SPACE ELECTROCHEMICAL RESEARCH AND TECHNOLOGY

NASA Lewis Research Center
Cleveland, Ohio
April 11-13, 1989

NASA CP-10029
AGENDA
SPACE ELECTROCHEMICAL RESEARCH AND TECHNOLOGY CONFERENCE
NASA LEWIS RESEARCH CENTER
CLEVELAND, OHIO
APRIL 11-13, 1989

Tuesday, April 11, 1989

7:30 a.m. Registration, coffee and doughnuts (Adm. Bldg.)

8:30 a.m. Welcome
J. Stuart Fordyce,
Director, Aerospace Technology Directorate, NASA Lewis
Research Center

8:40 a.m. Henry W. Brandhorst, Jr.,
Chief, Power Technology Division, NASA Lewis Research Center

8:50 a.m. Opening Remarks
Gregory Reck,
Director, Propulsion, Power, & Energy Division, NASA
Headquarters

Related Overviews

9:00 a.m. Introduction
Patricia O'Donnell,
Deputy Chief, Electrochemical Technology Branch,
NASA Lewis Research Center

9:05 a.m. LEO & GEO - Overview of Battery Usage in NASA/GSFC
LEO & GEO Missions
John Serlemitsos, NASA Goddard Space Flight Center

9:20 a.m. Planetary - The Importance of Batteries in Unmanned Missions
John W. Klein, Jet Propulsion Laboratory

9:35 a.m. Advanced Mission Studies - Human Exploration Mission Studies
Robert L. Cataldo, NASA Lewis Research Center

9:50 a.m. Air Force - Air Force Space Battery/Fuel Cell Program
R. A. Marsh, Wright Research & Development Center

10:05 a.m. Break

Technical Sessions

10:15 a.m. Advanced Concepts
Chairperson
John Appleby, Texas A&M University
Co-Chairperson
Michelle Manzo, NASA Lewis Research Center

10:20 a.m. A Survey of Advanced Battery Systems for Space Applications
Alan I. Attia, Jet Propulsion Laboratory
10:40 a.m. Novel Nitrogen-Based Organosulfur Electrodes for Advanced Intermediate Temperature Batteries  
S. J. Visco, Lawrence Berkeley Laboratory

11:00 a.m. Advanced Rechargeable Sodium Batteries With Novel Cathodes  
S. Di Stefano, Jet Propulsion Laboratory

11:20 a.m. Monolithic Solid Oxide Fuel Cell Development  
K. M. Myles, Argonne National Laboratory

11:40 a.m. The Electrochemical Generation of Useful Chemical Species From Lunar Materials  
Anthony F. Sammells, Eltron Research, Inc.

12:00 noon A New Concept for High-Cycle-Life LEO: Rechargeable MnO2-Hydrogen  
A. J. Appleby, Texas A&M University

12:20 p.m. Lunch

1:40 p.m. Characterization Testing of a 40 Ahr Bipolar Nickel Hydrogen Battery  
Jeffrey C. Brewer, NASA Marshall Space Flight Center

2:00 p.m. Advanced Double Layer Capacitors  
P. Lessner, GINER, INC.

2:20 p.m. Hydrogen-Oxygen Fuel Cells and Electrolyzers  
Chairperson  
James Huff, Los Alamos National Laboratory  
Co-Chairperson  
Paul Prokopius, NASA Lewis Research Center

2:25 p.m. Recent Advances in Solid Polymer Electrolyte Fuel Cell Technology With Low Platinum Loading Electrodes  
Supramaniam Srinivasan, Texas A&M University

2:45 p.m. The Application of Dow Chemical's Perfluorinated Membranes in Proton-Exchange Membrane Fuel Cells  
G. A. Eisman, Dow Chemical Company

3:05 p.m. Hydrogen-Oxygen Proton-Exchange Membrane Fuel Cells and Electrolyzers  
J. McElroy, Hamilton Standard

3:25 p.m. Break

3:35 p.m. Electrocatalysts for Oxygen Electrodes in Fuel Cells and Water Electrolyzers for Space Applications  
Ernest Yeager, Case Western Reserve University

3:55 p.m. Oxygen Electrodes for Rechargeable Alkaline Fuel Cells  
L. Swette, GINER, INC.

4:15 p.m. Non-Noble Electrocatalysts for Alkaline Fuel Cells  
P. Lessner, GINER, INC.
4:35 p.m. Corrosion Testing of Candidates for the Alkaline Fuel Cell Cathode
Joseph Singer, NASA Lewis Research Center

5:30 – Social
7:30 p.m. (Visitor Information Center)

Wednesday, April 12, 1989

8:00 a.m. Registration, coffee and doughnuts

8:25 a.m. **Nickel Electrode**
**Chairperson**
Albert Zimmerman, Aerospace Corporation

**Co-Chairperson**
Margaret Reid, NASA Lewis Research Center

8:30 a.m. Structural Comparison of Nickel Electrodes and Precursor Phases
Bahne C. Cornilsen, Michigan Technological University

8:50 a.m. Impedance Studies of Ni/Cd and Ni/H Cells Using the Cell Case as Reference Electrode
Margaret A. Reid, NASA Lewis Research Center

9:10 a.m. The Application of Electrochemical Impedance Spectroscopy for Characterizing the Degradation of Ni(OH)₂/NiOOH Electrodes
Digby D. Macdonald, SRI International

9:30 a.m. KOH Concentration Effect on the Cycle Life of Nickel-Hydrogen Cells. IV. Results of Failure Analyses
H. S. Lim, Hughes Aircraft Company

9:50 a.m. Advances in Lightweight Nickel Electrode Technology
James R. Wheeler, Eagle-Picher Industries, Inc.

10:10 a.m. Break

10:20 a.m. **Advanced Rechargeable Batteries**
**Chairperson**
Gerald Halpert, Jet Propulsion Laboratory

**Co-Chairperson**
John Smithrick, NASA Lewis Research Center

10:25 a.m. Multi-Mission Ni-H₂ Battery Cell for the 1990's
Gary Dodson, Eagle-Picher Industries, Inc.

10:45 a.m. Nickel-Hydrogen Capacity Loss on Storage
Michelle A. Manzo, NASA Lewis Research Center

11:05 a.m. Hydrogen Embrittlement in Nickel-Hydrogen Cells
Sidney Gross, Boeing Aerospace

11:25 a.m. Sodium-Sulfur Battery Flight Experiment Definition Study
Rebecca R. Chang, Ford Aerospace Corporation
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| 11:45 a.m. | Advanced High-Temperature Batteries  
Paul A. Nelson, Argonne National Laboratory                                                                                           |
| 12:05 p.m. | Advances in Ambient Temperature Secondary Lithium Cells  
S. Subbarao, Jet Propulsion Laboratory                                                                                              |
| 12:25 p.m. | Lunch                                                                                                                                   |
| 1:35 p.m.  | Introduction to Workshops  
Patricia O'Donnell, NASA Lewis Research Center                                                                                     |
| 1:45 - 4:45 p.m. | Workshop Sessions                                                            |
| 4:45 - 5:45 p.m. | Workshop Summary Preparation                                                 |
| 6:00 - 8:00 p.m. | Social and Dinner  
(Main Cafeteria)                                                                    |

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**Workshop Summary Presentations**

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| 9:30 a.m.  | Workshop Summaries  
Chairperson Remarks  
Patricia O'Donnell, NASA Lewis Research Center                                                                                   |
| 9:40 a.m.  | Advanced Concepts Workshop Summary                                                                                                    |
| 10:10 a.m. | Hydrogen-Oxygen Fuel Cells and Electrolyzers Workshop Summary                                                                        |
| 10:40 a.m. | Nickel Electrode Workshop Summary                                                                                                    |
| 11:10 a.m. | Advanced Rechargeable Batteries Workshop Summary                                                                                      |
| 11:40 a.m. | Closing Remarks                                                                                                                        |
| 12:00 noon| Adjourn                                                                                                                                |
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Co-Chairperson: Michelle Manzo, NASA Lewis Research Center

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OVERVIEW OF BATTERY USAGE IN NASA/GSFC LEO & GEO MISSIONS

Thomas Yi
NASA Goddard Space Flight Center
Greenbelt, Maryland

An overview of the batteries used in the LEO and GEO missions at Goddard Space Flight Center is described.

In July, 1989, Cosmic Background Explorer (COBE) will be launched from a Delta rocket to study the big bang theory. COBE, which is in a LEO/Polar orbit, will have two 20 Ah NiCd batteries, 18 cells per battery, made by McDonnell Douglas Company. The predicted mission DOD is 0 to 24% over one 63-day eclipse season, the predicted mission temperature, 16°C to 22°C, and the specification mission duration, 1 year.

In December, 1989, National Oceanic and Atmospheric Administration (NOAA-D) will be launched from an Atlas rocket for weather observation purposes. NOAA-D, which is in a LEO/Polar morning orbit, will have two 26.5 Ah NiCd batteries, 17 cells per battery, made by GE-Astro East Windor. The predicted mission DOD is 0 to 16%, the predicted mission temperature, 5°C, and the specification mission duration, 2 years. NOAA-I, which is scheduled for May, 1991 launch in a LEO/Polar afternoon orbit, will have three 26.5 Ah NiCd batteries, 17 cells per battery, made by GE-Astro East Windor. The predicted mission DOD is 18%, the predicted mission temperature, 5°C, and the specification mission duration, 2 years. NOAA-J is scheduled for July, 1992 launch, and NOAA-K, November, 1993.

In April, 1990, Gamma Ray Observatory (GRO) will be launched from STS37 to study the gamma ray radiation phenomenon. GRO, which is in a LEO orbit, will have two modular power systems (MPS) made by McDonnell Douglas, each MPS consisting of three 50 Ah NiCd batteries, 22 cells per battery. The predicted mission DOD is 15%, the predicted mission temperature, 15°C, and the specification mission duration, 2 years.

In July, 1990, Geostationary Operational Environmental Satellite (GOES-I) will be launched from an Atlas I rocket for weather observation purposes. GOES-I, which is in a GEO orbit, will have two 12 Ah NiCd batteries, 28 cells per battery, made by Ford Aerospace and Communications Company. The predicted mission DOD is 60%, the predicted mission temperature, 70°C, and the specification mission duration, 5 years. GOES-J is scheduled for November, 1991 launch, and GOES-K, for May, 1992 launch.

In December, 1990, Tracking and Data Relay Satellite (TDRS-E) will be launched from STS43 for communication purposes. TDRS-E, which is in a GEO orbit, will have three 40 Ah NiCd batteries, 24 cells per battery, made by TRW. The predicted mission DOD is 50%, the predicted mission temperature, 5°C, and the specification mission duration, 10 years. TDRS-F is scheduled for December, 1992 launch, and TDRS-G for May, 1994 launch.

In August, 1991, Extreme Ultraviolet Explorer (EUVE) will be launched from a Delta rocket. EUVE, which is in a LEO orbit, will have one modular power system (MPS) made by McDonnell Douglas. The predicted mission DOD is 15%, the
predicted mission temperature, 15°C, and the specification mission duration, 3 years.

In December, 1991, Upper Atmosphere Research Satellite (UARS) will be launched from STS50 to study the Earth's ozone layer and other environmental concerns. UARS, which is in a 56° inclination LEO orbit, will have one modular power systems (MPS) made by McDonnell Douglas. The predicted mission DOD is 0 to 24%, the predicted mission temperature, 10° to 16°C, and the specification mission duration, 3 years.

In addition to these missions, the GSFC has a number of Smaller Explorer missions to be launched from the Scout rockets. The battery requirements for these spacecrafts have not yet been determined.
THE IMPORTANCE OF BATTERIES IN UNMANNED MISSIONS

John W. Klein
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

The author will present a brief overview of the current set of unmanned missions that are currently in operation and those planned for the next 5 to 10 years. In this discussion, the author will detail the important role that batteries have come to play in the development of successful missions.

The author will discuss the workhorse battery, the NiCd, and its use throughout historical missions. Its role on Observers and Landers will be discussed and the success those batteries had.

The author will also spend time discussing the recent events in the issues of quality and life for NiCd batteries. These discussions will focus on the current design activities for Mars Observer, TOPEX, and Mariner Mark II. Of particular note will be the discussion on separator selection and the need for uniform testing procedures to develop a quality battery product that can perform to mission requirements. The recent experiences with the GRO battery failure and the other events have led JPL to the decision to develop a testing program in conjunction with other NASA centers to determine the best separator material for these two missions. Timing, however, is critical. The decision for separator material and battery design must be made a year from now. Thus there will not be time to perform a total 2-year accelerated test. So as in all cases, compromises will be made. The author will discuss JPL's plan for coping with this compromise.

The author will close with a discussion of where NiH₂ batteries are beginning to have an impact and the difficulties from a system point of view with their implementation. Such missions at EOS and the NOAA series of satellites rely upon NiH₂ for success but were not chosen for TOPEX or MO due to their large volume requirements.
The nation's efforts "to expand human presence and activity beyond Earth orbit into the solar system" was given renewed emphasis in January of 1988 when the Presidential Directive on National Space Policy was signed into effect. The expansion of human presence into the solar system has particular significance, in that it defines long-range goals for NASA's future missions. To embark and achieve such ambitious ventures is a significant undertaking, particularly compared to past space activities.

Two major efforts recently released, the National Commission on Space report, "Pioneering the Space Frontier," 1986, and astronaut Dr. Sally Ride's task force report, "Leadership and America's Future in Space," 1987, have helped set goals and give focus to NASA's future direction. Dr. Ride's task force formulated a plan to achieve the Commission's proposed agenda for the civilian space program. The task force recommended four initiatives: (1) Mission to Planet Earth, (2) Exploration of the Solar System, (3) Outpost on the Moon, and (4) Humans to Mars. The first two initiatives, to a great degree, are being pursued by NASA's Office of Space Science and Applications. However, the last two initiatives prompted the task force to recommend that a special NASA office be established to coordinate and lead human exploration studies. Therefore, the Office of Exploration was established to provide a focal point for these activities. These include establishing a mature understanding of mission options and opportunities and defining those near-term activities that can provide the greatest impact on future missions.

The Office of Exploration has established a process whereby all NASA field centers and other NASA Headquarters offices participate in the formulation and analysis of a wide range of mission strategies. These strategies were manifested into specific scenarios or candidate case studies. The case studies provided a systematic approach into analyzing each mission element. First, each case study must address several major themes and rationale including: national pride and international prestige, advancement of scientific knowledge, a catalyst for technology, economic benefits, space enterprise, international cooperation, and education and excellence. Second, the set of candidate case studies are formulated to encompass the technology requirement limits in the life sciences, launch capabilities, space transfer, automation and robotics in space operations, power, and propulsion.

The first set of reference case studies identify three major strategies: (1) human expeditions, (2) science outposts, and (3) evolutionary expansion. During the past year, four case studies were examined to explore these strategies. The expeditionary missions include the Human Expedition to Phobos and Human Expedition to Mars case studies. The Lunar Observatory and Lunar Outpost to Early Mars Evolution case studies examined the later two strategies. This set of case studies established the framework to perform detailed mission analysis and system engineering to define a host of concepts and requirements for various space systems and advanced technologies. This paper describes the details of each mission and, specifically, the results affecting the advanced technologies required to accomplish each mission scenario.
AIR FORCE SPACE BATTERY/FUEL CELL PROGRAM

R. A. Marsh
Wright Research & Development Center
Wright-Patterson Air Force Base, Ohio

(Abstract was not available at time of printing.)
The results of a survey on advanced secondary battery systems for space applications are presented. The objectives were: (1) to identify advanced battery systems capable of meeting the requirements of various types of space missions, with significant advantages over currently available batteries, (2) to obtain an accurate estimate of the anticipated improvements of these advanced systems, and (3) to obtain a consensus for the selection of systems most likely to yield the desired improvements. 205 battery experts from government, industry, and universities were invited to respond to a questionnaire on advanced batteries and their potential applications in space; 55 responded.

In the opinion of the respondents, few advanced systems are likely to exceed a specific energy of 150 Wh/kg and meet the additional requirements of safety and reliability within the next 15 years. The few that have this potential are:

1) Regenerative fuel cells, both alkaline and solid polymer electrolyte (SPE) types for large power systems.

2) Lithium-intercalatable cathodes, particularly the metal oxides intercalatable cathodes (MnO₂ or CoO₂), with applications limited to small spacecrafts requiring limited cycle life and low power levels.

3) Lithium molten salt systems (e.g., LiAl-FeS₂).

4) Na/Beta" Alumina/Sulfur or metal chlorides cells.

Likely technological advances that would enhance the performance of all the above systems are also identified, in particular:

1) Improved bifunctional oxygen electrodes.

2) Improved manufacturing technology for thin film lithium electrodes in combination with polymeric electrolytes.

3) Improved seals for the lithium molten salt cells.

4) Improved ceramics for sodium/solid electrolyte cells.
Advanced secondary batteries operating at intermediate temperatures (100 to 200°C) have attracted considerable interest due to their inherent advantages (reduced corrosion and safety risks) over higher temperature systems. Current work in this laboratory has involved research on a novel class of intermediate temperature Na/beta'-alumina/RSSR batteries conceptually similar to Na/S cells, but operating within a temperature range of 100 to 150°C, and having an organosulfur rather than inorganic sulfur positive electrode. The organosulfur electrodes are based on the reversible, two electron reduction of organodisulfides to the corresponding thiolate anions, \( \text{RSSR} + 2e^- \rightarrow 2\text{RS}^- \), where R is an organic moiety. Among the advantages of such a generic redox couple for battery research is the ability to tailor the physical, chemical, and electrochemical properties of the RSSR molecule through choice of the organic moiety. The viscosity, liquidus range, dielectric constant, equivalent weight, and redox potential can in fact be verified in a largely predictable manner. The current work concerns the use of multiple nitrogen organosulfur molecules, chosen for application in Na/RSSR cells for their expected oxidizing character. In fact, a Na/RSSR cell containing one of these materials, the sodium salt of 5-mercapto-1-methyltetrazole, yielded the highest open circuit voltage obtained yet in our laboratory; 3.0 volts in the charged state and 2.6 volts at 100% discharge. Accordingly, the cycling behavior of a series of multiple nitrogen organodisulfides as well as polymeric organodisulfides are presented in this manuscript.
Various high energy density rechargeable batteries are being considered for future space applications. Of these, the sodium-sulfur battery is one of the leading candidates. The primary advantage is the high energy density (760 Wh/kg theoretical). Energy densities in excess of 180 Wh/kg were realized in practical batteries. Other technological advantages include its chemical simplicity, absence of self-discharge, and long cycle life possibility.

More recently, other high temperature sodium batteries have come into the spotlight. These systems can be described as follows:

$$\text{Na/}\beta''-\text{Al}_2\text{O}_3/\text{NaAlCl}_4/\text{Metal Dichloride}$$

Sodium/metal dichloride systems are colloquially known as the zebra system and are currently being developed for traction and load leveling applications. The sodium-metal dichloride systems appear to offer many of the same advantages of the Na/S system, especially in terms of energy density and chemical simplicity, e.g.,

1. $2 \text{Na} + \text{FeCl}_2 \rightarrow 2 \text{NaCl} + \text{Fe}$, ~730 Wh/kg (theoretical)
2. $2 \text{Na} + \text{NiCl}_2 \rightarrow 2 \text{NaCl} + \text{Ni}$, ~790 Wh/kg (theoretical)
3. $2 \text{Na} + \text{CuCl}_2 \rightarrow 2 \text{NaCl} + \text{Cu}$, ~800 Wh/kg (theoretical)

These metal dichloride systems offer increased safety and good resistance to overcharge and operate over a wide range of temperatures from 150-400°C with less corrosion problems.

We at JPL are evaluating various new cathode materials for use in high energy density sodium batteries for advanced space applications. Our approach is to carry out basic electrochemical studies of these materials in a sodium cell configuration in order to understand their fundamental behaviors. Thus far, our studies have focused on alternate metal chlorides such as CuCl$_2$ and organic cathode materials such as TCNE. The preliminary findings of our studies will be presented.
The Monolithic Solid Oxide Fuel Cell (MSOFC) is being developed by a recently formed team comprised of Argonne National Laboratory, Allied-Signal Aerospace/AirResearch, and Combustion Engineering. The MSOFC is an oxide-ceramic structure in which appropriate electronic and ionic conductors are fabricated in a "honeycomb" shape similar to a block of corrugated paperboard. The electrolyte that conducts oxygen ions from the air side to the fuel side is yttria-stabilized zirconia (YSZ). All the other materials are electronic conductors including the nickel-YSZ anode, the strontium-doped lanthanum manganite cathode, and the doped lanthanum chromite interconnect (bipolar plate). These electronic and ionic conductors are arranged to provide short conduction paths to minimize resistive losses. The power density achievable with the MSOFC is expected to be about 8 kW/kg or 4 kW/L, at fuel efficiencies over 50%, because of small cell size and low resistive losses in the materials. The MSOFC operates in the range of 700 to 1000°C, at which temperatures rapid reform of hydrocarbon fuels is expected within the nickel-YSZ fuel channels.

Tape casting and hot roll calendering are used to fabricate the MSOFC structure. The tape casting process consists of spreading a ceramic slurry (slip) uniformly on a substrate, such as glass or polymer film, using a doctor blade. After the slip is dry, the ceramic layer is stripped off the substrate in the form of a flexible "tape." The hot roll calendering process consists of mixing ceramic powder with organic binder and plasticizer and rolling the warm mixture into a thin tape. The green tapes are cut to the desired dimensions, and the electrode tapes are corrugated to form the gas flow channels. The corrugations are formed by folding the tape onto a warm mold. After cooling, the tape retains the corrugated shape. Corrugated electrode tapes and flat electrolyte and interconnect composite tapes are stacked up to form the MSOFC structure. The layers are bonded together in the green state by heating the polymer binder slightly above its glass transition temperature under a small weight. The bonded green structure is then heated according to a precise firing schedule to the sintering temperature to form the monolithic ceramic structure.

The performance of the MSOFC has improved significantly during the course of development. The limitation of this system, based on materials resistance alone without interfacial resistances, is 0.093 ohm-cm² area-specific resistance (ASR). The current typical performance of MSOFC single cells is characterized by ASRs of about 0.4 to 0.5 ohm-cm². With further development the ASR is expected to be reduced below 0.2 ohm-cm², which will result in power levels greater than 1.4 W/cm².

The feasibility of the MSOFC concept has been proven, and the performance has been dramatically improved. The differences in thermal expansion coefficients and firing shrinkages among the fuel cell materials have been minimized. As a result of good matching of these properties, the MSOFC structure has been successfully fabricated with few defects, and the system shows excellent promise for development into a practical power source.
To be discussed here will be the current status of work in our laboratory on an electrochemical technology for the simultaneous generation of oxygen and lithium from a Li\textsubscript{2}O containing molten salt (Li\textsubscript{2}O-LiCl-LiF). The electrochemical cell utilizes an oxygen vacancy conducting solid electrolyte, yttria-stabilized zirconia, to effect separation between the oxygen evolving and lithium reduction half-cell reactions. The cell being studied possesses the general configuration:

\[
\begin{array}{|c|c|c|}
\hline
\text{FeSi}_{2}\text{Li}_{10} & \text{Li}_{2}\text{O}(20 \text{ m/o})\text{LiCl, LiF} & \text{O}^{2-}\text{-conducting} \\
\hline
\text{yttria-stabilized} & \text{zirconia} & \text{La}_{0.89}\text{Sr}_{0.11}\text{MnO}_{3} \\
\hline
\end{array}
\]

The cell, which operates at 700-800°C, possesses rapid electrode kinetics at the lithium-alloy electrode with exchange current density (\(i_0\)) values being \(>60\) mA/cm\(^2\), showing high reversibility for this reaction. When used in the electrolytic mode, lithium produced at the negative electrode would be continuously removed from the cell for later use (under lunar conditions) as an easily storable reducing agent (compared to H\(_2\)) for the chemical refining of lunar ores via the general reaction:

\[2\text{Li} + \text{MO} \rightarrow \text{Li}_{2}\text{O} + \text{M}\]

where MO represents a lunar ore. Emphasis to this time has been on the simulated lunar ore ilmenite (FeTiO\(_3\)), which we have found becomes chemically reduced by Li at 432°C. Furthermore, both Fe\(_2\)O\(_3\) and TiO\(_2\) have been reduced by Li to give the corresponding metal. The resulting Li\(_2\)O reaction product could then be removed from the solid-state reaction mixture by sublimation and reintroduced into the negative electrode compartment of the electrolytic cell. Hence, this electrochemical approach provides a convenient route for producing metals under lunar conditions and oxygen for the continuous maintenance of human habitats on the Moon's surface.

Because of the high reversibility of this electrochemical system, it has also formed the basis for the lithium-oxygen secondary battery. Prototype single cells are currently being fabricated and tested in our laboratory. This secondary lithium-oxygen battery system possesses the highest theoretical energy density yet investigated.

ACKNOWLEDGEMENTS

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A NEW CONCEPT FOR HIGH-CYCLE-LIFE LEO: RECHARGEABLE MnO₂-HYDROGEN

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The nickel-hydrogen secondary battery system is now the one of choice for use in GEO satellites. It offers superior energy density to that of nickel-cadmium, with a lifetime that is at least comparable in terms of both cycle life and overall operating life. While the number of deep cycles required for GEO use is small, LEO satellites with long lifetimes (5 to 10 years) will require secondary battery systems allowing 30,000 to 60,000 useful cycles which are characterized by an approximately 2C charge rate and C average discharge rate. These requirements are extremely difficult to attain with any existing battery system, though they can be attained with individual half-cells, especially those with non-consumable catalytic electrodes producing and consuming gaseous products.

The best example of such a system is the rechargeable bifunctional hydrogen electrode familiar from the nickel-hydrogen cell. This uses a platinum-based catalyst, which is immune to corrosion under all conditions. However, corrosion of the sintered nickel support of the nickel positive, combined with lattice contraction and expansion of active material during charge, eventually result in breakdown. This is a function of initial KOH concentration and range of discharge. As a result, the nickel-hydrogen system must be derated for LEO use, so that it offers only about 20 Wh/kg, instead of about 60 Wh/kg for a system designed for 100% depth-of-discharge.

Recent work has shown that birnessite MnO₂ doped with bismuth oxide can be cycled at very high rates (6C) over a very large number of cycles (thousands) at depths-of-discharge in the 85% - 90% range, based on two electrons, which discharge at the same potential in a flat plateau. The potential is about 0.7 V vs. hydrogen, with a cut-off at 0.6 V. At first sight, this low voltage would seem to be a disadvantage, since the theoretical energy density will be low. However, it permits the use of lightweight materials that are immune from corrosion at the positive. The high utilization and low equivalent weight of the active material, together with the use of teflon-bonded graphite for current collection, result in very light positives, especially when these are compared with those in a derated nickel-hydrogen system. In addition, the weight of the pressure vessel falls somewhat, since the dead volume is lower. Calculations show that a total system will have 2.5 times the Ah capacity of a derated nickel-hydrogen LEO battery, so that the energy density, based on 1.2 V for nickel-hydrogen and 0.7 V for MnO₂-hydrogen, will be 45% higher for comparable cycling performance.

Present work on this system concept, which involves microcalorimeter studies of self-discharge as well as cycling performance, will be described.
CHARACTERIZATION TESTING OF A 40 Ahr BIPOLAR NICKEL HYDROGEN BATTERY

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In a continuing effort to develop NiH₂ bipolar technology to a point where it can be used efficiently in space flight, Lewis Research Center (LeRC) has begun testing a second 40 Ahr, 10-cell bipolar battery. This battery, put on test in March, 1988, has undergone extensive characterization testing to determine the effects of such operating parameters as charge and discharge rates, temperature, and pressure.

The fundamental design of this actively cooled bipolar battery is the same as the first battery, also tested at LeRC. Most of the individual components, however, are from different manufacturers. Different testing procedures as well as certain unique battery characteristics make it difficult to directly compare the two sets of results. Some comparisons, however, can and will be made.

In general, the performance of this battery throughout characterization produced expected results. Varying the charge rate between C/4, C/2, and C had little effect on efficiencies while varying the discharge rate between C/4, C/2, C, and 2C had great effects on efficiencies, with C/4 producing the best results and 2C the worst. Temperature variations produced more puzzling results. Temperatures of 0°C, 10°C, 20°C, and 30°C were all used but not one of them showed a consistent efficiency advantage over the other three. End of charge voltages, however, did change -- decreasing as temperatures increased. Mid-point discharge voltages increased as temperatures increased, but only at the C and 2C rates. Initial tests also indicate a slight efficiency increase with an increase in vessel pressure from 200 to 400 psi. End of charge voltage appears to be unaffected by the increased pressure, but mid-point discharge voltages are slightly higher at the C/4 and C/2 discharge rates. An even greater difference is seen at the C and 2C rates.

The main differences seen between the first and second batteries occurred during the high-rate discharge portion of the test matrix. For the second battery, end-of-discharge voltage limits were reached within 15 seconds on the 10C constant current discharge rate and efficiencies of less than 30% were attained at the 5C constant current rate. Only during one-second-on, four-seconds-off SC pulse current cycle were reasonable results produced. The first battery also had poor high-rate discharge results, although better than those of the second battery. Minor changes were made to the battery frame design used for the first battery in an attempt to allow better gas access to the reaction sites for the second build and hopefully improve performance. The changes, however, did not improve the performance of the second battery and could have possibly contributed to the poorer performance that was observed. There are other component differences that could have contributed to the poorer performance of the second battery. The H₂ electrode in the
second battery was constructed with a Goretex backing which could have limited the high-rate current flow. The gas screen in the second battery had a larger mesh which again could have limited the high-rate current flow. Small scale 2" x 2" batteries are being tested to evaluate the effects of the component variations.

LEO cycle life testing at 40% DOD and 10°C is scheduled to follow the characterization.
There is a need for large amounts of power to be delivered rapidly in a number of airborne and space systems. Conventional, portable power sources, such as batteries, are not suited to delivering high peak power pulses. The charge stored at the electrode-electrolyte double layer is, however, much more accessible on a short time scale. Devices exploiting this concept have been fabricated using carbon (SOHIO) and metal oxides (Pinnacle Research) as the electrodes and sulfuric acid as the electrolyte.

One problem with using a solid electrode and a liquid electrolyte module is the possibility of leakage of the electrolyte because of the rupture of seals due to pressure external changes, overcharge, and other factors. The sulfuric acid electrolyte is highly corrosive, and leakage would be expected to lead to premature failure of the module. The approach reported here replaces the liquid sulfuric acid electrolyte with a solid ionomer electrolyte. The challenge is to form a solid electrode-solid ionomer electrolyte composite which has a high capacitance per geometric area.

The approach to maximize contact between the electrode particles and the ionomer has been to impregnate the electrode particles using a liquid ionomer solution and to bond the solvent-free structure to a solid ionomer membrane. Ruthenium dioxide is the electrode material used and is prepared in powder form by thermal decomposition of RuCl₃ in the presence of a fluxing agent. The ionomer solution chosen for the initial phase of the work contains Nafion 117 (Nafion ionomers are perfluorosulfonated ionomers made by E. I. DuPont). It is purchased as a 5% solution in alcohol-water solvent. Three strategies are being pursued to provide for a high area electrode-ionomer contact:

1. Mixing of the RuOₓ with a small volume of ionomer solution followed by evaporation of the solvent,
2. Mixing of the RuOₓ with a large amount of ionomer solution followed by filtration to remove the solvent, and
3. Impregnation of the ionomer into an already formed RuOₓ electrode.

After impregnation and solvent removal, electrodes are bonded to a Nafion 117 membrane and their electrochemical behavior is examined by cyclic voltammetry and AC impedance techniques. The reference (Hg/HgSO₄) and counter electrodes are in 1M H₂SO₄. Voltammograms showed the beginning of voltammetric waves at -0.275 V and +0.65 V vs. Hg/HgSO₄. The cathodic wave is due to the reduction of RuOₓ while the anode wave is limited to the beginning of oxygen evolution. The 0.925 V window between these reactions represents the usable voltage range. Capacitances were derived by plotting current density vs. sweep rate at 0.1 V vs. Hg/HgSO₄. Capacitances of up to 60 mF/cm² have been observed.

RuOₓ powder and electrodes have also been examined by non-electrochemical techniques. X-ray diffraction has shown that the material is almost pure RuO₂. BET surface area of the powder is approximately 50 m²/g. The electrode structure depends on the processing technique used to introduce the Nafion. Impregnated electrodes have Nafion concentrated near the surface. Electrodes prepared by the evaporation method show large aggregates of crystals.
surrounded by Nafion. Research is focusing on methods to make more uniform electrode-electrolyte contact.

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RECENT ADVANCES IN SOLID POLYMER ELECTROLYTE FUEL CELL TECHNOLOGY
WITH LOW PLATINUM LOADING ELECTRODES

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There is great enthusiasm for the development of high power density fuel cell systems for defense and civilian applications. Taking into consideration the main causes for efficiency losses—activation, mass transport and ohmic overpotentials—the only fuel cell systems capable of achieving high power densities are the ones with alkaline and solid polymer electrolyte. High power densities (0.8 W/cm² at 0.8 V and 1 A/cm² with H₂ and O₂ as reactants), have already been well demonstrated in the International Fuel Cells/United Technologies Corporation alkaline fuel cell systems used in NASA’s Apollo and Space Shuttle flights as auxiliary power sources. Even higher power densities (4 W/cm²—i.e., 8 A/cm² at 0.5 V) have been reported by the USAF/International Fuel Cells in advanced versions of the alkaline system.

Historically, the first type of fuel cell system to find a major application (auxiliary power source in the Gemini Space Vehicles) is the one with solid polymer electrolyte as the electrolyte. These fuel cell systems were developed by the General Electric Company. Since the sixties, great strides have been made in increasing the power density from 50 mW/cm² to about 2-3 W/cm². The latter performance was achieved at Ballard Technologies Corporation which used practically the same technology as General Electric Company/United Technologies Corporation—Hamilton Standard. The platinum loading in these fuel cells is 4 mg/cm² on each electrode.

Research and Development at Los Alamos National Laboratory and in our laboratory has led to the attainment of high power densities (~1 watt/cm²) in solid polymer electrolyte fuel cells with ten times lower platinum loading in the electrodes (i.e., 0.4 mg/cm²). The necessary criteria and the methods used to attain these goals are as follows:

1. Extension of the three dimensional reaction zone by the impregnation of a proton conductor (i.e., the ion-exchange membrane) into the electrode structure.
2. Hot pressing of the proton-exchange membrane and electrodes at a temperature above the glass transition temperature and at a pressure of 50 atm.
3. Adequate humidification of the reactant gases by passing these gases through humidification chambers set at temperatures of 10°C for H₂ and 5°C for oxygen or air higher than the cell temperature.
4. Enhancement of the electrode kinetics of the hydrogen oxidation and the oxygen reduction reactions and particularly of the mass transport rates of the reactant gases to the electrode by operation at elevated temperatures and pressures, say 95°C and 5 atm.
5. Localization of the platinum near the front surface of the electrode to reduce the thickness of the active layer and provide a higher concentration of platinum sites on the front surface to reduce mass transport and ohmic overpotentials within the porous electrode and at the electrode/electrolyte interface.
Improvement of the conductivity and water retention of the solid polymer electrolyte by use of perfluorinated sulfonic acid membranes with lower equivalent weight (i.e., more sulfonic acid groups per polymer molecule) than Nafion.

Using all the above methods, it is now possible to reach a cell potential of 0.620 V at a current density of 2 A/cm² and at a temperature of 95°C and pressure of 4/5 atm with H₂/O₂ as reactants. The slope of the linear region of the potential-current density plot for this case is 0.15 ohm-cm². With H₂/air as reactants and under the same operating conditions, mass transport limitations are encountered at current densities above 1.4 A/cm². Thus, the cell potential at 1 A/cm² with H₂/air as reactants is less than that with H₂/O₂ as reactants by 40 mV, which is the expected value based on electrode kinetics of the oxygen reduction reaction, and at 2 A/cm² with H₂/air as reactant is less than the corresponding value with H₂/O₂ as reactants by 250 mV, which is due to the considerably greater mass transport limitations in the former case.
THE APPLICATION OF DOW CHEMICAL'S PERFLUORINATED MEMBRANES IN PROTON-EXCHANGE MEMBRANE FUEL CELLS

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Dow Chemical's research activities in fuel cell devices revolves around the development and subsequent investigation of the perfluorinated ionomeric membrane separator useful in proton-exchange membrane systems. Work is currently focusing on studying the effects of equivalent weight, thickness, water of hydration, pretreatment procedures, as well as the degree of water management required for a given membrane separator in the cell. The presentation will include details of certain aspects of the above as well as some of the requirements for high and low power generation.
Hydrogen-oxygen SPE fuel cells and SPE electrolyzers (products of Hamilton Standard) both use a Proton-Exchange Membrane (PEM) as the sole electrolyte. These solid electrolyte devices have been under continuous development for over 30 years. This experience has resulted in a demonstrated ten-year SPE cell life capability under load conditions.

Ultimate life of PEM fuel cells and electrolyzers is primarily related to the chemical stability of the membrane. For perfluorocarbon proton-exchange membranes an accurate measure of the membrane stability is the fluoride loss rate. Millions of cell hours have contributed to establishing a relationship between fluoride loss rates and average expected ultimate cell life. Figure I shows this relationship. Several features have been introduced into SPE fuel cells and SPE electrolyzers such that applications requiring >100,000 hours of life can be considered.

**FIGURE I.** EXPECTED LIFETIMES OF SPE CELLS WITH PERFLUOROCARBON PROTON-EXCHANGE MEMBRANES
Equally important as the ultimate life is the voltage stability of hydrogen-oxygen fuel cells and electrolyzers. Here again the features of SPE fuel cells and SPE electrolyzers have shown a cell voltage stability in the order of 1 microvolt per hour. That level of stability has been demonstrated for tens of thousands of hours in SPE fuel cells at up to 500 amps per square foot (ASF) current density. SPE electrolyzers have demonstrated the same at 1000 ASF.

Many future extraterrestrial applications for fuel cells require that they be self recharged (i.e., regenerative fuel cells). This requirement means that a dedicated fuel cell and a dedicated electrolyzer work in tandem as an electrical energy storage system. Some applications may find advantage with a unitized regenerative fuel cell (i.e., one cell that operates alternately as a fuel cell and as an electrolyzer). Electrical energy storage for earth orbits via hydrogen-oxygen regenerative fuel cell systems can have specific energies in excess of 50 watt-hours/kg. For extraterrestrial surface electrical energy storage the hydrogen-oxygen regenerative fuel cell can have significantly increased specific energies:

- Mars Base ~ 500 watt-hours/kg
- Lunar Base ~ 1000 watt-hours/kg

To translate the proven SPE cell life and stability into a highly reliable extraterrestrial electrical energy storage system, a simplification of supporting equipment is required. Static phase separation, static fluid transport and static thermal control will be most useful in producing required system reliability. Although some 200,000 SPE fuel cell hours have been recorded in earth orbit with static fluid phase separation, no SPE electrolyzer has, as yet, operated in space.

Under NASA sponsorship a flight experiment of a unitized regenerative fuel cell is being studied. If selected for actual flight under the NASA OAST Outreach Project, several advanced features will be tested in space:

- reversible SPE cell (unitized)
- passive fuel cell product water separation and removal
- passive electrolyzer process water introduction
- passive electrochemical gas pumping
- passive heat management

The objective of the flight experiment is to test the space viability of the incorporated features, and not to imply that the specific configuration of the flight experiment is optimum for any given extraterrestrial application. With a successful flight experiment, supported by terrestrial experiments, the system designer can select the proven advanced system features that are appropriate for any particular extraterrestrial application.
In most instances separate electrocatalysts are needed to promote the reduction of \( \text{O}_2 \) in the fuel cell mode at to generate \( \text{O}_2 \) in the energy storage - water electrolysis mode in aqueous electrochemical systems operating at low and moderate temperature \((T < 200^\circ \text{C})\). This situation arises because, even with relatively high performance catalysts, the \( \text{O}_2 \) reduction and generation reactions are still quite irreversible with much overpotential. The potentials of the \( \text{O}_2 \) electrode in the cathodic and anodic modes are separated by typically 0.6 V and the states of the catalyst surface are very different. Interesting exceptions are the lead and bismuth ruthenate pyrochlores in alkaline electrolytes. These catalysts on high area carbon supports have high catalytic activity for both \( \text{O}_2 \) reduction and generation \((1,2)\). Furthermore, rotating ring-disk electrode measurements provide evidence that the \( \text{O}_2 \) reduction proceeds by a parallel four-electron pathway. The ruthenates can also be used as self-supported catalysts to avoid the problems associated with carbon oxidation, but the electrode performance so far achieved in the research at CWRU is considerably less. The possibility exists, however, of supporting these catalysts on a stable electronically-conducting high area oxide support such as a perovskite.

At the potentials involved in the anodic mode the ruthenate pyrochlores have substantial equilibrium solubility in concentrated alkaline electrolyte. This results in the loss of catalyst into the bulk solution and a decline in catalytic activity. Furthermore, the hydrogen generation counter electrode may become contaminated with reduction products from the pyrochlores (lead, ruthenium).

A possible approach to this problem is to immobilize the pyrochlore catalyst within an ionic-conducting solid polymer, which would replace the fluid electrolyte within the porous gas diffusion \( \text{O}_2 \) electrode. For bulk alkaline electrolyte, an anion-exchange polymer is needed with a transference number close to unity for the \( \text{OH}^- \) ion. Such a membrane may not block completely the transport of the lead and ruthenium, which are expected to be in complex anionic forms. Preliminary short-term measurements with lead ruthenates using a commercially available partially-fluorinated anion-exchange membrane as an overlayer on the porous gas-fed electrode indicate lower anodic polarization and virtually unchanged cathodic polarization. The leakage of soluble Pb and Ru species from the catalyst through the ionomer membrane will be evaluated. Other methods of applying polymer layers over the gas-fed electrodes or incorporating the polymer within the electrode will be discussed.

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References:


The primary objective of this program is the investigation and development of electrocatalysts and supports for the positive electrode of moderate temperature single-unit rechargeable alkaline fuel cells. Viable candidate materials must meet the following requirements: (1) good electrical conductivity (a more demanding requirement for supports than electrocatalysts), (2) high resistance to chemical corrosion and electrochemical oxidation and/or reduction, and (3) electrocatalysts, in addition, must exhibit high bifunctional electrocatalytic activity (O₂ evolution and reduction). Advanced development will require that the materials be prepared in high surface area forms, and may also entail integration of various candidate materials, e.g., one or two electrocatalysts distributed on a less active support material.

Candidate support materials have been drawn from transition metal carbides, borides, nitrides (Ti, Zr, Hf, Nb) and oxides (La, Sr, Cr, Mo, W, Mn, Ni) which have high conductivity (>1 ohm-cm⁻¹). Candidate catalyst materials have been selected largely from metal oxides of the form ABOₓ (where A = Pb, Cd, Mn, Ti, Zr, La, Sr, Na, and B = Pt, Pd, Ir, Ru, Ni, Co) which have been investigated and/or developed for one function only, O₂ reduction or O₂ evolution. The electrical conductivity requirement for catalysts may be lower, especially if integrated with a higher conductivity support. For initial evaluation, materials have been purchased when available; subsequently, in-house preparations have been attempted, to affect surface area and composition, if necessary.

All candidate materials of acceptable conductivity are subjected to corrosion testing in three steps. Preliminary corrosion testing consists of exposure to 30% KOH at 80°C under oxygen for several days. Materials that survive chemical testing are examined for electrochemical corrosion activity; the material is held at 1.4 V versus RHE in 30% KOH at 80°C for 15 to 20 hours. An acceptable anodic current is on the order of a few microamps/mg of material. For more stringent corrosion testing, and for further evaluation of electrocatalysts (which generally show significant O₂ evolution at 1.4 V), samples are held at 1.6 V or 0.6 V for about 100 hours. The surviving materials are then physically and chemically analyzed for signs of degradation (visual examination, electron microscopy, X-ray diffraction).

To evaluate the bifunctional oxygen activity of candidate catalysts, Teflon-bonded electrodes are fabricated and tested in a floating electrode configuration. Many of the experimental materials being studied have required development of a customized electrode fabrication procedure. For preliminary testing, catalysts of interest should show <500 mV polarization (from 1.2 V) in either mode at 200 mA/cm². In advanced development, our goal is to reduce the polarization to about 300-350 mV.

Approximately six support materials and five catalyst materials have been identified to date for further development. The test results will be described.
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NON-NOBLE ELECTROCATALYSTS FOR ALKALINE FUEL CELLS

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Noble metals, when used as electrocatalysts for oxygen reduction in alkaline fuel cells, suffer from the disadvantages of high cost, susceptibility to poisoning and sintering. Carbons activated with macrocyclics have attracted increasing attention as alternative electrocatalysts for oxygen reduction. Initial activity of these catalysts is good, but performance declines rapidly. Pyrolyzing the macrocyclic on the carbon support leads to enhanced stability and the catalysts retain good activity.

Despite this promising method of treating macrocyclic-activated carbon catalysts, the performance decay is still too large to be acceptable. The approach described here is designed to develop bulk doped catalysts with similar structures to pyrolyzed macrocyclic catalysts. The transition metal and coordinated ligands are dispersed throughout the bulk of the conductive carbon skeleton.

Two approaches to realizing this concept are being pursued, both involving the doping of carbon precursors. In one approach, the precursor is a solid phase carbon-containing ion-exchange resin. The precursor is doped with a transition metal and/or nitrogen, and the resulting mixture is pyrolyzed. In the other approach, the precursor is a gas-phase hydrocarbon. This is introduced with a transition metal species and nitrogen species into a reactor and pyrolyzed. This paper will mainly discuss work conducted using the solid-phase pyrolysis approach.

For the solid-phase precursors, ion-exchange resins were selected. Weak acid cation-exchange resins and chelating resins have been used. Dopants have included Fe$^{3+}$ (from FeCl$_3$), Fe(bipy)$_3$SO$_4$ and NH$_4$OH. Typical pyrolysis temperatures have ranged from 700-900°C.

Gas-phase pyrolysis is carried out in a tube furnace. The gas-phase precursor, ammonia (the nitrogen source), and the iron-containing organometallic are introduced into the reactor. The heated zone of the furnace is maintained at a temperature of 1000°C.

Electrochemical tests are performed using the floating electrode technique. The electrodes are tested at 80°C in 7M KOH.

Several studies have been conducted to determine if there is a synergistic effect between the transition metal and nitrogen and the effect of different methods of introducing the M-N coordination on performance.

One approach was to introduce the metal and nitrogen separately, for example, by sequentially doping FeCl$_3$ and NH$_4$OH into the resin. Catalysts were prepared from an undoped ion-exchange resin, a resin doped only with N, a resin doped only with Fe, and a resin doped with both Fe and N. Introduction of nitrogen alone has no beneficial effect on the performance of the catalysts. The introduction of the Fe alone significantly improves the performance in both the high and low current density regions. When both Fe
and N are introduced, the performance at lower current densities ("catalytic activity") is increased beyond that of the Fe-doped carbon, but the performance at higher current densities is similar to the carbon containing only Fe.

Catalysts prepared from resins-Fe(bipy)$_3$SO$_4$ precursors have performance that is only slightly less than CoTMPP adsorbed and pyrolyzed on Vulcan XC-72. Their performance is much better than carbons which have had the N and Fe introduced separately.

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CORROSION TESTING OF CANDIDATES FOR THE ALKALINE FUEL CELL CATHODE

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It is desirable to employ a corrosion screening test for catalyst or support candidates for the fuel cell cathode before entering upon optimization of the candidate or of the catalytic electrode. To this end, corrosion test electrodes, intended for complete immersion and maximum wetting, have been made with 30-40 vol. % Teflon; with perovskites this is about 10-15 wt %. The candidates were synthesized by methods intended for single-phase product without special emphasis on high surface area, although the substances tested were no coarser than 2 m²/g. A typical loading was 25 mg/cm² of the pure substance, usually on gold screen, a few mm² of which were left bare for contacting. Contact to the gold lead wire was made by welding with a micro-torch or a spot-welder.

Corrosion testing consisted of obtaining current-voltage data under flowing inert gas in the potential region for reduction of O₂. The electrode was immersed in 30% KOH. Observations were made at 20°C and 80°C, and the results compared with data from gold standards. Results with some perovskites, pyrochlores, spinels, and interstitial compounds will be discussed.

Collaboration on this program with Physical Sciences, Inc. (Contract No. NAS3-25119) is gratefully acknowledged.
The solid state structure of the nickel electrode controls the electrochemical properties. Proton diffusion and electron conduction are examples of properties which critically depend upon the structure. Undesirable phases can cause battery failure. If we can define the critical structural components (including nonstoichiometry and disorder in fine particle size materials), it is possible to control the empirical variables to optimize the electrochemical properties. To do this we must know both how the structure controls properties and how the structure can be controlled during electrode preparation, including deposition and formation. Definition of structure allows one to sort out the complex property-preparation relationship. This third side of the triangle, which provides control of electrochemical properties, is defined if we know the other two sides, structure-property and structure-preparation.

In this paper we shall summarize our previous Raman spectroscopic results and discuss important structural differences in the various phases of active mass and active mass precursors. Raman spectra provide unique signatures for these phases, and allow one to distinguish each phase, even when the compound is amorphous to x-rays (i.e. does not scatter x-rays because of a lack of order and/or small particle size). The structural changes incurred during formation, charge and discharge, cobalt addition, and aging will be discussed and related to electrode properties.

Important structural differences include NiO₂ layer stacking, nonstoichiometry (especially cation-deficit nonstoichiometry), disorder, dopant content, and water content. Our results indicate that optimal nickel active mass is non-close packed and nonstoichiometric. The formation process transforms precursor phases into this structure. Therefore, the precursor disorder, or lack thereof, influences this final active mass structure and the rate of formation. Aging processes induce structural change which is believed to be detrimental. The role of cobalt addition can be appreciated in terms of structures favored or stabilized by the dopant.

In recent work, we have developed the in situ Raman technique to characterize the critical structural parameters. An in situ method is necessary if one wishes to relate structure, electrochemistry, and preparation. We collect in situ Raman spectra of cells during charge and discharge, either during cyclic voltammetry or under constant current conditions.

With the structure-preparation knowledge now on-hand, and the new in situ Raman tool, it will be possible to define the structure-property-preparation relations in more detail. This instrumentation has application to a variety of electrode systems.
Impedance Studies of Ni/Cd and Ni/H Cells Using the Cell Case as Reference Electrode

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Many impedance studies have been carried out on Ni electrodes and Ni/Cd and Ni/H batteries. Some studies have been made while the cells were being discharged, others at various open circuit voltages. The impedances have been found to be strongly dependent on depths-of-discharge and/or voltage and on the procedure used to obtain the measurements. The studies have been similar qualitatively but not quantitatively. In addition to the problem of reproducibility, a second problem arises when measuring complete cells which have no reference electrode as to which portion of the impedance can be attributed to the anode and which portion to the cathode. In order for impedance to become a diagnostic tool, accurate and reproducible measurements must be made, and some way of separating the contributions of the individual electrodes must be found.

Recent studies in our laboratories using the PAR and the Solartron impedance equipment have found that consistent measurements can be made if the cells or electrodes are equilibrated at the voltage of interest. In the charged state, equilibration times required are short, on the order of a few hours or less, but the equilibration time required becomes progressively longer as the voltage is lowered. We have also found that the cell case can be used as a reference electrode during impedance measurements. The voltage of the case with respect to the electrodes is unimportant provided that it does not change appreciably during the course of the measurement. Measurements have been made with several uncycled Ni/Cd cells, one from a lot which was known to have faulty Cd electrodes and another from a lot which showed excellent cycle life and presumably had good Cd electrodes. The impedances of the Ni electrodes vs. the case were similar, while the impedance of the poor Cd electrodes vs. the case were an order of magnitude greater than that of the good Cd electrode vs. the case. A 50 AH Ni/H cell has also been investigated. After subtraction of the ohmic resistances, the sums of the impedances of the individual electrodes were very close to the impedance of the total cell. This indicates that the method is valid for examining the characteristics of the individual electrodes in situ.
In this paper we describe the use of wide-band electrochemical impedance spectroscopy for characterizing the degradation of porous Ni(OH)$_2$/NiOOH electrodes in concentrated KOH electrolyte solutions. The impedance spectra are interpreted in terms of a finite electrical transmission line and the changes in the components of the electrical analog are followed as a function of cycle number. We show that the degradation of the capacity of rolled and bonded Ni(OH)$_2$/NiOOH electrodes is caused by rupture of ohmic contacts within the active mass and by restructuring which results in a decrease in the number of active pores.
KOH CONCENTRATION EFFECT ON THE CYCLE LIFE OF NICKEL-HYDROGEN CELLS.

IV. RESULTS OF FAILURE ANALYSES

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Effects of KOH concentrations on failure modes and mechanisms of nickel-hydrogen cells have been studied using long cycled boiler plate cells containing electrolytes of various KOH concentrations ranging 21 to 36%. Life of these cells were up to 40,000 cycles in an accelerated low earth orbit (LEO) cycle regime at 80% depth of discharge. An interim life test results were reported earlier in J. Power Sources, 22, 213-220, 1988. The present report will discuss the results of final life test, end-of-life cell performance, and teardown analyses. These teardown analyses included visual observations, measurements of nickel electrode capacity in an electrolyte-flooded cell, dimensional changes of cell components, SEM studies on cell cross section, BET surface area and pore volume distribution in cycled nickel electrodes, and chemical analyses.

Cycle life of a nickel-hydrogen cell was improved tremendously as KOH concentration was decreased from 36 to 31% and from 31 to 26% while effect of further concentration decrease was complicated as described in our earlier report. Failure mode of high concentration (31 to 36%) cells was gradual capacity decrease, while that of low concentration (21 to 26%) cells was mainly formation of a soft short. Long cycled (25,000 to 40,000 cycles) nickel electrodes were expanded more than 50% of the initial value, but no correlation was found between this expansion and measured capacity. All electrodes cycled in low concentration (21 to 26%) cells had higher capacity than those cycled in high concentration (31 to 36%) cells.
Studies are currently underway to further the development of lightweight nickel electrode technology. Work is focused primarily on the space nickel-hydrogen system and nickel-iron system but is also applicable to the nickel-cadmium and nickel-zinc systems. The goal is to reduce electrode weight while maintaining or improving performance thereby increasing electrode energy density. Two basic electrode structures are being investigated. The first is the traditional nickel sponge produced from sintered nickel-carbonyl powder and the second is a new material for this application which consists of a non-woven mat of nickel fiber. Electrodes are being manufactured, tested and evaluated at the electrode and cell level.
A sufficient production, test and operational database is now available to permit design technology optimization for the next decade. The evolved battery cell design features standardized technology intended to support multiple type missions (e.g., both GEO and LEO). Design analyses and validation test cells demonstrate improved performance plus attractive specific-energy characteristics will be achieved.
Nickel-hydrogen batteries are rapidly becoming accepted for use in low-earth-orbit and geosynchronous orbit applications. With their increased use it has become evident that the storage procedures commonly used for nickel-cadmium cells are not adequate for the nickel-hydrogen system. Frequently cells that have been stored, under varied conditions, have exhibited a significant loss of capacity. However, due to variations in test and handling procedures, much of the data available on capacity loss has been confusing and often conflicting. As a result, members of the Electrochemical Technology Branch at the Lewis Research Center conducted a controlled determination of the capacity loss exhibited by nickel electrodes from various manufacturers when exposed to different storage conditions.

A comprehensive test matrix was developed to evaluate capacity loss in nickel electrodes from four different manufacturers. Two types of tests were run; individual electrode tests, which involved flooded capacity and impedance measurements before and after storage under varied conditions of temperature, hydrogen pressure, and electrolyte concentration; and cell tests which primarily evaluated the effects of state-of-charge on storage. The electrode tests were run using electrodes from Hughes, Gates Aerospace Batteries, Whittaker-Yardney, and Eagle-Picher Industries, Inc. - Joplin. The cell tests were run only with Hughes electrodes. The cell tests evaluated capacity loss on cells stored open circuit, shorted and trickle charged at C/100 following a full charge.

The results indicate that capacity loss varies with the specific electrode manufacturing process, storage temperature and hydrogen pressure. In general, electrodes stored at low temperatures or low hydrogen pressures exhibited a smaller loss in capacity over the twenty-eight day storage period than those stored at high pressure and high temperature. The capacity loss appears to correlate with the level of cobalt in the nickel electrode, with the most significant loss of capacity occurring in electrodes with higher cobalt levels. Impedance measurements appear to correlate well with the capacity loss observed for a given type of electrode but do not correlate well with the capacity loss between electrodes fabricated by different manufacturers. There was a definite correlation between the electrode potential measured immediately following storage and the measured capacity loss.
HYDROGEN EMBRITTLEMENT IN NICKEL-HYDROGEN CELLS

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It has long been known that many strong metals can become weakened and brittle as the result of the accumulation of hydrogen within the metal. When the metal is stretched, it does not show normal ductile properties, but fractures prematurely. This problem can occur as the result of a hydrogen evolution reaction such as corrosion or electroplating, or due to hydrogen in the environment at the metal surface.

High strength alloys such as steels are especially susceptible to hydrogen embrittlement. Nickel-hydrogen cells commonly use Inconel 718 alloy for the pressure container, and this also is susceptible to hydrogen embrittlement. Metals differ in their susceptibility to embrittlement, however.

Hydrogen embrittlement in nickel-hydrogen cells is analyzed in this paper, and the reasons why it may or may not occur are discussed. Although Inconel 718 can display hydrogen embrittlement, experience has not identified any problem with nickel-hydrogen cells. No hydrogen embrittlement problem is expected with the 718 alloy pressure container used in nickel-hydrogen cells.
SODIUM SULFUR BATTERY FLIGHT EXPERIMENT DEFINITION STUDY

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Sodium-sulfur batteries have been identified as the most likely successor to nickel-hydrogen batteries for space applications. One advantage of the Na/S battery system is that the usable specific energy is two to three times that of nickel-hydrogen batteries. This represents a significant launch cost savings or increased payload mass capabilities. Na/S batteries support NASA OAST's proposed Civil Space Technology Initiative goal of a factor of two improvement in spacecraft power system performance, as well as the proposed Spacecraft 2000 initiative.

The sodium-sulfur battery operates at between 300 and 400°C, using liquid sodium and sulfur/polysulfide electrodes and solid ceramic electrolyte. The transport of the electrode materials to the surface of the electrolyte is through wicking/capillary forces. These critical transport functions must be demonstrated under actual microgravity conditions before sodium-sulfur batteries can be confidently utilized in space.

Ford Aerospace Corporation, under contract to NASA Lewis Research Center, is currently working on the sodium-sulfur battery space flight experiment definition study. The objective is to design the experiment that will demonstrate operation of the sodium-sulfur battery/ cell in the space environment with particular emphasis on evaluation of microgravity effects. Experimental payload definitions have been completed and preliminary designs of the experiment have been defined.
ADVANCED HIGH-TEMPERATURE BATTERIES

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Work has been under way for about two decades on high-temperature batteries having lithium or sodium negative electrodes. These efforts have met with some success but the original promise of very high specific energy and power has not yet been achieved for practical battery systems. This paper discusses some recent new approaches to achieving high performance for lithium/FeS$_2$ cells and sodium/metal chloride cells.

The main problems for the development of successful LiAl/FeS$_2$ cells have been (1) the instability of the FeS$_2$ electrode, which has resulted in rapidly declining capacity, (2) the lack of an internal mechanism for accommodating overcharge of a cell, thus requiring the use of external charge control on each individual cell, and (3) the lack of a suitable current collector for the positive electrode other than expensive molybdenum sheet material. Much progress has been made at ANL in solving the first two problems. Reduction of the operating temperatures to 400°C by a change in electrolyte composition has increased the expected life to 1000 cycles. Also, a lithium shuttle mechanism has been demonstrated for selected electrode compositions that permits sufficient overcharge tolerance to adjust for the normally expected cell-to-cell deviation in coulombic efficiency. Recent new work on bipolar cells indicates that the third problem might be solved for a bipolar battery by the use of a coating on the positive side of the cell dividers, which could result in a low-cost means of transmitting current from the positive electrode. Also, bipolar cells are very efficient in the use of structural material and other non-active materials in the cell. Calculations show that a specific energy of 200 Wh/kg and 300 W/kg could be achieved with this design for moderately thick electrodes. Tests of very thin electrodes of this type have demonstrated very high power for periods of less than a second; batteries having such electrodes may be appropriate for pulse-power applications.

Sodium/sulfur batteries and sodium/metal chloride batteries have demonstrated good reliability and long cycle life. For applications where very high power is desired, new electrolyte configurations would be required. Design work has been carried out at ANL for the sodium/metal chloride battery that demonstrates the feasibility of achieving high specific energy (190 Wh/kg) and high power (>400 W/kg at two-thirds open circuit voltage) for large (>200 Ah) battery cells having thin-walled high-surface area electrolytes. These electrolytes can be configured as small tubes (5 to 8 mm dia) joined together by a ceramic or metallic header or as a flat-plate compartmented electrolyte structure. Such structures were studied at ANL for the sodium/metal chloride system because of the limited power capabilities of that system at its operating temperature of 250°C or lower. The conclusion reached in that study, that high power can be achieved for large cells of this design, would seem to be valid for sodium/sulfur cells as well.

Future efforts to improve the performance and reliability of both lithium and sodium anode high-temperature batteries are expected to result in battery systems that meet the goals that were originally set when the development
efforts were first initiated: specific energy of about 220 Wh/kg and specific power of 300 to 400 W/kg.
JPL is involved in a R & D program sponsored by NASA/OAST on the development of ambient temperature secondary lithium cells for future space applications. Some of the projected applications are planetary spacecraft, planetary rovers, and astronaut equipment. The main objective of the program is to develop secondary lithium cells with greater than 100 Wh/kg specific energy while delivering 1000 cycles at 50% DOD. To realize these ambitious goals, the work was initially focused on several important basic issues related to the cell chemistry, selection of cathode materials and electrolytes, and component development. We have examined the performance potential of Li-TiS₂, Li-MoS₃, Li-V₆O₁₃ and Li-NbSe₃ electrochemical systems. Among these four, the Li-TiS₂ system was found to be the most promising system in terms of realizable specific energy and cycle life. Some of the major advancements made so far in the development of Li-TiS₂ cells are in the areas of cathode processing technology, mixed solvent electrolytes, and cell assembly. Methods were developed for the fabrication of large size high performance TiS₂ cathodes. Among the various electrolytes examined, 1.5M LiAsF₆/EC + 2-MeTHF mixed solvent electrolyte was found to be more stable towards lithium. Experimental cells activated with this electrolyte exhibited more than 300 cycles at 100% DOD. Work is in progress in other areas such as selection of lithium alloys as candidate anode materials, optimization of cell design, and development of 5 Ah cells. This paper summarizes the advances made at JPL on the development of secondary lithium cells.
This document contains the proceedings of NASA's second Space Electrochemical Research and Technology Conference, held at the NASA Lewis Research Center on April 11-13, 1989. The objectives of the conference were to examine current technologies, research efforts, and advanced ideas, and to identify technical barriers which affect the advancement of electrochemical energy storage systems for space applications. The conference provided a forum for the exchange of ideas and opinions of those actively involved in the field, with the intention of coalescing views and findings into conclusions on progress in the field, prospects for future advances, areas overlooked, and the directions of future efforts. Related overviews were presented in the areas of NASA advanced mission models. Papers were presented and workshops were conducted in four technical areas: advanced concepts, hydrogen-oxygen fuel cells and electrolyzers, the nickel electrode, and advanced rechargeable batteries. This document contains the overviews, the technical papers, and summaries of the technical workshops.