton, PA 19341
(215) 363-6500

Charles Russell Greer
Code 663.2
NASA/GSFC
Greenbelt, MD 20771
(301) 344-6817

Ian Gutridge
MPD Technology Corp.
681 Lawlins Road
Wyckoff, NJ 07481
(201) 891-7911

Douglas Hafen
Lockheed Missiles & Space
D/62-16, B/151, P. O. Box 504
Sunnyvale, CA 94086
(408) 742-4371

Gerald Halpert
NASA/GSFC, Code 711.2
Greenbelt, MD 20771
(301) 344-5752

Frederick C. Hallberg
Code 683.1
NASA/GSFC
Greenbelt, MD 20771
(301) 344-8712

James D. Harkness
Naval Weapons Support Center
Bldg. 2919, Code 3053
Crane, IN 47522
(812) 854-1593

Dr. A. G. Hellfritzsch
608 Winona Court
Silver Spring, MD 20902
(301) 649-2664

Ed Hendee
Telesat Canada
333 River Road
Ottawa, Ontario
CANADA, KIL-8B9
(613) 746-5920

Thomas J. Hennigan
Bedford Engineering Corp.
900 Fairoak Avenue
W. Hyattsville, MD 20783
(301) 559-0613

Don Hess
Department of the Navy
NESEA
St. Inigoes, MD 20684
(301) 862-8067

H. Peter Hirschler
Building 126-T
Naval Underwater Systems Center
Newport, RI 02840
(401) 841-3884

Gerhard L. Holleck
EIC Laboratories Inc.
55 Chapel Street
Newton, MA 02158
(617) 965-2710

H. T. Holter
Naval Sea Systems Command
Washington, DC 20362
(202) 692-2080

Franklin J. Hornbuckle
Fairchild Space and Electronic
20301 Century Blvd.
Germantown, MD 20767
(301) 428-6221

Paul L. Howard
P. L. Howard Associates Inc.
P. O. Box K
Millington, MD 21651
(301) 928-5101

H. C. Huber
Navy Dept., Code AIR-54901H
Naval Air Systems Command
Washington, DC 20361
(202) 692-7150

Mathew Imamura
Martin Marietta Aerospace
P. O. Box 179
Denver, CO 80201
(303) 977-3000

Bruce Jagid
President
Power Conversion Inc.
70 MacQuesten Parkway S.
Mt. Vernon, NY 10550
(914) 699-7333

Dr. Stanley D. James
NSWC/White Oak
Code R-33/New Hampshire Ave.
Silver Spring, MD 20910
(301) 394-2730

Daniel Johnson
Union Carbide
P. O. Box 6056
Cleveland, OH 44101
(216) 631-3100

Dr. Joseph D. Jolson
Catalyst Research Corp.
1421 Clarkview Road
Baltimore, MD 21209
(301) 296-7000

Gordon L. Juvinall
TRW Ballistic Missiles Div.
P. O. Box 1310, MS 524/420
San Bernadino, CA 92402
(714) 382-5797

Gail Kaczorowski
NASA/GSFC
Code 205
Greenbelt, MD 20771
(301) 344-5894

Emanuel Karageorge
Code 663.1
NASA/GSFC
Greenbelt, MD 20771
(301) 344-5382

Joseph M. Keogh
U.S. Army
1409 Patrick Circle
Vienna, VA 22180
(703) 698-1344

Randy Kientz
General Electric Company
P. O. Box 114
Gainesville, FL 32601
(904) 462-3911

Dr. William P. Kilroy
NSWC/White Oak
R-33/New Hampshire Avenue
Silver Spring, MD 20910
(301) 394-1513

Kwang Yil Kim
Honeywell CTC
10701 Lyndale Avenue South
Bloomington, MN 55420
(612) 931-6460

Michael P. Kimmey
3503 Woodmoor Rd.
Baltimore, MD 21207
(301) 265-6435

Charles Koehler
Ford Aerospace & Communications
G-3
Palo Alto, CA 94303
(415) 494-7400 X5053

Paul W. Kuhl
Electrochem Ind. Inc.
9990 Wehrle Dr.
Clarence, NY 14031
(716) 759-2828

Vasanth L. Kunigahalli
Code 711
Bldg. 22, Room 341
Goddard Space Flight Center
Greenbelt, MD 20771
(301) 344-5751

Irving Kurman
Aerospace Corporation
P. O. Box 92957
Los Angeles, CA 90009
(213) 648-7573

Joseph Lackner
DND/DREO/ECD
Shirley Bay
Ottawa, Ontario
CANADA, K1A 0Z4
(613) 836-1731

Terry M. Lamb
USAF
P. O. Box 92960; SD-YRE
Los Angeles, CA 90009
(213) 643-2850

Robert D. Lane
Electrochem Industries Inc.
9990 Wehrle Dr.
Clarence, NY 14031
(716) 759-2828

John W. Lear
Martin Marietta Corp.
6819 N. Ridgeway Circle
Parker, CO 80134
(303) 977-1511

Harold F. Leibecki
NASA Lewis Research Center
MS 302/1
2100 Brookpark Road
Cleveland, OH 44135
(216) 433-4000

Joseph H. Letourneau
NASA/GSFC
Code 205
Greenbelt, MD 20771
(301) 344-7444

Samuel Levy
Division 2523
Sandia National Labs
P. O. Box 5800
Albuquerque, NM 85185
(505) 844-8029

Hong S. Lim
Hughes Research Laboratories
3011 Malibu Canyon Rd.
Malibu, CA 90265
(213) 456-6411

David Linden
78 Lovett Avenue
Little Silver, NJ 07739
(201) 741-2271

Chuck Lurie
M1/1406
TRW DSSG
Redondo Beach, CA 90278
(213) 535-0777

John S. Lynch
Vought Corp. (Unit 51700)
P. O. Box 225907
Dallas, TX 75265
(214) 266-7144

Gary Lyons
Howard Textile Mills, Inc.
20 Roosevelt Avenue
Roslyn, NY 11576
(516) 621-4414

George H. Mackie
Canadian Dept. of Commerce
P. O. Box 11490, Station H
Ottawa, Ontario
CANADA, K2H 5K3
(613) 828-8629

Dr. Tyler X. Mahy
Apt. T-1, 130 Duvall Lane
Gaithersburg, MD 20760
(703) 351-2908

Don Mains
Naval Weapons Support Center
Code 3053
Crane, IN 47522
(812) 854-1593

Paul Malachesky
Exxon Enterprises
P. O. Box 45
Linden, NJ 07036
(201) 474-6369

Lynn Marcoux
Hughes Aircraft Company
Building S 12, MS V330
P. O. Box 92919 Airport Station
Los Angeles, CA 90009
(213) 615-7200

Charles H. Marcus
NASA/GSFC
Code 205
Greenbelt, MD 20771
(301) 344-7441

G. T. Marsh
Martin Marietta Corp.
P. O. Box 179
Mail Stop S0550
Denver, CO 80201
(303) 977-4485

James H. Masson
Martin Marietta Corp.
P. O. Box 179,
Mail Stop S0550
Denver, CO 80201
(303) 977-4485

D. W. Maurer
Rm. 1E243
Bell Laboratories
Murray Hill, NJ 07974
(201) 582-3000

Joseph H. McCann, Jr.
RCA/PSEG-Suitland
9012 Stevens Lane
Lanham, MD 20801
(301) 459-0791

Patrick McDermott
NASA/GSFC
Code 711.2
Greenbelt, MD 20771
(301) 344-5752

Bruce McDonald
Duracell International,
Lithium Systems Division
175 Clearbrook Road
Elmsford, NY 10523
(914) 592-3556

George J. Methlie
2705 N. Jefferson Street
Arlington, VA 22207
(703) 533-1499

C. J. Meyer
GTE Sylvania
1800 N. Kent Street
Arlington, VA 22307
(703) 841-9020

Nora Middlemiss, PhD.
Ontario Research Foundation
Sheraton Park,
Mississauga, Ontario
CANADA, L5K 1D3
(416) 822-4111 X 247

Ronald P. Mikkelson
General Dynamics/Convair
MZ 41-6070, P. O. Box 80847
San Diego, CA 92138
(714) 277-8900 X1486

Lee Miller
Eagle-Picher Ind., Inc.
P. O. Box 47, C & Porter St.
Joplin, MO 64801
(417) 623-8000

A. J. Miserendino
GTE Sylvania Inc.
520 Winter Street
Waltham, MA 02154
(617) 890-9200

Carl Mueller
NSWC/White Oak
Code R33, Room 4-171
Silver Spring, MD 20910
(301) 394-2472

Vernon C. Mueller
McDonnell Douglas Astro. Co.
Dept. E-454, Bldg. 106
MS 408, P. O. Box 516
St. Louis, MO 63166
(314) 232-1003

Edward B. Murphy
MIT Lincoln Lab
Box 73
Lexington, MA 02173
(617) 862-5500 X450

Dr. Robert M. Murphy
Electrochem Industries, Inc.
9990 Wehrle Drive
Clarence, NY 14031
(716) 759-2828

Buddy D. Murray
Martin Marietta
5873 W. Alder Ave.
Littleton, CO 80123
(303) 977-4485

Dr. J. Myatt
Building 152
AERE
Harwell, Oxfordshire OX11ORA
England
235-24141

Walter Nagel
Code 745.2
NASA/GSFC
Greenbelt, MD 20771
(301) 344-5939

T. O'Sullivan
Bell Labs
Murray Hill, NJ 07974
(201) 582-3000

Burton Otzinger
Rockwell International
SL-10/12214 Lakewood Blvd.
Downey, CA 90241
(213) 594-3783

Charles J. Pace
GTE Products
SSD Div.
89 B Street
Needham, MA 02192
(617) 449-2000

Charles F. Palandati
Code 711.2
Bldg. 22, Rm. 290
NASA/GSFC
Greenbelt, MD 20771
(301) 344-5379

John M. Parry
Arthur D. Little Inc.
25 Acorn Park
Cambridge, MA 02140
(617) 864-5730

Dr. Ben Patton
Theromo Electron Corp.
1736 I St., N.W.
Suite 807
Washington, DC 20006
(202) 861-0510

Dr. W. F. Payne
Canadian Astronautics Ltd.
1024 Morrison Dr.
Ottawa, Ontario
CANADA, K2H 8K7
(613) 820-8280

Florido S. Pe
Bedford Engineering Corp.
Alexandria, VA
(703) 549-3930

Wilfredo Perez
Rm. 171 (R33)
NSWC/White Oak
Silver Spring, MD 20910
(301) 394-1318

Tim Potts
Eagle-Picher Ind.
C & Porter Sts.
Joplin, MO 64801
(417) 623-8000 X345

Dr. A. J. Prasad
Hyderabad Batteries Ltd.
D-31, I.D.A., Jeedimetla
Hyderabad, India 500854

Dr. Vincent J. Puglisi
Yardney Nickel Battery Division
82 Mechanic Street
Pawtucket, CT 06379
(203) 599-1100

Rod K. Quinn
Org. 2523
Exploratory Batteries Div.
Sandia National Laboratories
Albuquerque, NM 87185
(505) 844-1933

Matiar Rahman
Bedford Engineering Corp.
3805 Mt. Vernon Ave.
Alexandria, VA 22305
(703) 549-3930

N. S. Raman
Duracell International
N. Tarrytown, NY
(914) 631-4014

Guy G. Rampel
General Electric
Box 114
Gainesville, FL 32602
(904) 462-3521

Bert E. Reeves 2-35160
Vought Corporation
P. O. Box 225907
Dallas, TX 75265
(214) 266-4160

Edward Reiss
Electronics R & D Command
DELET-PB
Ft. Monmouth, NJ 07703
(201) 544-4211

Don Righter
Code 661
NASA/GSFC
Greenbelt, MD 20771
(301) 344-6816

M. K. Riseborough
British Aerospace Dynamics Grp.
Site B, Gunnelswood Road
Stevenage Hertfordshire
England
0438-3456

Paul F. Ritterman
TRW
1 Space Park
Redondo Beach, CA
(213) 535-0777

G. B. Robinson
Code 480
NASA/GSFC
Greenbelt, MD 20771
(301) 344-8934

Dr. Howard H. Rogers
Hughes Aircraft Company
B S-12/MS V330, P. O. Box 92919
Los Angeles, CA 90009
(213) 648-0480

Douglas Rusta
TRW/DSSG
One Space Park, M1/1208
Redondo Beach, CA 90278
(213) 535-4321

Milan Ruzicka
Bureau of Natl. Affairs, Inc.
1231 25th Street, N.W.
Washington, DC 20037
(202) 452-4417

Albert C. Sadilek
JHU/APL
Johns Hopkins Road
Laurel, MD 20810
(301) 953-7100

William R. Sadler
8800 Nero St.
Annandale, VA 22003
(703) 978-9193

Irwin Schulman
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, CA 91103
(213) 354-6094

Ronald Schwartz
Naval Air Development Center
Code 30421
Warminster, PA 18974
(215) 441-2181

Willard R. Scott
TRW Defense & Space Systems Grp.
M1-1406, One Space Park Dr.
Redondo Beach, CA 90278
(213) 535-0777

Charles Scuilla
5501 Starboard Dr.
Fairfax, VA 22030
(703) 351-2908

Dr. Harvey N. Seiger
Harvey N. Seiger Associates
8 Beacon Hill Drive
Waterford, CT 06385
(203) 443-5886

Keith Senderak
Naval Weapons Support Center
Code 3052
Crane, IN 47522
(812) 854-1593

Eddie T. Seo
The Gates Rubber Company
P. O. Box 5887
Denver, CO 80217
(303) 744-4614

Philippe P. Seurin
SAFT America Inc.
711 Industrial Blvd.
Valdosta, GA 31601
(912) 244-7390

John Sindorf
Johnson Controls
900 E. Keefe Ave.
Milwaukee, WI 53218
(414) 228-2719

Dennis Sorenson
Gould Inc.
931 No. Vandalia St.
St. Paul, MN
(612) 645-8531

Steven J. Stadnick
Senior Project Engineer
Hughes Aircraft Company
Space & Communications Group
P. O. Box 92919
Los Angeles, CA 90009
(213) 648-9322

Irv Stein
Jet Propulsion Labs
4800 Oak Grove Dr., MS 198-220
Pasadena, CA 91103
(213) 354-6048

David Stewart
RCA - American Communications
400 College Road East
Princeton, NJ 08540
(609) 734-4122

Joseph Stockel
COMSAT Laboratories
Clarksburg, MD 20734
(301) 428-4545

Dr. R. A. Sutula
NSWC/White Oak
Bldg. 24-9, New Hampshire Ave.
Silver Spring, MD 20910
(301) 394-2730

L. Swette
Giner, Inc.
14 Spring Street
Waltham, MA 02154
(617) 899-7270

Michael Tasevoli
Code 711.2
Bldg. 11, Rm. E208
NASA/GSFC
Greenbelt, MD 20771
(301) 344-6691

David Taub
Electrochem Industries
9990 Wehrle Drive
Clarence, NY 14031
(716) 759-2828

Dr. H. Taylor
Duracell Internat'l, Inc.
Lab. of Physical Science
Northwest Industrial Park
3rd Avenue
Burlington, MA 01803
(617) 272-4100 X23

H. E. Thierfelder
General Electric Space Division
Box 8555
Philadelphia, PA 19101
(215) 962-3028

Sid Tiller
Code 711.2
NASA/GSFC
Greenbelt, MD 20771
(301) 344-5379

Dr. Harri Vaidyanathan
Energy Research Corporation
#3 Great Pasture Road
Danbury, CT 06810
(207) 792-1460

G. Van Ommering
Ford Aerospace & Comm.
3939 Fabian Way - MS-G31
Palo Alto, CA 94303
(415) 494-7400 X6359

Dr. D. Verma
Embassy of India
2107 Massachusetts Ave., N.W.
Washington, DC 20008
(202) 677-0519

Scott A. Verzwyvelt
Hughes Research Laboratories
3011 Malibu Canyon Road
Malibu, CA 90265
(213) 456-6411

B. Vyas
Bell Labs
600 Mountain Ave., Room 1E-207
Murray Hill, NJ 07974
(201) 582-3000

C. Richard Walk
Bedford Engineering Corp.
3805 Mount Vernon Ave.
Alexandria, VA 22305
(703) 549-3930

Donald L. Warburton
NSWC/White Oak
Code R33
Silver Spring, MD 20910
(301) 394-2316

Don R. Warnock
AFWAL/POOC-1
Wright-Patterson AFB, OH 45433
(513) 255-6235

Robert A. Warriner
Hughes Aircraft Co.
10181 Firwood Dr.
Cupertino, CA 95014
(408) 745-3148

Donald A. Webb
McDonnell Douglas Astro. Co.
Dept. E-454, Bldg. 106
MS 408, P. O. Box 516
St. Louis, MO 63166
(314) 232-1003

Howard Weiner
The Aerospace Corporation
Bldg. A-1, MS 5066
P. O. Box 92957
Los Angeles, CA 90009
(213) 648-6272

John L. Westrom
NASA/GSFC
Code 711.3
Greenbelt, MD 20771
(301) 344-8885

Robert Wigand
Code 853
GSFC
Greenbelt, MD 20771
(301) 344-8681

Dr. A. H. Willis
MS 8C62
Boeing Aerospace Corporation
P. O. Box 3999
Seattle, WA 98124
(206) 773-2994

P. Willmann
ESA-ESTEC
Zwarteweg 62 2200 AG
Noordwijk, The Netherlands

I. David Yalom
10813 East Nolcrest Drive
Silver Spring, MD 20903
(301) 593-1973

Dave Yedwab
Arradcom Bldg. 65 N.
Dover, NJ 07801
(201) 328-3058

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16. Abstract

This, the 13th Annual Battery Workshop was attended by manufacturers, users, and government representatives interested in the latest results of testing, analysis, and development. The purpose of the Workshop was to share flight and test experience, stimulate discussion on problem areas, and to review the latest technology improvements.

The papers presented in this document have been derived from transcripts taken at the Workshop held at the Goddard Space Flight Center on November 18-20, 1980. The transcripts were lightly edited with the speaker's vugraphs assembled at the end of each presentation for uniformity.

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