Status of the DOE Battery and Electrochemical Technology Program V

R. Roberts

Roberts Consultants, Inc.
Chevy Chase, Maryland

June 1985

Prepared by Roberts Consultants, Inc.
for Pacific Northwest Laboratory
under Contract DE-AC06-76RLO 1830
with the U.S. Department of Energy

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

NTIS Price Codes
Microfiche A01

Printed Copy

Pages	Price Codes
001-025	A02
026-050	A03
051-075	A04
076-100	A05
101-125	A06
126-150	A07
151-175	A08
176-200	A09
201-225	A010
226-250	A011
251-275	A012
276-300	A013

STATUS OF THE DOE BATTERY AND
ELECTROCHEMICAL TECHNOLOGY
PROGRAM V

R. Roberts

Roberts Consultants, Inc.
Chevy Chase, Maryland

June 1985

Prepared by Roberts Consultants, Inc.
for Pacific Northwest Laboratory
under Contract DE-AC06-76RL0 1830
with the U.S. Department of Energy
under Agreement B-L4300-A-V

Pacific Northwest Laboratory
Richland, Washington 99352

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to the participants at the Sixth DOE Electrochemical Contractor's Review (June 1984) for their cooperation in furnishing supplemental information and reviewing the technical content of the report. The continuing encouragement, advice, and assistance of the contract monitors: Carl H. Imhoff, Pacific Northwest Laboratory, and Jonathan Hurwitch, Battelle-Columbus Laboratories; and of Albert R. Landgrebe of DOE have been of great value.

Special thanks go to Susie Armstrong for her assistance in the preparation of the report, and D.M. Rutherford of Pacific Northwest Laboratory for his able handling of contractual arrangements.

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Energy Systems Research, Division of Energy Storage of the U.S. Department of Energy under Contract No. DE-AC06-76RL0 1830 through Subcontract B-L4300-A-V.

ABSTRACT

This report reviews the status of the Department of Energy (DOE) Electrochemical Energy Storage Branch (ECS) Program as of June 1984. Activities of related programs investigating the applicability of batteries and fuel cells in transportation, stationary energy storage, and solar energy systems are summarized.

The ECS program consists of two activities, Technology Base Research (TBR) managed by the Lawrence Berkeley Laboratory (LBL) and Exploratory Technology Development and Testing (ETD) managed by the Sandia National Laboratories (SNL).

The status of the Battery Energy Storage Test (BEST) Facility is presented, including the status of the batteries to be tested. ECS program contributions to the advancement of the lead-acid battery and specific examples of technology transfer from this program are given.

The advances during the period December, 1982 to June, 1984 in the characterization and performance of the lead-acid, iron/nickel-oxide, iron/air, aluminum/air, zinc/bromine, zinc/ferricyanide, and sodium/sulfur batteries and in fuel cells for transport are summarized. Novel techniques and the application of established techniques to the study of electrode processes, especially the electrode/electrolyte interface, are described.

Research with the potential of leading to improved ceramic electrolytes and positive electrode container and current-collectors for the sodium/sulfur battery is presented. Advances in the electrocatalysis of the oxygen (air) electrode and the relationship of these advances to the iron/air and aluminum/air batteries and to the fuel cell are noted. The quest for new battery couples and battery materials is reviewed.

New developments in the modeling of electrochemical cell and electrode performance with the approaches to test these models are reported. Of special note is the application of microelectronic technology to the preparation of a mosaic microelectrode for the study of gas bubble formation and the associated mass transport at an operating electrode.

EXECUTIVE SUMMARY

The Sixth Department of Energy (DOE) Electrochemical Contractor's Review, June 25-29, 1984, covered past accomplishments, continuing improvements in battery and electrochemical system performance, and related basic and applied research. These activities form the scientific and technological base for exploring alternative solutions and new approaches to energy conservation through advanced electrochemical technologies. Selected highlights from recent research are summarized below.

The past accomplishments resulting in technology transfer to industry or to mission-oriented federal agencies, such as the Department of Defense, were noted in the program of the Electrochemical Energy Storage (ECS) Branch. These accomplishments included:

- Gould, Inc.'s development of a maintenance-free, 6 volt, 100 ampere hour lead-acid battery for use in solar energy systems.
- Diamond Shamrock Corporation's and Case Western Reserve University's development of a platinum-based air electrode now being funded and evaluated by ELTECH Systems, Inc. for reducing energy in the chlor-alkali process.
- The Prototech-developed hydrogen electrode, which is being evaluated by EXXON for energy savings in zinc recovery.
- The initiation by the U.S. Air Force of the development of the Ford sodium/sulfur battery for satellite applications.
- The completion of negotiations between SOHIO and the National Aeronautics and Space Administration for continuing the development of the Redox battery.

In addition to Gould's development, several other advances in lead-acid battery technology are being used or evaluated by industry.

Sandia National Laboratories (SNL), under its Exploratory Technology Development and Testing (ETD) activities, is continuing its testing of batteries for solar energy systems and other stationary battery applications. SNL is also coordinating the activities of the Electric Vehicle Battery Testing Task Force.

Under the ETD activity, the combination of photovoltaics and battery storage has been shown to meet the daily variations in load demands for residential power at the Jacarilla Indian Reservation. The

Electric Vehicle Battery Task Force has reviewed and modified the electric vehicle battery test procedures.

The operation of the Battery Energy Storage Test (BEST) Facility by the Public Service Gas and Electric Co. has demonstrated the compatibility of lead-acid battery energy storage with the operation of an electric utility. The testing of a 500 kWh zinc/chlorine battery, developed by Energy Development Associates with partial DOE support, had been initiated at the BEST Facility and had completed baseline cycle tests in April, 1984.

The ETD activity is emphasizing the development of the zinc/bromine and the sodium/sulfur batteries. Improvements in the performance of the zinc/bromine battery are continuing and lower cost processing technology has been developed. A 20 kWh, 120 V battery has been built and is being tested. This battery is to be evaluated by SNL for energy storage in a photovoltaic system. Earlier design studies of an 80 kWh zinc/bromine battery for stationary energy storage in utilities and of a 10-100 kWh battery for electric vehicles projected the cost for the large-scale production of this battery to be \$28/kW (1980\$).

The sodium/sulfur battery investigations emphasize solutions to the problems of early cell failures and the corrosion of the positive container and current collector. Three modules of a stationary energy storage battery, a total of 384 cells, underwent a 32-month test. A statistical analysis of the cell performance indicated a characteristic life for these cells of approximately 1500 days.

The effort to develop a low-cost corrosion-resistant positive current collector and container for the sodium/sulfur battery has been increased. Doped chromium oxide and lanthanum chromite have been shown to be corrosion-resistant under battery operating conditions. Fabrication of coatings made from these materials is to be attempted. It has also been observed that composites of aluminum with silicon carbide have good corrosion-resistance while retaining satisfactory conductivity.

The toughening of the beta-alumina electrolyte with zirconia has been demonstrated. This approach is expected to improve the lifetime of the ceramic electrolyte used in the sodium/sulfur battery.

The Technology Base Research activity includes applied research on battery couples, and fundamental studies on electrode phenomena and electrochemical engineering.

The major battery system being studied is the aluminum/air cell. This is a mechanically rechargeable system in which aluminum negative plates are mechanically replaced, the aluminum hydroxide formed removed, and water added. Research is continuing on improved alloys for the

negative electrode, the collection process for the aluminum hydroxide produced, and catalysts for the air electrode. Heat-treated cobalt macrocyclics have given improved air-electrode performance with a lower rate of carbon substrate corrosion than platinum catalyzed electrodes. The improved catalysis of the air electrode has also impacted on the iron/air and fuel-cell technologies.

To advance electrocatalysis, improved and new techniques for studying electrode surfaces, especially in-situ measurements, have been developed. One approach is surface-enhanced Raman spectroscopy. Another is high-resolution electron energy loss spectra being used at Brookhaven National Laboratory. An in-situ electron scattering technique is being developed at Los Alamos National Laboratory for studying the electrode-electrolyte interface.

Studies of alternative electrolytes for the zinc/nickel-oxide battery with lower zincate ion or zinc hydroxide solubility and pulsed charging indicate enhanced reversibility of the zinc electrode.

The studies of the engineering principles for electrochemical cells have given improved cell and electrode modeling capabilities. These have been applied to flow-through and flow-by porous electrodes, fluidized- and falling-bed electrodes, and descriptions of mass and heat transfer. A novel technique, based on microelectronics, has been developed and applied to the study of gas evolution at electrodes.

The completed electrochemical process investigations included electro-organic synthesis. The study of the simultaneous oxidation and reduction of glucose to two useful products, gluconic acid and sorbitol, has shown that this is a more economic approach than producing the same products in separate cells.

TABLE OF CONTENTS

	<u>Page</u>
LIST OF TABLES	x
LIST OF FIGURES	xi
1.0 INTRODUCTION	1
1.1 The Role of Energy Storage	1
1.2 Overview of the Electrochemical Energy Storage Program	2
1.3 ECS Program Planning	4
1.4 Program Structure	8
1.5 Report Structure	11
2.0 ELECTROCHEMICAL SYSTEMS APPLICATION STUDIES	13
2.1 Stationary Electrical Storage in Utility Systems	13
2.2 Solar System Battery Storage	16
2.3 EHV Battery Program	20
2.3.1 Battery Requirements for EV's	24
2.4 Battery Test Program and Facilities	31
2.5 Technology Analysis and Transfer	36
3.0 AQUEOUS NON-FLOW BATTERIES	42
3.1 Lead-Acid Batteries	42
3.1.1 Stationary Lead-Acid Batteries	43
3.1.2 EV Lead-Acid Batteries	46
3.2 Alkaline Batteries	52
3.2.1 Iron/Nickel-Oxide Batteries	52
3.2.1.1 Overview of Iron/Nickel-Oxide Battery Status	57
3.2.2 Zinc/Nickel-Oxide Batteries	58
3.2.3 Alkaline Battery Research	58
3.2.3.1 Iron Electrode Research	59
3.2.3.2 Zinc Electrode Research	61
3.2.3.3 Zinc/Nickel-Oxide Battery Separator Research	64
3.2.3.4 Nickel-Oxide Electrode Research	68

TABLE OF CONTENTS

	<u>Page</u>
4.0 ALKALINE BATTERIES WITH GASEOUS REACTANTS	73
4.1 Hydrogen/Nickel-Oxide Battery	73
4.2 Iron/Air Battery	75
4.3 Aluminum/Air Battery	80
5.0 FLOW BATTERIES	93
5.1 Zinc/Bromine Battery	93
5.2 Zinc/Chlorine Battery	96
5.3 Zinc Deposition in Acidic Electrolytes	97
5.4 Zinc/Ferricyanide Battery	100
5.5 Chromous/Ferric Redox Battery	104
6.0 NON-AQUEOUS BATTERY SYSTEMS	106
6.1 Organic Electrolyte Batteries	106
6.1.1 Sulfolane Electrolyte Batteries	106
6.1.2 Conducting Polymeric Electrode Cells	107
6.1.3 Organic Electrolyte Battery Research	108
6.2 Molten Salt Systems	111
6.2.1 Li-alloy/FeS Batteries	111
6.2.2 Research on Li-alloy/Metal Sulfide Batteries	113
6.2.3 Research on Alternative Molten Salt Cells	117
6.3 Solid Electrolyte Batteries	118
6.3.1 Sodium/Sulfur Battery	119
6.3.1.1 Beta"-alumina Research	125
6.3.1.2 Na ₂ S _x /S Transport Properties	130
6.3.1.3 Corrosion in Polysulfide Melts	130
6.3.2 Sodium/Trichlorosulfonium Ion Cell	134
6.3.3 Novel Solid Ionic-Conductor Research	135

TABLE OF CONTENTS

	<u>Page</u>
7.0 FUEL CELLS FOR TRANSPORT	139
7.1 Fuel-Cell Technology	139
7.2 Methanol Reforming	145
7.3 Fuel-Cell Membrane Research	146
7.4 New Acid Electrolytes	147
7.5 Fuel-Cell Electrocatalysis	148
8.0 ELECTROCHEMICAL ENGINEERING AND TECHNOLOGIES	154
8.1 Electrochemical Engineering	154
8.2 Electrochemical Technologies	157
REFERENCES	159
APPENDIX A ABBREVIATIONS	165

LIST OF TABLES

TABLE NUMBER		<u>Page</u>
1	BATTERY TECHNOLOGY STATUS AND POTENTIAL	6
2	BATTERY TECHNOLOGY NEEDS	7
3	EV BATTERY PROGRAM GOALS	23
4	TOTAL AND AVERAGE VEHICLE WEIGHT	25
5	BATTERY PERFORMANCE PARAMETERS	26
6	BATTERY AND VEHICLE COSTS	28
7	COMPARISON OF DRIVING CYCLES OF VEHICLE TEST PROFILES	33
8	BATTERY APPLICATION MATRIX (EXAMPLE)	38
9	LEAD-ACID LOAD-LEVELING BATTERY GOALS	44
10	NBTL TEST RESULTS OF EXIDE LOAD-LEVELING BATTERY	47
11	SEALED LEAD-ACID BATTERY CYCLE TEST SUMMARY	48
12	IRON/NICKEL-OXIDE BATTERY PERFORMANCE GOALS	53
13	RELATIVE IMPORTANCE OF THERMAL PARAMETERS IN A TYPICAL IRON/NICKEL-OXIDE CELL	72
14	EXPERIMENTAL HYDROGEN/NICKEL-OXIDE BATTERIES	74
15	JPL ESTIMATES OF IRON/AIR BATTERY CHARACTERISTICS	78
16	Al/AIR BATTERY PROJECT ORGANIZATION	81
17	Al/Air BATTERY WEIGHT ESTIMATION	86
18	Al/AIR CATHODE PERFORMANCE	89
19	METAL SULFIDE EQUILIBRIUM POTENTIAL AND NUCLEATION OVERPOTENTIALS	116

LIST OF TABLES (concluded)

TABLE NUMBER		<u>Page</u>
20	ELECTRIC VEHICLE ENGINEERING MODEL-1 DESIGN GOALS	123
21	BETA"-ALUMINA TEST MATRIX	126
22	ANL CORROSION TEST RESULTS	132
23	GLASS COMPOSITIONS AND PROPERTIES	137
24	KEY TO FIGURE 11	143

LIST OF FIGURES

FIGURE NUMBER		<u>Page</u>
1	FUNDING BY TECHNOLOGY AREA (TBR)	10
2	FUNDING BY ELEMENT (ETD)	12
3	BATTERY BREAK-EVEN CAPITAL COST (5-hr. BATTERY)	17
4	SOLAR-ARRAY/BATTERY ENERGY PROFILE	19
5	IMPACT OF RANGE AND DoD ON LIFE-CYCLE COST	30
6	NBTL DERIVED RAGONE PLOTS FOR AQUEOUS MOBILE BATTERIES	35
7	MACROCYCLIC CROWN ETHERS	67
8	Al/AIR WEDGE CELL SCHEMATIC	82
9	Al/AIR BATTERY SYSTEM SCHEMATIC	85
10	RAGONE PLOT FOR Na/S EV CELL	122
11	SPER ^R CELL HARDWARE CROSS SECTION	142

1.0 INTRODUCTION

This is the fifth in a series of reports on the status of the Department of Energy (DOE) program on batteries and electrochemical technologies for energy conservation. The research and development aspects of this program are conducted by the Energy Storage Division (STOR) of the Office of Energy Systems Research (ESR). The evaluation of the resulting battery developments are conducted in collaboration with the Electrical Energy Systems Program (EES), the Electric and Hybrid Vehicle Program (EHV), and the Renewable Energy Program (RE) of DOE.

The four preceeding reports (referencea 1-4) reviewed the status of the ECS program as of June 1978, December 1979, June 1981, and December 1982, resp. These reports included background on battery storage program objectives, battery and electrotechnology research and development, summaries of the assessments of the potential contributions of batteries and electrotechnologies to energy conservation, and the economics of the introduction of batteries in the utility, transportation, and commercial sectors of the national economy.

This report is based on the status of the battery storage program at the time of the 6th DOE Battery and Electrochemical Contractor's Conference (BECC-6) held June 25-29, 1984.

The goals of this and the earlier reviews, as expressed by Albert R. Landgrebe, the program director, were:

- to discuss progress that has been made to date (June 1984)
- to delineate those electrochemical topics in which further research might prove fruitful in expediting the development and engineering of these systems
- to identify new R&D thrusts

1.1 The Role of Energy Storage

Alan J. Streb, DOE Deputy Assistant Secretary for Conservation, noted in his welcoming remarks that energy storage, in general, and electrochemical technology, in particular, contribute in a significant way to the overall enhancement of energy use efficiency. The Federal role is to encourage improved energy efficiency through conservation by helping to provide a good technical and economic environment. Cooperation between government and industry is essential to stimulate the development of technologies leading to energy conservation.

The improved energy efficiency brought about by conservation is evidenced by the 20 percent decline, since 1973, in the energy requirement to produce a constant dollar of gross national product. This emphasizes the prominence that energy conservation plays in the overall national energy plan.

The Electrochemical Energy Storage (ECS) Program is one of the DOE conservation efforts oriented toward providing the technology base required for the more effective application of electrochemical systems to various end-uses. The primary need is to develop the technology for rechargeable batteries for energy storage. The ECS research activities are designed to ensure the availability of the technologies that will permit the orderly development of electrochemical systems. These are targeted for eventual use in transportation, electrical network, solar energy, and industrial energy systems.

The transfer of technology is a major activity of the ECS program. Recent examples of technology transfer include:

- the development of a maintenance free 6V, 100 Ah lead-acid battery which is being marketed by Gould
- the development of a platinum-based air electrode for which ELTECH Systems has funded a pilot plant to demonstrate applicability to the chlor-alkali process
- the initiation of an Air Force program to develop the sodium/sulfur battery for satellite power

Streb was highly optimistic regarding the potential markets for electrochemical energy storage systems. One such market that requires successful battery developments is transportation. Another potential market is for load-leveling in utility systems. Streb also expressed the belief that it is no exaggeration to say that we are in the formative stages of an entirely new energy storage industry with all that entails--jobs, profits, and beneficial effects on our balance of trade--to name just a few.

1.2 Overview of the Electrochemical Energy Storage Program

The aim of the Electrochemical Energy Storage (ECS) Program, according to Landgrebe, is to develop energy storage technologies that will assist the private sector in providing efficient, reliable, economic, safe, and environmentally acceptable technology to:

- underpin industrial development of electrochemical power sources for transportation
- increase the operating economy of electric utilities through load leveling
- enable intermittent renewable resources to provide continuous service
- increase productivity by improving the efficiency of industrial electrochemical processes

The ECS program supports activities in Technology Base Research (TBR) and Exploratory Technology Development and Testing (ETD). Technology base research encompasses fundamental research to provide the basis for improvements in existing battery systems and the identification and development of new battery and fuel-cell systems. Crosscutting electrochemical and materials research in support of battery and fuel-cell development programs is also conducted. The ETD activity includes the development and evaluation of high performance, long-life, economical, and producible batteries for future mobile and stationary energy storage applications. This activity is designed to fill the gap between fundamental research on promising electrochemical systems and the product engineering capabilities of industry.

Results of the ECS program leading to technology transfer reported by Landgrebe, in addition to those noted by Streb, include:

- mathematical modeling of the Hall-Heroult cell for the electrolytic preparation of aluminum which has shown opportunities for a 4-25 percent improvement in cell efficiency
- improvements in the lead-acid battery which are being introduced into commercial batteries:
 - a) single-point watering for maintenance cost reduction
 - b) plastic grids for weight and cost reduction
 - c) gas recombination to reduce maintenance and to improve safety
 - d) improvements in active material formulation
 - e) charging system improvements to reduce charging time without reducing life

In addition, the continued development of several technologies has been undertaken by industry or mission-oriented government agencies. Examples include:

- the zinc/chlorine battery has been integrated into an electric vehicle by Energy Development Associates (EDA) and a 500 kWh zinc/chlorine battery is under test at the Battery Energy Storage Test (BEST) Facility
- Ford Aerospace has cost shared in the development of a 100 kWh sodium/sulfur battery
- the Prototech developed hydrogen electrode for the electrowinning of zinc is being evaluated by Exxon in a pilot plant
- Standard Oil of Ohio (SOHIO) has completed negotiations for exclusive rights to the NASA developed chromous/ferric Redox battery technology

Based on the recent rapid and successful developments in electrochemistry, Landgrebe observed that electrochemistry can be safely said to be one of the most promising branches of chemistry. Theoretical studies of the mechanism of metal corrosion in aggressive media is an immediate task with great potential for cost reduction and energy savings. Corrosion research requires the use of a variety of methods and approaches because of the number of disciplines and the complexity of the problems involved. The future progress of theoretical and applied electrochemistry will probably be connected with acquiring greater and deeper knowledge of the chemical stages in electrochemical processes.

1.3 ECS Program Planning

James E. Quinn, DOE, reviewed the Office of Energy Systems Research (ESR) planning activities as they relate to the ECS program. The boundary conditions for this planning are the National Energy Policy Plan and the DOE guidance based on this policy. Within these boundary conditions, the DOE program is directed toward:

- fostering an adequate supply of energy at reasonable cost
- minimizing Federal control and involvement in energy markets
- promoting a balanced and mixed energy resource system

The Federal role in research and development is to concentrate in areas where the energy-use potential is high and the incentives for and the availability of private investment are severely limited or non-existent. The strategy of the Electrochemical Energy Storage Program is to:

- identify requirements for batteries and electrochemical processes in applications which include electric vehicles, utility load-leveling, and stationary energy storage
- provide a technology base for advanced electrochemical processes, components, and materials
- develop promising technologies until the concept is proven or disproven
- test and evaluate new systems in a controlled laboratory environment to verify performance
- transfer technical information to industry to assure further product development and commercial use

The general planning process assesses opportunities for application, reviews technical status and potential, establishes technology needs, develops and scopes program options, evaluates and prioritizes projects, and selects programs within the budget constraints. The major applications, requirements, and current and projected technology capabilities for batteries are given in Table 1.

Research needs in the electrochemical program have been determined by experts from industry, academia, government, and DOE National Laboratories. Through the use of topical seminars, meetings, and industry groups, e.g., the Electric Power Research Institute (EPRI), areas of basic and applied technology needs have been identified. These are listed in Table 2.

An evaluation process is used to rank projects and define programs within given budget constraints. The ranking criteria include:

- impact on energy use
- contribution to U.S. competitive position
- contribution to national defense
- environmental and other societal benefits
- probability of technical and market success
- cost and economics
- appropriateness of federal role

TABLE 1
BATTERY TECHNOLOGY STATUS AND POTENTIAL

Requirement	Electric Vehicle	Electric Utility Load Leveling	Remote Stand-Alone (Solar)	Residential Grid-Connected (Solar)
Capacity	20-50 kWh	20 to 100 MWh	100 kWh	25 kWh
Footprint	Not Applicable	80 kWh/m ²	Not Applicable	Not Applicable
Efficiency	70%	65%	70%	70%
Life	6 years 1600 cycles	30 years 7500 cycles	20 years 6000 cycles	20 years 6000 cycles
Specific Power	130 W/kg	Not Applicable	Not Applicable	Not Applicable

Source: Reference 5 (Quinn)

TABLE 2
BATTERY TECHNOLOGY NEEDS

Technology Base Research

- Develop and characterize new catalysts with high activity, long life, and low cost.
- Perform research on electrochemical corrosion processes.
- Develop an aluminum/air battery system which offers the potential of powering a vehicle 300 miles or more between mechanical recharges.
- Investigate catalysts, electrode structures, electrolytes, and advanced reformers for alkaline, phosphoric acid, and solid polymer electrolyte fuel cell systems for transportation.
- Research additional metal/air battery systems including zinc/air and iron/air.
- Develop long-life, efficient, low-cost battery systems for stationary storage applications including zinc/ferricyanide and hydrogen/nickel-oxide system.
- Research intermediate-temperature molten salt systems, lithium/metal-disulfide batteries, and thermally regenerative batteries.
- Research the organic electrolyte lithium battery systems as these offer the highest theoretical specific energy of any battery under development.

Exploratory Development and Testing

- Conduct R&D on high-performance sodium/sulfur battery systems that can lead to safe, reliable, and efficient cells and modules.
- Develop a zinc/bromine battery system emphasizing increased performance, low cost, and increased life.
- Provide facilities for testing and evaluating secondary battery systems.
- Develop a battery performance data base and analysis of failure modes to identify major problem areas.

Source: Reference 5 (Quinn)

After initial rankings and presentation of appropriate data, projects are split into various funding levels and reordered by management judgement.

1.4 Program Structure

The current ECS program, as stated by Landgrebe, consists of two major activities:

- Technology Base Research (TBR)
- Exploratory Technology Development and Testing (ETD)

The responsibility for TBR activities has been assigned to the Lawrence Berkeley Laboratory (LBL) at the University of California, and that for ETD activities to Sandia National Laboratories (SNL). The fiscal year 1984 and the projected 1985 budgets are:

	1984 \$M	1985 \$M
Technology Base Research	7.4	9.35
Exploratory Technology Development and Testing	10.6	7.5
Total	18.0	16.85

Battery systems, which have been characterized earlier in the ECS program and have demonstrated performances that can be extrapolated to meeting the requirements for a specific application, have become the responsibility of the respective program of the Office of Energy Systems Research of the Office of Energy Conservation (EC) of the DOE. The status of the evaluation and testing of these batteries for specific applications is reviewed in Section 2 of this report and technology details in Sections 3 through 8.

The LBL TBR activity supports the DOE effort to provide the basic and applied research required to establish the technology base for the stationary storage and electric vehicle applications.⁽⁵⁾ The primary objective of the TBR is to identify the most promising electrochemical technologies and transfer these technologies to the ETD activity or to one of the DOE end-use programs for ultimate transfer to industry for possible commercialization. The TBR activity is subdivided into general research and applied research.

The general research areas of the TBR activity include:

- identification of new electrochemical couples for advanced batteries
- determination of the technical feasibility of new couples
- improvements in battery components and materials
- establishment of engineering principles applicable to electrochemical energy storage and conversion
- investigation of fuel-cell technology for transportation applications

The applied research aspects of the TBR activity are targeted toward batteries that will lead to superior performance and lower life-cycle costs. The principal applied research topics of the TBR activity include:

- electrochemical studies of new reversible electrochemical couples and metal/air cells
- supporting research which includes the engineering and modeling of cells and cell components and research on cell materials
- electrochemical processes including corrosion in electrochemical systems, three phase electrochemical systems, and non-electrochemically-regenerative cells
- fuel-cell (FC) research emphasizing systems for transportation

The distribution of the fiscal year 1984 (FY '84) funds among the TBR areas is shown in Figure 1.

The objective of the ETD activity at SNL is the development and evaluation of high-performance, long-life, economical, and producible batteries for mobile and stationary storage applications.⁽⁵⁾ This activity is designed to bridge the gap between the TBR basic and applied research efforts and commercialization. The ETD activity follows-up on the battery couples, materials, and engineering shown to be promising by the TBR activity. The ETD activity consists of five elements:

- aqueous batteries
- nonaqueous batteries

FUNDING BY TECHNOLOGY AREA (TBR)
FY 1984
FIGURE 1

- engineering analysis
- performance testing and evaluation
- project analysis

The planned distribution of FY '84 funds among the ETD activity elements is shown in Figure 2.

The evaluation of the performance of the improved and advanced batteries in stationary and transportation systems, as previously noted, is partly or wholly supported by other programs of the Office of Energy Conservation.

1.5 Report Structure

This review of the ECS program will not adhere to the management organization of the program. The technology and research on specific battery systems are integrated. Generic research is reported in the technology section most closely related to the research or in Section 8.

The battery couples will be written: negative/positive. When the electrolyte is included the components will be written: negative/electrolyte/positive. The major exception will be the lead-acid battery for which the common name will be used.

The primary source of the information summarized in this report was the extended abstracts published as part of the proceedings of the "Sixth DOE Electrochemical Contractor's Review" (BECC-6) held 25-29 June 1984⁽⁵⁾. This has been supplemented by information from the project summaries issued as part of BECC-6,⁽⁶⁾ the annual summaries of the TBR and ETD activities,^(7,8) and various publications.

Total Activity
\$ 10.6 M

FUNDING BY ELEMENT (ETD)
FIGURE 2

2.0 ELECTROCHEMICAL SYSTEMS APPLICATION STUDIES

The majority of the battery applications and electrochemical technologies activities, previously wholly or partially included in the ECS program, which are not being continued by industry or another federal agency, have been transferred to the DOE end-use programs or discontinued. Current ECS efforts on stationary storage are targeted toward solar systems - photovoltaics and wind power - and on electrochemical storage for utility systems.

2.1 Stationary Electrical Storage in Utility Systems

The remaining effort on the evaluation of battery energy storage for load-leveling in electrical utility systems is the operation of the Battery Energy Storage Test (BEST) Facility. At this facility testing of battery storage under utility operating conditions and the evaluation of battery storage for application to utility systems is conducted. The sponsors of the BEST Facility include DOE Electric Energy Systems (EES), the Electric Power Research Institute (EPRI), and the Public Service Electric and Gas Company (PSE&G). The BEST Facility serves energy technology developers, electric utilities, and the project sponsors. The test program, described in reference 2, was based on schedules developed jointly among the program sponsors, equipment suppliers, and PSE&G. The BEST Facility provides for testing of batteries, ac/dc power conversion equipment, and of complete battery energy storage systems.

The BEST Facility operation of a base-line system during 1982-1983 was reported to have given the first useful information regarding the characteristics of a utility operated battery energy storage system.⁽⁵⁾ The base-line system consists of a 1.8 MWh state-of-the-art (SOA) lead-acid battery, a 2.5 MW ac/dc converter, and a control and data processing computer system. It operates in a 13.8 kV interconnection with the PSE&G electric distribution grid. The tests conducted included repetitive cycling in eight different application modes representing typical operations. These tests were successful. They verified that a SOA battery energy storage system can provide load-leveling, peak shaving, spinning reserve, load-following, and special customer applications functions. A 75

percent dc/dc energy conversion efficiency was achieved, this efficiency included the overcharge energy. A total of 200 MWh of energy were exchanged with the PSE&G distribution grid.

The SOA lead-acid battery was configured as a series string of 64, 12 V modules. The battery was typically discharged to provide an average power of 400 kW at 730 V. No difficulties were encountered in operating at higher voltages (1000 Vdc) or at lower voltages (250 V dc). The observed temperature variation in the batteries during cycling was within a safe value. However, it was observed that the battery tops on the positive side lifted, indicating positive plate growth.

The BEST operation of the SOA lead-acid battery gave facility operating personnel experience in battery storage systems operation, and in the use of the on-line monitoring and control system. Based on the test results, it was concluded that SOA lead-acid batteries with the associated conversion equipment can perform the many applications required by electric utilities and their customers. Future operations of the BEST Facility are expected to give valuable information on battery life and operating and maintenance costs.

PSE&G has also completed the test bay for the installation of a 500 kWh zinc/chlorine battery. The development and operation of this battery, including a description of the 50 kW modules used, has been reviewed in the preceding status reports, references 1 through 4, and in Energy Development Associates (EDA) reports to DOE and EPRI. The battery system was installed at the BEST Facility by EDA during August 1983. A nine-month zinc/chlorine developmental test program was initiated in February, 1984. This test phase is to verify operation and maintenance procedures and to obtain test data under operating conditions in a user environment. The zinc/chlorine battery completed 30 baseline cycles (April 1984); the baseline cycles consisted of seven hours of charge and five hours of discharge without a "charged-stand" period. The average dc/dc energy efficiency was 62 percent. The projected ac/ac efficiency for a commercial, optimized battery energy storage system operating under utility conditions is estimated by the developer as 7-10 percent lower than the dc/dc efficiency.

A 500 kWh (one-hour rate) load-leveling GNB Batteries, Inc. lead-acid battery has also been supplied for testing. The battery was procured by EPRI. Testing was initiated in February 1984. Midway in the nine-month test program a matched ac/dc converter and control unit are to be added to the test system. This will enable the evaluation of a battery designed for load-leveling. The battery is rated as having an eight-year, two-thousand cycle life.

Future BEST plans include the testing of a sodium/sulfur, a zinc/bromine, and a 1-MWh zinc/chlorine battery by the late 1980's.

PSE&G is also working on a project titled, "Technical and Economic Assessments of Electrochemical Energy Storage Systems."⁽⁵⁾ The major tasks and the areas included are:

- Task 1 - Overall Technical Assessment

An overall technical assessment of four advanced batteries zinc/chlorine, zinc/bromine, sodium/sulfur, and lead-acid has been completed. These batteries were evaluated with respect to the design and engineering, total battery plant costs including balance of plant, reliability of the overall battery facility, efficiency of the facility, environmental and regulatory issues, and credible accident assessments.

- Task 2 - System Stability Impact Assessment

A simulation of system response in which all components affecting system stability and dynamic performance are represented. The EPRI Transient/Mid-Term Stability Program was used in this assessment.

- Task 3 - Overall Economic Assessment

An overall economic assessment of battery systems on generation planning representing breakeven costs of battery plants with respect to various parameters such as capital costs, escalation, load factor, efficiency, plant life, salvage value, charge hours, storage hours, and effective forced outage ratio has been completed.

- Task 4 - Battery Cost Methodology

A battery cost methodology and sensitivity analysis of the critical cost components for the battery and balance of plant was completed for zinc/chlorine, zinc/bromine, sodium/sulfur, and lead-acid batteries.

Background information for Task 1 was obtained directly from the battery developers. This included data on the battery configuration, battery operation, auxiliary systems, and cost of a 100 MWh plant. The information was used by the PSE&G staff to develop the balance of plant (BOP) interface for each of the battery systems. Based on these results, working documents were prepared which contained the design, plant description, and cost for each of

the above battery systems. These working documents were reviewed by the participating battery developers before being forwarded to DOE for comment.

In Task 2, a system stability impact assessment was performed through the development of valid mathematical models for the storage battery and associated AC/DC conversion equipment. The equations were solved using a digital computer program. Both line-commutated and self-commutated (forced-commutated) converter systems were modeled. A large number of computer runs have been made covering a variety of disturbances under various operating conditions in a large reference power system. The results suggested that the battery storage systems are not likely to have significant impact on a power system.

The Task 3 results on the breakeven cost relationship as a function of battery penetration for the "base" study assumptions are shown in Figure 3. The breakeven cost for batteries is the installed capital cost of a battery plant which is economically equivalent to a conventional capacity option. The three components of the breakeven cost: peak shaving, spinning reserve, and capacity credits are shown in Figure 3. The results show a marked decrease in the battery breakeven capital cost as battery penetration increases. A sensitivity analysis of the battery breakeven costs for variation in battery plant characteristics, utility system characteristics, and financial data is also reported.

In Task 4, the battery cost methodology covers the battery and balance of plant. The battery cost methodology was primarily based on A.D. Little Standard Costing Methodology. The BOP cost methodology was based on standard utility practice and experience. A sensitivity analysis of the critical cost components was performed for each battery type. This analysis represents the fluctuation of cost impact on the battery and BOP costs.

2.2 Solar System Battery Storage

The SNL field testing program for the battery electrical storage component of solar energy systems (photovoltaic and wind) was described in reference 4 and its status is up-dated in this report. The SNL test results on specific batteries for solar energy systems are included in the technology sections.

A stand-alone battery and photovoltaic residential power test is located on the Jicarilla Apache Indian Reservation. This test is sponsored by the Public Health Service. The system consists of a 490 watt photovoltaic array and 24 kWh, 24 V battery. When the array cannot supply the demand, the required supplemental power is

**BATTERY BREAKEVEN CAPITAL COST
(5-HR. BATTERY)
FIGURE 3**

obtained from the battery. This system is being monitored to obtain battery performance data, and the energy mix between the photovoltaic array and battery for a daily load profile is shown in Figure 4.⁽⁵⁾

A second photovoltaic test involves a 40 kWh lead-acid battery which will be tied to a large photovoltaic array and grid connected. Prior to including the batteries in the system they were tested for over 100, 80 percent depth-of-discharge (DoD) cycles.⁽⁵⁾

The wind energy systems include a 2 kW wind turbine with a 24 V, 1000 Ah lead-acid battery at the Rocky Flats Small Wind System Test Facility and a project being performed by the Hawaii Natural Energy Institute (HNEI).

The Rocky Flats project has been in progress for over a year. Wind turbine, battery, and load satisfaction data have been collected and analyzed. The results indicated that for the month of March, 1984 the combined energy systems were able to supply the system load.

The HNEI project is in Phase II of a three phase program. The objective is to design and construct a wind energy-battery storage (WEBS) system for connection to a utility grid serving a small community on Molokai Island.⁽⁵⁾ Phase I activities included meteorological data collection for siting the wind turbine generators, performance projections, load profile data collection for the community and island, and development of a numerical (computer) simulation of the system. The Phase II efforts included expanding and improving the computer model, including:

- interaction with the utility
- collection of additional wind and load data
- updating information on WEBS components
- finalizing the design of a battery storage facility
- applying the simulation to various configurations and operating strategies

The computer simulation has been improved both in design and function. A major accomplishment was the addition of the utility with two generation systems, in an active role, to the model. This resulted in the following:

SOLAR-ARRAY/BATTERY ENERGY PROFILE
FIGURE 4

- development of two additional strategies for the use of the WEBS system
- save fuel costs by using the battery to reduce the use of the more expensive generating equipment or to reduce load fluctuations at the utility

The model simulation studies assisted in the preparation of a design for a 250 kWh expandable battery storage facility. A final design, drawings, and specifications for the system have been delivered by a consulting engineering firm.

The plan for Phase III includes system construction, testing, and operation; however, the implementation of phase III is not definite. Enhancement of the computer model to expand its capabilities would also be undertaken.

The net results of the project are expected to include the following:

- a net savings in imported oil for electricity generation
- a field experiment for the use of battery storage to increase wind energy penetration

2.3 EHV Battery Program

Earlier status reports have described the evolution of the Electric and Hybrid Vehicle Program, including the Fuel Cell for Transport Program. Current emphasis in the EHV program is on the test and evaluation of alternative components and power trains to delineate technical problems and lower future initial and operating EV and EHV costs.

Robert Kirk, Chief of the Technology and Systems Development Branch (TSD) of the Office of Vehicle and Engine R&D, DOE, presented an overview of the status of the electric and hybrid vehicles (EHV) research and development program.⁽⁵⁾ Various aspects of the TSD program have been assigned to DOE contractor operated laboratories. The organizations and the aspects of their activities impacting on battery and fuel-cell technology are:

- The Aerospace Corporation - management of the Ford ac propulsion and battery technology development effort and conducting of studies and analyses
- Argonne National Laboratory (ANL) - aqueous non-flow battery development activities and modeling of EV battery applications

- Jet Propulsion Laboratory (JPL) - management and testing of vehicles system and propulsion subsystem and advanced technology assessments
- Sandia National Laboratories (SNL) - management of the zinc/bromine EV battery systems development
- Los Alamos National Laboratory (LANL) - management of fuel cells for transport program

The cooperative program with the Lewis Research Center of the National Aeronautics and Space Agency (NASA) was discontinued at the end of fiscal year 1983 and the agreement with JPL is to conclude at the end of fiscal year 1984.

The specific objectives of the TSD program is to establish the technology base required for a totally or near-totally petroleum-free vehicle. Three types of vehicles are being emphasized:

- all-electric commercial van, limited range
- all-electric passenger car, limited range
- hybrid passenger car, unlimited range

The critical technology needs, with respect to batteries, enumerated by Kirk were:

- reduced cost
- increased cycle life
- increased specific energy and specific peak power
- reduced degradation due to age and temperature effects
- reduced maintenance requirements

The TSD program contains a number of studies and analyses on the impact of various available and projected technologies on EV and EHV performance. These studies assist in establishing vehicle performance capabilities and advances required to achieve performance objectives. The study at JPL has assigned rankings for various batteries and fuel cells as the power source or part of a hybrid power plant for advanced electric vehicles.

Electric vehicle test results have shown that Electric Test Vehicle-1 (ETV-1), which was designed for mass production, using an advanced lead-acid battery was capable of achieving a range of 123

mi (198 km) at 35 mph (56 km/h) and 90 mi (144.8 km) at 45 mph (72 km/h). The ETV-1 had a top speed of 70 mph (113 km/h). The Ford Motor Company advanced ac propulsion system, which has a coaxial motor and transaxle (ETX), is to be tested using lead-acid, zinc/bromine, and sodium/sulfur batteries. The Ford ETX vehicle has shown improved performance when compared with the ETV-1. The Eaton advanced-van propulsion technology effort includes the use of iron/nickel-oxide batteries.

Based on the in-vehicle tests and various system studies, battery performance and cost development goals have been established. These are shown in Table 3. Studies of batteries for hybrid vehicles indicate the need for a high power density battery, such as zinc/nickel oxide. Effort is being continued on advanced batteries and fuel cells for EV and EHV applications.

The EHV test and evaluation program, reviewed by Kenneth F. Barber (DOE, EHV), consists of three elements:

- vehicle site operations
- technology suitability testing
- engineering evaluation testing

Here the activities and results impacting on battery technology will be emphasized.

A group of vehicle site operators has formed a Users Task Force for selecting and evaluating technologies for eliminating present EV shortcomings. According to Barber the major problems with present technology are low reliability and high operating cost.⁽⁵⁾ Battery life is an important component of operating costs. However, the results of testing of some advanced batteries indicate that considerable progress is being made in increasing battery life. The fleet operation has shown that the costs for current batteries can be reduced by conducting routine battery capacity checks and by the use of on-board systems to detect weak or defective modules enabling the taking of corrective action before damage to the remainder of the battery pack. The fleet operation has also shown that watering of the lead-acid battery is labor intensive and significantly increases the operating cost. To help decrease this cost a watering wand has been developed and is being field tested. Preliminary results indicate a large, as high as 75 percent, decrease in watering time. An alternative route to decreased watering time is the gel-electrolyte battery to be discussed in Section 3.2.

TABLE 3
EV BATTERY PROGRAM GOALS

Battery Parameter	Developmental Goal	Expected Vehicle Performance
Specific Energy	56 Wh/kg	100 mi (160 km)/charge in an urban driving schedule
Specific Power	104 W/kg	Acceleration 0 to 30 mph (48 km/h) in 8 sec; hill climbing
Cycle Life	800 cycles	60,000 mile (46,000 km) life
Cost (1981\$)	\$70/kWh (\$0.11/kWh/cycle)	\$2000 battery cost/vehicle 7¢/mile (4.8¢/km) (life cycle)

Reference 5 (Kirk)

Characterization testing of the Hybrid Test Vehicle (HTV), under the engineering evaluation testing element, has been completed by the Jet Propulsion Laboratory. The results indicated a fuel economy savings of 44 percent over an annualized basis. The reference vehicle was a 1985 Buick of the same size as the HTV. Chassis dynamometer testing, using the ETV-1 and Jet-750 pickup as test vehicles, was carried out using the Globe EV-2300 lead-acid and the Eagle-Picher iron/nickel-oxide batteries. Battery testing is also underway at the National Battery Test Laboratory (NBTL) of the Argonne National Laboratory (ANL). The charge/discharge studies of the Globe EV-2300 lead-acid battery are to determine the minimum overcharge requirement as a function of the depth-of-discharge. The pulse discharge characteristics of the Eagle-Picher iron/nickel-oxide battery are being determined to aid motor controller designers in synthesizing a circuit model with minimum energy losses. The effect of battery temperature and depth-of-discharge on cycle life is also being investigated at NBTL.

2.3.1 Battery Requirements for EV's

William J. Walsh and William W. Marr, ANL, have developed a computer system to assist in the establishment of battery requirements for electric and hybrid vehicles. This program has been given the acronym "EVA". The computer program includes:

- mission-specified vehicle requirements
- comprehensive battery modeling
- avoidance of premature or unnecessary assumptions
- least-cost analysis

Equations were developed for calculating various weight, performance, and cost parameters for the battery and the vehicle. These relationships are shown in Tables 4, 5, and 6, respectively.

Battery data used in the EVA program included the 1984 performance of lead-acid and iron/nickel-oxide batteries and the 1990 performance for these batteries and several of the advanced batteries based on projected 1990 technology. The advanced batteries include Na/S, Li-Al/FeS, Zn/Br₂, and Zn/Cl₂.

The results of the EVA program for the estimation of life-cycle cost vs. range as a function of DoD are shown in Figure 5. The EVA computer program is to be ready for users during the summer of 1984 and will be obtainable from ANL at no cost to USA requestors.

TABLE 4
TOTAL AND AVERAGE VEHICLE WEIGHT

$$W_T = \frac{W_{PL} + W_{BD}}{1 - \beta_D - \beta_F - \beta_B}$$

$$\bar{W}_T = W_T - (1-r) W_{PL}$$

Where:

W_T = total vehicle weight (kg)

$\bar{W}_T$ = average vehicle weight (kg)

W_{PL} = payload of vehicle

W_{BD} = weight of body

β_D = weight fraction of drive-train based on W_T

β_F = weight fraction of frame based on W_T

r = average fractional payload onboard

β_B = weight fraction of battery based on W_T

Reference 5 (Walsh and Marr)

TABLE 5
BATTERY PERFORMANCE PARAMETERS

EV Battery Specific Power:

$$P_B = \frac{P_v}{\beta_B \eta_{VP}}$$

$$P_B = \frac{E_v R_c}{\beta_B \eta_{VE} T_C}$$

Specific Power vs. Specific Energy

$$P_B = a_0 \cdot E_B + (1/3 - a_0) \cdot E_3$$

Peak Power vs. Specific Energy and DoD

$$PP = (a_1 + a_2 \cdot \text{DoD}) \cdot E_3 + a_3$$

Cycle Life vs. DoD

$$L_B = L_{B0} \cdot e^{\alpha (1-\text{DoD})}$$

Where:

P_B = Peak specific power (w/kg)

P_B = Average specific power (w/kg)

P_v = Vehicle power-to-weight requirement (w/kg)

η_{VP} = Vehicle drive-train power efficiency

η_{VE} = Vehicle drive-train energy efficiency

β_B = Battery weight fraction

E_v = Vehicle energy consumption with distance (Wh/kg-km)

R_c = Range of a typical drive-cycle, km

TABLE 5
BATTERY PERFORMANCE PARAMETERS (concluded)

T_c = Time period corresponding to R_c , hrs
 a_0 = Ragone slope (Figure 6)
 $\bar{E}_B$ = Average specific energy (wh/kg)
 E_3 = Specific energy at 3-hour rate (wh/kg)
 PP = Peak power
 a_1, a_2, a_3 = battery coefficients
 DoD = Depth of discharge
 L_B = Battery life cycles
 L_{B0} = Battery life at $DoD = 1.0$ cycle
 α = Battery coefficients

Reference 5 (Walsh and Marr)

TABLE 6
BATTERY AND VEHICLE COSTS

Battery Costs

$$C_B = C_{B1} + C_{B2} E_T + C_{B3} P_T$$

Vehicle First Cost

$$C_V = (1 + \delta_D) \left\{ \underbrace{[(C_{BD1} + C_{BD2} W_{BD})]}_{\text{Body} = BD} + \underbrace{[(C_{D1} + C_{D2} \beta_D W_T)]}_{\text{Drive train} = D} \right\} +$$

Dealer Markup

Body = BD

Drive train = D

$$+ \underbrace{[(C_{F1} + C_{F2} \beta_F W_T)]}_{\text{Frame} = F} + \underbrace{[(C_{T1} + C_{T2} W_T)]}_{\text{Tires} = T} +$$

Frame = F

Tires = T

$$+ \underbrace{[(C_{B1} + C_{B2} E_T + C_{B3} P_T)]}_{\text{Battery} = B} + C_{1E} + C_{1P}$$

Battery = B

Replacement Cost of Components

$$C_{R1} = \underbrace{(1 + \delta_M)}_{\text{Markup}} \cdot C_1 \cdot \underbrace{\exp(xt)}_{\text{Escalation}} \cdot \underbrace{\exp(-yt)}_{\text{Present-worth}}$$

Markup

Escalation

Present-
worth

TABLE 6
BATTERY AND VEHICLE COSTS (concluded)

Where:

- C_B = total battery cost
- C_{B1} = battery fixed cost
- C_{B2} = energy cost coefficient
- C_{B3} = power cost coefficient
- E_T = total battery energy
- P_T = total battery peak power
- C_V = total vehicle first cost \$
- δ_D = dealer markup fraction
- C_1 = cost of component in initial year
- C_2 = cost of component
- β = fractional weight of designated component
- W = weight of component
- C_{R1} = cost of replacement of component 1
- C_{1E} = cost for improved energy performance
- C_{1P} = cost for improved power performance
- δ_M = manufacturer's markup fraction
- x = cost escalation rate fraction
- y = discount rate fraction
- t = replacement period from initial year

**IMPACT OF RANGE AND DoD
ON LIFE-CYCLE COST
FIGURE 5**

2.4 Battery Test Program and Facilities

The EHV Battery Testing Working Task Force (Task Force) was established by the EHV and Energy Storage Technology (STOR) Divisions of DOE in January 1983. The purpose of the Task Force is to review and make recommendations for improvements of the DOE sponsored EV battery testing activities at national laboratories and contractors under a variety of test conditions.⁽⁵⁾ A major goal of the Task Force is to coordinate the testing methods used at the various laboratories and suggest standard test procedures and reporting practices.

A review was made of the EV battery testing programs of the organizations of the Task Force: Aerospace Corp., Argonne National Laboratory, Jet Propulsion Laboratory (JPL), Sandia National Laboratories, and Tennessee Valley Authority (TVA). Generally, SNL evaluates battery systems that are in an early state of development for both EV and stationary storage applications. NBTL tests more mature technologies in application-specific tests. JPL and TVA perform system and on-road tests of engineering prototype units.

The Task Force reviewed the test program at NBTL. There was general concurrence with the tests being conducted, however, several additional tests were proposed. The recommended procedure changes included:

- Ragone test - specific energy vs. specific power and maximum power based on thermal or safety limitations
- sustained power test - 45 W/kg discharge is repeated at various states-of-charge leading to the determination of the depth-of-discharge which supports a six-minute discharge
- effect of age on Ragone characteristics, driving cycle, and self-discharge characteristics

Another concern of the Task Force is the identification of a simplified composite driving-cycle battery-life test. The Federal Urban Driving Schedule (FUDS) cycle was selected as the starting point. The simplifications, based on JPL EV modeling codes, consisted mainly of constructing constant power segments from the detailed FUDS structure and shortening the basic cycle to about three minutes. In all cases, the primary features of the modified cycle tests were within 10 percent of the original, based on a statistical comparison.

NBTL, in cooperation with the EHV Battery Testing Task Force, has conducted an evaluation of the suitability of various proposed versions of FUDS as a standard for testing batteries. According to F. Hornstra, et. al., the distinguishing characteristics of FUDS are its long cycling time (0.38 h-12 km per cycle), its low average velocity (~ 32 km/h), and high acceleration requirements.⁽⁵⁾ When applied to ETV-1, with vehicle current and voltage constraints ignored, the battery requirements are characterized by high peak power (90 W/kg requiring currents approaching 900 A) and low average power (10 W/kg). Batteries operated under these conditions achieved ranges comparable to those achieved with the SAE J227 ad schedule which has peak power requirements of ~ 47 W/kg, an average power requirement of ~ 15 W/kg, and an average velocity of ~ 48 km/h. Table 7 gives a comparative summary of the test profiles of two versions of FUDS and the SAE J227ad urban driving schedule.

Following the development of the test cycle, it is planned to disseminate the recommended procedures to organizations outside of the Task Force laboratories.

The testing programs of batteries for electric vehicles and stationary energy storage are conducted at NBTL and SNL.

The NBTL facilities and the results of some of the tests conducted have been described in earlier status reports, references 1-4. Batteries developed under the DOE programs and by private industry are tested at the NBTL facilities. Included are batteries for EV's and EHV's, electric utility load leveling, and solar energy storage.⁽⁵⁾

The facility at NBTL has space for the simultaneous testing of 76 independently operated batteries under various environmental conditions and over a wide range of voltages and currents. The NBTL has four major components:

- the control room and main test area where ambient and elevated temperature testing are conducted
- the environmental annex, for low temperature and zinc/halogen battery testing
- the Battery Components Technology (BCT) Laboratory, where special instrumentation and software are installed to allow systematic parametric variation and optimization and other studies
- the high temperature test area which was recently added to test lithium/sulfur and sodium/sulfur cells

TABLE 7
COMPARISON OF DRIVING CYCLES OF VEHICLE TEST PROFILES

PARAMETER	PROFILE		
	FUDS*	FUDS CLAMPED**	SAE J227aD**
1. Time/Cycle	1371s; 0.38h	same	121s; 0.034h
2. Range/Cycle (mi)	7.45	~ same	0.94
3. Average Velocity (mph)	20	~same	~30
4. Specific Power Requirements (W/kg)			
A. Average	9.9	9.7	14.9
B. Peak	90	71 to 58	48
5. Energy/Mile (Wh/mi)			
A. Energy Consumption	246	241	263
B. Regenerative Braking (Returned to Battery)	54 = 22%	56 = 23%	56 = 21%
6. Achieved Range			
A. ISOA Lead-Acid	68 $\pm$ 7.5	83 $\pm$ 7.5	73 $\pm$ 1
B. Fe/NiO(OH)	N.A.	104 $\pm$ 7.5	95 $\pm$ 1

(Vehicle = Improved ETV-1 with 488 kg of Batteries)

*Applied as if vehicle had no current or voltage limitations, i.e., currents up to 900 A and voltages down to 1 V/cell average were allowed to occur.

**IETV-1 compatible (currents less than 400 A and voltages greater than 1.3 V/cell average were maintained (Tests conducted at NBTL-ANL)

Reference 5 (Barber)

Over 1000 cells have been evaluated at NBTL. Most of these have been as 3 to 6 cell modules, but batteries of up to 140 cells have been included. Performance-characterization assessments are conducted under a series of charge/discharge cycles with constant current, constant power, peak power, and computer simulated dynamic load profile conditions. Charging algorithms are provided to accommodate the battery under test. Special studies are conducted in the BCT laboratory to explore and optimize charge procedures, to investigate the impact of unique load demands on battery performance, and to analyze the thermal management requirements of battery systems.

Scaling and normalization techniques developed and practiced at NBTL permit full-sized battery performance to be projected on the basis of 3 to 6 cell modules. Larger units are tested as the specific battery technology matures.

The mapping of the battery specific energy as a function of the specific power at which it is discharged (Ragone plot) is one of the most useful of the EV battery tests performed. Figure 6 depicts the Ragone plots obtained for various aqueous mobile-batteries tested. All of the batteries included, except for the EV-106 lead-acid golf-cart and the Delco Remy zinc/nickel-oxide batteries, represent technology developed under the DOE program. Test results, other than the Ragone plots, are included in the discussions of the status of specific battery systems.

The goal of the battery tests at SNL is to evaluate their operation under a variety of conditions and to determine electrochemical performance, efficiency, and life. These data are to be used to direct the emphasis in the battery research and development efforts. The SNL test project is composed of two efforts. The first consists of laboratory bench scale testing of small, prototype cells and batteries. These include lead-acid, zinc/bromine (Zn/Br_2), chromous/ferric redox ($\text{Cr}^{+2}/\text{Fe}^{+3}$), zinc/ferricyanide ion ($\text{Zn}/\text{Fe}(\text{CN})_6^{3-}$), hydrogen/nickel oxide ($\text{H}_2/\text{NiO}(\text{OH})$), and cadmium/nickel oxide ($\text{Cd}/\text{NiO}(\text{OH})$). These cells and batteries have been evaluated under simulated solar application tests and parametric test plans. The second part involves testing batteries under field test conditions representative of photovoltaic and wind systems, either utility connected or in the stand-alone mode. Lead-acid batteries have been used to resolve test control and data acquisition systems. As in the case of the NBTL testing activities, the available results are reviewed in the sections on the respective battery technologies.

NBTL DERIVED RAGONE PLOTS FOR AQUEOUS MOBILE BATTERIES
FIGURE 6

2.5 Technology Analysis and Transfer

Technology analysis is being conducted by the Pacific Northwest Laboratory (PNL). The analyses are to assist the Energy Storage Technologies (EST) evaluations of programs, program information management, and system technology characterizations and assessments. The recently initiated efforts at PNL include several planning and support tasks. Included among these efforts are:

- the statistical analysis of battery failures
- the evaluation of the status of emerging technologies
- the development of R&D program evaluation techniques to support DOE headquarters
- the description of technical, economic, and environmental aspects of selected storage systems
- the automation of the work planning system for EST
- the assistance of technology transfer of EST funded research

The statistical analysis of battery failures is to develop analytical methods and the capability of:

- identifying preferred multi-cell module test configurations
- evaluating the potential battery performance and risks before actual testing

The approach of PNL is to develop a model based on past battery failure observations and analyses. The model is then to be adapted to include failure data on the Na/S battery. The results are to be validated by comparison of the simulated failure model with actual battery experience.

Part of the PNL support effort is an analysis of the patent literature for the Na/S battery. This should be of value in the analysis of the progress in the transferring of this technology.

BECC-6 included a study of a general electrochemical energy technology transfer plan and a summary of the transfer of technical advances in lead-acid battery technology resulting from the DOE program to lead-acid battery practice.

The DOE defines technology transfer as "the transformation of research and development into processes, products and services that can be applied to state and local governments and private sector needs." This suggests a sequential flow of technology from a research result to an end-use application or user.

The ECS technology transfer effort, according to Regis Scheithauer et. al., Jaycor, is intended to integrate end-use technical and economic requirements with institutional issues that may impede or facilitate the use of electrochemical energy storage technologies by the private sector.⁽⁵⁾ The effort has five major tasks:

- defining selected markets for electrochemical energy storage for load-leveling
- characterizing and identifying participants in electrochemical energy storage product development and commercialization
- documenting and analyzing selected previous efforts to transfer DOE-sponsored electrochemical energy storage technology to the private sector
- identifying and analyzing institutional issues which may affect the technology transfer of ECS-sponsored research and development
- developing a set of technology transfer recommendations tailored to specific end-use markets.

A preliminary characterization of the commercial and industrial economic sectors have identified several potentially receptive markets for load-leveling batteries. These have load shapes that complement customer-side-of-the-meter storage. Examples include: groceries, department stores, hospitals, new car dealers, and lumber, stone, and glass producers. Institutional characteristics for each market have been identified and potential market size calculated. The battery application matrix derived by Scheithauer is shown in Table 8. Several motive applications have also been identified: industrial fork lifts, airline ground support vehicles, lawn mowers, golf carts, and fleet EV's.

The results of a 1983 survey of eight domestic airlines showed an increase in the use of ground support EV's, from 5 percent in 1981 to 11 percent in '83. The airline respondents projected that by 1990 fifty percent of their 9,000 ground support vehicles will be battery powered. The respondents represented 26 percent of the

TABLE 8
BATTERY APPLICATION MATRIX (EXAMPLE)

Application	Stationary Applications						
	Zinc/Bromine	Sodium/Sulfur	Lead-acid	Zinc/Chlorine	Lithium/Metal sulfide	Iron/Nickel oxide	Hydrogen/Nickel oxide
Utility Load-Leveling	0	●	●	0	0	0	0
Remote Solar/Wind	●	0	●	0	0	0	●
- Buoys	0	0	●	0	0	0	●
- Farming	●	0	●	0	0	0	0
- Military	0	●	0	●	0	0	●
Customer Side-of-the-Meter							
- Groceries	0	0	●	0	0	0	0
- Hospitals	●	●	●	●	0	0	0
- Subways	●	●	●	●	●	●	●

● - Strong potential to satisfy all or most of application requirements

● - Moderate potential to satisfy all or most of application requirements

0 - Little potential to satisfy all or most of application requirements

Reference 5 (Scheithauer)

potential market. Eastern Airlines was reported as claiming the following:

- battery-powered vehicles cost \$137,000 less than their Diesel counterpart
- energy costs are lower per pushout, \$0.21 for battery charging vs \$2.41 for Diesel fuel

The pushout tractor is a 62,000 pound (23,130 kg) vehicle, including batteries. It has 2-40 hp electric motors, a top speed of 7 mph (11.2 km/h), and is capable of pushing a 425,000 pound (158,500 kg) aircraft up a two percent grade for 600 feet (182 m). The battery requirements are being met with SOA lead-acid batteries with the following specifications:

- 2-600 Ah batteries
- 64 cell batteries with 19 plates/cell
- total battery weight of 12,000 pounds (4475 kg)

The status of the various battery technologies has also been reviewed. The results of the analysis of the sodium/sulfur battery were detailed and specific conclusions on this battery technology are included in Section 6.3.1.

The study is also focusing on institutional factors which are likely to be important to the acceptance of a technology by the private sector. Included among the issues identified are:

- required return on investment
- capital availability and cost
- insurability
- ability to handle explosive and hazardous materials
- safety and environmental control requirements
- applicability of use-restrictions
- potential for building and code restrictions

To aid in making specific recommendations for technology transfer, case studies of previously successful transfers of ECS-sponsored technology to the private sector are being analyzed. These transfers have been described in Sections 1.1 and 1.2.

Scheithauer also discussed the advantages, disadvantages, and appropriate situation for seven different technology transfer mechanisms. These mechanisms, together with the battery requirements for the various potential end uses, will be synthesized into a set of technology transfer recommendations.

Walsh, ANL, conducted a case study of the transfer of lead-acid battery advances resulting from the research supported by DOE under the technical direction of the ECS program. Most of the related research and development was under the technical management of ANL. The study included:

- documentation of technical advances
- examination of relationship of federal/private R&D efforts
- description of private-sector outcomes
- analysis of the appropriate federal role

Among the positive impacts of the DOE lead-acid battery research and development program is an anticipated increase in private sector research and development following the phase out of DOE funding. Prior to the federal program, lead-acid battery research and development was relatively dormant.

Among the technology advances resulting from DOE sponsorship were:

- improvement of specific energy by 30-50 percent
- advances in cycle life
- improvements in auxiliaries and operating procedures (e.g., wand watering system, control instrumentation)

Specific commercial products that have resulted include:

- EV batteries are offered for sale
- batteries for fork-lift, golf cart, and other traction applications contain DOE-developed technology
- batteries for starting-lighting-ignition containing DOE program advances in positive electrode technology are being planned

Walsh has concluded that the program has resulted in a greatly improved national competitive position in lead-acid batteries. Furthermore, the USA now appears to have the best lead-acid battery technology in the world. However, there remains the potential for further advances in lead-acid battery technology involving long-range high-risk research and development. Specifically, this would involve high-rate lead-acid batteries capable of 50-60 Wh/kg and could include bipolar battery construction. Walsh is of the opinion that this type of effort is essential to maintaining the USA front position in lead-acid battery technology.

3.0 AQUEOUS NON-FLOW BATTERIES

This section on aqueous batteries is limited to those couples in which all negative and positive reactants are included in the electrodes and are not added to the cell during discharge. These batteries have been discussed in earlier status reports, references 1-4, as part of the Near-Term Battery Program. Included are the lead-acid, iron/nickel-oxide, and zinc/nickel-oxide couples. The present ECS effort on these battery systems is limited to basic and applied research to establish the basis for overcoming some of the shortcomings in these systems as defined by battery system scale-up and EV demonstrations. The definition of required improvements, based on simulated and in-vehicle testing, is part of the Aqueous Mobile Battery (AMB) project of the EHV program. The AMB project is under the technical monitorship of ANL.

Efforts are also continuing on selected aspects of the use of lead-acid batteries in stationary storage for load-leveling in electric utility systems and for stand-alone and grid-connected solar systems.

This section will up-date the results of the developmental and testing activities reported since status report IV, reference 4, and the results of continuing research and testing. Some of the earlier advances in lead-acid battery technology resulting from the DOE program were noted in Chapters 1 and 2.

3.1 Lead-Acid Batteries

The lead-acid battery, because of its commercial availability and high state-of-development, is continuing to be used in system evaluations for both stationary and mobile battery applications. It is the reference system for establishing required battery system improvements, both technical and economic, and for establishing whether or not improved or advanced battery technologies will meet the established goals. These goals for both stationary and mobile applications have been detailed in earlier status reports, references 1-4.

The major reported R&D effort on stationary lead-acid batteries has been the completion of the Exide development and testing of selected battery variables. The development of some of the technology involved was supported by the DOE program and others were commercially developed and made available by manufacturers for testing by DOE.

3.1.1 Stationary Lead-Acid Batteries

The Exide investigations relating to stationary batteries for utility application have been detailed in a final report⁽⁹⁾ and included in the BECC-6 Extended Abstracts⁽⁵⁾. The overall goals of this program are shown in Table 9. Three accelerated tests, detailed in reference 3, were developed to establish a valid basis for extrapolating performance:

- continuous overcharging to test positive grid corrosion
- shallow cycling to test shedding of positive and negative active materials from plates
- deep cycling (80 percent DoD) at elevated temperature to test capacity loss during cycling, active material shedding, positive grid corrosion, cell case/cover materials, and seals

The major results were:

- overcharge corrosion testing verified that the lead-alloy and grid design selected for the positive should satisfy the life-cycle goal
- the active material shedding test gave evidence that a new additive for the positive active material would reduce shedding during shallow cycling
- the deep-cycling test indicated that the equivalent of 6000 cycles at normal operating temperatures are achievable

Based on these results and Exide experience with the design and production of large submarine batteries, a manufacturing cost study was conducted. It was concluded that mechanization of assembly processes might require substantially less new capital investment if small battery dimensions could be used with automation similar to that developed for the production of SOA starting-lighting-ignition batteries. This approach promised an increased rate of production at competitive prices. The final decision was to develop a deep-cycling cell in the same geometry and with the same manufacturing tooling required for stationary float-type batteries which are currently being mass produced by Exide.

The selected battery design includes the following features:

- pasted flat-plate designs with the anticipation that plate wrapping of retainers and separation system could be automated

TABLE 9
LEAD-ACID LOAD-LEVELING BATTERY GOALS

Goal	State-of-The-Art	Advanced Battery
BEST Battery MWh	5	5
Life Stand, Yr	10	20
Cycles (80% DoD)	2,000	4,000
Energy Efficiency, Turnaround %	76-85	80
Energy Footprint kWh/m ²	43-54	75
Initial Battery Price, \$/kWh		
Lead 25¢/lb	42-58	37-50
58¢/lb	75-100	50-75
Battery Rebuild Price % of initial	46-79	50
Operating Temperature °C	4-50	4-50
Cycle Discharge h	5	5
Recharge h	7-10	5-7
Depth %	80	80
5-h rate		

Reference 9 (Chreitzberg)

- cell cases and covers of Lexan^R polycarbonate plastic were selected in sizes convenient for scaling-up from 5 to 35 plate cells
- terminal posts, straps, and plate grids were selected from available production designs and tooling

The cell development and testing reported in reference 9 has been continued under the support of SNL and Exide. Testing of competing 35-plate cell designs, initiated under the DOE supported contract, has been continued at Exide. The test group is composed of four design sets of two cells each. The major design parameters being examined are:

- positive active material (PAM) density, 4.0 and 3.2 g/cc
- anti-shedding additive in low density PAM to permit increase in utilization without failure from excessive PAM shedding
- retainer system glass mats of slyver or random glass fibers with and without perforated polyvinyl chloride (PVC) sheets
- type of spacing between plates
- negative to positive active material ratio of 0.8 and 1.0

Common features to all cells are:

- 17 positive plates with long life Pb-Sb alloy grid
- 18 negative plates with a Pb-Ca alloy grid and high active material density
- microporous rubber separator
- 1.285 sp. gr. sulfuric acid electrolyte
- one air-lift circulation pump in each cell
- polycarbonate jar and cover

The test cycle, after initial capacity build-up, consisted of 2-80 percent DoD cycles daily at the 5 hour rate to a minimum of 1.6 V/cell at ambient temperature and without cell cooling. Cell electrolyte temperatures ranged from 34-44°C. Once a month a capacity measuring discharge to 100 percent DoD, full charge plus an

equalization charge, and cool-down period were carried out. The number of cycles completed, as of 1 May 1984, was 1590, including the 80 percent and 100 percent DoD cycles.

Results of the cycling tests, as of 1 May 1984, included:

- based on the projections from the accelerated cycling tests, cells tested at 40°C had reached 72-percent of the cycling goal for this temperature
- the capacity of low PAM density plates remained 10 percent higher for 20 percent less active material than the high PAM density plates during the cycles conducted. Capacity increase with cycling was continuing as of 1 May 1984. PAM utilization in Ah/kg PAM was 40-45% higher than in high density plates

The data indicated the possibility that the high PAM density plates could, in time, exceed the capacity of the low PAM density plates.

Three batteries (one 36 kWh and two 18 kWh) of the final preprototype design were delivered for testing at NBTL. The key characteristics of the 36 kWh battery, as reported by NBTL, are given in Table 10. This battery was under test as of May 1984. The life-cycle tests are to be continued to failure.

Sealed lead-acid batteries are being tested at SNL for stand-alone and grid-connected solar systems.⁽⁵⁾ Over thirty, 6 V, 100 Ah Gould and Eagle-Picher (EP) batteries have been tested with several continuing on test (May 1984). Table 11 summarizes the results of these tests, including tests on a C&D flooded lead-acid battery. Cycle testing consists of both 80 percent DoD cycles and partial recharge cycles with test batteries operated between 80 and 20 percent DoD without complete recharge. For the Gould batteries, tested for over 1000 cycles at the 5-h rate, the failure mode was typically positive grid corrosion. Failure modes are being determined on units that failed after approximately 500 cycles. Although the earlier EP batteries had short cycle-lives, more recent units show performance equal to Gould batteries. The C&D flooded batteries also had performances comparable to the Gould batteries. The two types of test showed no differences in performance or life.⁽⁵⁾

3.1.2 EV Lead-Acid Batteries

The Globe Battery Division of Johnson Controls, Inc. (Globe) has detailed its efforts on the EV lead-acid battery for

TABLE 10
NBTL TEST RESULTS OF EXIDE LOAD-LEVELING BATTERY

	MODULE*
Rated Capacity (5h rate)	36 kWh
Actual Initial Capacity (5h rate)	41.75 kWh
Gravimetric Energy Density	25.3 Wh/kg
Volumetric Energy Density	48.0 Wh/l
Energy Footprint	38.3 kWh/m ²
Projected Life	4000 cycles
Accumulated Cycles	
Actual at 50°C	943
Equivalent 25°C	2650
	(66% of cycle life goal)
Present Capacity	40.9 kWh
	(98% of initial and 114% of rated)

*Includes weight and volume of six-cell module tray and accessories.

Reference 5 (Hornstra)

TABLE 11
SEALED LEAD-ACID BATTERY CYCLE TEST SUMMARY

<u>Manufacturer/Type</u>	<u>ID#</u>	<u>Test Mode</u>	<u>Cycles Completed</u>	<u>Percent of Rated Capacity</u>
Gould/Sealed Pb-Acid				
Group 2 (delivered 4/81)	137	DEEP	972	80*
	138	DPSOC H	1336	80*
	139	DPSOC	1002	80*
Group 3 (delivered 8/81)	157	DEEP	898	80*
	158	DEEP H	761	80*
	159	DPSOC	850	80*
Group 4 (delivered 11/81)	183	DEEP H	886	80*
	184	DPSOC	798	(125)*
	185	DEEP	729	80*
Group 5 (delivered 3/82)	196	DEEP	495	80*
	197	DPSOC H	394	80*
	198	DPSOC H	567	80*
Group 6 (delivered 3/83)	331	DPSOC-S	598	80*
	332	DPSOC-S	390	80*
	333	DPSOC-S	387	80*
	334	DPSOC-S	385	80*
Group 7 (delivered 1/83)	311	DEEP	789	93
	312	DPSOC	780	72*
	313	DPSOC H	932	75*
Group 8 (delivered 1/83)	335	DEEP @ 2.5V	856	81
	336	DEEP @ 2.6V	401	80*
	337	DEEP @ 2.7V	306	80*
EP/Sealed Pb-Acid (delivered 1/82)	179	DEEP H	944	80*
	180	DPSOC H	670	79*
	181	DEEP H	919	91
	182	DPSOC H-S	1141	106
C&D/Flooded Pb-Acid	98	DEEP	710	80*
	99	DPSOC	931	80*

*Cycle testing terminated

(Date as of May 1, 1984)

Test Modes: DEEP - 80% DoD @ C/5 rate
DPSOC - Deep Partial State of Charge @ C/5 Rate
H - indicates horizontal plate orientation
-S - indicates series test station configuration

1982.(10) These results were partially covered in reference 4 and are expanded here based on the additional data available.

One objective of the Globe research effort is the improved utilization of the active material in the lead-acid battery. One approach has been the investigation of the effects of plate thickness on active material utilization. Three different positive electrode thicknesses were investigated at various current densities. A 20 percent improvement in the active material utilization was found when the electrode thickness was decreased 42 percent. Replacing an 11 electrode test cell with a 15 thin negative and positive electrode cell, the material utilization immediately after formulation was increased by approximately 25 percent. It was also shown that decreased positive paste density led to the expected greater utilization of active material.

Studies on the lead-plastic composite electrodes has continued. The formation efficiency of these electrodes has been found to be satisfactory. Deep-discharge cycling of test cells with the composite grids has been initiated.

Studies were conducted on the role of antimony, released by the positive grid during the cycling of the battery, on cell performance degradation. The cycling of an ISOA cell with Pb-Sb positive grids showed that antimony accumulated in the negative plate and this was the cause of the marked decline in cell capacity. Lead micro-electrode studies showed that decreased charge efficiency of the lead negative due to antimony could be suppressed by the presence of 20 ppm of Maracell C. Lignin. Further investigation is required to clarify the mechanism of the suppression of the harmful effect of antimony on negative electrode charge efficiency. Tests were also conducted on the removal of antimony from the negative electrode as a function of the negative charging potential. It was shown that the antimony content of the negative plate was decreased with increasing charging potential relative to a reference electrode.

Cycling tests on 15 electrode test cells showed that cell cycle life was determined by the positive electrode. Plate integrity was extremely good in all cells. Furthermore, physical and microscopic examination showed the grid to be in good condition. Microscopic examination of the grid/active material interface indicated defects in this interface. It was also observed that the positive material was easily dislodged. These observations suggest that the positive plate degradation is due to the weakening of the active material/grid interaction. This observation was tested in electrodes with larger areas of active material between grid connections. The cells with the larger free active material areas showed more rapid capacity loss.

Studies were conducted to test patent claims of the improved deep-discharge cycle life of lead-acid batteries using bonding agents, hydroxyethyl methacrylate or polyacrylic acid with polytetrafluoroethylene (PTFE), in the positive plate. Following formation, the acetic acid content of the cell was 1100 $\mu\text{g/ml}$ compared to 60 $\mu\text{g/ml}$ in standard cells. The overall cycle-life performance of these cells was poorer than the standard cell and the patent claims were not confirmed.

The effort to develop a monitoring system that accurately displays the percent state-of-charge of the battery pack at Globe has not been successful. The major difficulty was interference from the electric vehicle controller which prevented valid conclusions.

Thermal management of EV batteries has also been examined. During a 3h discharge and 7h charge (5 percent overcharge) of a battery module, temperature excursions of 15-20°C were observed when the ambient temperature was 25°C. The highest temperatures reached were between 40° and 45°C in the center of the electrode stack. Forced air convection on the sides of the module reduced the overall temperature excursion. The use of the Globe developed air-pulse pump for acid circulation reduced the temperature rise and promoted uniform temperature distribution.

Effort was reported at Globe to replace the electronically controlled electrolyte circulation system by a pneumatic system. This system was demonstrated to work but its reliability requires improvement. It was projected that the pneumatic system will cost approximately one-eighth that of the current electronically controlled electrolyte circulating system. Several Globe lead-acid modules with the electronic electrolyte circulating system have been submitted to NBTL for testing.

Earlier it was noted that the use of a watering wand decreased the watering time for lead-acid batteries. An alternative route to decreasing the watering problem is being investigated as part of the Technology Suitability Testing element. Gel/cell^R (Globe) sealed lead-acid batteries are being studied. The temperature sensitivity of charge/discharge, cycle life characteristics, and overall performance when subjected to urban driving conditions are being evaluated. Although the battery was initially developed for industrial applications, it is being tested as an EV battery because of its potential for reducing operating costs. The test program is to include field testing of approximately 40 vehicles starting in early FY 1985.

Studies were conducted to assess the impact of temperature on the cycle life of Globe ISOA lead-acid modules. This assessment was made as guidance to the thermal control requirements for optimized performance and cycle life of EV batteries. In these tests, modules were discharged for a fixed relative number of Ah's (80 percent DoD, based on room temperature capacity measurements), independently of operating temperature, in order to simulate a vehicle with a temperature-independent fixed mission. Under these conditions, a marked decrease in cycle life was observed at temperatures of 15°C and 52°C. Optimum cycle life appeared to be achieved over a temperature range between 30°C and 44°C.

A test program at the University of Alabama in Huntsville (UAH) was designed to assess the battery problems encountered when EV's are operated at various temperatures and to provide an engineering data base for the elimination of these problems. Three different 96 V EV lead-acid batteries were compared between the temperatures of -16°C to 54°C.⁽¹¹⁾ An attempt was made to correlate the performance observed with the design features of the batteries tested.

Various devices for electrolyte mixing to improve active material utilization and cycle-life of lead-acid batteries have been designed and evaluated at UAH.⁽¹²⁾ A simple low cost pump device, operated on pulsed air, that gave improved cell performance was developed.

Tests of the Globe EV batteries have been included in the NBTL program. Figure 6 is the result of the Ragone plots obtained on lead-acid and other batteries tested at NBTL. The Globe Advanced I battery shows the advances made in the combined specific energy and specific power performance of lead-acid batteries.

Some of the achievements of the lead-acid battery program were noted by Streb and by Landgrebe (Sections 1.1 and 1.2). More specific achievements were summarized by Kirk:⁽⁵⁾

Characteristic	1977	Performance Achieved	Goal
Specific Energy Wh/kg	32	43	56
Specific Power W/kg	92	104	104
Cycle Life cycles (80% DoD)	250	560	800

3.2 Alkaline Batteries

The major effort is on developing iron/nickel-oxide batteries for vehicles. There is no DOE supported developmental effort on the zinc/nickel-oxide battery. Testing of the commercially developed Delco Remy zinc/nickel-oxide battery is being conducted at NBTL. Research is being continued on the fundamental aspects of the iron, zinc, and nickel-oxide electrodes.

3.2.1 Iron/Nickel-Oxide Batteries

The iron/nickel-oxide battery program goals and 1982 objectives are given in Table 12.

The iron/nickel-oxide battery efforts at Eagle-Picher (EP) are emphasizing the following:⁽¹³⁾

- process improvements for nickel-plaque development and its impregnation to increase the battery specific energy
- overall system improvements to facilitate battery maintenance
- reduce and eliminate any potential ignition hazards in the battery

Plaque-substrate development has centered on a comparison of woven wire configurations vs. expanded metals. This included a comparison of pure nickel and nickel-plated products. A majority of the electrodes have been based on woven 0.18 mm. diameter wire, 20 x 20 mesh screens. The same wire was used for both the thin and thicker electrodes. Different woven wire and expanded metal configurations were analyzed in terms of cost, projected current carrying ability for the desired 3.4 mm thick electrode, and processability.

Concern was expressed with respect to nickel-plated substrates which are being acquired for further examination. The conductivity of the alternative substrates and their potential for contamination of the acidic impregnation bath and the cell environment are two concerns which are to be investigated.

The development of an advanced nickel plaque requires an incremental increase in thickness from 2.0 to 3.4 mm. An increase in porosity from 80 percent to 85 percent is also desired. The improved plaque must have the capability of active material impregnation to a loading of 1.6 g/cc.

TABLE 12
IRON/NICKEL-OXIDE BATTERY PERFORMANCE GOALS

	FY-1986 Goals	1982 Objective
Specific Energy (C/3 rate)	56 Wh/kg	54 Wh/kg
Volumetric Specific Energy	120 Wh/l	115 Wh/l
Specific Power - Peak (30 sec.)	104 W/kg	104 W/kg
Duty Cycle - Discharge	2-4 hrs	2-4 hrs
Charge	4-8 hrs	4-8 hrs
Energy Efficiency (Round trip)	70%	65%
OEM Price (1981 \$ for 10,000, 25 kWh batteries/yr)	\$70/kWh	\$150/kWh
Cycle Life (80% DoD to 75% capacity)	800 cycles	800 cycles

Attempts have been made to develop a slurry impregnation formulation capable of being applied to a 3.4 mm thick plaque. No entirely satisfactory slurry was achieved, as of the report date. Plaque strengths varied from 660 to 1630 psi (4.5-11.1 MPa). Modification of slurry formulations to include pore formers is being explored. Conditions for plaque drying and sintering are also being investigated. The reported plates had average thicknesses of 2.0 to 2.7 mm, porosities of 81.0 to 84.8 percent, and break strengths of 692 to 1035 psi (4.7-7.1 MPa).

Groups of plate types were impregnated using the step-current method, pH-2.4, and 2.4 M nickel nitrate. Various problems arose during impregnation. Blistering was the most significant. Various process modifications to eliminate blistering are being studied. Another problem encountered was plate bowing. This has been corrected by modifying the slurry application process. The studies have shown that the desired level of loading can be achieved. For the highest estimated capacity, an active material loading of 1.6 gm/cc of plaque was selected for cell testing. A comparison of a lightly loaded and a more heavily loaded plaque, at cycle no. 90 in a test cell, showed the capacity advantage of heavy loading:

Plaque Loading g/cc	Utilization Percent	Output Ah
1.35	86	154
1.55	80	164

During the period reported in reference 13, experimental three-cell modules were constructed and tested. Except for specific energy and cost the program achieved the objectives for 1982.

The multi-cell watering system was modified by the addition of a flow control device and the coupling of this device to the battery. This eliminated the non-uniformities. Active battery tests showed that the filling rate should be approximately one cell per minute. This requires a two foot (61 cm) head.

Attempts were made to develop a flame arrestor which would prevent the accidental ignition of the hydrogen and oxygen which form during charging. Catalytic hydrogen and oxygen devices and flame arrestors were tested but none were completely successful.

Cells that were tested at NBTL and had shown charge voltage deviations and self-discharge after 760 cycles were disassembled for visual inspection. The following observations were reported:

- The positive plates were in good condition. There were some small blisters which probably had only a small effect on performance.
- The negative plates showed evidence of corrosion, especially at the outer edges. The central portions were intact.
- All the positive plates showed growth in width and length of approximately 1.5 percent. The stability was great enough to project that they would have survived an additional 800 cycles.
- The separator appeared to be loaded with sludge. Although the folded edges of the separator had been split by positive plate growth, the separator had not lost its effectiveness.

Some of the above shortcomings had been recognized prior to the cell inspection and changes were made in later cell designs. These included larger sludge space and placing the separator around the negative instead of the positive electrode.

The overall Westinghouse approach to the iron/nickel-oxide battery was summarized in reference 4. Details of the investigation of various approaches taken to achieve low-cost batteries that could meet performance objectives are included in reference 14.

Improvements in the processes for making the various components in order to meet program goals continued through 1982. Some emphasis was placed on the preparation of pasted positive plates. The pasting composition developed earlier, consisting of a mixture of hydrated nickel oxide, nickel carbonate, and hydrated cobalt oxide continued to be used. Various commercially available hydrated nickel oxides have been evaluated for their effect on paste rheology, plate formation, and in cell performance. Evaluation of the best of these materials was continuing at the end of the report period.(14)

Various plating procedures, both electroless and electrolytic, were investigated for coating the positive grid. A combination of both methods was found to be most effective for the prevention of grid corrosion. Alternative separators to the Celanese K501 standard separator were also investigated. Based on the tests conducted, an alternative separator was selected for full cell testing. However, this material is more expensive than the standard material.

Reduction in battery weight and volume is another major improvement objective of the Westinghouse program. An integrated five or six cell module to replace the single cells used in the modules under test can reduce the number of "heavy" cell walls. Other improvements considered the use of through-the-wall connectors instead of top mounted terminals with cell interconnect cables, and internal ducting for electrolyte circulation.

Charge optimization is being investigated to increase cycle energy efficiency from 50-55 percent to the desired 70 percent. This efficiency was achieved by discharging only 67 percent of the nominal C/3 capacity and charging at constant current to 105 percent of the current discharged.

The testing of iron/nickel-oxide batteries has continued beyond that reported by Eagle-Picher and Westinghouse. (13)(14) The tests at NBTIL have shown that the specific energy and cycle life of iron/nickel-oxide batteries exceed those of lead-acid batteries. However, the iron/nickel-oxide batteries require a significant overcharge to achieve full capacity. Repeatable iron/nickel-oxide battery operation was achieved over a wide range of overcharge levels (10-50 percent). Discharge capacity increased with the level of overcharge. An overcharge level of 25 percent was typically required to obtain the manufacturer's rated capacity for the modules tested. Discharge capacities in excess of the rated value were achieved with overcharges of more than 25 percent. The maximum capacity obtained was 114 percent of the rated value. The combination of iron/nickel-oxide battery capacity and efficiency can be optimized for a particular application by the selection of the overcharge level.

The overcharge level required to achieve iron/nickel-oxide battery rated capacity was shown to be dependent on the battery's initial DoD level. A 75 percent overcharge was needed to attain rated capacity from a 100 percent DoD condition. From DoD levels of 25, 50 and 75 percent, overcharges of about 50 percent were required. The greatest ampere hour overcharge level was required for a 75 percent DoD and caused the greatest evolution of hydrogen and of water consumption.

The rate of self-discharge of iron/nickel-oxide batteries was observed to be directly related to the standtime after charging and the state-of-charge of the battery. The self-discharge rate decreased rapidly during either stand-by or discharge. A four hour standtime, after a recharge to provide full capacity, resulted in a 5.5 percent loss in capacity. In contrast, a four hour standtime at a 20 percent DoD level resulted in no measurable loss in capacity.

The NBTL Ragone curve for the iron/nickel-oxide battery, Figure 6, showed a higher specific energy at a given specific power than the lead-acid batteries tested.

Kirk summarized the advances made in the iron/nickel-oxide battery under the DOE program:⁽⁵⁾

Characteristic	1977	Performance Achieved	Goal
Specific Energy Wh/kg	38	48	56
Specific Power W/kg	86	102	103
Cycle Life (80% DoD)	510	930	800

3.2.1.1 Overview of Iron/Nickel-Oxide Battery Status

The potential for long cycle-life, 800 or more cycles, for this cell is well established. Its major performance deficiency is its low energy efficiency. This is largely due to the requirement of a high overcharge to restore the battery capacity.

Eagle-Picher has observed sludge formation during recycling. The probability of shorting due to the sludge was decreased by increasing the dead-space in the cell bottom. EP has also addressed the problem of the hazard due to hydrogen and oxygen accumulation, in part, related to the high overcharge requirement but which also can occur during the self-discharge after charging. Overcharging also leads to the need for a watering capability for large batteries such as those required for EV's. Westinghouse also recognizes the need to improve the safety, performance, and reliability of the electrolyte management system. The need for maintenance free cells has also been noted by Westinghouse.

The achievability of the cost objectives for the iron/nickel-oxide battery, in spite of projections, needs to be better established. The Westinghouse approach to lower cost grids and pasted positive plates and lower cost cell and battery assemblies are targeted toward this need.

A fundamental concern is whether or not the high overcharge requirement for the iron/nickel-oxide battery is inherent to the cell electrochemistry or is in part due to electrode structure. This overcharge requirement limits the cycle efficiency, increases the lifetime cost, and contributes to the hazard potential of the iron/nickel-oxide battery.

3.2.2 Zinc/Nickel-Oxide Batteries

The decision to discontinue the DOE support for the development of the zinc/nickel-oxide battery was reported in reference 4. That report included a summary of the status of the various Zn/NiO(OH) battery development programs as of the time of their conclusion. The only Zn/NiO(OH) battery investigation during 1983 and early 1984 was the earlier noted NBTL testing of the privately developed Delco-Remy battery. The Ragone plot for the Delco-Remy battery is included in Figure 6. Tests of this battery are continuing at NBTL to obtain additional information on cycle-life and other performance characteristics.

3.2.3 Alkaline Battery Research

The research on the alkaline battery electrode reactions, electrolyte, and separators is being continued as guidance to improved material selection, electrode composition, and electrode construction. These studies include electrolyte and electrode thermodynamics, electrode kinetics and mechanism, and zinc-ion transport through separators.

Earlier results of the study under Digby D. Macdonald on the thermodynamic framework for estimating the characteristics of alkaline battery electrolytes and the electrode reactions, were included in reference 4. The completed efforts have been reported and represent an extension of the earlier summarized calculations of electrolyte thermodynamic properties and preparation of pH-potential diagrams.⁽¹⁵⁾ The thermodynamic data has been used to calculate reversible cell potentials for a number of battery systems; these calculations assume well defined electrode reactions. The calculated reversible cell potentials were compared with observed cell voltages to compute the voltage efficiencies for various alkaline batteries. Included here are the results of metal/air and hydrogen/nickel-oxide couples which are to be reviewed in Chapter 4.0.

The calculated cell voltages varied with the concentration of alkali metal hydroxide and temperature. These variations can be summarized in four groups:

- Al/air, Zn/air, and Zn/NiO(OH) - the cell potential increased with alkali concentration but decreased with an increase in temperature
- Li/air and to a lesser extent Fe/air - the cell potential decreased with alkali concentration but increased with an increase in temperature

- Fe/NiO(OH) - the cell potential decreased with an increase in alkali concentration or an increase in temperature
- H₂/NiO(OH) - the cell potential is independent of concentration but decreases with temperature

The efficiencies of H₂/NiO(OH), Fe/NiO(OH), and Zn/NiO(OH) test cells were between 90 and 100 percent. The high efficiencies imply that, at least on open circuit, there is little, if any, contribution from parasitic redox couples to the cell potentials for the above couples. The efficiency of the Fe/air test cell was relatively low (72 percent). This may have been determined by the nature of the redox couple at the air electrode.

The above reported estimates are limited in accuracy because of the limitations of the approximation methods used to calculate the thermodynamic quantities required.

An experimental program has been established to eliminate the uncertainties of the above calculations. The uncertainties include:

- the stoichiometric mean molal activity coefficient
- the ion-association constant
- the ionic product of water

To obtain more accurate data, equilibrium potentials are to be measured in an electrochemical cell. The cell arrangement permits the simultaneous measurement of equilibrium potentials for three different cells. Two of the cells give concentration-cell potentials relative to KOH (1 mol/kg), and give data on the electrode/electrolyte properties. The third potential measurement enables the determination of water activity in the test alkali solution.⁽⁵⁾

3.2.3.1 Iron Electrode Research

Investigations have also been conducted on the chemical and electrochemical reactions at the various anodes and cathodes of alkaline cells. M.C.H. McKubre has used potentiodynamic sweep voltammetry and coulometry, rotating disc, and AC impedance measurements for studying anodic and cathodic reactions of alkaline battery active material.⁽¹⁶⁾ The impedance measurements and their interpretation were summarized in references 3 and 4.

The measurements have led McKubre to postulate a mechanism for the formation and discharge of an oxide film on iron via a number of dissolved intermediate species. The thermodynamically favored

reaction paths for the iron charge and discharge reactions at high and low temperatures have been derived from the dynamic electrochemical measurements. These favored reaction paths, together with the impedance measurements, were used to propose a mechanism as a working hypothesis for future investigations. Some of the features of the mechanism include different pathways for the oxidation and reduction reactions as a function of temperature. FeO_2^{2-} is an intermediate species at low temperature whereas HFeO_2^- is a high temperature intermediate. The evidence indicates that the oxidation and reduction of iron proceed via the formation and discharge of an oxide film and involve a number of dissolved species. The exchange current at zero charge, i_0 , showed that the kinetic constraints for the charge/discharge process decrease with increasing temperature. However, the principal kinetic limitations of charge and discharge originate within the oxide film and not with charge transfer at the interface.⁽¹⁶⁾ Although the measurements were made in NaOH, the general conclusions are considered to be applicable to KOH.

D.S. Poa, et. al., have also investigated the mechanism and kinetics of iron dissolution reactions but used KOH as the electrolyte.⁽¹⁷⁾ Both cyclic voltammetry and rotating ring-disc electrode (RRDE) techniques were used. The measurements were made in 0.5 to 10.0 M KOH with and without additives.

The RRDE experiments in 5 to 7.5 M KOH showed that the reversibility of the electrode is relatively higher at these concentrations, and the coulombic inefficiency and loss of reactant relatively lower during both charge and discharge, than in lower alkali concentrations. More concentrated electrolytes (8-10 M) indicated a greater probability of efficiency loss due to oxidative dissolution and the increased formation of solid film products under anodic conditions. These factors may make the iron electrode less reversible in the high alkali concentration electrolytes.

Poa and coworkers also investigated the effect of additives, such as K_2S , LiOH , and FeO , on the behavior of the iron electrode. The results were interpreted as follows:

- K_2S - the optimum concentration of K_2S improves the reversibility of the iron electrode during charge and discharge cycling. K_2S can improve the high-rate discharge performance and increase the hydrogen overvoltage of the iron electrode
- LiOH - the RRDE measurements indicated that LiOH decreases the extent of oxidation of Fe to valence states higher than 2, may improve the Fe electrode reversibility, and significantly reduces the formation of solid film products

- FeO - the effect of FeO was interpreted as indicating a decrease in solid-film product formation, the possible increase in soluble Fe(III) species, and increase in the hydrogen overvoltage

3.2.3.2 Zinc Electrode Research

The limited reversibility of the zinc electrode was the primary cause for discontinuing the development of the Zn/NiO(OH) battery. The observed effects leading to the low cycle life of this battery are zinc dendrite formation, change in the shape of the active zinc area, zinc densification, and loss of zinc from the negative electrode. Several research efforts have been undertaken under the LBL TBR activity to give guidance for increasing the cycle life of the zinc electrode.

Elton J. Cairns and associates at LBL are investigating factors affecting the cycle life of the alkaline zinc electrode.⁽⁵⁾⁽¹⁸⁾ Earlier studies, reference 4, had shown that pulsed-charging at low peak current density and low charge per pulse gave the best cycling results. Further studies have included the effect of changes in electrolyte composition on cell performance. The test cell configuration used two sintered nickel-oxide electrodes and one pasted zinc electrode. The negative electrode paste consisted of 94 percent ZnO, 2 percent PbO, and 4 percent polytetrafluoroethylene (PTFE). The electrolytes included:

- 30 percent KOH, 1 percent LiOH saturated with ZnO
- 15 percent KOH, 1 percent LiOH saturated with ZnO
- 15 percent KOH, 15 percent KF saturated with ZnO and LiOH
- 22 percent K₃BO₃, 1 percent Li₃BO₃

The various cells were operated at 100 percent DoD at constant current. The cell capacity was determined at a fixed cut-off voltage of 1.1 V. The zinc electrode changes were followed by mass balance, x-ray, and scanning electron microscopy. The change in shape factor was determined by the ratio of retained capacity to the electrode area loss.

Zinc loss due to migration was shown to be 30-50 percent. The capacity loss rate was decreased by the presence of the alkali borate and the alkali fluoride, and zinc dendrite formation was also suppressed. The cell capacity after cycling was determined by the redistribution of zinc on the electrode (change in shape) and charge acceptance by the positive electrode. The shape change varied

between electrolytes with the shape change decreasing with the decreasing solubility of zinc hydroxide (as zincate ion) in the electrolyte. The electrolyte containing 15 percent KF showed the least shape change and little change in the uniformity of active material distribution over the zinc electrode.

The earlier studies by T. Katan on the reaction profiles developed during the cycling of porous zinc electrodes, reported in references 2, 3, and 4, have been continued. The experimental technique is to observe the electrochemical behavior in a simulated zinc pore having dimensions similar to those of a real pore i.e., about 20 microns. The reference electrodes were prepared by vapor depositing silver onto an alumina substrate. To obtain the spacing between reference electrodes, photographic procedures employing photoresists were used. The substrate was embedded in epoxy and polished to obtain reference electrodes for measurements in the simulated 20 micron pore.⁽⁷⁾

A computer controlled data acquisition and programming system was used for data collection. Potential-profile information was obtained for both constant current and cycled current operation. The pore penetration depth was observed as a function of current density. The potential distribution indicated a pore penetration depth of 0.08 cm. This corresponds to 0.02 cm for a typical commercial electrode. The penetration depth was a function of applied current, the greater penetration occurring at the lower currents. In addition, edge effects became more pronounced with increased current density. The movement of the reaction front, ZnO formation on the surface, was followed by a zone of relatively lower reaction rate. The precipitation of ZnO resulted in pore blockage, masking the pore surface and forcing the reaction front to move deeper into the pore. Hydroxyl ion concentration gradients resulted from the formation of ZnO. These gradients were sufficient to form concentration cells, corresponding to zinc dissolution and precipitation currents of about 0.8 mA/cm².

Potential profiles developed from the edges of the zinc electrode toward the center, in the transverse direction, and from the front towards the rear axially. The results indicated, that for a cross-sectional current density of 50 mA/cm², there was a potential difference of about 6 mV between the edge and interior of the pore.

The photomicrograph of the pore showed the movement of the zinc from high current density toward lower current density points during cycling. The tendency of zinc to form on the edge was observed to decrease with cycling. The effect was to force the zinc toward the center of the plate and to regions of lower current density where the separation diminished the current.

Based on these studies, Katan attributed shape change to the current density distribution and the reactant concentration distribution. Pore penetration was a function of current density and cycling.

Cairns and coworkers have also conducted model single-pore experiments to study the discharge behavior of the zinc electrode.⁽⁷⁾ The cell design enabled the simultaneous microscopic and potential observations using pores of dimensions comparable to those in commercial electrodes. The reference electrode was a quartz-supported cadmium thin film and was used to provide pore potential-distribution and hydroxyl-ion concentration data. Discharge behavior was studied in pores of effective radii between 14-20 microns at 7, 30, and 1250 mA/cm² in 7.7 M KOH. The results obtained were consistent with the dissolution-precipitation mechanism. SEM studies showed significant variations in electrode surface morphology with location in the pore and rate of discharge. Significant hydroxyl-ion gradients, with slow relaxation times at the 30 mA/cm² rate, were found to exist within the pore. There was no evidence of electrode passivation at current densities of 7 and 30 mA/cm², but passivation was observed at 1250 mA/cm².

Closely related studies were conducted by McKubre.⁽¹⁶⁾ He and coworkers investigated the influence of convection and zincate-ion concentration on the dissolution kinetics and passivation of the anodic (discharge) reaction of zinc. As in the studies on iron, these studies used rotating disc and impedance measurements. Based on the observations, McKubre proposed that the dissolution proceeds via consecutive one electron changes with Zn⁺¹ as an adsorbed intermediate species. Zinc hydroxide, in a porous and loosely adherent form, was suggested as the first discharge product. At potentials below the passivation potential, the zinc hydroxide separates from the surface as a colloid and is in equilibrium with the zincate ion in solution. This equilibrium is controlled by the hydroxyl-ion concentration. The dissolution of the zinc is hypothesized to be catalyzed by the zincate ion, and the rate of dissolution controlled by the rate of diffusion of the zincate ion to the electrode. This autocatalytic effect was confirmed by the impedance measurements, and McKubre suggested that this is a plausible mechanism for shape change of zinc electrodes.

Various studies on the effect of the addition of heavy metal oxides to the zinc electrode were reported in references 3 and 4. James McBreen and Ellen Gannon have extended these studies to the inclusion of bismuth oxide in the mix of a pasted zinc electrode.⁽¹⁹⁾ The effect of Bi₂O₃ additions was investigated by the use of cyclic voltammetry, chronopotentiometry, polarization measurements, and scanning electron microscopy. The results

indicated that during plate formation most of the Bi_2O_3 was reduced to metallic bismuth prior to the reduction of the zinc oxide. The bismuth formed a needle-like matrix in the active material paste. The presence of Bi_2O_3 did not greatly affect the electrode polarizability or the current distribution on the zinc electrode. The deposit of zinc on bismuth was found to be more active than the earlier studied deposit of zinc on lead or indium. It was suggested that the beneficial effect of Bi_2O_3 may be in the prevention of densification of zinc formed during charge.

Earlier studies on the effect of pulsed charging on the reversibility of the zinc electrode were noted in references 3 and 4. McBreen and coworkers have compared dc charging of the zinc electrode with dc charging with superimposed ac square waves of various amplitudes and frequencies, 0.1-5000Hz.⁽²⁰⁾ In the case of dc charging, the faradaic conductance passed through a maximum at $\sim 75 \text{ mA/cm}^2$. The decrease in the faradaic conductance at higher current densities (100 mA/cm^2) was related to the formation of dense zinc deposits on the electrode surface. At low dc current densities ($\sim 30 \text{ mA/cm}^2$), superimposition of ac promotes growth of zinc close to the current collector and results in small amounts of dispersed hexagonal zinc deposits on the current collector. The low current density pulsed charging was beneficial in that it increased the electrode faradaic conductance and promoted growth of the zinc deposit close to the current collector. Based on the relaxation time of the double layer, it was suggested that the optimum frequency for pulsed charging was between 1 and 10 Hz.

3.2.3.3 Zinc/Nickel-Oxide Battery Separator Research

Previous studies have shown that the separator, both micro-porous and ion exchange types, and its physical arrangement affect the cycle life of Zn/NiO(OH) batteries. This has led to a more intensive investigation of the modeling, composition, and structure of separators as they influence zinc electrode reversibility.

Douglas N. Bennion and coworkers have been developing models of membrane transport. Earlier results are being published.^(a) This model describes solute and solvent transport across neutral or ion exchange membranes. The model is based on concentrated electrolyte theory and Stefan-Maxwell transport equations. The result of the model is a correlation of salt and solvent fluxes through the membrane along with the concentration, pressure, and electrical profiles in the membrane. The model contains two equilibrium and six transport parameters when applied to the transport of a single salt and water.

(a) Pintauro, P., and D.N. Bennion, "Mass Transport of Electrolytes in Membranes, I Development of Mathematical Model," I&EC Fundamentals, in press.

Measurements of the equilibrium properties for the NaOH-H₂O-Nafion^R membrane were conducted to assist in the testing of this model.^(5,22) Various techniques were used to determine the following parameters:

- membrane-anion concentration
- membrane-water concentration
- membrane fixed-ion concentration
- wet-membrane density

It was determined that at a fixed temperature the water concentration in the membrane decreased with the external concentration of the alkali (NaOH). The other parameters increased with alkali concentration. The concentration difference and the volumetric flow rate through the membranes were measured, and the membrane-cation transference number determined.

Reverse osmosis experiments were also conducted at NaOH concentrations of 1, 4 and 8 molar and at various temperatures. The results showed that at a given temperature the flow rate through the membrane decreased with increasing NaOH concentration; the flow rate for a given concentration increased with temperature.

Related measurements using radiotracers were conducted by R.T. Ruggeri and T.R. Beck.⁽²³⁾ They concluded that the use of radiotracers is a viable technique for determining multiple transport numbers and self-permeability coefficients in a single experiment. The radiotracer method was reported as being of equal accuracy to the conventional Hittorf method and can be effectively used in the study of multicomponent mass transport in a wide variety of membranes.

The high cost of Nafion^R and the availability of models for membrane transport have led to the attempt to synthesize alternative materials. Based on the models developed by Bennion and coworkers, which includes parallel hydroxyl-ion and water transport, it was postulated that anionic exchange membranes would decrease shape change, dendrite formation, and voltage loss in Zn/NiO(OH) batteries. The investigation of the synthesis of such membranes was reported at BECC-6.⁽⁵⁾ The capability of crown ethers to dissolve inorganic salts led to the selection of these compounds for exploration. The size of the ether ring determines the cation selectivity of the crown ether. The incorporation of the macrocyclic crown ethers into the ion exchange membrane is expected to enhance the ion transport in the Zn/NiO(OH) battery and to lead to better performance.

The eighteen different macrocyclic crown ethers synthesized for investigation are shown in Figure 7. The macrocyclic crown ether most extensively studied, as of June 1984, was compound 7. This was converted to the potassium salt using potassium thiocyanate. Membranes containing this salt and polypropylene or a vinylidene chloride-vinyl chloride copolymer were prepared. The presence of the macrocyclic crown ether improved the uptake of 4M KOH and the membrane conductivity. However, a greater increase in conductivity is required for a practical membrane.

R.S. Yeo and J. Lee are also attempting to synthesize improved membranes for alkaline electrolyte batteries.⁽⁵⁾ Their approach is to prepare hybrid separators which contain the properties of both microporous and ion exchange materials. The ultimate objective is a separator material which is highly specific for fast transport of the electrolyte while inhibiting zincate-ion diffusion.

The separators are being prepared by the radiation grafting of a monomer, such as methyl acrylic acid, onto a microporous substrate. The extent of grafting was controlled by the concentration of monomer and the radiation dosage. The ion-exchange capacity was directly proportional to the extent of grafting. The ion selectivity of the individual hybrid separators was as effective as that exhibited by the corresponding ion exchange membrane. The zincate ion permeability was much lower for the hybrid separator. The hydraulic permeability was higher.

Based on the above observations and a model of the hybrid separator performance, it was concluded that the new separator materials should lead to improved cell cycle-life. This is to be examined in cell studies.

The initial studies of J. P. Pemsler and M. D. Dempsey on supported liquid membrane (SLM) separators were briefly summarized in reference 4. These membranes consist of a microporous separator, such as Celgard^R (polypropylene) or a cellulosic material, infiltrated with highly-specific organic reagents.⁽⁵⁾ The latter assist in the control of the transport properties across the separator. A number of ion-exchange reagent/solvent/modifier systems have been investigated. Details with respect to the reagent/solvent/modifier combination were not available due to the status of the corresponding patent applications.

The separators showed high specificity, low cost, and low resistivity. Zincate ion transport across the separator was decreased, and there was no penetration of dendrites across the modified separator during cycling.

**MACROCYCLIC CROWN ETHERS
 FIGURE 7**

A modified zinc/nickel-oxide cell design was used to test the performance of the supported liquid membranes. The new cell design allowed for the total thickness of the electrodes (one negative and two positives), wicks, and the SLM separator without causing excess pressure on the electrode package. Excess gassing, localized heating, and electrolyte-wick dry out were attributed to the pressure on the electrodes in the earlier cell designs.

The cells were life-cycle tested at C/2 to 100 percent DoD. Two SLM systems showed cycle-lives of 250 and 306 resp. This was better than the use of one or two layers of Celgard^R but inferior to the use of three Celgard^R layers. The performance testing of SLM separators is continuing.

The study of the application of SLM membranes to the zinc/ferricyanide cell and other research related to flow battery systems will be discussed in Chapter 5.

3.2.3.4 Nickel-Oxide Electrode Research

Various studies on the electrochemistry, kinetics, and structural changes in the nickel-oxide electrode were reported in references 1 through 4. This positive electrode is common to the Fe/NiO(OH), Zn/NiO(OH), and H₂/NiO(OH) batteries.

The earlier studies of M. J. Madou, summarized in reference 4, have been extended and the results of studies of impedance and photoeffects of the nickel-oxide electrode have been published. (24)(25) The experimental methods used in these studies were primarily photocurrent measurements as a function of voltage, wavelength, and chopper speed as well as the previously referenced impedance measurements as a function of frequency and voltage. The measurements were performed on nickel-oxide films of various thicknesses on a nickel substrate. It was found that depending on the electrode potential, an n-type or p-type semiconducting oxide can be present at the surface of a nickel electrode. Under illumination the n-type oxide gives rise to anodic photocurrents and the p-type oxide, to cathodic photocurrents.

The impedance measurements show that a solid-state diffusion process, presumably of protons through the oxide film, dominates the impedance behavior for the charged electrode. In the case of the discharged electrode, the impedance behavior is dominated by the space-charge inside the p-type oxide.

The effect of secondary ions in the electrolyte, in addition to Li⁺ from LiOH which is used as an electrolyte constituent, on the nickel-oxide electrode was studied. The ions included Co⁺²,

Fe^{+2} , Ba^{+2} , and Zn^{+2} which can be present as beneficial additives or unintentional impurities. Three types of electrodes were studied: bare nickel, single crystal NiO, and an electrodeposited NiO film. In the case of the NiO film, the secondary ions were codeposited with the NiO. The observed effects included:

- the rate of oxygen evolution on nickel-oxide electrodes increases with time
- the presence of Li^{+} delays the aging of the nickel-oxide electrode and increases the overpotential for oxygen evolution
- the presence of iron increases oxygen evolution from the nickel-oxide electrode
- the presence of Li^{+} does not affect single crystal nickel oxide
- the addition of CoSO_4 to the alkaline electrolyte was more effective than the codeposition of cobalt and nickel oxides

These studies resulted in the suggestion that addition of CoSO_4 to the electrolyte be investigated as a method for improving the nickel-oxide electrode performance to replace the codeposition of cobalt oxide.

Earlier studies of the nickel-oxide electrode using impedance and electrochemical techniques have been reported by McKubre.⁽¹⁶⁾ These used 20, 24, and 28 weight percent NaOH as the electrolyte. The temperature range for these studies was -20° to 120°C . Two principle sources of irreversibility were postulated to explain the observations. Although the thermodynamic properties of the Ni(II) to Ni(III) reaction are similar to those for oxygen evolution, the former predominates at low temperature because of the large over-voltage for oxygen evolution. With increasing temperature the exchange current density for oxygen evolution increases markedly, leading to a decreased charge capacity and coulombic efficiency.

An irreversibility of the nickel-oxide electrode was observed to be associated with deep or prolonged discharge, particularly at elevated temperatures. This was demonstrated by using various cathodic hold times during the cyclic voltammetry of the nickel-oxide electrode. The ensuing anodic process required a higher potential and consumed a higher charge with increasing hold time. This can contribute to cell inefficiency depending on the charge conditions and temperature.

Parallel studies on the effect of temperature on the morphological changes occurring during the cycling of the nickel-oxide electrode have been conducted by Macdonald and his associates. The transmission line model (TLM) which they developed for the interpretation of impedance measurements was summarized in reference 3. Roll-bonded and sintered nickel-oxide electrodes were used in these studies.

Parameters of the TLM were curve-fitted to the experimental data for porous electrodes at different stages of cycling. The changes in these parameters with cycling time were consistent with experimental observations, and could be attributed to various electrode phenomena. At 23°C these included:⁽⁷⁾

- the average pore length decreased with cycle number, but always remained larger than the thickness of the electrode
- the average solid phase resistivity increased with cycle number
- the solution resistance within the pores remained virtually unchanged during the cycle life of the electrode
- the number of active pores decreased after the first few cycles
- the average resistance per pore of the solution and solid phases decreased during cycling with the corresponding decrease in potential across the electrode
- the total impedance of the porous electrode was relatively insensitive to the impedance of the solution/backing-plate interface indicating that little current flows along the entire pore length in the solution.

Degradation of roll-bonded electrodes became more rapid at elevated temperatures, 60 and 100°C. At the elevated temperatures, the oxygen evolution reaction proceeds at significant rates simultaneously with the nickel-oxide charging reaction. Sintered electrodes showed more abrupt failures than the roll-bonded electrodes and broke down rapidly at 100°C. This indicated that oxygen evolution can also affect the cycle life of sintered electrodes.

The experimental data for roll-bonded electrodes were generally consistent with a degradation mechanism which involves the simultaneous restructuring of the active material and rupture of particle-particle ohmic contacts. The restructuring accounts for

the decrease in average pore length, decrease in the number of pores, and decrease in the average solution resistance per pore during cycling. The restructuring process was postulated as resulting from dissolution/precipitation processes occurring in the pores during cycling causing a redistribution of material. The rupture of particle-particle contacts could result from the stresses generated due to volume changes upon the cyclic interconversion of Ni(OH)_2 and NiO(OH) .

The above reported studies of McKubre and Macdonald show the importance of temperature control on the performance of the iron/nickel-oxide battery as well as other systems containing nickel oxide. J. Lee, et. al., applied the earlier derived ANL mathematical model for the thermal balance in batteries to the design of iron/nickel-oxide batteries.⁽²⁶⁾ Modifications made to the earlier model were summarized in reference 4, and presented in greater detail in reference 27. The modifications included:

- dividing a cell into two thermal regions,
 - (a) the "core" consisting of electrodes and separators
 - (b) the "boundary region" consisting of the cell case and electrolyte adjacent to the case
- adding the thermal resistances imposed by boundary electrolyte and cell case
- accounting for boundary mass accumulation due to internal convection

To improve the correlations between the results of the solution of the model and the cell design, the dimensionless parameters have been regrouped and the total heat dissipation separated into heat fluxes through individual surfaces via the various heat transfer modes.

Table 13 shows the relative importance of some of the thermal parameters on the thermal balance during cell discharge and cell temperature uniformity. These results indicate that the temperature rise of a single cell is strongly affected by the heat generated, boundary conduction, and convective heat transfer. The importance of boundary conduction and convective heat transfer decreases in a five-cell module because of the relative decrease in external surface area. At higher rates of discharge, C or C/2, the thermal resistance of the cell case and surrounding electrolyte becomes very significant. The temperature uniformity in a cell is most strongly affected by boundary conduction and convective heat transfer. The model has been applied to the design of iron/nickel-oxide cells.

TABLE 13
RELATIVE IMPORTANCE OF THERMAL PARAMETERS
IN A TYPICAL IRON/NICKEL-OXIDE CELL

Thermal Parameters	Cell Temperature Rise		Cell Temperature Uniformity
	High Rate Discharge	Low Rate Discharge	
<u>Energy delivered</u> <u>Heat capacity</u>	X	X	
<u>Total Reaction Heat</u> <u>Heat capacity</u>	X	X	
Heat conduction	X		X
Heat convection (due to porosity change)			X
Boundary conduction	X		X
Convective heat transfer	X	X	X
Ambient heat transfer	X	X	

4.0 ALKALINE BATTERIES WITH GASEOUS REACTANTS

Several battery systems that involve a gaseous electrode in an alkali electrolyte are being investigated. These include hydrogen/nickel oxide, iron/air, and aluminum/air. Although no effort on the zinc/air battery is included in this report, consideration is being given to renewing investigation of this system. All of these systems, except for aluminum/air, are electrochemically reversible; aluminum/air is being approached as a mechanically rechargeable battery with the potential for a much longer duration vehicle between recharges than the electrochemically reversible batteries.

4.1 Hydrogen/Nickel-Oxide Battery

The use and design of the $H_2/NiO(OH)$ cell as an aerospace system and the design modifications required for terrestrial application in stationary electrical storage systems were reviewed in reference 3. Based on the earlier design study, a contract to conduct the research and cell design investigations needed to develop a low cost $H_2/NiO(OH)$ battery was negotiated. This is a joint effort of COMSAT and Johnson Controls, Inc.

The objectives of this investigation of the $H_2/NiO(OH)$ battery, in addition to lower cost, are a sealed, 100 Ah battery capable of maintenance free operation for 20 years. Alternative prismatic cell designs, rather than the aerospace cylindrical cell, are being investigated. As of June 1984, nine-different 100-Ah cell configurations had been tested. These, together with the cell components used, are listed in Table 14. Cells 3 and 9 are being tested at SNL, and were reported to have completed approximately 30 cycles at 60 to 70 percent DoD, and at least one cell had undergone 500 cycles at 70-80 percent DoD (June 1984).

Cell 9 is the most advanced of the experimental cells. It has a back-to-back electrode construction. The electrochemically impregnated positive electrodes contain cadmium as an additive. Cadmium has been found to give a positive electrode with improved high temperature performance. Cobalt additives were found to produce better low temperature performance. The high platinum loading of the aerospace hydrogen electrode, 7 mg Pt/cm², has been markedly reduced by using a carbon substrate with 0.4 mg Pt/cm².

A 7.5 V (6 cell) 100-Ah battery was fabricated using the more cost effective technology. The cell was operated inside of a pressure vessel. Initial cycles were used to evaluate capacity, cell matching, and cycle performance stability at various temperatures. The measured capacity was in excess of the 100-Ah design goal. Pressure and voltage stability with cycling were achieved,

TABLE 14
EXPERIMENTAL HYDROGEN/NICKEL-OXIDE BATTERIES

Cell Number	Positive ^a		Negative ^b		Separator ^c	Design
	Number	Type	Number	Type		
1	22	JCI	22	Platinum	W. R. Grace	Back-to-back
2	22	JCI	22	10% Platinum/Carbon	W. R. Grace	Back-to-back
3	22	JCI	22	10% Platinum/Carbon	Asbestos	Back-to-back
4	22	255 JCI	22	10% Platinum/Carbon	Asbestos	Back-to-back
5	22	255 JCI	22	10% Platinum/Carbon	Asbestos	Recirculating
6	21	255 JCI	22	10% Platinum/Carbon	Asbestos	Recirculating
7	21	JCI*	22	10% Platinum/Carbon	Asbestos	Recirculating
8	21	255 JCI	21	10% Platinum/Carbon	Asbestos	Back-to-back
9	21	JCI	21	10% Platinum/Carbon	Asbestos	Back-to-back

^aPositive Electrodes

JCI : 0.76-mm thick wet slurry plaque, aqueous impregnation process with cadmium additive.

255 JCI : 0.76-mm thick dry sinter plaque, aqueous impregnation process with cobalt additive.

JCI* : 0.76-mm thick wet slurry plaque, aqueous impregnation process with cobalt additive.

^bNegative Electrodes

Platinum : Standard aerospace platinum catalyst with 6 to 8 mg Pt/cm² surface area.

10% Platinum/
Carbon : Carbon/platinum catalyst with 0.4 mg Pt/cm² surface area.

^cSeparator

W. R. Grace : Inorganic/organic composite consisting of nonwoven polyolefine with inorganic filler material.

Asbestos : Quin-T fuel cell grade asbestos.

Reference 5 (Dunlop)

and cell matching, evidenced during capacity measurements, was maintained at 3.5 Ah to 1.0 V for all cells in the battery.

The self-discharge characteristics of the battery were similar to those of individual cells. The uniform capacity of the individual cells indicated the absence of electrolyte bridging or leakage between cells.

A manufacturing process for the cells has been developed. The battery cost has been reduced by a factor of 10, from \$35,000/kWh to an estimated \$3,500/kWh. Further cost reduction is required to meet the cost goals for a solar stationary battery application.

4.2 Iron/Air Battery

The past efforts on applied research and development of the iron/air battery have been described in the earlier status reports, references 1-4. The need for a long cycle-life bifunctional (charge and discharge) oxygen (air) electrode has led to emphasis on the characterization and improved performance of this electrode. Specific objectives are to reduce the polarization at the air electrode and to extend the cycle life to 1000 cycles. The air electrode performance desired is -60 mV vs. Hg/HgO at 25 mA/cm² on discharge and 480 mV vs. Hg/HgO at 12.5 mA/cm² on charge.

E.S. Buzzelli, Westinghouse, reported on recent efforts to improve the oxygen electrode performance.⁽⁵⁾ A study was made of various types of carbon for use in the positive electrode. The high-surface-area furnace black, Black Pearls 2000, showed a high rate of corrosion, especially at charging potentials. Shawinigan Black (SB), a medium-surface-area acetylene black, showed a low corrosion rate and high activity for oxygen evolution. Shawinigan Black is also active for peroxide generation.

Binders to reduce the cost of positive electrode fabrication have also been investigated.⁽²⁸⁾ This has resulted in finding two alternative binders as potential replacements for PTFE and FEP (fluorinated polyethylene). The materials are fibrillated polyethylene and fibrillated polypropylene which are marketed by Hercules/Solvay as Pulpex^R E and Pulpex^R P, respectively. These fibrillated polyalkanes have large surface areas (10 m²/gm), large diameters (20 μ), and a length of 1mm. The high surface area gives the fiber strong binding ability and decreases the amount of Pulpex^R necessary. The large diameter compensates for lower stability. Both Pulpexes^R are sufficiently hydrophobic to be used to prevent wetting without the use of fluorinated polymers. Electrodes fabricated from Pulpex^R and carbon (0.03 cm thick) showed no leakage of 25 percent KOH at room temperature for over 1500 hours.

The electrodes for in-cell testing were made using Pulpex^R P in the hydrophilic layer and Pulpex^R E in the hydrophobic layer. The electrodes were pressed at 135°C with a small amount of PTFE used as a dusting agent. Two electrodes were cycled in the bi-functional mode using a four-hour 25 mA charge and a four-hour 12.5 mA discharge. The performance was better than similar Teflon^R-based electrodes. Further evaluation is required before these new electrodes can be considered as replacements for the more expensive fluorinated materials.

Investigations to improve oxygen electrodes containing polytetrafluoroethylene (PTFE) as the hydrophobic agent were also conducted. It was found that a PTFE microdispersion with a cationic wetting agent produced longer-lived and better performing electrodes than the earlier used non-ionic wetting agent. This improvement was attributed to the gelling of the wetting agent by KOH.

The addition of a mixture of nickel (II), iron (II), and cobalt (II) hydroxides as the cathode catalyst produced a high peroxide elimination rate as well as good performance as an air electrode.

The efforts on an improved bifunctional air electrode has led to the following operating characteristics (June 1984):

Best performance		
Discharge (25 ma/cm ²)		-100 mV*
Charge (12.5-62.5 ma/cm ²)		490 mV
Best polarization		
Discharge (25-125 ma/cm ²)		75 mV
Charge (12.5-62.5 ma/cm ²)		30 mV
Best Cycle Life		
Above -150 mV		250 cycles
Above -175 mV		555 cycles

*All voltages vs. Hg/HgO electrode

Based on the electrode investigations to date, it was concluded that improvement in the air electrode structure are more important for achieving performance goals than are gains in performance achievable with catalysts as active for peroxide generation as platinum. The life of the air electrode is limited by the rate of electrolyte penetration. This rate of penetration is a function of electrode composition, structure, processing, and the charge potential. The rate of carbon oxidation is a function of the charge potential as well as the catalyst present.

To supplement the research efforts, a study of the prospects for the iron/air battery was conducted at the Jet Propulsion Laboratory. The battery system was modeled mathematically to obtain estimates of battery performance, cost, weight, and size for various EV missions. The input to the battery model was the laboratory performance data for the individual electrodes. The results of these model calculations for both near-term (late 1980's) and projected long-term performance are given in Table 15.

Research to understand the functioning and to improve the overall performance of the bifunctional electrode has continued. Earlier studies have been reviewed in references 1 to 4.

Ernest Yeager and coworkers, Case Western Reserve Univ. (CWRU), have continued investigations on the oxygen reduction and generation reactions in alkaline electrolytes.⁽⁷⁾ Various catalysts, including transition-metal macrocyclics, carbon, graphites, and metal oxides are being examined.

As part of the investigation of graphites, various quinones which are adsorptively attached to the basal plane of the graphite substrate have been used as models for studying the reduction of oxygen. The quinones were shown to be active in the reduction of oxygen, the onset of reduction correlating with the voltammetric peak potential for the first one-electron reduction of the quinone to semiquinone. The concluded studies on the generation of the superoxide-radical anion on the basal plane of highly-ordered pyrolytic graphite in alkaline solution showed that the reduction of oxygen to peroxide was inhibited. This is in contrast to other carbon surfaces.

The investigation of oxygen reduction using transition-metal macrocyclic complexes adsorbed on carbon have shown that the state of adsorption and aggregation are critical. Mossbauer spectroscopy and transmission electron microscopy showed that iron phthalocyanine (FePC) on Vulcan XC-72 carbon consisted almost entirely of adsorbed material. Cyclic voltammetry showed a highly irreversible reduction of the iron center from Fe(II) to Fe(I) that leads to a less effective oxygen reduction catalyst.

An electrocatalyst based on a partially-pyrolyzed metal-free tetramethoxyphenyl porphyrin (H_2TMPP) on Shawinigan acetylene black (SB) with added hydroxides of nickel, iron, and cobalt has been shown to have superior activity for oxygen reduction and generation. The $H_2TMPP-SB-Ni,Fe,Co$ hydroxide system was more active than related systems containing only Co. Other combinations of metal hydroxides also have high activity for oxygen reduction. Yeager suggested that these mixed systems involve different species

TABLE 15
JPL ESTIMATES OF IRON/AIR BATTERY CHARACTERISTICS

Near-Term Battery Characteristics

<u>Mission</u>	<u>Energy</u> (kWh)	<u>Power</u> (kW)	<u>Sp. Ener.</u> (Wh/kg)	<u>Pk. Power*</u> (W/kg)	<u>Cost</u> (\$/bat.)	<u>Volume</u> (l)
Commuter	12	25	98	203	889	102
Hybrid	15	50	72	240	1524	208
EV or Van	25	60	90	215	1831	279
Full Perf	50	50	130	130	1744	260

Advanced Technology Battery Characteristics

<u>Mission</u>	<u>Energy</u> (kWh)	<u>Power</u> (kW)	<u>Sp. Ener.</u> (Wh/kg)	<u>Pk. Power*</u> (W/kg)	<u>Cost</u> (\$/bat.)	<u>Volume</u> (l)
Commuter	12	25	126	262	636	81
Hybrid	15	50	93	309	1031	147
EV or Van	25	60	115	277	1230	187
Full Perf	50	50	181	181	1197	204

*From 100% to 20% SOC

Jet Propulsion Laboratory Report (Contract No. 956731)

as catalysts for different reactions; for example, one type for oxygen reduction and another type for peroxide decomposition. The long-term stability of the $\text{H}_2\text{TMPP-SB-Ni,Fe,Co}$ hydroxide system is still to be examined.

Philip N. Ross and H. Sokol, LBL, have studied the corrosion of carbon in acetylene black and an HAF-type furnace black (ASTM-N330)⁽⁷⁾. Heat treatment of these carbons had little effect on the microstructure of the acetylene black but a marked effect on the microstructure of the HAF-type furnace black. The precursor and heat treated carbons all had the same nominal Brunauer, Emmett, Teller (BET) surface area, but their corrosion rates in alkaline solutions varied significantly, indicating that microstructure is an important fundamental property.

Effort has continued on the use of ^{14}C labeling of acetylene black, together with mass spectroscopy, to determine the current efficiencies for oxygen evolution, carbon dissolution to carbon dioxide, and carbon gasification (to CO) during corrosion.^(5,7,29) The current efficiencies were found to depend dramatically on potential, temperature, and the presence of an oxygen evolution catalyst, Co_3O_4 . With the uncatalyzed carbon, three corrosion regimes were identified:

- at potentials < 500 mV vs. Hg/HgO and temperatures $< 50^\circ\text{C}$, carbon dissolution is the primary anodic process
- at $500\text{--}600$ mV vs. Hg/HgO and $< 50^\circ\text{C}$ carbon dissolution and oxygen evolution occur at equivalent rates
- at potentials > 600 mV vs. Hg/HgO or above approximately 60°C at practical potentials (> 450 mV) oxygen evolution and carbon gasification are the dominant anodic processes

Below 500 mV vs. Hg/HgO and 50°C the current efficiency for oxygen evolution from uncatalyzed acetylene black is sufficiently small that the total anodic current is essentially the corrosion current.

The current efficiency for oxygen evolution increased in the presence of Co_3O_4 . The rate of the carbon oxidation reactions were also accelerated relative to the uncatalyzed carbon. In addition, significant quantities of organic products were formed in the presence of Co_3O_4 . Only trace amounts of organics formed when the carbon was uncatalyzed.

The observations indicate that cobalt oxide does not have to be in physical contact with the reacting carbon black aggregate to produce an accelerating effect on the corrosion reactions.

Accelerating the rate of oxygen evolution from within the electrode in itself causes accelerated corrosion of the carbon. Ross postulated that a Co(II)/Co(III) redox mechanism is a factor in the catalysis of oxygen evolution and in the catalysis of the anodic corrosion of the carbon. The Co(II)/Co(III) mechanism may involve transient solvated species that reside within the porous structure.

4.3 Aluminum/Air Battery

The mechanically rechargeable aluminum/air battery is the subject of one of the major efforts of the ECS program. The current research and system component performance evaluation continues to be under the technical direction of the Lawrence Livermore National Laboratory (LLNL). Various aspects of the program are being carried out by subcontractors. Table 16 shows the participating organizations and the aspects of the cell technology each is investigating.⁽⁵⁾

The objective of the Al/air effort continues to be the development of a power source for general purpose electrical vehicles. The technical effort centers on the evaluation of the ability of this power source to provide the range, acceleration, and rapid refueling capability of internal combustion engines at equivalent cost and overall energy efficiency.

The evolution of the Al/air cell has been covered in the preceding status reports, references 1-4. A summary of the status of the development of the battery system, as of late 1983, is included in reference 30.

In the Al/air cell system, Figure 8, the aluminum anode feeds by gravity into a wedge shaped cell. The sodium hydroxide electrolyte circulates between the cell and a crystallizer, where the supersaturated solution of sodium aluminate decomposes to regenerate the electrolyte. The aluminum hydroxide product is removed periodically for recycling to the aluminum industry.

The reference battery design used in the on-going program is the wedge shaped cell with wet-side current collection, Figure 8. The wedge angle is 3 to 6 degrees and the anode area is 600 cm^2 . Reliable performance requires very uniform consumption of the aluminum during cell operation, and a circuit analysis of the performance of the cell was undertaken. The equations were solved for empirical values of anode and cathode polarization, inter-electrode resistance, and current collector/anode junction and bus resistances. The current density, j , normalized to the current at the maximum value where the wedge enters the cell, depends on the distance from the leading edge according to:

TABLE 16
Al/AIR BATTERY PROJECT ORGANIZATION

Lawrence Livermore Laboratory - A. Maimoni

- Program Management
- System integration
- Cell/crystallizer model

ELTECH Systems Corp - D. J. Wheeler

- Prime Industrial Subcontractor
- Project management
- Air cathode fabrication and performance
- Cell component fabrication and performance
- Fabricate prototype sub-systems
- Design integrated system

Associate subcontracts

Alcan - B. O'Callaghan

- Crystallization kinetics
- Crystallizer/separator development
- Crystallizer/separator design
- Fuel (Al) cycle economics

Case Western Reserve University - E. Yeager

- Cathode electrodes and catalysts
- Fundamental oxygen electrochemistry

Electromedia, Inc. - F. Solomon

- Cathode fabrication
- Cathode structure improvements
- Cathode cost reduction

SRI International - D.D. Macdonald

- Novel aluminum alloys
- Characterization of aluminum dissolution reactions
- Alloy microstructure effects

Full utilization of aluminum
Rapid recharge

Precipitates Al(OH)_3 (hydrate) on seed
Regenerates electrolyte
 $\text{NaAl(OH)}_4 \rightarrow \text{NaOH} + \text{Al(OH)}_3$

AL/AIR WEDGE CELL SCHEMATIC
FIGURE 8

$$j = \cosh(x r^{1/2}) / \cosh(r^{1/2})$$

where x is the relative wedge displacement and r is a dimensionless ratio of the resistances operating parallel to the electrodes to those operating normal to the surface. The estimated current uniformity was ± 3 percent. The maximum deviation from planarity was estimated to be less than 5 micrometers. This is well within the elastic limits of the cell.

The continuity and constancy of the rate of fall of the aluminum anode and the magnitude of the voltage losses at the anode/current-collector sliding junction are critical tests of the effectiveness of the wedge cell. The experimental data showed that at constant current the fall rate is constant, continuous, and not far from that calculated based on the cell geometry and Faraday's law. The junction losses (7 mV) were approximately 0.5 percent of the cell voltage.

A reference cell has been designed in order to better evaluate the performance of alternative cell materials and configurations. The cell was designed to minimize electrolyte holdup in the cells, to observe the current distribution constraints, and to provide electrolyte and air distribution manifolding. The cells were designed and manufactured from NORYL^R (polyphenylene oxide) using computer controlled machining. Two complete five cell stacks have been produced. Initial tests are to be conducted on a one cell assembly to evaluate the performance of the air distribution manifold and air cathode assembly procedures.

Performance, overall system efficiency, and economics will be strongly affected by the ability to recover the spent aluminum in the form of hydrargillite. This crystalline form of aluminum hydroxide is compatible with current aluminum recovery technology. The equipment selected by LLNL for the evaluation of hydrargillite recovery was the hydrocyclone. A commercial hydrocyclone supplied by Krebs Engineers was selected for testing in combination with a crystallizer and a wedge cell. Ninety-eight percent of the cyclone overflow was returned to the crystallizer because the unit was large enough to handle the flow from 30-50 cells. Measurements on the suspension of relatively fine particles ($120 \text{ m}^2/\text{kg}$) indicated that a separation of 99 percent for a cutoff near an average particle diameter of $13 \text{ } \mu\text{m}$, could be obtained. Based on the tests conducted, it was estimated that three hydrocyclones of the size tested would suffice for the operation of a vehicle battery. The total power requirement of the three units was estimated as 105 W, less than one percent of the gross average power of a 100 cell, 18 kW vehicle battery.

In the first experiment centrifugal pumps were used to circulate the suspension. The particle population was found to increase, with a steady decrease in average particle size. This was attributed to attrition by the pump impeller and secondary nucleation. Peristaltic pumps, combined with a hydrocyclone, led to lower particle attrition. Further studies are to be conducted using the peristaltic pump and hydrocyclone coupled to a cell and crystallizer. There is particle size regrowth during system rest periods.

The Alcoa rate equation was evaluated during operation of the separator system. The observed rate was then investigated to predict the accumulation of solid $\text{Al}(\text{OH})_3$ -hydrargillite. These results agreed with the separate experimental mass balance measurements based on Faraday's law; changes in aluminate concentration, and anode weight loss. The conclusions of these tests were:

- the Alcoa rate equation applies to the simultaneous operation of prototype cell and hydrocyclone/crystallizer
- the rate equation was verified within the range of critical vehicular operation conditions

The coupling between the production of aluminum hydroxide in the cell, its crystallization, and separation is an important step in determining the total battery system operation. A schematic for the total system is shown in Figure 9. The understanding of the processes and their interactions is required. At LLNL a first version of a computer code, CRYSP, to describe the evolution of the particle size distribution as a function of the system components and vehicle operating conditions has been completed. There is, however, a lack of the information needed to describe the various processes for crystal nucleation, aggregation, and abrasion. An experimental-calculational study is being conducted to obtain the needed input data. Initially the particle growth model, based on the correlation derived by Alcoa, is being used.

Based on the experimental results, an estimate has been made of the weight for a 70 kWh battery. The system components, the basis for the weight determination, and estimated weights are given in Table 17.

John F. Cooper (LLNL) has recently estimated the cost of aluminum fuel.⁽³¹⁾ The technical developments and aluminum ingot price increases between 1979 and 1982 were used in the cost projection. The estimate was based on the U.S. Industry Published Price for a distributed 50-lb. ingot modified by fabrication,

Numbers indicate flow rates ml/s

**AL/AIR BATTERY SYSTEM SCHEMATIC
FIGURE 9**

TABLE 17
Al/AIR BATTERY WEIGHT ESTIMATION
(70 kWh, 31 kW (peak))

Component	Basis for Estimation	Weight (kg)
Cells	M3 wedge cassettes: 1.1 g/cm^2 ; $5-7 \text{ kW/m}^2$	69-49
Cyclones	Krebs PC-1; PVC construction	2
Electrolyte	Contained in cells, crystallizer, cyclones and manifolding	35 ^a
Seed	Alcoa rate equation; $C_{Sn} = 0.06 \text{ M}$	18 ^a
Aluminum	Fuel requirement, 4-5 kWh/kg	17.5-14
Wedge	3° angle geometry	26
Water	Reaction and evaporation loses	32
Storage	Water, electrolyte, hydrargillite storage tanks	3
Misc.	Cell case, impellers, air-pretreatment, drive motor, startup battery etc. (estimate)	30
Total:		209-233

^aTemperature = 70° at maximum $C_{Al} = 2.7 \text{ M}$; seed area/mass ratio = $66.1 \text{ m}^2/\text{kg}$; seed area/electrolyte volume ratio = $30 \text{ m}^2/\text{liter}$.

Reference 30 (Cooper)

alloying, premium purity, and retail markups analogous to gasoline. A credit for recycled hydrargillite was included. Another important assumption was the energy yield of aluminum as measured by the vehicular fuel efficiency. For vehicular energy efficiencies of 36-42 gross ton-km/kg-Al, fuel estimates are equivalent to liquid fuel costing \$0.56-0.94/liter (\$2.12-\$3.54/gal) (mid-1981 U.S. dollars) used in automobiles with fuel efficiencies of 13.5-19.3 gross-ton-km/l (35-50 gross-ton-miles/gal-fuel).

The ELTECH program, initiated mid-January 1984, increases the scope of the previous ELTECH efforts on the air electrode and aluminum alloys for the anode. This subcontract now includes the investigation of system components and their integration.

The fabrication and testing of alternative electrode structures is being conducted by Electromedia and ELTECH. The performance of various cathode modifications and their failure modes during cycling and intermittent stand are being evaluated. The ELTECH test cycle consists of:⁽⁴⁾

- 3 minutes at 100 ma/cm²
- 0.5 minutes at 600 ma/cm²
- 10 minutes at 200 ma/cm²
- 2 hours at standby, electrolyte drained

Gas diffusion electrodes catalyzed by platinum or thermally treated cobalt tetrameso-p-methoxy phenyl porphyrin (CoTMPP) were tested.

Failure mode analysis of the platinum catalyzed electrode identified that over 75 percent of the platinum was lost during 500 cycles; 90 percent was lost in 600 cycles. The thermally-treated CoTMPP showed a loss of 20 percent in 800 cycles. Both types of electrodes showed a reduction of micropore surface area and micropore volume. The presence of aluminate and stannate in the electrolyte increased the air electrode cycle life. It was also observed that the presence of platinum catalyzed the oxidation of the carbon electrode.

A stronger, more hydrophobic conductive wetproof layer was developed at ELTECH. This allowed the air-side electrical contact desired for simplified battery construction. No loss in voltage performance was observed between electrodes with air and electrolyte side contacts. Combining the improved electrode structure with heat-treated CoTMPP catalyst led to an electrode formulation which

attained over 1400 cycles, close to the 1500 cycle goal established by earlier LLNL studies. Table 18 gives the performance as of late 1983, technical goal, and LLNL specifications for the air electrode initial performance.

The study of the effects of alloying agents on the aluminum anode was performed at Ohio State University and at ELTECH. Current cell testing is being performed using 99.999% pure aluminum in an electrolyte containing about 0.06 M sodium stannate. The alloy RX-808 used in previous cell testing is high purity aluminum (99.999%) with small additions of Sn and Ga. The presence of Sn in the alloy or the electrolyte reduces the corrosion of aluminum by the electrolyte, while Ga tends to decrease the overpotential at high current densities. However, the tin deposit is exfoliated from the surface during cell operation, accumulates in the electrolyte and might cause shorting of the cell at small anode/cathode separations.

Thirteen alloys were prepared from 99.99 percent pure aluminum for testing in 4M NaOH. The alloys had varying amounts of gallium, thallium, indium, and phosphorous. The alloys showed open circuit stability without the presence of inhibitors greater than the stability of RX808, the present reference alloy, plus inhibitor. The stability improvement, depending on the alloy, was gained at the expense of 100 to 300 mV in open circuit anode potential.

Anode polarization data identified a dependence of parasitic corrosion rate on alloy composition. Both a positive difference effect and a negative difference effect were observed with the alloys tested, and these affects were correlated to alloy composition. Alloys were developed with coulombic efficiencies superior to RX-808 at current densities at or below 200 mA/cm² and were equivalent at higher current densities. On the other hand, the overpotential was greater for most of these alloys.

Preliminary AC impedance studies of the alloys developed show that hydrogen evolution and alloy dissolution exhibit markedly different transfer functions, and that these two phenomenon may be delineated by the appropriate selection of the dc polarization potential. The ac impedance measurement also appears to be useful in assessing the effects of solution phase inhibitors.

The improvements in the oxygen electrode performance, especially the incorporation of thermally-treated CoTMPP as the catalyst, are in part the result of collaboration between ELTECH and Case Western Reserve University (CWRU). Earlier studies at CWRU on electrocatalysis for bifunctional air electrodes (iron/air cell), for oxygen cathodes for industrial processing, and for fuel cells

TABLE 18
Al/AIR CATHODE PERFORMANCE

Current Density kA/m ²	Best Obtained CoTMPP V vs. RHE	Technical Goal V vs. RHE	LLNL Specs V vs. RHE
1	807	841	836
2	766	830	796
3	741	823	756
4	706	816	716
5	667	810	676
6	583	805	636

RHE - Reversible Hydrogen Electrode

Reference 30 (Cooper)

have been summarized in earlier status reports, references 1-4, and publications by Yeager and coworkers.

The investigation of alternative oxygen reduction electrocatalysts, electrode structures, and the mechanism of electrode deterioration are included in the CWRU effort. Both electrochemical kinetic techniques, e.g., linear sweep voltammetry, rotating ring disc, and oxygen generation and non-electrochemical methods for surface composition and structure determination are being used.

The emphasis is on the use of metal macrocyclics for electrocatalysts and on the carbon electrode supports. Over 30 different macrocyclics have been investigated. The elements of the first, second, and third transition groups of the periodic table are included in the metals studies. Included among the ligands used are the phthalocyanines, porphyrins, tetraazaanulene, a hexaazamacrocyclic, and polymeric phthalocyanines. The macrocyclics, with and without metal ions, have been incorporated into the electrode and studied both before and after heat treatment.

Since the December 1982 BECC meeting, much of the CWRU research has been investigating iron tetrasulfonated phthalocyanine (FeTSPC) as a catalyst. This compound has been found to catalyze the four electron reduction step of oxygen to water or hydroxyl ion over a substantial potential range without the formation of hydrogen peroxide. Much electrochemical and spectroscopic data have been obtained for FeTSPC as well as for Co, Cu and H₂TSPC's. Results with surface enhanced Raman spectroscopy (SERS) of monolayers of these compounds on silver single crystals support earlier findings on polycrystalline silver, i.e., the TSPC's are oriented perpendicular to the surface. The corresponding non-sulfonated macrocyclics are probably oriented parallel to the surface.

Molecular orbital (MO) calculations conducted at CWRU indicated that substituent groups on the phthalocyanine ligand or replacement of carbon atoms in the benzo rings with nitrogens should only affect the MO energy levels by a minor extent. Experimentally the voltammetry for FePC was found to be similar to that of FeTSPC.

The effect of the replacement of C-atoms by N-atoms was examined by using Fe(II)-tetra-3,4-pyridinoporphyrazine (FeTPPA). Its voltammetry and the pH dependence of the voltammetric peaks are similar to those for FeTSPC. The oxygen reduction behavior was somewhat different from that of FeTSPC, but it still exhibited a relatively wide potential region in which the O₂ reduction appeared to involve 4 electrons, with no detectable generation of peroxide.

To assist in the interpretation of the cyclic voltammetric peaks observed during the investigation of the oxygen electrocatalysis of Fe(II)TSPC, Mossbauer spectroscopy is being used. This gives information on the bonding between the oxygen and iron during the reaction. Based on the Mossbauer spectrum taken with the electrode held at -1.05 V vs. Hg/HgO led to the conclusion that the oxygen reduction proceeds by an electrochemical step (E) followed by a chemical step (C), i.e., an EC mechanism:

As noted under the summary of the activities of ELTECH, thermal treatment of Co-TMPP leads to a catalyzed electrode with longer cycle life and less degradation than Pt catalyzed electrodes. Part of the research at CWRU is to understand the transformations that take place and why these lead to an improved electrode.

High catalytic activity has been observed in both alkaline and acid media using electrodes containing the products of the pyrolysis of iron or cobalt macrocyclics (e.g., porphyrins, tetraazaannulenes, phthalocyanines). The volatile pyrolysis products have been determined using gas chromatography and mass spectroscopy. The residual material on the electrode has been investigated by cyclic voltammetry and Mossbauer spectroscopy. The evidence showed the presence of iron or cobalt oxide. The Mossbauer spectra did not show evidence for metal-nitrogen bonding in the residue. However, other observations indicate that some of the nitrogen remains in the electrode.

The research on the heat treatment process indicates the need for the presence of a metal atom. The catalytic activity of metal-free H₂TMPP pyrolyzed on a carbon substrate has been attributed to the presence of metal impurities in the carbon. Active electrodes can be obtained by adding an iron or cobalt salt to a carbon electrode containing the preadsorbed metal-free macrocycle and then pyrolyzing. It has also been shown that a catalytically active electrode can be formed when the metal hydroxide is added to the pyrolyzed macrocyclic on a carbon substrate.

The optimum heat treatment temperature is in the range of 450-500°C in a nitrogen or argon atmosphere. The temperature depends on the macrocycle, the metal and how it is added, and the carbon substrate.

In alkaline solution, electrodes containing the pyrolyzed metal macrocyclic catalyze the decomposition of hydrogen peroxide. In acid electrolytes, the overall oxygen reduction reaction is catalyzed. Still uncertain is the role of the residual nitrogen,

assumed to be bonded to the metal, on electrocatalysis or electrode stability.

It has been observed that with low activity Shawinigan Black the oxygen reduction activity is enhanced by the addition of a second metal hydroxide, such as nickel hydroxide, to the pyrolyzed-catalyzed electrode. This approach is considered to produce different catalytic sites for oxygen reduction and peroxide decomposition.

It has also been observed that the presence of the pyrolyzed metal macrocyclics modifies the hydrophobicity of the carbon surface and improves the mass transport of oxygen within the electrode.

5.0 FLOW BATTERIES

The flow batteries include those systems which use the electrolyte as the carrier for one or more of the electrode reactants during discharge and charge. The exploratory engineering related to the operation of the flow battery systems is being conducted under the Exploratory Technology Development and Testing Project (ETD), Sandia National Laboratories (SNL). The supporting studies on membranes for flow batteries is also a part of the ETD effort. Supporting research on electrode processes and the modeling of the electrochemical engineering of flow batteries is conducted under the Technology Base Research (TBR) Project of the Lawrence Berkeley Laboratory (LBL).

Four battery systems were discussed in the earlier status reports (references 1-4). These are: Zn/Br₂, Zn/Cl₂, Zn/ferricyanide, and the chromous/ferric Redox battery. Advances in the technology of all but the Redox battery were reported at BECC-6. The continuation of the effort on the zinc/chlorine battery is supported by the Electric Energy Systems Program of the DOE and by EPRI.

5.1 Zinc/Bromine Battery

The effort on the Zn/Br₂ battery is targeted at systems for stationary electrical storage and for transport. The electric vehicle related investigations are partly supported by the DOE-EHV program. The schematic of this battery system was presented in reference 4. The system essentially consists of two separate electrode systems with two electrolytes separately circulated using a microporous separator to minimize their rate of mixing. The zinc-bromide anolyte contains a supporting salt, e.g., KCl, to maintain the conductivity of the electrolyte. The bromine in the catholyte is complexed with an organic reagent thus increasing bromine availability and decreasing the free bromine concentration. Bipolar cells are used with an Exxon developed "tunnel" shunt current protection system. This was described in reference 4.

During the year preceding BECC-6, Exxon developed a new two piece unit cell with an electrode area of 1200 cm². A 1 kWh battery had completed over 400 cycles, and a 10 kWh, 78 cell, bipolar battery had completed over 100 cycles (June 1984). This battery also demonstrated the "tunnel" shunt current protection technique. A 200 V, 15 kW battery was constructed and operated for 50 cycles. A 120 V, 20 kWh battery has been built and is under test. Assembly and part tolerance problems delayed the initiation of testing.

The battery developments since BECC-5 (December 1982) have enabled improvement in the control of earlier recognized failure mechanisms, such as pH increases, cathode fouling by residues adhering to its surface, and battery stack sealing problems. More recently identified problems were the warpage of electrodes with cycling and wear of the brushes on the D.C. motors used for electrolyte circulation.

The warpage problem was investigated using x-rays, scanning electron microscopy, and differential scanning calorimetry. The studies indicated that the carbon-plastic composite bipolar electrode plate absorbs bromine causing a linear expansion of the plate leading to warpage. To overcome the changes in the plate morphology, both thinner and thicker plates were investigated along with the use of reinforcement posts to physically limit the warpage. It had been noted that thicker electrodes, used in an older cell design, had sustained 600 cycles without warpage. The overcoming of the warpage problem leaves the brush wear problem, a system auxiliary failure, the primary outstanding difficulty requiring resolution.

Previously reported cathode failures due to the accumulation of separator residues have been decreased. This was accomplished by the better pre-extraction of the residues from the separator before battery assembly.

Extended tests of electrolyte life had completed over 5000 hours or 1000 cycles as of June 1984. These tests showed no decline in electrolyte performance and no evidence of degradation of the bromine complexing agents. Laser Raman spectroscopy and C^{13} nuclear magnetic resonance (NMR) were used to study liquid phase complexation and chemical changes in the bromine complexing agent. To understand the relationship of the ratio of bromine to complexing agents on coulombic efficiency, phase equilibrium studies of complexing agents have been conducted. The effect of bromine transport into the anolyte on zinc deposition has also been investigated. These studies have led to new information which is guiding the modification of some of the system components.

The use of additives in the electrolytes has shown the possibility of extending performance to -16°C . No data on the effect of these additives on cell life was reported. The high temperature operation was, in part, limited by the softening of the polyvinyl chloride (PVC) fittings above 70°C .

The exchange-current densities for bromine on carbon have been determined. These enable the estimation of the minimum surface areas required in the cathode activation layer. This has con-

tributed to the development of a new layer for bromine activation having a low kinetic polarization at current densities as high as 150 mA/cm². One kWh and 15 kWh battery testing of this new layer showed improved voltaic performance. The use of carbon-plastic composite electrodes has increased bromine resistance and reduced the electrode cost.

A new class of resilient plastics, which is resistant to bromine, has been identified. These plastics promise to reduce the battery stack sealing problem.

The earlier developed computer model has been extended to include weight, volume, and state-of-charge effects. Graphic presentations of this model permit design projections for critical battery variables such as separator characteristics, electrolyte conductivity, and zinc utilization.

In addition to the specific improvements noted, improved processing of components offers reduction of cost. An example is the continuous production of the Daramic separator. These processing improvements, together with the use of low cost plastics, have led to the estimate of a battery cost for large scale production of approximately \$28/kW (1980\$).

Richard J. Bellows and coworkers have published a design projection for 80 kWh Zn/Br₂ batteries for bulk energy storage.⁽³²⁾ Some of the characteristics of this system which are important to this application include:

- specific energy-65 Wh/kg, specific power-140-W/kg, and overall dc/dc efficiency approaching 70 percent
- over 400 deep discharge cycles demonstrated
- good charge retentivity on prolonged stand
- low cost materials and potentially low manufacturing costs
- ease of electrolyte maintainability and battery repairability
- modular design flexibility

An earlier design study of a Zn/Br₂ battery for electric vehicles had similar manufacturing costs.⁽³³⁾ The projected performance characteristics were similar:

EV	SES
36-240 V	120 V
60-80 Wh/kg	65 Wh/kg
130-205 W/kg	140 W/kg
10-100 kWh capacity	80 kWh

The EV battery physical design consists of side by side location of the electrolyte storage and circulating compartment and battery stack.

The design of the 20 kWh stand-alone battery that is to be delivered to SNL for evaluation in a photovoltaic system simulation test has the following characteristics:⁽⁵⁾

- 1200 cm² battery electrodes
- 120 V on discharge, capacity 80 kWh, peak power (kW-20sec) 30
- two high voltage stacks on either side of a common manifold
- modules above the anolyte and catholyte reservoirs and the centrifugal circulating pumps

5.2 Zinc/Chlorine Battery

The remaining DOE support for the zinc/chlorine battery is limited to the cooperative effort with EPRI and PSE&G on the testing of the 500 kWh unit at the BEST Facility (Section 2.2). This battery system has been developed by Energy Development Associates (EDA), a Gulf+Western Company. Further development of this system for Electrical Energy Storage and for EV application is being continued by EDA.

The 500 kWh power source consists of 10-50 kWh batteries, see reference 4 for details. The 500 kWh unit was qualified at a Detroit Edison Substation. This consisted of 11 cycles. The battery showed a dc/dc efficiency of greater than 63 percent and delivered more than the rated 500 kWh of energy. The system was installed in the BEST Facility in September, 1983 and power applied in October, 1983. The PSE&G baseline operation consisted of 30 cycles. The system had a 91 percent availability. Through mid-June 1984, 40 MWh were delivered. EDA has the objective of installing a 6 MWh, 2 MW(3hr), utility battery in 1985.

A 50 kWh Zn/Cl₂ battery was installed at NBTL in April 1984 for independent testing and started-up on June 11, 1984. The energy

output was 49 kWh. The electrolyte in this unit had a higher concentration of supporting electrolyte, 4M in KCl plus NaCl, rather than 2M in KCl.

EDA is also continuing its development of an EV Zn/Cl₂ battery. Commercial vans have been used as the battery test vehicles. A range of 97 miles (155/km) was obtained at 30 mph (48 km/h) and 90 miles (144 km), at 35 mph (56 km/h). It showed an acceleration of 0-30 mph (0-48 km/h) in 14.5 seconds and a maximum speed of 55 mph (88 km/h).

Among the R&D issues noted by Charles J. Warde (EDA) are the rate of chlorine-hydrate formation, the chlorine dissolution rate, and the reduction of the store storage pressure, currently 4 psig (1.21×10^2 kPa). The life-time of the graphite electrodes has been shown to be in excess of 1700 cycles.

The target for the installed cost of the Zn/Cl₂ EV battery is less than \$50/kW.

5.3 Zinc Deposition in Acidic Electrolytes

A common feature of the zinc/halogen systems is the re-deposition of zinc from an acidic electrolyte during charge. Investigations to understand the effects of additives and of flow conditions on the morphology of the zinc deposits formed are in progress.

The studies at Brookhaven National Laboratory (BNL) are concerned with the mechanism and morphology of zinc deposition and the role of metal-ion additives on the related phenomena. One of the guiding principles of these studies are the conclusions of earlier studies that high exchange current densities favor dendrite formation.(34)(35)

The rate of zinc deposition on a glassy carbon substrate was determined to obtain a measure of the relative kinetics of deposition from high-purity zinc-chloride and zinc-bromide electrolytes. The primary technique was the potential-step method. The resultant current transient was related to a simple model for the instantaneous formation of zinc nuclei and zinc growth under kinetic control. It was observed that the current transient reaches a steady state. The steady state value is a measure of the rate of growth of zinc perpendicular to the substrate. The results showed that the kinetics of zinc deposition are much faster in zinc bromide than in zinc chloride. Additions of KCl as a supporting electrolyte moderately decreased the deposition rate from zinc bromide. The addition of aluminum chloride to zinc bromide resulted in a marked

decrease in deposition rate. These results indicated a decreased deposition rate in the presence of a complexing agent with the deposition rate being a function of the strength of the complex.

Experiments on zinc deposition on polycrystalline zinc indicated that the zinc growth habit depended on crystal orientation. Preliminary experiments on deposition on zinc single crystals showed that the rate of zinc deposition is much faster on the basal plane than on the plane perpendicular to the basal plane. According to McBreen and Gannon the rising current transient for the basal plane is consistent with simultaneous layer growth and the nucleation and growth of three dimensional centers. The flat current transient for the plane perpendicular to the basal plane was interpreted as being consistent with a layer growth mechanism. McBreen and Gannon noted that earlier investigations had shown that beneficial additives, e.g., lead, promote growth perpendicular to the basal plane whereas deleterious impurities, e.g., copper, promote growth parallel to the basal plane.

An extensive study was conducted at BNL on the effect of additions of Pb^{+2} , Bi^{+3} , and Tl^{+3} ions on zinc deposition. The cyclic voltammetry experiments indicated that in some cases the additive is deposited on the substrate prior to the deposition of zinc. The addition of Bi^{+3} and Pb^{+2} markedly decreased the rate of zinc deposition at a given potential; the effect of Pb^{+2} was greater than that of Bi^{+3} .

The study of the effect of the superimposition of square wave pulses on the morphology of zinc deposits showed this to be mostly one of deposit orientation. In general, pulsed charging yielded smooth adherent deposits.

W.C. Hsie and J.R. Selman (IIT) are investigating the following aspects of zinc deposition in zinc/halogen batteries:^(5,7,36)

- analysis of transport processes in battery electrolytes and their effect on the electrode kinetics of zinc deposition and hydrogen evolution
- experimental determination of the growth rate and morphology of microprofiles of dendritic type in electrodeposition from battery electrolytes
- determination of the relationship of the dendritic growth characteristics to the electrolyte transport processes and to the electrode kinetics of zinc deposition and hydrogen evolution

The laboratory investigation consisted of a matrix of experimental measurements of zinc profiles on a rotating concentric cylinder electrode (RCCE). The matrix conditions included: rotation speed, pH, and current density. Data were obtained for the following:

- growth rate of nodules or dendrites
- overpotential vs. time characteristics
- impedance components

The morphology of the deposit was studied by means of in-situ optical microscopy and post deposition SEM.

The increase in rotation speed increased the growth rate of profiles; however, the apparent induction time for dendrites to be visible increased with increasing convection. At 500 rpm and 46 mA/cm² a charge loading density of 380 mAh/cm² could be realized without dendrite formation.

Gas bubbles were observed to cling to most nodule or dendrite tips at pH < 2. A few gas bubbles were observed at higher pH (2-5). The SEM photographs showed that the relationship between gas coverage and micromorphology of the profile tips was apparently due to localized corrosion and shielding by bubbles. The formation of ridges in the flow direction was characteristic of the deposits observed for low-pH deposition at moderate current densities. These characteristics appeared to be connected with gas evolution. The profiles disappeared and single nodules dominated at higher deposition rates.

Impedance measurements over a frequency range of 0.1 Hz to 10 kHz were made during deposition under various conditions of the matrix variables. The measurements were made during current interruptions at regular intervals. The capacity at the high frequency, 10 kHz, showed an unusual dependence on loading. This dependence was qualitatively explained by the effect of gas bubbles on the profiles. In the presence of hydrogen bubbles the growth model corresponded more to preferential tip growth or tip-and-lateral growth. Increased convection tends to change the growth pattern from periodically inhibited vertical growth to preferred tip or tip-and-lateral growth.

Zinc deposition kinetic parameters were determined from polarization measurements of the RCCE at short deposition times. The exchange current density was found to be in the range of 3-30 mA/cm² for 1 M ZnCl₂ (with 3 M KCl) at 25°C. There were significant unexplained variations in the exchange current densities.

The equations for the growth of a dendritic profile in a flow channel with perturbed flow and concentration field were developed. These equations were used to calculate primary and secondary current distributions at or near a two-dimensional profile. The effect of various parameters, such as the ratio of dendrite height to channel height, on the current density near the tip was systematically investigated. The specific results are to be published.

5.4 Zinc/Ferricyanide Battery

The evolution of the zinc/ferricyanide battery has been described in references 2, 3 and 4. The system, being investigated by the Lockheed Missiles and Space Co., consists of anode and cathode compartments separated by an ion-exchange membrane, such as Nafion^R. The negative electrode is an inert substrate on which zinc is deposited during charge. The positive electrode is carbon at which the ferricyanide ion is reduced to the ferrocyanide ion. The anolyte is a solution of zincate ion in sodium hydroxide; the catholyte is a solution of sodium ferricyanide in sodium hydroxide. Both are circulated during cell operation. During discharge zinc oxide and/or zinc hydroxide precipitates from the anolyte and a mixture of sodium ferri- and ferrocyanide from the catholyte. An external storage space is required for each of the electrolyte streams. Solution of the solids is required during charge. The overall battery performance has changed only moderately from that given in reference 4.

The effort, since December 1982, has emphasized the investigation of the membrane.⁽⁵⁾ The endurance, resistance, and cost of the membrane are critical issues in determining the practicality of this battery system. A number of cost effective membranes were cyclically evaluated to determine the effects of ferricyanide on membrane cycle-life. The results indicated the potential for a marked improvement over some of the earlier membranes tested. Some alternative membranes endured the ferricyanide electrolyte with little or no change in performance. The preliminary evaluation tests consisted of 100 capacity cycles at 70 mAh/cm². The cycle life of selected membranes under cell operating conditions is to be determined. Further modifications of the membranes are required in order to meet the requirements for resistance and ferricyanide transport. Several membranes exhibited a good coulombic efficiency but also had a high resistance and thus, a lower voltage efficiency. Based on these observations, the tailoring of membranes to the cell requirements is being undertaken.

One approach to alternative Zn/ferricyanide battery membranes is that of the SNL staff. Studies of various commercial and developmental membranes, were the basis of a stability

ranking.⁽⁵⁾ The best of these was a Japanese material which consisted of a membrane structure of poly(trifluoroacrylic) acid on a base of polyfluoroacrylic acid and Teflon. In general radiation grafted membranes were slightly more stable than the homogeneous membranes. These observations led to the preparation by RAI Corporation of grafted membranes as specified by SNL. The eight custom-made membranes were varied by substrate film type (PTFE or fluorinated ethylene-propylene (FEP)), substrate thickness, and extent of crosslinking.

The membranes were tested and, in general, had moderately good stability in the alkaline ferricyanide electrolyte and provided good coulombic and voltage efficiencies. Cycle lives of 200 and overall energy efficiencies of 70 percent were obtained. However, these were not sufficient to provide the cell performance objectives.

The study of the relationship between membrane structure and properties showed that PTFE backings exhibited better selectivities than poly FEP backings at comparable film thickness. The membrane resistances increased with membrane thickness and, in some cases, improved selectivity was observed at high crosslink densities. After cycling, the membranes lost 60-80 percent of the grafted material and this was accompanied by a loss of ion-exchange capacity and water. It was also demonstrated that the graft loss was attributable to oxidative attack by the electrolyte and this led to decreased coulombic efficiency. Further syntheses are planned in an attempt to overcome these deficiencies.

The development of supported liquid membranes (SLMs) at Castle Technology Corp (Section 3.2.3.5) includes SLMs for the zinc/ferricyanide battery. SLMs with PTFE as the microporous support have passed short term stability tests. The combinations tested exhibited a selectivity of hydroxyl ion over ferricyanide and zincate ions of 10^4 - 10^5 with separator resistances of 1-10 ohm cm. The retention of organic reagents in the flowing alkaline electrolyte has been a problem.

The group at Lockheed have continued to investigate zinc/ferricyanide cell design and the auxiliaries required for battery operation. The crystallizer that was used to ensure that the electrolyte would be free of solids has been replaced by a hydrocyclone downstream from the pump and upstream of the electrolyte reservoir of the cell. The solids are separated by vortex action. The solids in the recirculating electrolyte were less than 50 microns and did not clog the electrolyte circulation system. The required pumping power was estimated as 2-5 percent of the cell output.

The solubility of sodium ferricyanide has been determined and an empirical equation derived for the solubility as a function of temperature and sodium hydroxide concentration.

Cells with Nafion^R membranes have been tested. The electrode areas have varied from 60 to 1000 cm². One of the smaller cells, using Nafion^R N-117 as the membrane, had a cycle life of 1413. The largest cell, 1000 cm², had a cycle life of over 340. The voltaic efficiencies of the Nafion^R membrane cells varied from 79-91 percent, the coulombic efficiency from 83-92 percent, and the energy efficiency from 68 to 84 percent.

Degradation mechanisms were investigated on 60 and 200 cm² cells after test termination. The observed failure modes included separator failure, zinc accumulation, ferrocyanide accumulation in the porous graphite felt electrode, gradual oxidation of the porous felt electrode, increased contact resistance between the graphite felt and the current collector plate, formation of high resistance films of ferrous hydroxide on electrode or felt surfaces, and general oxidation of contact surfaces.

Bipolar electrode technology is being developed. This is based upon a nickel coated graphite fiber in a thermoplastic compatible with the battery conditions and electrolyte. The composite has a resistivity of between 1 and 0.05 ohm-cm, and readily lends itself to extrusion or thermopressing operations for mass production. The bonding of the composite to a metal end-plate has been demonstrated.

The earlier conceptual engineering design for the zinc/ferricyanide system has been refined. Currently it includes a model for ferro-ferricyanide solids management, an improved model of the battery, and projected costs as a function of electrolyte volume and solid to liquid ratio. The model requires certain thermodynamic properties of sodium ferro- and ferricyanide which are not available in the literature. These are to be determined.

Modeling of a 1.57 kW module has been undertaken by Selman of the Illinois Institute of Technology (IIT). He has estimated that under adiabatic discharge conditions, with a solid to liquid ratio of 0.5, the temperature rise in the battery would be 25°C, with a solid to liquid ratio of 0.25, a temperature rise of 15°C was estimated. The model also indicated that adiabatic operation should be more cost effective than isothermal operation.

The use of particulate bed electrodes is most readily adaptable to systems with circulating anolyte. The studies of James W. Evans, LBL, center on zinc deposition on particulate-bed electrodes in alkali electrolytes.^(5,7) Although most closely related to the

current effort on the zinc/ferricyanide battery, it could also be adapted to the other zinc-negative batteries. For this to be attractive, the performance of the electrode would have to compensate for the additional complexities of a circulating electrolyte such as lower overall efficiency, pumping and associated plumbing, external volume for the electrolyte, and increased weight. This may be counterbalanced by improved cell performance, increased cycle-life, simpler thermal regulation, and less stringent separator requirements.

The gross behavior of particulate bed electrodes was investigated following their invention in the late sixties. Most of these studies did not investigate the transient behavior of these electrodes. The research at LBL has emphasized the potential transients and the electrochemical reaction rates of the processes taking place at the particle surface under unsteady conditions. The research also investigated the mechanism of electronic transport in the particulate electrode and the controlling factors.

The research has centered on fluidized-bed electrodes, i.e., the particles are kept in suspension by the hydrodynamics of an upward flowing liquid, and on falling bed electrodes, i.e., the particles fall through the electrolyte and are mechanically returned to the top of the electrode. The hydrodynamics of these electrodes make potential transients inherent.

The experimental apparatus employed a dual probe (a Luggin capillary for electrolyte potential measurement and a means for particle potential measurement). The signals were fed into a digital oscillograph. All the measurements of the dual probe were with respect to the electrolyte potential adjacent to the cell diaphragm. The potential traces were transferred to a microcomputer for statistical analysis. Potential histograms, autocorrelograms, and power spectra were generated for any point in the electrode. The time average of the observed overpotentials showed extremes at the current feeder and the cell diaphragm. These results are consistent with the mathematical models developed for fluidized-bed and porous electrodes.

Potential transients were measured in fluidized- and moving-bed electrodes consisting of copper particles, zinc-coated copper particles, and Sorapac particles. The last are zinc-coated polymer particles for battery applications that are being commercially developed by a French company. The polymeric particles are between 300 and 400 μm in diameter. The particles are first coated with an electroless deposit of nickel, followed by an electroplated coating of cadmium. The zinc is in contact with the cadmium coating.

The transients observed in the fluidized beds were distinctly different for the different electrode particles. These differences were attributed to the varying hydrodynamics of the fluidized bed as a function of the difference between particle and fluid density. The large density differences between the zinc-coated copper and the electrolyte leads to "bubbling" i.e., regions of relatively low particle density. This results in fluctuations in the local resistivity of the bed. The fluctuations in the case of Sorapec, with a smaller density difference, are less. In spite of the differences in fluctuation rates, the local reaction rate is not directly affected.

5.5 Chromous/Ferric Redox Battery

The $\text{Cr}^{+2}/\text{Fe}^{+3}$ battery system differs from the Zn/halogen and Zn/ferricyanide batteries as it operates with both anode and cathode reactants in solution. The earlier developments were based on the separation of the reactants in the anolyte and catholyte and have been summarized in references 1-4. A major change in the battery operation was reported at BECC-5 and was reviewed in reference 4. This change involves the use of mixed electrolytes, i.e., anolyte and catholyte contain chromium and iron ions.

Bismuth has been shown to be an excellent catalyst for the electrochemical oxidation and reduction of chromium ions in the mixed-reactant electrolyte at 65°C. In addition to its enhancement of the rate of the anodic and cathodic reactions, the high hydrogen overvoltage of bismuth decreases the rate of hydrogen evolution. Another significant feature of bismuth is the ease with which it can be stripped from the surface of the electrode at the end of discharge. The bismuth redeposits at the beginning of the subsequent charge cycle. This makes the negative electrode highly forgiving to operational mistakes, such as overcharging which leads to iron deposition.

Another operational aspect of the mixed reactant system is its symmetry. When fully discharged the anolyte and catholyte are indistinguishable. This makes it possible to electrically reverse the system if desired. This reversal can be of benefit in countering the electroosmosis and electrodialysis processes that can occur during normal operation. Polarity reversal has been carried out in the laboratory with no harmful effect on cell performance.

The use of a rebalance cell is required due to the evolution of hydrogen at the anode which leads to a lower anodic coulombic efficiency than for the cathode causing an unbalance of reactant concentrations. The earlier rebalance technique was described in reference 1. This has been replaced by an iron/chlorine rebalance

cell. In this cell, the iron reactant is discharged while chlorine is evolved at a graphite anode. An HCl electrolyte is used. Energy must be supplied to the rebalancing cell resulting in a system energy penalty. This is small as the hydrogen represents only one percent of the charge capacity.

The use of the mixed ion reactants has changed the requirements for the membrane. This is a result of the diminished need for high membrane selectivity to keep the chromium and iron ions separate. The emphasis is on a low resistance membrane, stable to the reactant solutions. The membranes selected for testing, primarily cation exchange materials, were characterized with regard to resistivity and selectivity and then evaluated in a cell. A performance mapping approach was used. This involved constant-current cycles over a range of current densities. These tests showed that for each membrane there was a current density at which the round-trip energy efficiency was a maximum. The observed optimum current density depended on the membrane characteristics. Energy efficiencies of eighty percent or more were obtained at current densities up to 100 mA/cm².

Negotiations have been completed with Standard Oil of Ohio (SOHIO) for the scale-up and possible commercialization of the NASA Lewis Laboratory chromous/ferric battery. Direct support of this battery by DOE has been discontinued.

6.0 Non-Aqueous Battery Systems

Three different classes of nonaqueous electrolytes, with corresponding differences in temperature range, have been included in the ECS program. These are in order of increasing operating temperature range: organic, molten salt, and solid electrolytes. Both the organic and molten salt systems concentrate on lithium anodes. Although sulfur or sulfur compound cathodes are emphasized, other cathodes are being explored.

6.1 Organic Electrolyte Batteries

The DOE support of two different approaches to organic electrolyte batteries were completed in the first half of calendar year 1984. The two systems were lithium batteries with sulfolane as the electrolyte solvent and the application of conducting polymers, primarily polyacetylene, to batteries. The efforts in these two systems prior to December 1982 have been summarized in references 1-4. Research on organic electrolyte systems is being continued.

6.1.1 Sulfolane Electrolyte Batteries

The studies at EIC Laboratories, Inc. have been emphasizing the critical factors governing the use of sulfolane:^(6,37)

- the conductivity of sulfolane electrolytes
- the stability of sulfolane electrolytes
- the ability to cycle lithium in sulfolane electrolytes

High purity sulfolane is required to obtain a reliable reference base for the conductivity and stability of sulfolane electrolytes. Several purification techniques were evaluated. The procedure giving the highest purity material consisted of:

- adsorption on activated charcoal
- vacuum distillation
- treatment with alumina

Melting point, the ultraviolet spectrum, and cyclic voltammetry were used to determine the purity of the solvent.

Sulfolane has a high dielectric constant. The conductivities of 1M lithium perchlorate (LiClO_4) and lithium hexafluoroarsenate (LiAsF_6) were determined as ~ 0.0024 and $0.0027 \text{ ohm}^{-1} \text{ cm}^{-1}$,

respectively. The electrolyte conductivity increases when an ether is added. The sulfolane electrolytes are liquid at room temperature, however, pure sulfolane melts at 29°C. Sulfolane electrolytes were found to be stable to lithium for weeks when stored at 70°C.

The cycling stability of sulfolane electrolytes was investigated using a lithium half-cell with a lithium counter-electrode. The cell separator was Celgard^R 3501 (a treated microporous polypropylene) and a 10 mil polypropylene felt wick. The electrodes and separator were held in compression in a prismatic glass container. These cells were cycled at ambient temperature and at 50, 70, and 90°C. The efficiencies increased with temperature. The sulfolane-LiClO₄ electrolyte showed the best overall efficiencies, ranging from 78 percent at ambient temperature to 88 percent at 90°C. The stability of sulfolane to lithium was attributed to the formation of protective films on the metal.

J. S. Foos and L. M. Rembetsy noted the advantages of sulfolane electrolytes for use in lithium secondary batteries:

- the stability of sulfolane to Li and its ~5 V electrochemical window are comparable with a high voltage cell
- the high thermal stability of sulfolane
- the safety of sulfolane, electrolytes with LiClO₄ have been heated to decomposition (250°C) without explosion

6.1.2 Conducting Polymeric Electrode Cells

The earlier studies of G.C. Farrington and A.G. MacDiarmid on the use of polymeric electrodes, primarily polyacetylene, as lithium battery electrodes were summarized in reference 4. The electrochemical cell investigated was Li/LiClO₄ in tetrahydrofuran/(CH)_x.⁽⁵⁾ Current time curves were determined for cells having an anode of (Li_mCH)_x where m = 0.01 to 0.07. A study of the current-time curves for the reduction of acetylene at a controlled potential, 1.1 V vs. Li/Li⁺, showed that a fresh film had an initial current density of 4-5 mA/cm². This decayed within 30-60 seconds to a plateau of about 0.7 mA/cm². When this was repeated by oxidizing the polyacetylene to m=0 and reducing at 1.1 V, the initial discharge current density was about the same, but the magnitude of the plateau current was reduced. This trend continued with cycling until the plateau disappeared. This indicated that the current density polyacetylene negative electrodes can sustain during reduction grows smaller with cycling. Cycling efficiency also

tended to decrease as m was increased. At the higher values of m (0.06 to 0.07) there was a marked loss in capacity on standing for 24 hours.

Polyacetylene, when oxidized in a non-aqueous cell containing 1.0 M LiClO_4 in propylene carbonate, developed a voltage of 3.4-4.0 V vs. $\text{Li/Li}^+\text{ClO}_4^-$. Oxidation levels of at least $(\text{CH}(\text{ClO}_4)_{0.10})_x$ were achieved electrochemically. Reduction to an uncharged state had a coulombic efficiency of nearly 100 percent. However, the electrochemical doping process was only efficient in the presence of a minimum of liquid electrolyte and ultra-clean conditions. The results were similar when an LiAsF_6 containing electrolyte was used.⁽³⁸⁾

The general conclusion of the studies on the use of doped polyacetylene cells was, that although these show high coulombic efficiency, the low charge acceptance, loss in capacity on cycling, and chemical instability of doped polyacetylene, make this an unpromising material for high energy density batteries.

6.1.3 Organic Electrolyte Battery Research

Rolf H. Muller and coworkers are continuing their investigations on the structure, composition, and mode of formation of layers on lithium in lithium organic batteries.^(5,7) The electrolytes studied were polypropylene carbonate (PC) and 2-methyl tetrahydrofuran containing LiClO_4 or LiAsF_6 .

A thin-layer cell with electrode separation of 50 microns was used. This was to minimize the amount of electrolyte and the effect of electrolyte impurities. The cell was operated inside an inert-atmosphere glove box filled with recirculating helium containing less than 1 ppm O_2 , N_2 , and H_2O . Lithium-amalgam was used to reduce the water content of the solvents and of the helium.

Surface layers formed in the PC- LiClO_4 electrolyte were examined by infrared spectroscopy. The film contained lithium carbonate and polymerized propylene carbonate. Electron surface chemical analysis (ESCA) and ion etching showed that the polymerized PC formed in the inner film next to the lithium and the inorganic compound in the outer layer. The polymer film was determined to be poorly ordered. ESCA analysis also showed that chlorine in various oxidation states had formed, indicating reaction of the ClO_4^- . The relative concentration of the various chlorine oxidation states varied with film depth.

The presence of water in the electrolyte leads to the formation of a protective lithium oxide film on the lithium. This is bene-

ficial for shelf life but has low conductivity and can hinder the recharging of the cell.⁽³⁹⁾

Lithium deposited on Li, Cu, and Pt substrates in 1M-LiClO₄ in PC or in 2-methyl hydrofuran was found to be very porous. The stripping of the lithium deposit from these electrodes showed that the initial deposit had formed an alloy with the Cu, Pt, and Au substrates. Surface layers were only present on the unalloyed outer parts of the deposits. This observation led to the conclusion that electrochemically-formed lithium alloys can give active electrodes but with a very limited capacity. The addition of various inhibitors to the electrolyte did not change the lithium morphology or prevent reaction with solvents.

Various protective-surface layers were formed by reaction with lithium. Lithium nitride, a material with high ionic conductivity, appeared to be promising. Investigation of this protective-surface is continuing with the objective of finding methods of forming thin, uniform films of lithium nitride that are ionic conductors and protective in PC and 2-methyl tetrahydrofuran. The films must also withstand cycling.

Alternative cathodes for use in organic electrolytes are also being investigated. Charles W. Tobias and Karrie Hanson at LBL have studied the electrochemistry of the I₂/I₃⁻ in propylene carbonate containing 0.004 M KI and 0.5 M KAsF₆. The cyclic voltammetry of the reaction was studied. Based on the observed voltammograms, the following reaction sequence was proposed:

The validity of the proposed reactions was tested by following the reaction in an optically transparent thin layer cell. Cyclic voltammograms and the changes in the UV spectra were determined simultaneously. The absorbance of the triiodide ion can be readily distinguished from that of the iodine. The formation and disappearance of the triiodide ion were followed by scanning the UV-visible spectrum every 30 seconds during a slow (1 mV/sec) voltammetric sweep. The absorption spectra were consistent with the proposed mechanism.

A general transport model to simulate the voltammograms was developed in collaboration with M. Matlosz (LBL).⁽⁴⁰⁾ The important features of the mechanism are the presence of two electron-transfer steps which have a more complex stoichiometry than 1:1. In addition to the electrochemical steps, the model includes

the effects of mass transport. The results of the comparison of the model to the scan rates below 500 mV/sec indicated that the first of the above reactions, iodide ion to iodine, is kinetically inhibited whereas the electrochemical reaction involving the triiodide ion is reversible.

In addition to the cyclic voltammetry experiments, the stability of propylene carbonate in the presence of chlorine, bromine, and iodine was studied. It was found that the Cl_2 and Br_2 reactions with PC were very sensitive to the presence of small amounts of water. The order of stability of the halogens in PC was:

It was also observed that iodine and bromine disproportionate in PC, forming the corresponding trihalide ions and probably positively charged halogen ions.

Research on cathodes for organic electrolyte cells was also conducted at Stanford Univ. by Robert A. Huggins and associates. Tungsten and vanadium oxide bronzes have been investigated as lithium insertion type positive electrodes. The kinetics of the electrochemical insertion of lithium into sodium tungsten bronzes, Na_xWO_3 (where $0.4 < x < 0.7$), to form mixed alkali bronzes, $\text{Li}_y\text{Na}_x\text{WO}_3$ (where $0 < y < 0.5$, $x+y < 0.93$), have been studied.⁽⁴¹⁾ Single crystals of the bronzes were prepared to measure lithium diffusion rates. Powder x-ray diffraction, thermogravimetric analysis, and chemical titration were employed to determine the sodium stoichiometry of the tungsten bronze samples. Either galvanostatic or potentiostatic techniques were used to measure the chemical diffusion coefficient of lithium in the bronze samples. Thermodynamic quantities were determined by measuring the Emf as a function of temperature for the cell:

The chemical diffusion coefficient of lithium in the mixed cubic tungsten bronzes, $\text{Li}_y\text{Na}_x\text{WO}_3$, at ambient temperature was as high as 10^{-7} cm²/sec for low values of y, but decreased with increasing alkali metal content. Samples with $x = 0.7$ accommodated very little lithium and the diffusion coefficient decreased rapidly with the increase in Li concentration. The measured diffusion coefficient of lithium in the mixed tungsten bronzes was many orders of magnitude greater than the diffusion coefficient of lithium in cubic Li_xWO_3 .

Studies of lithium insertion in vanadium oxide bronzes have also been reported.⁽⁴²⁾ The cell used was similar to that for the

tungsten bronze studies discussed above. In beta-phase vanadium bronzes, $M_xV_2O_5$ ($M = Na, K$), it was observed that almost two lithium atoms may be accommodated per formula weight. The shape of the titration curve for $Li_yK_{0.25}V_2O_5$, i.e., the Emf vs. Li content, was explained as the filling of sites within the tunnels of the bronze. The kinetics of the Li insertion reaction have also been studied.

6.2 Molten Salt Systems

The major effort on molten salt systems, through FY82, was the research, development, and performance evaluation of the Li-alloy/molten salt/FeS battery. This program, centered at ANL, was reviewed in references 1-4, with a summary of the status of this system at the end of FY82 included in reference 4. Additional details on the status of this battery system have been published in references 43 and 44 which post-date reference 4. These add details but do not change the summarized information. This section will briefly summarize the status of this system, additional information reported, and research on related systems with the potential for improved specific energy and specific power.

6.2.1 Li-alloy/FeS Batteries

The final version of the Gould Li-alloy/FeS battery consisted of a mixed Li-Al, Li-Si powder negative, a FeS positive, and a ternary lithium salt electrolyte retained in a magnesium oxide powder separator and in the electrodes.⁽⁵⁾ The electrolyte content of the various battery components provided good ionic conductivity with good electrolyte retention. The cell operating temperature was 460°C.

The improved cells had specific energies in the range of 80-85 Wh/kg and 180-190 Wh/l at the C/3 rate. Cell lifetimes of greater than 400 cycles to 100 percent DoD and a peak power of approximately 100 W/kg at 80 percent DoD were routinely achieved. There were no "infant mortalities" even when cells had been subject to at least one freeze-thaw cycle. Several Gould cells are under test at NBTL.

The Eagle-Picher status cells consisted of a Li-Al anode, LiCl-KCl electrolyte, BN felt separator, and FeS cathode. The various cells and groups of twelve status cells showed a wide range of cycle-lives, Group I from 238 to 1031 and Group IX from 193 to 517.

By reducing the hole size in the negative electrode retainer, EP achieved improved cell cycle-life. As of the end of 1983, five of these cells under test at NBTL had achieved the longest cycle

lives ever realized for EP Li-Al/FeS cells and were still under test at that time.⁽⁸⁾ These cells indicate that the modified cell construction may have overcome cell-shortting by protrusions from the negative electrode.

Work at ANL had shown that the use of a heavier positive current collector gave a marked increase in the specific power of the Li-alloy/FeS cells. Both the Gould and EP cells showed the benefit of the heavier current collector. The Gould cell showed an 80 percent increase and the EP cell a 30 percent increase in power output by this change in cell design.

Chen and Gibbard have determined the rate of thermal generation in 200 Ah lithium-aluminum/iron-sulfide cells.⁽⁴⁵⁾ Five-plate, prismatic cells containing three negatives and two positives, boron nitride nonwoven separators, and molten LiCl-KCl-LiF electrolyte were used in these studies. Two independent methods were employed. The first was based on precise measurements of the cell voltage as a function of temperature and state-of-charge combined with measurements of the overpotential during discharge. It was found that the temperature derivative of the cell potential varied strongly with temperature and DoD. For fully charged or discharged cells the temperature coefficients of the electromotive force were negative. However, for partially discharged (23-27 percent DoD) cells, two linear portions were observed. Over the lower portion of the temperature range the temperature coefficients were negative; over the higher portion of the temperature range the coefficients were positive. This behavior was attributed to the transition between J-phase ($\text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl}$) and x-phase (Li_2FeS_2) formation. For cells discharged 50 percent or more, only negative slopes were found over the temperature range of 400-500°C.

A high temperature battery calorimeter was designed and built for the direct experimental measurement of the rate of thermal energy generation. The calorimeter was designed with a temperature range of 400-500°C, a sensitivity of 1 mW, and an upper limit of heat flow of 50 W. Problems with the nickel foil heaters limited the calorimeter operating temperature to 410-435°C.

There was good agreement between the heat generation calculated from the thermodynamic data and the direct calorimetric measurements. The temperature derivative of the cell potential of the Li-Al/FeS cell was a complicated function of temperature and state of charge. The cell reaction for fully charged and fully discharged cells was exothermic. Above 430°C, a part of the discharge process was endothermic.

6.2.2 Research on Li-alloy/Metal Sulfide Batteries

The conclusion of the Li/alloy/FeS battery development effort has led to the reinitiation at ANL of research on related systems with the potential for providing alternative cells with greater specific energy and power, and which can satisfy the other criteria of cycle-life, cost, and suitability for EV or stationary energy storage. Some of the earlier efforts were summarized in references 1-3. The current effort is emphasizing the investigation of the kinetic and thermodynamic properties of Li-Si, Li-Al-Si, FeS₂, Ni₃S₂, NiS, and NiS₂ as electrode materials.⁽⁴³⁾

New methods were developed for characterizing active materials according to usable specific power and power sustaining capability. Half-cell experiments were designed with electrodes of 0.7 cm² with capacities of 0.25-1.5 Ah/cm². The test conditions gave a nearly one-dimensional current distribution. Working electrode potentials were measured using reference electrodes developed by L. Redey and D.R. Vissers of ANL.⁽⁴⁶⁾ The electrode performance was evaluated by galvanostatic cycling, by current-interruption electrode potential relaxation (CIPR) measurements, and by high current pulse techniques. The measurements were used for the numerical characterization of the electrode kinetics in terms of the area specific resistance (ASR) (ohm-cm²). The ASR values are obtained by dividing the time-instant values of either the polarization during high intensity pulses ($jASR_t$) or the potential relaxation after current interruption ($oASR_t$) by the applied current density. The values for the area specific resistance were independent of the current density in the range of 0-200 mA/cm². The ASR values were used to compare the kinetic behavior of different electrodes.

To compare the power-related performance of electrodes, Redey and coworkers introduced the parameter, power indicator (PI). This parameter quantitatively indicates the peak-power and the peak-power-sustaining characteristics of the electrode. The PI was calculated from the ASR and the potential span that was available for useful electrical work during a specific duration of a high intensity current pulse. This approach also enabled the estimation of charge acceptance during a high charging pulse, such as regenerative braking.

Alloys of Li-Al-Si were investigated to determine whether or not such a mixture would retain the power capability of Li-Al and the capacity of Li-Si.⁽⁵⁾ Two compositions of the Al-Si alloy matrix for use in tertiary-alloy negative electrodes were prepared: Al_{0.88}Si_{0.12} and Al_{0.5}Si_{0.5}. The electrolyte used was 9.6 w/o LiF-22.0 w/o LiCl-68.4 w/o LiBr. The ASR's for the ternary

alloys were significantly lower than for Li-Si alloys of the same Li content. The specific energies of the ternary mixtures were higher than for comparable Li-Al negative electrodes. The ternary electrode offers a compromise of the power capability and capacity of the binary Li-Al and Li-Si electrodes, resp.

Spectroscopic studies of the LiS_x species formed during the charging of Li-Al/FeS cells have been reported.⁽⁴⁷⁾ Two methods of preparation of LiS_x were used, one chemical and one electrochemical. The results of the observations confirmed earlier studies that more than one sulfide/polysulfide species was involved. Based on the observations it was concluded that at higher sulfur activities increasing amounts of soluble polysulfide species can form in Li-Al/S and Li-Al/ MS_x cells (M = Fe, Co, Ni).

Iron disulfide and nickel sulfide were investigated as alternative active materials for the Li-alloy/FeS cell. Earlier results on FeS_2 were summarized in reference 4. The chemistry of the four plateaus observed during the discharge of FeS_2 was summarized by the following compositional changes:

The ASR values showed that the high resistance of the electrode during discharge limits its usable capacity and power. The resistance was especially high in the $\text{Li}_3\text{Fe}_2\text{S}_4$ stage of the discharge sequence.⁽⁷⁾

The thermodynamics of the transition:

were determined at various values of x in the temperature range 382–455°C.⁽²⁾ An equation was derived relating the electromotive force (Emf) for the reaction to the temperature:⁽⁷⁾

$$E = 1.37902 + 0.00066T \text{ (}^\circ\text{C)}.$$

A comparative study of the electrochemistry of FeS_2 , CoS_2 , and NiS_2 electrodes in molten LiCl-KCl electrolytes at 400°C was conducted at ANL.⁽⁴⁸⁾ Cyclic voltammetry was used to determine the Emf's for the changes taking place during the cathodic and anodic transformations. Galvanostatic cycling was used for the identification of the various phases formed. The cells were cycled repeatedly at current densities of 12 to 60 mA/cm². The cells were stopped at various states of charge for subsequent phase studies. The positive electrodes, after removal from the cells, were analyzed by x-ray diffraction and metallographic techniques.

It was observed that the transformations during the electrochemical reduction and reoxidation of CoS_2 and NiS_2 were less complex than for FeS_2 . The sequences of phases occurring were summarized as follows:

The sequences are given in the order of decreasing potential vs. Al, Li-Al independently of the sweep direction.

Extended repeated cyclic voltammetry experiments on the same electrode showed that sulfur was lost by the disulfide electrodes. The losses were attributed to nonequilibrium species that were involved in the electrochemical formation of the disulfides from their precursors. The cyclic voltammetry peaks were also used to derive anodic and cathodic nucleation overpotentials. The reactions, their Emf's vs. Al, Li-Al, and nucleation overpotentials are given in Table 19.⁽⁴⁸⁾

In further studies of the performance of porous nickel-sulfide electrodes, Redey and Vissers studied the following electrodes:⁽⁴⁹⁾

- 2.5 mm thick electrode with 545 mah/cm² capacity in 44.2 w/o LiCl-55.8 w/o KCl electrolyte
- 2.5 mm thick electrode with 545 mah/cm² capacity in 9.6 w/o LiF-22.0 w/o LiCl-68.4 w/o LiBr electrolyte
- 4.6 mm thick electrode with 437 mah/cm² capacity in the all Li cation electrolyte

The capacities are based on the $\text{Ni} \rightleftharpoons \text{NiS}$ transition.

Electrode potentials were recorded against a Li-Al reference electrode during galvanostatic cycling, current interruption, and the application of high intensity current pulses. Area specific resistance (ASR) quantities were determined.

Results of slow cycling at low current densities gave the phase transformation sequence of reference 48 (see above). At higher current densities the potential shifts occurred prior to the passage of the theoretical number of coulombs for the given transition. This shift was attributed to the potential value being determined by the surface-layer composition which preceded the internal reaction. The observed current efficiency of less than one was attributed to polysulfide-ion formation which diffused to the negative electrode and caused self-discharge.

TABLE 19
METAL SULFIDE EQUILIBRIUM POTENTIAL AND NUCLEATION OVERPOTENTIALS

Electrode phases (peaks) ^a	Emf ^b (mV)	cn ^c (mV)	an ^d (mV)
$\text{FeS}_2 \rightleftharpoons \text{Li}_3\text{Fe}_2\text{S}_4$	1750 $\pm$ 5	6	95 ^e
$\text{Li}_3\text{Fe}_2\text{S}_4 \rightleftharpoons \text{Li}_{2.2}\text{Fe}_{0.8}\text{S}_2$ and Fe_{1-x}S	1660 $\pm$ 10	30	50
$\text{Li}_2\text{FeS}_2 \rightleftharpoons \text{Fe}$ and Li_2S	1328 $\pm$ 5	18	17
$\text{CoS}_2 \rightleftharpoons \text{Co}_3\text{S}_4$ and Li_2S	1718 $\pm$ 5	9	56 ^e
$\text{Co}_3\text{S}_4 \rightleftharpoons \text{Co}_9\text{S}_8$ and Li_2S	1620 $\pm$ 5	15	50
$\text{Co}_9\text{S}_8 \rightleftharpoons \text{Co}$ and Li_2S	1373 $\pm$ 5	56	5
$\text{NiS}_2 \rightleftharpoons \text{NiS}$ and Li_2S	1748 $\pm$ 5	8	27 ^e
$\text{NiS} \rightleftharpoons \text{Ni}_7\text{S}_6$ and Li_2S	1605 $\pm$ 5	14	13
$\text{Ni}_7\text{S}_6 \rightleftharpoons \text{Ni}_3\text{S}_2$ and Li_2S	1559 $\pm$ 5	14	4
$\text{Ni}_3\text{S}_2 \rightleftharpoons \text{Ni}$ and Li_2S	1365 $\pm$ 2	7	3

^aPhases from reaction sequences, Section 6.2.2

^bEstimated from cyclic voltammograms

^cCathodic nucleation overpotential (Emf- V_{cn})

^dAnodic nucleation overpotential (Emf- V_{an})

^eLower limits

Reference 48 (Preto et al.)

The ASR values determined from the experimental data indicated that both power and active material utilization were higher in the all Li cation electrolyte. For the same electrolyte, the higher loading density electrode gave better power performance. The j_{ASR} vs. pulse duration plots indicated that the nickel sulfide electrode had good peak-power and peak-power sustaining characteristics.

6.2.3 Research on Alternative Molten Salt Cells

The effort of Huggins and collaborators at Stanford U. on alternative anodes, cathodes, and electrolytes for molten salt and solid electrolyte batteries is continuing. The results of earlier investigations have been summarized in status reports 1-4. The molten salt related investigations, since BECC-5 (December 1982), have emphasized systems which are liquid below 200°C and their compatibility with both high lithium activity electrodes and useful positive electrodes.

Further studies on the $\text{LiNO}_3\text{-KNO}_3$ molten salt system have shown that the melting point can be decreased by the addition of CsNO_3 .⁽⁷⁾ The eutectic composition had a melting point of $96 \pm 2^\circ\text{C}$. A solid lithium electrode was found to behave reversibly in this ternary electrolyte. Oxidation and reduction potentials of the electrolyte were measured, and $\text{Li}_{1-x}\text{CoO}_2$ was shown to be a reversible positive electrode in the melt.

Molten alkali nitrites were also investigated for use as intermediate-temperature lithium electrolytes. $\text{LiNO}_2\text{-KNO}_2$, with a eutectic melting at 120°C , was studied by cyclic voltammetry. Lithium and high-lithium activity alloys tend to form a protective layer, attributed to Li_2O , when immersed in the salt. This is similar to the behavior of Li in alkali nitrate melts. The growth of the protective layer did not follow the parabolic law. The resistance of the layer decreased with increasing temperature. Alloy electrodes, e.g., Li-Sb, Li-Bi, behaved reversibly in the melt. The corrosion rate of lithium in the nitrite melt was also determined.

The characterization of aluminum as the negative electrode in LiAlCl_4 as the electrolyte has continued.⁽⁷⁾ The oxidation limit of LiAlCl_4 with respect to aluminum deposition and stripping were examined in both basic and acidic melts using complex-impedance spectroscopy and cyclic voltammetry. Diffusion was important in basic melts, and the morphology of the aluminum deposits was poor. Much higher current densities, ($\sim 100 \text{ mA/cm}^2$) could be passed in acidic melts before mass transport became important. Lithium vanadium bronzes were determined to be stable in the acidic LiAlCl_4 electrolytes.

The initiation of studies at Stanford on ternary alloys for the negative electrodes in molten salts was noted in reference 4. Related work on the Li-Al-Si system performed at ANL was described earlier in this section. At Stanford the thermodynamics of Li-Al-Si were determined electrochemically. The phase diagrams for Li-Al-Si and for Li-Al-Sb at 400°C were also determined.

The Stanford research activities included an investigation of the thermodynamic parameters, phase equilibria, and electrochemistry of lithium transition metal oxide (Li_xMO_y) compounds. (50) LiMnO_3 , Li_5FeO_4 , LiFeO_2 , and LiCoO_2 were investigated as possible positive electrodes for high temperature cells having a lithium or lithium alloy negative and LiCl-KCl molten salt electrolyte. The usefulness of the transition metal oxides depends on their tendency to reduce to lower valence state oxides. The oxygen partial pressure of the compound is a measure of this tendency. The equilibrium partial pressure of oxygen above the two oxides in equilibrium is a measure of the free energy of the transition from one valence state to the other.

The reduction of the lithium metal transition compound was investigated in cells of the type:

The electrochemical reactions were found to be reversible at 400°C. The current densities used for the discharge and charge reactions was 5-15 mA/cm². Up to 3.0 mols of Li could be reversibly reacted. The measurement of the Emf of the cathode as a function of the lithium content, i.e., the number of coulombs passed, gave a measure of the free energy change with composition and a means of calculating the oxygen equilibrium pressure.

The ternary compounds with the highest cathodic potential vs. Li were also the ones of lowest stability, i.e., highest oxygen partial pressure. The relationship between cell voltage and oxygen partial pressure imposes a maximum voltage of 1.820 V vs. Li on LiCl-KCl electrolyte cells using oxide cathode materials. This is equivalent to an oxygen partial pressure of 10^{-25} atm. This requirement puts a strong limitation on the possibility of developing high voltage Li molten salt cells with oxide cathodes.

6.3 Solid Electrolyte Batteries

The solid electrolyte systems center on the use of β'' -alumina as the electrolyte in elevated temperature batteries. The Ford sodium/sulfur battery is one of the major research and development

efforts of the ECS program and is part of the ETD activities. The other solid-electrolyte battery system, which is in the laboratory research stage, is the sodium/trichlorosulfonium ion cell (Na/SCl_3). This uses the β "-alumina as an ion exchange membrane separator along with a molten salt electrolyte. This effort, and research on alternative solid ionic conductors, both crystalline and glass, are part of the TBR activity. Corrosion by sulfur and sodium polysulfides is also being investigated to aid in material selection for the Na/S system. Included are related studies of corrosion by lithium sulfides.

6.3.1 Sodium/Sulfur Battery

Summaries of the patent background and status of the sodium/sulfur battery, which were part of the technology analysis and transfer studies included in Section 2.5, are summarized as additional background to the current status of this battery. Descriptions of the cell and its evolution, up to December 1982, have been presented in references 1-4. Essentially the basic Na/S cell consists of a sodium anode inside of a β "-alumina solid electrolyte cylinder, and a sulfur cathode. An electronic conducting material is included with the sulfur and a chromium-plated steel cylinder acts as the positive current collector.

The patent search at the Pacific Northwest Laboratory (PNL) identified 285 patents on the Na/S battery that had been issued between 1968 and 1984.⁽⁵⁾ The patent activity reached a peak in 1976 and 1977 with 41 and 40 patents, respectively, being issued in these two years. Recent activity has fallen to about one-half of the peak number of patents. W. Bradford Ashton and coworkers placed these patents in four categories:

- electrode materials or designs
- electrolyte designs (including fabrication techniques)
- seals and containers
- overall designs and operational consideration

Of the 285 patents, 58 percent belong to U.S. assignees and the remainder to foreign assignees. British organizations hold 55 of the foreign patents, Federal Republic of Germany - 28, French - 19, and Japanese - 17.

The U.S. assignees hold a disproportionately large share of patents related to electrolyte designs and seals and containers. Foreign assignees own a greater share of overall design patents.

The study of the status of the sodium/sulfur battery, at Jaycor, listed the following as the Na/S battery characteristics:

- molten anode and cathode reactants separated by a solid electrolyte
- medium operating voltage, 1.6-1.8 V
- operating temperature, 300-500°C
- cell energy efficiency, 70-80 percent
- high specific energy, 75-125 Wh/kg
- life, 80-1000 cycles (100 kWh battery completed 675 cycles)
- commercialization, 1990
- cost, ~\$85/kWh (1980\$) in year 2000

The Na/S battery problems noted in the same study included:

- restarting difficult if cells are allowed to cool and solidify
- infant mortality of cells
- development of inexpensive, corrosion resistant containment
- insulation need to maintain temperature
- failure of ceramic electrolyte and cost of electrolyte

The current effort at the Ford Aerospace & Communications Corp. on the Na/S battery is concerned with demonstrating the capabilities of the cells resulting from earlier investigations and continuing efforts to improve the performance and durability of cells made with lower cost materials.

The design, construction, and testing of Na/S batteries for electric vehicles and stationary electrical storage applications has been emphasized in the current program. The Electric Vehicle Engineering Model-1 (EVEM-1) cell has been designed and constructed. This cell was optimized for specific energy leading to a small sacrifice in specific power. In spite of this sacrifice in specific power, a high power capability was achieved. This is important in reducing the total number of cells required for an EV battery.

The EVEM-1 cell had a specific energy at C/3 of 145 Wh/kg and an energy density of 300 Wh/l. An EVEM-1 cell had completed over 1000 cycles and tests were continuing as of June 1984. Figure 10 is a Ragone plot for laboratory EV cells and for production EVEM cells. Special tests on these cells showed them to be safe and rugged. The special tests included shock and vibration, freeze and thaw cycles between standard charge-discharge cycles, and safety of cells in which the electrolyte was intentionally caused to fail. The projected design goals for the EVEM-1 battery are presented in Table 20.

A battery of 480 EVEM-1 cells was constructed and bench tested. The battery was refurbished following the bench tests by the replacement of failed cells. The refurbished battery was placed in an insulated container and shipped to Ford Dearborn for further testing. Shorting of two thermocouples to their buses led to the full discharge of two of the eight modules. After examining the six undamaged modules, they were reconfigured and assembled into a 360-cell, 240-V battery which is to be tested.

The general features of the 100 kWh stationary energy storage (SES) Na/S battery were described in reference 4. This 512 cell battery was assembled in January and February 1981 from cells fabricated in the last half of 1980. Ninety-eight percent of the fabricated cells were satisfactory. The battery was placed on test in February 1981 and as of October 1983, three of the four modules had completed 675 cycles with a greater than ninety-five percent availability. Testing of the fourth module was discontinued after ~100 cycles as this module had been damaged due to an equipment failure. Due to removal of this module and additional cell failures and capacity decline, the available energy decreased from 100 kWh to 60 kWh with a cycle energy efficiency decrease from 75 to 60 percent. This decrease was primarily due to coulombic inefficiency. The battery was refurbished and the 295 useable cells were retained after x-ray inspection and open circuit voltage measurement. The tests of the refurbished battery were initiated in April 1984 and had completed 50 cycles with 100 percent coulombic efficiency at the time of BECC-6, June 1984.

Inspection of the failed cells indicated some sulfur side leakage due to container corrosion and also some leakage at the sodium pinch-off.

The three modules (384 cells in all) of the 100 kWh stationary energy storage system described above underwent a 32 month test. A Weibull statistical analysis of the data indicated the characteristic life of these cells to be ~1500 days.

**RAGONE PLOT FOR THE Na/S EV CELL
FIGURE 10**

TABLE 20
ELECTRIC VEHICLE ENGINEERING MODEL-1 DESIGN GOALS

Nominal voltage	240 V dc
Rated capacity	166 Ah at C/3
Delivered energy	36 kWh at C/3
Peak power (30 sec pulse)	54 kW at 0-50% DoD 44 kW at 80% DoD
Continuous power	16 kW to 80% DoD
Weight	402 kg
Volume	283 l
Thermal loss	300 W at 350°C
Life	200 cycles; 1 year

Reference 5 (Harlow)

The fusing of individuals cells, reference 4, was found not to be entirely effective because of leakage currents. Modification of the fusing by placing two or three cells in series with the fuse enables the blocking of the leakage current. The modified fusing procedure causes the additional loss of one or two operating cells per failure. A module containing 48 parallel units with two cells and a fuse in series (96 cell total) has been tested. As of June 1984 the module had undergone 50 daily cycles consisting of:

- 5 hour discharge at 960 A
- 2 hour idle period
- 10 hour tapered charge at <600 A
- 7 hour idle period
- 7 hour recharge of 83 percent of capacity
- 76 percent dc-dc voltage efficiency
- 100 percent coulombic efficiency

The status of the module as of June 1984 was:

- 1 two cell string with torn fuze
- 6 strings with failed cell
- 41 good strings remaining

Test cells have also been constructed with lower cost, pitch-based current collector matrix materials. These showed excellent performance for test periods of up to 29 months. Cell testing of a low-cost conductive glass as a cathode corrosion protection coating continued to show promise.⁽⁵⁾

Ceramtec continued to supply the β "-alumina electrolytes. The location of the Ceramtec facilities was changed and the new pilot plant facilities are capable of producing 1500 electric vehicle electrolytes and 1000 load leveling electrolytes (500 mm long) per year. The β "-alumina electrolytes are produced with high density-alumina header rings for cell assembly.

Electrolytes prepared by the lower cost slurry-solution spray-drying process have been produced and tests in Mark-II and EV size cells have been initiated. The Mark II cells had completed over 170 cycles, and the EV-size cells had completed 625 cycles as of June 1984.

6.3.1.1 Beta"-alumina Research

Research is continuing to better understand the properties of β "-alumina, the causes for electrolyte tube failures, and methods for improving the lifetime of the electrolyte.

An investigation has been initiated at SNL to provide an independent statistical characterization, establish manufacturing capabilities and tolerance limits, and provide a reference base against which improvements in the β "-alumina electrolyte can be compared.⁽⁵⁾ The SNL test matrix is shown in Table 21. It includes both chemical and physical testing at various stages of the process starting from the raw materials to the final sintered body. Properties are also being measured at several locations on each electrolyte tube. Sufficient data had not been determined at the time of BECC-6 for statistical analysis.

In addition to studies of the β "-alumina electrolytes produced, electrolytes from failed cells are also being examined at SNL. X-ray diffraction and surface chemical analysis techniques are to be used in addition to the tests listed in Table 21.

The axial and radial AC conductivities of the electrolytes are being determined. The axial AC conductivity is being measured by using ionically reversible electrodes made from sodium salts. The measurements cover the temperature range 225 to 375°C. The radial AC conductivity is being measured over the temperature range of 25 to 600°C by the use of ionically-blocking gold electrodes. Both sets of measurements cover the frequency range from 5 Hz to 10 MHz. The measurements gave a value for the axial resistance of ~6 ohm-cm at 300°C (Ceramtec value 6 ohm-cm at 300°C) and the radial resistance of a disc shaped sample (not a part of an electrolyte tube) was ~6 ohm-cm at 300°C. The measurements of the axial resistance showed no variation from the top to the bottom of the electrolyte tube. The tube also had uniform density.

Earlier results of studies by L.C. deJonghe at LBL on the chemical and electrochemical characteristics of β and β "-alumina were summarized in reference 3. Additional results have been reported in references 51 and 52 and are included in this summary.

The effect of the microstructure on the initiation of failure in β "-alumina electrolytes was investigated by acoustic emission detection in Na/Na cells. Two types of ceramic electrolyte failures have been identified. The first type, Mode 1, involves a rapid, catastrophic crack propagation. Mode 1 failure was described as being due to the pressure caused by capillary streaming of sodium through a small pre-existing surface flaw on the sodium side of the

TABLE 21
BETA"-ALUMINA TEST MATRIX

Test, Measurement	Processing Steps*			Electrolyte
	1	2	3	
Green density			X	
Thermal analysis		X	X	
Surface area	X	X		
Particle size	X	X		
Chemical analysis	X			X
Phase analysis				X
Microstructure				X
Fracture strength				X
Fracture toughness				X
Ionic conductivity				X
Young's modules				X
Thermal expansion				X
Density				X
Dimensional				X
Surface roughness				X
1 - Raw materials				
2 - Milling				
3 - Isotactic pressing				

Reference 5 (Grothaus and Hellstrom)

electrolyte. This pressure is caused by crack extension above some critical value of the current density. The observed average critical current densities were 145 and 640 mA/cm² for large and for small grained electrolytes, resp. Micrographs of electrolytes following electrolysis showed preferential degradation along the grain boundaries of large grains, in agreement with the acoustic data.

It is generally agreed that in Mode I failure the critical current density for failure initiation is proportional to the critical stress intensity factor raised to some power.⁽⁵²⁾ According to the models, this power has a value of 4 so that the fracture toughness of the electrolyte has a very profound effect on its durability.⁽⁵³⁾

Nearly all electrolytes from used Na/S cells examined at LBL, showed Mode I cracks. This was true even in the case of relatively short use (20 Ah/cm⁻²). However, such electrolytes operated for extended times with little deterioration in performance. Thus, the exact correlation between Mode I crack formation in the laboratory tests and electrolyte failure in operating cells is not quantitatively established.

The second type of degradation, Mode II, is slow. In several used electrolytes a layer of damage was found to have developed from the sodium side of the electrolyte. The observed damage indicated that a slow grain boundary deterioration was taking place in certain electrolytes. In some cases such layers contained calcium. This surface damage layer was not universal; some electrolytes used in long-term cell experiments were free of a surface damage layer. These observations suggest that subtle compositional differences may have significant effects on the life of the electrolytes.

Evidence also indicated that slow crack growth had occurred. The evidence included:

- tapered discoloration profiles around the cracks
- morphology of old cracks
- current rate increase dependent critical current density levels

A suggested mechanism proposes that the strong reducing conditions, created by the sodium that is electrolyzed into the crack during cell charging, chemically destroys the electrolyte at the crack tip. This effect has been incorporated into a model which predicts that the electrolyte is fairly unaffected by short current pulses,

and that a decrease in the current density can increase the total number of coulombs that a cell can cycle prior to failure.

Other electrolyte changes observed during the LBL studies included:

- darkening of solid electrolyte in contact with molten salt
- rapid or slow crack penetration through the electrolyte, causing practical or total short circuits
- cracking and electrode imprinting on the sulfur side of the electrolyte

The chemical coloration was associated with a partial reduction of the electrolyte.

Sulfur-side attack is found frequently in electrolytes that have been used for extended periods in Na/S cells. Laboratory experiments have indicated that the polysulfide discharge composition may be very corrosive, especially if the metal is in equilibrium with solid Na_2S_2 . Such conditions can exist locally at the positive side of the electrolyte surface during the discharge cycle.

The fracture toughness of sodium β'' -alumina crystals was determined by a hardness-indent method. Cracks with habit planes normal to the 00.1 planes had fracture toughness values of $\sim 2 \text{ MPa}\cdot\text{m}^{1/2}$; cracks running parallel to the 00.1 planes had values of $\sim 0.16 \text{ MPa}\cdot\text{m}^{1/2}$. This extreme anisotropy was considered as partially explaining the difference between calculated and observed critical densities for Mode I failure initiation of polycrystalline solid electrolytes and the variation in failure initiation from crack to crack.

The efforts at Ceramtec and Rockwell International Science Center on the transformation toughening of β'' -alumina, reported in reference 4, has continued. Corporate research at Ceramtec on transformation toughened β'' -alumina was reported at BECC-6. Beta-alumina electrolytes, transformation toughened by the addition of zirconia, have been prepared by the use of the zeta process. Strengths in four-point bending toughness, as indicated through critical stress intensity factors, sodium-ion resistivity, and critical current densities for mechanical failure have been measured. At around 15 percent zirconia there is an area of overlap of the region of high toughness and the region of low resistivity. This overlap region suggests compositions that could be considered for Na/S battery application.

The effort of D.J. Green at Rockwell on transformation toughening of β'' -alumina is emphasizing the determination of the optimum zirconia concentration and method of fabrication.⁽⁵⁾ The studies on the effect of zirconia concentration have shown that up to 15 v/o ZrO_2 can be added to β'' -alumina without causing a large increase in resistivity. It was also found that with over 10 v/o ZrO_2 grain growth of the β'' -alumina phase was limited, which helps eliminate failures caused by the presence of large grains of β'' -alumina.

The β'' - $\text{Al}_2\text{O}_3/\text{ZrO}_2$ composites were slip cast from colloidal dispersions of the powders in alcohols, usually 1-butanol. The cast material was sintered at 1535°C. The resulting ceramic bodies had densities ~97 percent of theoretical or greater. A comparison of the properties of toughened β'' -alumina materials showed that the fabrication process required careful control. Uniform mixing of the two powders and particle size control were important factors. It was necessary to limit the size of the zirconia particles to one micron. The removal of larger agglomerates from the zirconia was accomplished by sedimentation. On the other hand, it was observed that reduction in the β'' -alumina large particle size content by sedimentation increased the resistivity and large particles gave a more desirable product in terms of ionic resistivity.

Additions of up to 20 percent of tetragonal ZrO_2 increased the fracture toughness up to 66 percent with a parallel strength increase of a factor of between 2 and 3. A comparison of the effects of tetragonal and cubic ZrO_2 showed that the major strengthening mechanism was the control of the grain-growth of the β'' -alumina with the associated decrease in critical flaw size. Microstructurally, it was found that this reduction was a result of the control of the β'' -alumina grain size by the zirconia preventing exaggerated grain growth. This eliminated the flaw population associated with large grains of β'' -alumina which occur in the single phase material.

The addition of 10-20 volume percent of zirconia to β'' -alumina gave products with the following properties:

- fracture toughness - 3.3 to 5.0 $\text{MPa}\cdot\text{m}^{1/2}$
- strength - as high as 440 MPa
- ionic resistivities (300°C) - 6-10 ohm-cm

Further increases in strength are considered to be feasible if further reduction in the relatively large processing flaws can be

achieved. Recent studies at LBL on zirconia toughened β'' -alumina electrolytes indicated that substantial performance improvement may be expected by zirconia toughening.

6.3.1.2 Na₂S_x/S Transport Properties

The knowledge of transport properties is important to cell performance modeling. The data on these properties, which are difficult to measure in the Na₂S_x/S mixture at the cathode, are at best limited. John Newman at the University of California, Berkeley has undertaken research to improve the data on the needed transport properties.^(5,7)

The fundamental transport properties of a multicomponent mixture, the binary transfer coefficients, are defined by concentrated solution theory. The mathematical equation relates the gradient of the electrochemical potential of a species to the binary transfer coefficient of this species with respect to other species in solution. These binary transfer coefficients can, in turn, be related to the conductivities, transference numbers, and diffusion coefficients determined experimentally as a function of concentration.

The transference number of the sulfur anions was calculated from literature data. The available literature values for diffusion coefficients in sodium polysulfide melts do not agree. This led Newman to investigate restricted diffusion as a method for measuring diffusion coefficients in sodium polysulfides. Experimentally, the species of unknown diffusivity is placed in a tall thin cylindrical cell, which is closed at each end by a reference electrode. The potential across the cell is measured as a function of time as the initial sharp concentration gradient is allowed to relax toward a final uniform concentration. At long times, the diffusion coefficient can be determined from the slope of the logarithmic plot of concentration difference vs. time.

6.3.1.3 Corrosion in Polysulfide Melts

Corrosion of the cathode current collector is an important factor in determining the lifetime of the Na/S battery. This problem also exists in the Li-Al/MS_x batteries when higher valence metal sulfide cathodes are used. This had led to an intensification of corrosion research related to these systems, with greatest emphasis on the Na/S battery positive-current collector. In addition to corrosion resistance, the current collector should have adequate conductivity, impermeability, preferential wettability by polysulfide rather than sulfur, mechanical stability, and economic viability.⁽⁵⁴⁾

A.P. Brown and coworkers at ANL have conducted static corrosion tests of various metals and alloys in sulfur and sodium polysulfide melts. The tests were conducted at 350°C with measurements of the reaction kinetics and the identification of scale morphology.

Nickel corrosion showed parabolic kinetics. The corrosion products formed a compact multilayered scale, with composition varying from the nickel substrate surface to the melt: Ni_3S_2 - Ni_7S_6 , YNiS , $\alpha\text{Ni}_{1-x}\text{S}$, NiS_2 . The deviation of the corrosion of iron from parabolic kinetics increased with the basicity of the polysulfide ($\text{Na}_2\text{S}_3 > \text{Na}_2\text{S}_4 > \text{Na}_2\text{S}_5$). The scale on iron in the presence of sulfur was FeS/FeS_2 ; in the presence of Na_2S_3 , Na_3FeS_3 formed. Molybdenum corroded significantly more slowly than either nickel or chromium.

Chromium-containing nickel and iron-based alloys containing less than 16 percent Cr corroded in Na_2S_3 . However, when the Cr content was greater than 20 percent, a protective scale of NaCrS_2 formed. Other alloys studied in Na_2S_3 included E-Brite-26-1 (Fe-26 Cr-1 Mo) and nichrome (Ni-20 Cr). On the E-Brite, the NaCrS_2 scale formed in Na_2S_3 ruptured and spalled due to the dissolution and recrystallization of Na_3FeS_3 in the melt. The scale on nichrome consisted of interwoven layers of NiS_2 and NaCrS_2 . Aluminum and various aluminum alloys also showed higher corrosion rates than in sulfur. A binary Al-0.6 Mg alloy corroded more slowly than pure aluminum in Na_2S_3 .

The results of the above corrosion studies, except for the aluminum alloys, are summarized in Table 22.

Halina S. Wroblowa and coworkers at Ford Dearborn noted that the obvious choice of current collector materials which are in contact with the polysulfide melt - metals - are thermodynamically unstable in the melt.⁽⁵⁴⁾ The only metals that can be used are those that passivate forming more or less protective and conductive layers; such metals include chromium, molybdenum, and tungsten. Aluminum passivates forming an insulating layer. Carbon in most of its forms is too porous. Non-porous glassy carbon is too expensive even as a thin lining.

The initial studies at Ford Dearborn were on chromium and doped chromium oxides, as well as certain aluminum composite materials, as positive current collector materials.⁽⁵⁴⁾ These materials were tested in a laboratory three-electrode glass cell in which the test piece was partly immersed in the sulfur/polysulfide melt and could be polarized using a potentiostat. The rates of chromium passing into the melt were measured in-situ at 350°C. The experimental parameters included:

TABLE 22
ANL CORROSION TEST RESULTS

Material	Medium	Penetration after 100 h cm	Parabolic Rate Constant, cm sec 1/2
Ni (Nickel-200)	S	8.3×10^{-3}	1.38×10^{-5}
	Na ₂ S ₃	7.4×10^{-3}	1.23×10^{-5}
Fe (AlSi-1008)	S	1.4×10^{-3} (25h)	2.35×10^{-6}
	Na ₂ S ₃	2.3×10^{-3} (25h)	Not parabolic
Molybdenum	S	5×10^{-6}	Test in progress
	Na ₂ S ₃	9.4×10^{-5}	Test in progress
Hastealloy B (Ni-28 Mo-5 Fe)	S	5×10^{-6}	Not determined
	Na ₂ S ₃	2.4×10^{-3}	1.52×10^{-6}
430SS (Fe-16Cr)	Na ₂ S ₃	1.3×10^{-3} (25h)	Not parabolic
E-brite 26-1 (Fe-26Cr-1 Mo)	S	6.5×10^{-5}	Logarithmic
	Na ₂ S ₃	6.3×10^{-5}	Linear $k = 1.9 \times 10^{-10}$ cm sec ⁻¹
Nichrome N9-20Cr)	Na ₂ S ₃	2.0×10^{-4}	Linear $k = 7.26 \times 10^{-10}$ cm sec ⁻¹

Reference 5 (Brown)

- polarization or cycling conditions
- level of additives to the melt
- plating conditions

The study of the corrosion of chromium involved use of a Cr^{51} labeled chromium plate on E-brite. The corrosion was measured by determining the increase of radioactivity in the melt as a function of the above noted experimental parameters. Changes in the surface layer were determined by scanning electron microscopy (SEM), electron dispersive x-ray spectroscopy (EDAX), and x-ray diffraction (XRD). The preliminary results were:

- at chromium potentials above approximately -0.2 V (Na_2S_5 reference) corresponding to Na_2S_x ($x > 3$) the chromium removal rate was 1-5 nm per day. The surface was covered with smooth black Cr_2S_5 crystals
- addition of H^+ and/or H_2O to the melt did not change the rate of chromium passing into the melt
- polarization to a region more cathodic than -0.2 V, where reduction to Na_2S_2 can occur, was a necessary but not a sufficient factor for inducing higher rates of corrosion
- higher rates of corrosion accompanied by blistering of the surface of the chromium sulfide surface layers occurred only under cycling conditions if the cathodic cut-off potential was lower than -0.2 V

Chromium oxide is thermodynamically stable in polysulfide melts but is an insulator. By the addition of lower valent dopants, particularly Li_2O and MgO , materials with resistivities of less than 15 ohm cm were obtained. Cycling in $\text{Na}_2\text{S}_x/\text{S}$ melts of the low resistivity materials caused an increase in resistance which stabilized at ~ 60 ohm cm. This is sufficiently low to be useable in thin coatings.

Lanthanum chromite (LaCrO_3) perovskites, substituted with Sr, had initial resistivities of the order of 1 ohm cm which increased on cycling at a rate of $\sim 7.5 \times 10^{-3}$ ohm cm/day. This would lead to a resistivity of less than 40 ohm cm after 10 years of cycling. No corrosive attack was observed after 6 months of cycling of doped single or mixed chromium oxides. Attempts are being made to form coatings of these materials on stainless steel or aluminum substrates.

Aluminum, in spite of its formation of a non-conductive coating in the $\text{Na}_2\text{S}_x/\text{S}$ melt, was considered of interest as a possible self-healing substrate or in certain composites as the container material. To overcome the problem of the resistivity of the coating formed, Al composites were produced by imbedding SiC particles into Al alloys.⁽⁵⁵⁾ These composites retain their conductivity even after several months of cycling in $\text{Na}_2\text{S}_x/\text{S}$ melts. Optical examination and melt analysis did not reveal corrosive attack on the surface nor along embedded particle-alloy interfaces over a 3 month (450 deep discharge cycles) period. The study of these materials under cell operating conditions has been initiated.

Cairns and McLarnon at LBL are investigating the corrosion of Mo, Cr, and 70 percent Cr-30 percent Fe alloy in molten mixtures of $\text{Na}_2\text{S-S}$ and $\text{Li}_2\text{S-S}$.⁽⁷⁾ Both static and electrochemical studies are underway. The melt compositions were chosen to reflect expected variations in sulfur activity and were generally within the single-phase liquid regions. Cross sections of the exposed materials were studied using SEM-EDAX techniques to determine the thickness and composition of the scale. Where possible, weight gain was used to calculate overall corrosion rates.

The electrochemical cell used was constructed from quartz, a molybdenum feed through was used as a reference electrode, and tungsten springs were used as current leads and to hold the electrodes in place. Tests were conducted by maintaining the metallic samples at a fixed potential relative to a Mo/MoS_2 reference electrode. The cell current and resistance of the scale were measured as a function of time to determine the rate of scale formation. The initial tests showed that Mo was resistant to corrosion at 400°C in $\text{Li}_2\text{S-S}$ melts, apparently independent of sulfur activity. Little specific data could be obtained on the composition of the film.

6.3.2 Sodium/trichlorosulfonium Ion Cell

The research on the chemistry of the Na/SCl_3^+ cell and its energy and power characteristics by Mamantov and coworkers has been reviewed in the earlier status reports, references 1-4. The essential features of this cell are: a sodium negative, a β'' -alumina membrane separator, and tetravalent sulfur in a molten electrolyte of $\text{AlCl}_3\text{-NaCl}$ as the positive. Like the Na/S cell, both the positive and negative reactants are molten. The operating temperature is $180\text{-}250^\circ\text{C}$.

The emphasis since BECC-5 has been on "sulfur-rich" laboratory cells. A sulfur-rich positive is defined as one in which the S/Al molar ratio is greater than 0.15. The positive discharges in two steps, the first representing a four electron change:

and the second, a two electron change

Several of the cells tested had specific energies (active material only) for the total six electron change as high as 442 Wh/kg, and for the four electron step of 439 Wh/kg at ~ 20 mA/cm². Some of these cells were operated at area current densities of ~ 360 mA/cm² showing area power densities in excess of 500 mW/cm². In some cells high area energy and area power density were achieved in the same cell. Five cells completed over 100 deep charge-discharge cycles.

6.3.3 Novel Solid Ionic-Conductor Research

In addition to the research on β "-alumina, described in Section 6.3.2.1, the TBR program has been exploring alternative solid ionic conductors. Both ceramics and glasses are being investigated.

The work of B.J. Wuensch at M.I.T. on NASICON ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$) was reviewed in references 2, 3 and 4. The earlier structural studies had shown the existence of different sodium-ion sites in the structure. The two sodium-ion sites assisted in the understanding of the conduction vs. composition behavior of NASICON. The observation that the phosphorous in NASICON contributed to its instability toward sodium has led to the consideration of the possible synthesis of related structures without phosphorus. The results of these studies have been detailed in reference 56.

Studies of mixtures with the composition of $\text{A}_2\text{MSi}_6\text{O}_{15}$ and $\text{A}_3\text{M}'\text{Si}_6\text{O}_{15}$ where A = Na or K, M = Ti or Zr, and M' = Y, Nd, or La have been initiated by Wuensch. Crystal structures had previously been determined for individual compositions, $\text{K}_2\text{TiSi}_6\text{O}_{15}$ and $\text{K}_3\text{NdSi}_6\text{O}_{15}$. These were shown to contain TiO_6 or NdO_6 octahedra and silicon tetrahedra which build a three dimensional system of channels. The alkali ions displayed unusually high thermal motion which may be indicative of high mobility. These systems also have the capability of accommodating cations of different volumes. This in turn permits variation of the concentration of alkali ions and the fraction of the interstices which are occupied. These compositions thus have a degree of crystal chemical flexibility which is analogous to the NASICON system.⁽⁷⁾

Initial attempts to synthesize the crystalline compounds led to glass formation. The use of high pressure (800-1200 atm) hydrothermal synthesis led to the successful preparation of well

crystallized powders. The main product of the reaction was the desired composition, however, also present was a trace of a rare earth oxide. Solid solutions in six glass systems, binary compositions of a member of the M and M' families of silicates, were prepared for hydrothermal crystallization. Complex impedance measurements as a function of temperature and frequency for these glasses indicate activation energies for conduction on the order of 0.7 to 0.9 eV and conductivities at 300°C as high as $10^{-4} \text{ ohm}^{-1}\text{cm}^{-1}$.

Work at Stanford on solid electrolytes, reference 4, has been extended to the preparation of solid solutions of Li_7TaO_6 and Li_8ZrO_6 . These solids are expected to be stable against lithium at unit activity. Layered alkali-zirconium phosphates, $\text{M}_2\text{Zr}(\text{PO}_4)_2$, were prepared by ion-exchange techniques. It was found that a high temperature modification of the lithium member of this family showed high ionic conductivity, comparable to lithium orthosilicate and lithium orthophosphate, which were discussed in reference 4.

The synthesis of glass electrolytes for possible application in the Na/S cell is being carried out at ANL. The efforts on NASIGLAS, glasses with compositions similar to NASICON, were described in reference 4. The current investigations are on soda-rich glasses of the $\text{Na}_2\text{O}-\text{ZrO}_2-\text{Al}_2\text{O}_3-\text{SiO}_2$ quaternary system.⁽⁵⁾ The compositions of interest, in mol fractions, consist of:

- Na_2O - 1/2 to 1/4
- ZrO_2 - 1/6 to 0
- Al_2O_3 - 1/4 to 0
- SiO_2 - 1/2 to 1/4

The properties of 14 glasses of the above compositions are being determined. The properties reported at BECC-6 are summarized in Table 23. Glasses with resistivities approaching the goal of 100 ohm-cm are shown. The corrosion of the glasses in Na and sodium polysulfide-sulfur melts is being investigated.

As an aid in understanding the properties of the glasses and as a guide in selecting new compositions for testing, multiple linear regression techniques are being used to generate response surfaces from the various sets of data. The resistivity response surface indicated a region of high conductivity and high glass transition temperature in the neighborhood of 42 m/o soda, 31 m/o silica, and 27 m/o alumina plus zirconia, where m/o is mol percent. The presence of glass-forming compositions in this region has been confirmed and the glass properties are being investigated.

TABLE 23
GLASS COMPOSITIONS AND PROPERTIES

Na ₂ O	Composition, m/o			Transition		Resistivity ohm-cm at 300°C	Activation Energy eV
	Al ₂ O ₃	ZrO ₂	Si O ₂	Temperature, Tg-°C a	b		
0.250	---	---	0.750	468	475	3704	0.684
0.460	---	---	0.540	397	---	192	0.555
0.250	0.125	---	0.625	---	544	3569	0.595
0.250	0.250	---	0.500	---	---	1119	0.586
0.370	0.125	---	0.500	---	526	697	0.605
0.400	0.120	---	0.480	501	502	484	0.630
0.410	0.166	---	0.417	540	---	364	0.562
0.370	---	0.125	0.500	---	645	324	0.488
0.410	---	0.083	0.500	532	---	195	0.541
0.440	---	0.100	0.456	562	564	181	0.517
0.460	---	0.110	0.430	519	548	144	0.507
0.290	0.125	0.083	0.500	---	685	1209	0.591
0.430	0.083	0.055	0.431	563	---	162	0.522
0.450	0.062	0.042	0.446	---	510	130	0.564

Tg = glass transition temperature

m/o = mol percent

a = 10°C/min temperature rise

b = 20°C/min temperature rise

Reference 5 (Roche and Kucera)

The earlier studies of H.L. Tuller at MIT on various lithium borate glasses as lithium-ion conductors were reviewed in references 3 and 4. More recent studies have emphasized the relationship between glass structure and ionic conductivity in the system $\text{Na}_2\text{O}-\text{NaCl}-\text{B}_2\text{O}_3$. The activation energies determined for sodium ion conductivity (~ 0.035 eV) were only slightly larger than those for lithium ion in spite of the larger size of the sodium ion. Density measurements showed that the sodium ion was accommodated by dilation. The various measurements support the conclusion that conduction in these glasses is dominated by strain effects on ion mobility rather than the dissociation of carrier complexes. New glass compositions are being examined using this guideline.

Major progress has been made in the development of electrochemical cells for the investigation of the corrosion of fast ion-conducting glasses in the presence of lithium. These cells enable the examination of a wide range of lithium activities and temperatures. In particular, electrochemical cells of the type:

which include a working and reference cell were used to vary the lithium activity from extremely low values to values approaching unity by the titration of Li from one Li-Al electrode into the Li-Sn electrode.

During continued titration, steps corresponding to the formation of Li-Sn compounds were observed. The relative shift of the position of the steps on the time axis was interpreted as indicative of lithium reaction with the glasses. This was confirmed by examination of the glass surface. Relationships relating the observed shift to the titration rate and temperature were developed and are being used to derive chemical diffusion coefficients for Li diffusion into the reaction layers. Glasses with a range of reactivities and effective diffusivities in their reaction layers are being examined. Some of these glasses exhibit near ideal electrolyte behavior.

7.0 Fuel Cells for Transport

The studies establishing the technical base and goals for fuel cells for transport have been reviewed in references (3) and (4). As a result of these studies and the evaluation of current and projected performance of acid-electrolyte fuel cells, the fuel cell for transport research and engineering program, managed by the Los Alamos National laboratory, was undertaken. This effort is supported by the ECS and EV programs of DOE. This effort is continuing to analyze fuel-cell-vehicle performance projections as an improved guide to establishing fuel-cell technology goals. In addition research is being conducted on improved reformers for converting fuel, primarily methanol, to hydrogen for reaction in the fuel cell, improved electrocatalysts, lower-cost long-lived membranes for the solid polymer electrolyte (SPE^R) fuel cell, and alternative acid electrolytes.

7.1 Fuel-Cell Technology

A study at United Technologies Corp. (UTC) was conducted to determine if there is any limitation, other than catalyst activity, to the operation of the phosphoric acid fuel cell at low temperature.⁽⁵⁾ The benefits to be achieved by low temperature operations include reduced start-up time for the fuel cell and reduced rate of electrocatalyst degradation. The conclusion of the study was, that provided very high cell performance goals can be met, systems can be designed to operate at 65°C and meet vehicle requirements. Thus, development of macrocyclic electrocatalysts that can fulfill the low-temperature operating goals becomes an important objective.

The fuel-cell power-plant configuration for automotive load testing and the test procedures for the 20-kW fuel-cell power plant have been developed at LANL. An analysis was made of a 20-kW fuel-cell powered General Motors X-car on the Federal Urban Driving Schedule (FUDS). The analysis determined the regions of drive-motor torque and speed that best represent the cycle load. A typical test map gave the times of recurrence of torque/speed windows for the FUDS with the fuel-cell power-plant limit and the probable load dynamometer limit. Based on these results, the fuel-cell-powered drive system would be tested at the various torque/speed points, and the fuel consumption for the drive schedule determined by weighting each of the test points by its relative duration from the maps. This test procedure corresponds to a standard automotive industry test procedure for internal combustion engines.

LANL has designed and assembled a six station, phosphoric acid, single cell test and measurement system to investigate the effects of rapid current pulsing, slow-load current ramping, and temperature cycling on phosphoric-acid single cells. The cathode reactant for the cells is filtered compressed air. The anode fuel is hydrogen for all stations except station one, where carbon dioxide is added to the fuel stream. All cells are maintained at 200°C when under load. As of June 1984, cells 1 and 2 were operating at a constant and continuous 200 mA/cm². Cell 3 was being pulsed at a constant and continuous 1 kHz between no-load and 400 ma/cm² to simulate chopper control. Cells 4 through 6 were being subjected to a varying current that takes 7.5 seconds to go from no load to 400 mA/cm² and returns to no load in 2.5 seconds. Cell 4 was operating in this mode continuously, while cells 5 and 6 were operating in this mode for 3 hours and then left on open circuit for 21 hours. Cell 5 was being maintained at 200°C during open circuit; cell 6 was being allowed to cool to ambient temperature during open circuit. This test program was initiated as of June 1984.

The Energy Research Corp. (ERC) is constructing a phosphoric acid fuel cell stack with a methanol reformer that is to provide a system for establishing baseline fuel-cell performance.⁽⁷⁾ The fuel cell and reformer are being sized for a breadboard power plant capable of delivering 20 kW of continuous output with a transient power capability of 30 kW. The fuel cell stack consists of 200 cells measuring 11 x 16 inches (28 x 41 cm). A single air blower provides both cooling air and process air to the cathode manifold. The stack is designed for a nominal output of 170 amperes at 124 volts. The methanol reformer uses a commercial copper-zinc shift catalyst. The reformer is constructed with a fuel vaporizer and burner, which is housed concentrically within a cylindrical catalyst bed.

The breadboard power plant is controlled manually. Liquid fuel is metered to the reformer at a rate about 1.5 times the stoichiometric-hydrogen requirement based on the reaction:

Water is mixed with methanol at a mole ratio of 1.3:1.

To warm the powerplant, liquid fuel is burned in the reformer burner, and electrically-heated air is circulated through the cooling-air loop of the stack. In the normal operating mode, the reformer operates with heat supplied solely by the exhaust tailgas from the fuel-cell stack.

As of June 1984, the design of the major components had been completed, and the fabrication and assembly of the fuel-cell stack and reformer were underway.

Special emphasis is currently being placed on the solid polymer electrolyte (SPER^R) fuel cell which was developed by the General Electric Co. (G.E.). Earlier studies indicated that the SPER^R fuel cell could become the sole power plant for electric vehicles. However, the current SPER^R technology is based on Nafion^R which is too expensive for the cost goals for the EV power plant. The study of the potential applicability and projected capabilities of the SPER^R fuel cell was summarized in reference 4.

The effort at G.E. on the SPER^R fuel cell is centered on the modification of the membrane-catalyst combination in order to reduce fuel cell cost without sacrificing performance. The technology developed at G.E. for the SPER^R-water and brine electrolyzer will be transferred to the SPER^R fuel cell, where appropriate.

Using the SPER^R electrolyzer technology as guidance, a baseline SPER^R fuel cell was designed and constructed. This is shown in cross section in Figure 11. The key to Figure 11 is given in Table 24. The hardware was designed to include low-cost molded carbon collector/separators, carbon-based flow field supports, pneumatic bladder stack compression, water cooling, and internal humidification of the process gases. The cell hardware consists of two endplates, six carbon collectors, one bus plate, two copper plates, a bladder, and tie rods. Attached to the cell hardware are quick coupling connectors on the fluid end plate and a valve on the pneumatic end plate.

Several unique features have been incorporated in the cell. One of these resulted in the development of a low cost design incorporating molded carbon/binder collectors. These collectors had been proven in the SPER^R electrolyzer to be low cost, stable, and manufacturable in large sizes without significant degradation of performance. The stack was designed for humidification of the process gases by water transport through a membrane between two collectors at the end away from the fluid endplate. This facilitates replacement of the membrane and electrode (M+E) without disturbing the humidifier section. The change from stiff endplates to a pressurized rubber bladder for providing the compressive load to the cell improved the uniformity of the compressive loading.

The SPER^R fuel cell system for laboratory testing was based on a simple modular concept. Results from the earlier automotive fuel cell study dictated a design operating envelope of:

SPE[®] CELL HARDWARE-CROSS SECTION
FIGURE 11

TABLE 24
KEY TO FIGURE 11

1. Anode coolant collector
2. Anode collector
3. Cathode collector
4. Cathode coolant collector
5. Positive bus
6. Humidifier collector - gas
7. Humidifier collector - water

M&E - Membrane and electrode

H&E - Humidifier membrane

CFP - Carbon fiber paper

- anode pressures from atmospheric to 30 psig (2.06×10^2 kPA)
- cathode pressures from atmospheric to 135 psig (9.28×10^2 kPA)
- temperatures to 240°F (115°C)
- anode feed: pure hydrogen; five gas mixtures of H₂ containing 0.17 v/o, 0.3 v/o, 1.0 v/o, 3.0 v/o, or 5.0 v/o carbon monoxide diluted to 25 v/o with CO₂, remainder 75 v/o H₂

System controls are included for the following functions:

- heating and cooling
- gas pressure, switching, and flow
- current and voltage
- safety functions

Since the design was for use in a developmental program, the fuel cell hardware can be easily replaced.

It was decided to establish a benchmark performance using baseline membrane and electrode assemblies. The cell operating conditions selected were:

- temperature - 180°F (82°C)
- fuel - 30 psig H₂ (2.06×10^2 kPA)
- oxidizer - 30 psig O₂ (2.06×10^2 kPA)
- current density - 500 amp/ft² (538 ma/cm²)
- voltage, dc - 0.740 V

Twenty five cells were evaluated with baseline membrane and electrode assemblies. The average of these tests was:

0.90 V at 100 a/ft² (108 ma/cm²)

0.72 V at 500 a/ft² (538 ma/cm²)

The G.E. efforts on membranes and electrocatalysts will be discussed with the related investigations on these components.

7.2 Methanol Reforming

Methanol is the concensus fuel for fuel cells for vehicles. This is due to the availability of methanol, the projection that methanol will be readily available via coal gasification, and the relative ease with which methanol can be converted to hydrogen for reaction in the fuel cell.

At IASL the thermodynamics of methanol reforming was reviewed. The equilibrium calculations showed that carbon monoxide concentrations, even at the lower operating temperatures, should be much larger than those observed. For example, a 1:1 stoichiometric mixture of methanol and water at 200°C was predicted to yield a hydrogen/carbon monoxide mixture containing 2.72 percent CO. The experimental results, Los Alamos and others, showed levels of 10 to 100 times lower.

The reaction mechanism for the methanol-water reaction is generally considered as proceeding through a methanol-cracking/water-gas shift mechanism, two heterogeneous processes. The other published mechanism suggests that steam reforming progresses through a methyl formate step.

The higher concentrations of CO projected by the crack/shift mechanism made it difficult to accept. The methyl formate route was considered to be more reasonable, although the first step involves considerable molecular rearrangement. This rearrangement conflicts with the observed rapid reaction as space velocities have shown kinetic parameters in excess of 5000 h^{-1} on CuO-ZnO catalysts. There is some agreement that this catalyst involves microclusters of copper dispersed on an oxide lattice.

The technical staff at LANL proposed a model to explain the reaction pathway for methanol reforming on CuO-ZnO catalysts. The catalytic site was represented as a Cu-Zn site on the surface of the catalyst. The Cu-Zn site was assumed to cycle between an oxidized site, stabilized by the interaction between CuO and ZnO, and a reduced site (Cu). It was further postulated that methanol reacted at the oxidized site to form a methoxy adduct, which bonded to the surface with the loss of a hydrogen molecule resulting in a "formyl-type" adduct. The remaining carbon-hydrogen bonds are weakened by the interaction of two oxygen atoms with the central carbon atom. After the second hydrogen molecule is produced, the C/O species left at the Cu-ZnO site decomposes to yield CO₂ and a "reduced" reaction site. Finally, water reacts with the reduced site to generate a copper-hydroxy species that reacts to regenerate the oxidized "entrance" site. The third molecule of hydrogen is produced during this step. Although this mechanism explains important

details of the methanol-water reaction further testing is required. The implication of the model of successive oxidation/ reduction steps is partially verified by color changes in the catalyst. The dull green-black color was associated with the oxidation step, and the reddish tinge of the fully activated catalyst with the reduction step. Infrared spectroscopy investigations support the proposed reaction pathway.⁽⁷⁾

Closely related studies have been conducted at Brookhaven National Laboratory (BNL). The BNL work has centered on the decomposition of methanol on a clean Pt(111) surface and a Pt(111) surface covered with hydroxyl ions. The technique being used is high resolution electron energy loss spectroscopy (HREELS). The HREELS spectra indicated that methanol is first chemisorbed on platinum via the oxygen atom, which forms a methoxy linkage with platinum, and the CH₃O group is dehydrogenated to a formaldehyde structure. When the last hydrogen atom comes off, the CO-remnant turns over and is bonded via the carbon atom to form a platinum carbonyl linkage. Desorption of this group is difficult, and it constitutes the poisoning species on platinum. In the case of the hydroxyl-ion-covered surface, the hydrogen adsorbed on the metal reacts with the hydroxyl groups to form water. These experiments were repeated with deuterated methanol, and the results confirmed the above conclusions.⁽⁷⁾

Preliminary results indicated that the adsorption of carbon monoxide differed considerably on clean platinum, platinum covered with adsorbed oxygen, and platinum covered with hydroxyl groups.

A computer code was developed at LANL to aid in reaction analysis and to predict optimum design of various fuel-processing schemes. The code calculates the mass and thermal fluxes through a plug-flow reactor.⁽⁵⁾ The model divides the plug flow reactor into a two-dimensional grid of smaller elements, cells. The code output consists of a listing giving temperature for each radial cell along with average compositions and temperatures for each of the axial cells through the reacting network.

7.3 Fuel-Cell Membrane Research

The GE approach to developing lower cost membranes was to investigate commercially available materials, purchase samples of selected membranes, and then evaluate both the physical-chemical properties and fuel cell performance-endurance characteristics.⁽⁵⁾ Twelve potential membrane sources were investigated; nine looked promising and the manufacturers were contacted. Samples were received from four vendors and evaluated for their physical-chemical properties. Three of these were operationally evaluated. One of

the membranes, with a projected cost of one-half that of the present membrane, exhibited performance equivalent to the baseline material.

At LANL a model is being developed that shows the influence of water transport across the membrane on fuel-cell performance.⁽⁷⁾ There is strong evidence that membrane transport properties are affected by water interactions and these interactions are partially controlled by polymer structure. In a study of proton-residence times, i.e., the average lifetime of a proton at a single anionic site, it was shown that proton-residence time decreased with increasing polymer equivalent weight. Furthermore, relatively minor changes in polymer structure can substantially influence polymer behavior.

Less has been investigated regarding the transport properties through ionomer membranes during fuel-cell operations than during electrosynthesis. Although proton fluxes are calculable from known current fluxes, the uniformity of current fluxes is uncertain. Engineering analyses suggested that the apparent water-to-proton ratio involved in the current-driven transport process is 0.6, this is below the values of 7 to 9 found in other experiments. Thus, water produced at the cathode is pumped through an activity gradient and, perhaps, a pressure gradient against the proton flux and concurrent water flow.

The rate of proton transport is determined by the current, whereas the countercurrent water flow is controlled through pressure differences. The water flow is highly influenced by dimensional changes within the polymer structure. These changes may, in part, result from the potential gradient that exists between the anode and cathode. At 500 mA/cm², the proton flux is 5.2×10^{-6} moles/s/cm². Water pumped as part of the anodic fuel accounts for only 3.3×10^{-6} moles/s/cm². Calculations indicated that dehydration of the anode zone occurred when the water flux decreased below 3.3×10^{-5} moles/s/cm². The rate of anode zone dehydration increased with increased current density.

7.4 New Acid Electrolytes

The interest in superacid electrolyte fuel cells for EV's to reduce the fuel-cell operating temperature was reviewed in references 3 and 4. The acids of greatest interest have been the fluorinated sulfonic acids of which trifluoromethane sulfonic acid (TFMSA) is the first member of the homologous series and disulfonic acids, such as methylene disulfonic acid and tetrafluoroethylene-1, 2-disulfonic acid (TFEDSA).

Studies by Cairns, Ross, and McLarnon, LBL, were conducted to characterize TFEDSA as a fuel-cell electrolyte.⁽⁷⁾ The kinetic currents for oxygen reduction in TFEDSA and TFMSA were measured using rotating disc experiments. The two acids showed similar behavior at pH=1. The reaction order with respect to oxygen concentration was measured in both electrolytes by using gases with various partial pressures of oxygen. The reaction order in both electrolytes was unity. Additional studies on alternative electrolytes are being supported by the fuel cell program of the Office of Fossil Energy, DOE.

7.5 Fuel-Cell Electrocatalysis

The major effort for the advancement of fuel-cell technology has been on improved electrocatalysts for the oxygen electrode. The cost and lifetime of the catalyst in acid fuel cells, emphasized in this and the stationary fuel-cell program, is a determining factor in the commercialization of fuel cells. Therefore, electrocatalysis has been an area of research emphasis. Work is also being conducted on CO tolerant anode catalysts. Electrocatalysis in alkaline media was discussed in reference to the iron/air and aluminum/air batteries in Sections 4.2 and 4.3. The LANL program includes investigations ranging from the performance testing of specific anode catalysts to quantum mechanical calculations of the oxygen/catalyst interactions. The program also includes the investigation of the mechanism of the electrocatalysis of oxygen reduction and new electrocatalysts.

G.E. is conducting a two-pronged approach to the improvement of the carbon monoxide tolerance of anode catalysts:

- reduction of catalyst cost by the reduction of catalyst loading
- improvement of catalyst performance with hydrogen fuel containing carbon monoxide

Four CO tolerant anode catalysts (designated A, B, C, and D) were prepared based on previous developments. A was selected as the baseline anode catalyst. Later two more catalysts, designated E and F, with slightly different compositions were prepared. Various methods of catalyst preparation were also investigated. Although all the anode catalysts showed CO tolerance, catalysts E and F showed exceptional tolerance. Two of the anode catalysts, not specifically designated, were reported to show superior performance in the presence of 1 percent CO. Catalyst loadings at both the anode and cathode were reduced 50 percent with some loss in cell performance.

John A. S. Bett at UTC has also been exploring anode catalysts for increased CO tolerance, which would enable lower anode operating temperatures. Past experience has shown that the anode catalyst used in the phosphoric fuel cell becomes more CO tolerant with increasing temperature. Based on the results of previous UTC efforts and a literature study, the following were selected as candidate anode catalysts: gold/platinum, platinum/ruthenium, platinum/bismuth, and three platinum-based UTC proprietary catalysts CSV-11, CSV-15 and CSV-36. The electrodes were tested at 100, 140 and 170°C in phosphoric acid with a dew point of -57°C.

The performance of the anode catalysts was evaluated by determining the increase in the polarization of a pure hydrogen anode on switching from pure hydrogen to fuel gas containing one percent CO. At 180°C, the CO-tolerance of Pt was superior to any of the candidate catalysts. CSV-11 and CSV-15 showed a clear advantage over Pt at 100 and 140°C. Au/Pd and Pt/Ru showed no advantage over platinum. The performance of CSV-11 at 140°C showed promise of satisfying the vehicle goals. This finding led to a shift in emphasis to the development of low temperature cathode catalysts, primarily metal ligands, for use with CSV-11.

At LANL a sensitive experimental technique was developed by S. Gottesfeld for determining the effect of anion adsorption on the pseudocapacitance for the oxide-formation reaction of a gold surface. Quantitative data was obtained on the adsorption of HSO_4^- , H_2PO_4^- , and CF_3SO_3^- on gold. Substantial adsorption of HSO_4^- and H_2PO_4^- was observed, but the extent of CF_3SO_3^- adsorption was minimal in the potential range studied. Rotating ring-disc electrode measurements in 0.05 M HF showed that HSO_4^- adsorption decreased the oxygen reduction kinetics, but H_3PO_4 or CF_3SO_3^- ions did not. The effects on the kinetics were more pronounced when Cl^- or Br^- was adsorbed.

The electrochemistry at the interface between the solid polymer electrolyte (Nafion^R) and various electrodes has been investigated at BNL.^(5, 1) The electrode materials included platinum and gold screens in direct contact with Nafion^R. Additional experiments were carried out on multiple combinations of platinum screens with either graphite felt or gold screen electrodes with only one of the electrodes in direct contact with the membrane. The goal of the experiments was the better understanding of the current generation mechanism and the factors controlling catalyst utilization at electrodes in contact with an ionic solid polymer. The measurement technique was cyclic voltammetry.

The voltammograms were determined for the electrodes in contact with Nafion^R and in an aqueous acid. In the case of the platinum and gold screens, these were very similar. The adsorption doubled

(a) McBreen, J., "Voltammetric Studies of Electrodes in Contact with Ionomeric Membranes" submitted for publication.

in the presence of a second screen which was not in direct contact with the Nafion^R. This indicated that the electrode remote from the ionic polymer was electrochemically active. When the gold or graphite electrodes were between the platinum screen and the Nafion^R, there was a considerable distortion of the platinum oxide reduction peak and the hydrogen adsorption and desorption peaks. This was consistent with a resistive path. There was no effect on the gold electrode upon the interposition of a platinum screen. The results infer that the platinum black catalyst used in the SPE^R fuel cell should have high utilization and that the incorporation of platinum in carbon, not practiced, would decrease cell performance.

There is being developed at LANL an in-situ ion beam-analysis technique to characterize electrode surfaces under conditions closely approximating a working electrochemical cell. To accomplish this a cell was designed and constructed with a thin platinum film sealing a small window and serving as the working electrode. The incident ion beam is to penetrate the platinum and scatter from the chemical species on the electrolyte side of the film electrode. A 1 μ m thick sputtered-platinum film was successfully placed over the window of the electrochemical cell. Electrochemistry was performed in the cell. The thickness of the platinum was such that the platinum signal partially obscured other signals. A platinum film/inert substrate is being fabricated that will allow better signal resolution and allow the cell beam aperture to be larger.

Supplementing the attempts to develop techniques for the direct determination of species on platinum surface is the recently LANL initiated ab initio quantum mechanical calculations of the structure of PtO. This molecule was selected as it is the simplest, in terms of composition, of the possible species which can be formed between platinum and oxygen. This is considered to be an important step in understanding the platinum-oxygen-water interactions at platinum catalyst surfaces.

Electrocatalysis at nearly ordered metallic surfaces is being investigated by Ross at LBL. Surface-analysis techniques, such as low energy electron diffraction (LEED), are being used.⁽⁵⁸⁾ A LEED apparatus has been interfaced directly with an electrochemical cell to determine which metal/metal oxide or Me/Me²⁺ systems can be emersed and examined in the metallic state. Gold, copper, and platinum were shown to be compatible with this technique whereas zinc causes a problem because of its reaction with air during emersion/evacuation.

Pt/PtO_x was selected for extensive study. A LEED analysis of the (100) surface indicated that cycling can alter the long-range ordering (~10 nm) of the surface, but local order (1.3-1.9 nm) is

always preserved. Cycling between the hydrogen adsorption region and the edge of the oxygen electroreduction region (0-0.83 V vs. RHE) caused no discernible change in the Pt(100) LEED pattern. Cycling into the oxygen electroreduction region (1.58 V vs. RHE) produced LEED patterns characterized by alternate broadened and sharp spots. The fluctuation of the spot breadth with incident electron beam energy was consistent with the formation of a correlated island-hole structure.⁽⁵⁹⁾

The restrictions imposed by the LEED system on cell geometry make it necessary to use transient methods with stationary electrodes to study the kinetics of the Me/Me^{2+} reaction and for the dissolution of atomic scale quantities of metal. A mathematical description of voltammetric curves for reversible metal deposition/dissolution was developed and confirmed using the Ag/Ag^+ electrode.⁽⁵⁸⁾ Preliminary experiments on copper deposition from dilute acidic Cu^{2+} solution indicated that LEED can be used to determine atomic-scale structural transformations that accompany the Cu/Cu^{2+} reactions during potential cycling of the substrate.⁽⁵⁹⁾

Jeffery T. Glass and coworkers, University of Virginia, are investigating the effects of various metallurgical variables on the electrocatalysis of the oxygen reaction. The effort has been subdivided into four phases:

- study the effect of increasing Cr content, and therefore decreasing lattice spacing, on the catalytic properties of Pt-Cr alloys within the Pt-rich terminal solid solution
- examine the effect of the order-disorder transition within the Pt-rich solid solution on catalysis
- study the differences between the intermetallic and solid solution phases in both their activities and stabilities
- determine the effect of dispersion within a matrix phase and the effect of metastable structures through the study of various heat treatments of samples consisting of two phases when in equilibrium.

Eight Pt-Cr alloy specimens of appropriate composition have been selected to cover the four phases of the study. To date, three of the eight specimens and pure Pt and Cr have been furnished for this research by James L. Smith at LANL. The specimens have been sectioned and metallographically polished for metallurgical characterization. Lattice parameters were measured via x-ray diffraction and structures were determined by comparison with standard x-ray data. Microscopy following chemical and electrochemical etching was

being conducted (June 1984) to document grain sizes and to look for impurities, such as oxides, in the specimens.

The free energies of Pt-Cr alloys, as well as those of alloys of Pt-Ti, Pt-Zr, and Pt-V, were calculated. These free energies gave data on the relative stability of the different alloys. According to these calculations, Pt-Cr and Pt-Zr had the highest negative free energies and were the most stable with respect to the alloying agents. The most stable composition for this group of alloys was at approximately 50 atomic percent. The applicability of these results to a fuel-cell system are to be tested by electrochemical studies of the stability of the Pt-Cr alloys.

Studies are in progress at UTC and BNL on the use of metal-macrocyclic ligands as catalysts or as catalyst sources for the oxygen electrodes. Related studies at Case Western Reserve and ELTECH were summarized in Section 4.3 as part of the review of the Al/air battery. The major difference is that the fuel cell research activities emphasize acid systems and the metal/air batteries, alkaline systems.

Bett at UTC is investigating thermally decomposed cobalt and iron macrocyclics as electrocatalysts for the oxygen electrodes for phosphoric acid fuel cells. The macrocycles ligands include phthalocyanines, tetraazaannulenes (TAA), and tetramethoxy phenyl porphyrins (TMPP). These are being investigated to:

- identify the catalyst with the highest intrinsic activity
- identify factors limiting catalyst performance in fuel-cell electrodes
- develop approaches for the improvement of catalysts prepared from metal macrocyclics

At UTC a large matrix of catalyst preparation and test variables has been investigated to determine factors influencing catalyst and electrode performance.

Several different carbons were selected as catalyst supports. These included Vulcan XC-72; Black Pearls-2000, a high-surface-area carbon; and RB carbon which had been used at Case Western Reserve Univ.

Supported CoTAA, thermally decomposed at 700°C, gave well defined Tafel behavior in cathodic polarization, with performance reflecting the intrinsic activity of the pyrolyzed macrocyclic compound. FeTMPP gave even higher performance than CoTAA at low

current density but with pronounced curvature of the polarization curve at high current density. The intrinsic activity of FeTMPP exceeds that of platinum in the temperature range chosen. The performance of FeTMPP catalyzed electrodes at high current density appeared limited by reactant gas diffusion and by ionic conductance in the electrolyte-filled porous structure. Improvement in these factors by modification of the support and control of pyrolysis conditions are considered by Bett to be approaches to achieving the performance goals for EV fuel cells.

At BNL several metal tetrasulfonated phthalocyanines (MTSP) were prepared including those of Mn, Cr, VO^{+2} , Fe(III), Fe(II), Co, Ni, Cu, Zn, Ga, Rh, Ir, and the demetalated tetrasulfonated phthalocyanine. The evaluation process consisted of H_2O_2 decomposition studies, investigation of the interaction of oxygen with the MTSP compounds, and a detailed screening of these materials as electrocatalysts for fuel-cell reactions. Preliminary H_2O_2 decomposition studies were carried out with the both the MTSP and the H_2O_2 in dilute solution, 10^{-5} M and 5×10^{-4} – 2×10^{-3} M, resp. All of the above listed MTSP's, except those of Rh, Ir, and H_2TSP , were evaluated. The MTSP compounds of Mn, Fe(II), Fe(III), Ru, and Co interacted strongly with H_2O_2 , decomposing both the H_2O_2 and the MTSP. The reactivity was apparently metal center dependent. There was also good correlation between the d-electron population at the metal center and the sensitivity toward hydrogen peroxide. The d-electron population also correlated well with the activity of the MTSP as an electrocatalyst for oxygen reduction. The work indicates that the MTSP compounds catalyze oxygen reduction because they can axially coordinate O_2 and H_2O_2 . Suitable metal centers can donate electron density to encourage heterolytic change of oxygen.

Exploratory studies were conducted on the electrocatalytic activity of CoTSP incorporated in polypyrrole films. The polypyrrole films were prepared by electrodeposition from an aqueous solution of pyrrole and CoTSP. The CoTSP acted as the counter ion in the film. The catalytic performance of these films was better than that reported for adsorbed macrocyclics on carbon.

8.0 Electrochemical Engineering and Technologies

8.1 Electrochemical Engineering

The ECS supported studies of the electrochemical engineering of industrial electrochemical processes, including performance modeling of specific battery systems, has decreased along with the efforts on battery commercialization and energy conservation in electrochemical process industries. The ECS program is continuing support of studies in generic electrochemical engineering for batteries, electrolytic cells, and other electrochemical technologies.

The initiation of studies by Selman, IIT, of the literature on experimentally-established mass- and heat-transfer correlations for the design of electrochemical systems was noted in reference 4. The search for, and compilation of, heat-and mass-transfer correlations in the literature have been completed. The correlations were collected from 33 journals and 13 standard textbooks or reference volumes. Approximately 420 mass-transfer correlations from 260 sources and 450 heat-transfer correlations from 240 sources were compiled. All correlations have been classified using a 13-digit decimal classification according to flow containment, flow regime and flow geometry, type of convection, transfer surface geometry and motion, and heat-transfer medium. The MIDAS data-acquisition system was used for data storage and retrieval.

A final draft report has been written. The draft report has been reviewed by several experts in fundamental and applied mass and heat transfer. The reviewed correlations will be published as a DOE-LBL report, as part of a professional journal, or as a chapter in a book.

Newman at the University of California, Berkeley is investigating methods for the design and scale-up of battery systems, analysis of thin-gap flow cells, and porous flow-through and flow-by electrodes. The overall objectives of this investigation are:

- to improve the performance of electrochemical cells used in the inter-conversion of electrical and chemical energy
- to develop mathematical models to predict the behavior of electrochemical systems and to identify important process parameters
- to experimentally verify the completeness and accuracy of the models

Experimental data for one-dimensional porous battery electrodes were combined with a model for the current and cell connectors to predict specific energy and maximum power for complete battery systems. The discharge behavior of the plate, including electrochemical and grid resistances, were combined with the voltage and weight penalties of the interconnecting bus and post, positive and negative active materials, and other cell components to give specific results for the Li-Al/FeS battery. These results can be used to optimize the battery for maximum energy or power, or a compromise design may be selected.

The use of porous flow-through electrodes for the electrolytic removal of small amounts of lead was selected as a model system for evaluating the porous electrode model. Experimental data were obtained on the removal of lead at a concentration of $4 \mu\text{g}/\text{cm}^3$ from a 1M H_2SO_4 feed stream in atmospheric and high pressure flow through reactors. The atmospheric reactor used reticulated-vitreous carbon that was coated with a mercury film. The best results showed removal of 98 percent of the lead from the feed stream. In the high-pressure experiments, pressures were varied up to 120 bars on electrode beds of copper- or lead-coated spheres. The copper spheres showed high rates of hydrogen evolution which inhibited lead deposition. The use of lead spheres inhibited the hydrogen evolution which had inhibited lead deposition. This inhibition often resulted in the formation of PbSO_4 layers.

A limiting-current model for the potential and concentration distribution for a flow-by electrode was developed. The model showed that for flow-by electrodes, the maximum solution-phase potential drop is dependent upon one relevant parameter: the product of the electrode width and the reciprocal of the penetration depth.

Design equations were also derived which related the fixed and variable costs to electrode design and operating variables. The sum of fixed and variable costs were then optimized for the flow-through and flow-by configurations to give the conditions under which each configuration is preferred.

Tobias at LBL has developed a novel approach to the understanding of gas evolution at electrodes, i.e., the use of a micro-mosaic electrode which is described in references 5 and 60. This electrode, which was prepared from a silicon wafer using integrated-circuit manufacturing technology, consisted of a 10×10 matrix of coplanar, electrically isolated, square platinum segments on 100-micron centers surrounded by a relatively large buffer segment. A computer-activated data acquisition and control system was assembled. The software was developed to monitor the current to

each individual segment and to control the potential of selected segments.⁽⁶¹⁾

The classical limiting current method was employed in performing mass transfer rate experiments in free convection, and later, to determine the effects of bubble separation and coalescence. Following a potential step, in the absence of bubble phenomena, the current to each segment of an electrode facing upward decreased inversely proportionately to the square root of time. However, 15-20 seconds after the potential step was applied, the fluid next to the electrode became less dense and convection was initiated.. A stable periodic current developed. The amplitude of the current fluctuations at a single segment of the mosaic electrode was greater than the average fluctuations over the total surface.

The micro-mosaic electrode, oriented horizontally and facing upward, was used to measure the effect of the disengagement of a single hydrogen bubble, and of the coalescence of two bubbles, on the limiting current of the reduction of ferric to ferrous ions.⁽⁶²⁾ The mass-transfer enhancement due to bubble disengagement was found to be small when compared to that due to coalescence. Increases in the mass-transfer rate of more than an order of magnitude over the free convection limiting current were observed for the coalescence phenomena. The development of a theoretical model of the phenomena involved has been initiated. The direction of the initial change in the limiting current was correctly modeled by the numerical solution of the convective-diffusion equation. This equation was derived for the flow generated by an ascending fluid sphere near a horizontal surface and for the flow in the wedge formed by the electrode and the bubble in the region near the collapse of the bubble contact area.

Observations of the growth and detachment of single bubbles by means of high speed motion pictures revealed that for large bubbles ($d > 1\text{mm}$) the time scale for the collapse of the contact area is in the order of milliseconds. Numerically implemented solutions of the Laplace-Young equation yielded the shape and maximum bubble size attainable on flat and curved surfaces. A correlation was developed to relate maximum bubble volume to angle of contact, surface tension, and radius of curvature of the surface.

The current distribution in the vicinity of a single attached bubble was computed by the use of the finite element method.^(5,7) In addition to the ohmic and kinetic effects, the analysis included the transport of the dissolved gas species and the contribution of the supersaturation to concentration overpotential. It was found that the familiar effect of ohmic obstruction by the bubble could be greatly overshadowed by the localized lowering of the concentration

overpotential. The result showed an enhancement rather than a depression of current density in the "shadow region" under the bubble. The magnitude of this effect depended on average current density and the thickness of the mass-transfer boundary layer.

8.2 Electrochemical Technologies

The background for the investigation by Sadoway on the effect of impurities on the electrowinning of magnesium was summarized in reference 4. The impurities selected were boron and sulfur as these are known to require careful control in industrial magnesium cells. The electrolyte used in the investigations corresponded to that used industrially in the "anhydrous" electrolytic processes (10 w/o MgCl_2 , 10 w/o CaCl_2 , 20 w/o KCl , and 60 w/o NaCl). The effects of boron and of sulfur were studied by the addition of 0.5 w/o boron as B_2O_3 or 0.5 w/o sulfur as MgSO_4 , resp.

With electrolytes that were contaminated with B or S, galvanostatic electrodeposition occurred at voltages too low to produce magnesium metal. Instead, what appeared to be nonmetallic deposits plated out on the cathode. In the case of the boron impurity, ESCA elemental analysis showed that the cathodic deposit formed contained some of the boron. The results were consistent with the presence of magnesium boride, magnesium oxide, and magnesium hydroxychloride. It was also proposed that the sodium in the deposit was present as Na_2O or magnesium sodium boride. The latter is in accordance with literature suggestions.

In the case of a sulfur source as the impurity, emission spectrography and infrared analysis of the cathodic deposit were consistent with the formation of magnesium oxide and magnesium sulfide. In either case, B or S contamination, the cathode surface becomes passivated by the formation of magnesium compounds.

The use of paired electroorganic synthesis, i.e., the simultaneous production of useful organic products at the anode and cathode of an electrolysis cell, was reviewed in the preceding status report, Reference 4. This gave the background for the investigation of the reduction of glucose to sorbitol and its oxidation to gluconic acid in a single cell. The previously reviewed investigations, conducted by M.M. Baizer and coworkers, showed that by the use of a zinc-amalgam (Zn(Hg)) cathode and the electrochemical generation of HOBr as an oxidant at the anode, the desired objective could be fulfilled. The earlier experiments helped define the following reaction conditions:

- pH 5-7 to minimize glucose isomerization

- temperature 55°C to minimize the parasitic δ -gluconolactone/glucose redox couple
- supporting electrolyte of CaBr_2 to facilitate the separation of products and reactants

The current efficiency for the oxidation of glucose to gluconic acid was 100 percent but was only 20 percent for the reduction to sorbitol.

To attempt to improve the overall cell performance a flow-through packed-bed reactor with a Raney nickel cathode and a graphite chip anode was constructed.^(5,7) The horizontal bed electrodes were separated by a fritted-glass disk. The electrolyte, 1.6M glucose and 0.4M CaBr_2 , entered at the top of the cell and exited through the bottom. The other operating conditions for the reactor were:

- applied current - 500 mA
- electrolyte flow rate - 100 ml/min
- current efficiencies (at 0.3 Faraday per mole) - sorbitol 80%; gluconic acid 100%
- product yields (at 0.3 Faradays per mole) - sorbitol 100%; gluconic acid 100%.

A method to separate the products and supporting electrolyte downstream of the electrochemical flow cell was devised. The product mixture was first dried and CaBr_2 removed with absolute alcohol. Water dissolved the sorbitol leaving calcium gluconate.

A preliminary economic analysis of the process showed that the cost of producing 1 lb (0.45 kg) of calcium gluconate with the simultaneous production of 0.68 lb (0.31 kg) of sorbitol in a paired synthesis (\$0.896) was considerably less than the cost of synthesizing the same products in separate electrochemical cells (\$1.20).

REFERENCES

1. Roberts, R., "Status of the DOE Battery and Electrochemical Technology Program," The MITRE Corporation, Report No. MTR-8026, September 1979.
2. Roberts, R., "Status of the DOE Battery and Electrochemical Technology Program II," The MITRE Corporation, Report No. MTR-80W15, December 1980.
3. Roberts, R., "Status of the DOE Battery and Electrochemical Technology Program III," The MITRE Corporation, Report No. MTR-81W223, February 1982.
4. Roberts, R., "Status of the DOE Battery and Electrochemical Technology Program IV," The MITRE Corporation, Report No. MTR-82W232, May 1983.
5. "Proceedings of the Sixth DOE Electrochemical Contractor's Review," CONF-840677, June 24-28, 1984.
6. "Project Summaries: Sixth DOE Electrochemical Contractor's Review," CONF-840677, June 1984.
7. Kinoshita, K., Editor, "Annual Report for 1983 Technology Base Research Project for Electrochemical Energy Storage," Lawrence Berkeley Laboratory, LBL-17742, May 1984.
8. Shoemaker, P., Editor "Exploratory Technology Development and Testing Project - Executive Summary" Annual Report for Calendar 1983, Sandia National Laboratories, June 1984.
9. Chreitzberg, A.M., "Research, Development, and Demonstration of Advanced Lead-Acid Batteries for Utility Load Leveling" Exide Management and Technology Company, Contract No. 31-109-38-4951, Argonne National Laboratory, Report No. ANL/OEPM-83-6, August 1983.
10. Bowman, D.E., "Annual Report for 1982 on Research, Development, and Demonstration of Lead-Acid Batteries for Electric Vehicle Propulsion", Globe Battery Division, Johnson Controls, Inc., Contract No. 31-109-38-4205, Argonne National Laboratory Report No. ANL/OEPM 83-9, August 1983.
11. Nowak, D., J. Electrochem. Soc. 130, 331 C, (1983).
12. Nowak, D., and K. Tomantschger, J. Electrochem. Soc. 130, 331C (1983).

REFERENCES

13. Broglio, E.P., "Annual Report for 1982 on Research, Development, and Demonstration of Nickel-Iron Batteries for Electric Vehicle Propulsion," Eagle-Picher Industries, Contract No. 31-109-38-6850, Argonne National Laboratory, Report No. ANL/OEPM-83-7, May 1983.
14. Westinghouse Electric Corporation, "Annual Report for 1982 on Research, Development, and Demonstration of Nickel-Iron Batteries for Electric Vehicle Propulsion," Argonne National Laboratory, ANL Report ANL/OEPM-83-8, May 1983.
15. Pound, B., B. Sundararay, R.P. Singh, and D.D. Macdonald, "Thermodynamic Framework for Estimating the Efficiencies of Alkaline Batteries," Final Report, Lawrence Berkeley Laboratory Report LBL-16806, October 1983.
16. McKubre, M.C.H., "Temperature Limitation of Primary and Secondary Battery Electrodes," Lawrence Berkeley Laboratory Report, LBL-16141, May 1983.
17. Poa, D.S., J.F. Miller, and N.P. Yao, "The Mechanism and Kinetics of Iron Electrode Dissolution in KOH Electrolytes," Extended Abstracts of Battery Division, The Electrochemistry Society, Inc., Fall Meeting, p. 17, October 9-14, 1983.
18. Adler, T.C., F.R. McLarnon, and E.J. Cairns, "Studies of the Zinc Electrode: Effects of Charging Regime and Electrolyte Composition," International Society of Electrochemistry, 35th Meeting, Extended Abstracts, p. 304, August 5-10, 1984.
19. McBreen, J., and E. Gannon, "The Role of Bismuth Oxide Additives in Zinc Electrodes," Extended Abstracts of Battery Division, The Electrochemistry Society, Inc., Fall Meeting, p. 13, October 9-14, 1983.
20. McBreen, J., E. Gannon, D-T. Chin and R. Sethi, J. Electrochem. Soc. 130, 1641 (1983).
22. Bhakta, S.D., "Battery Transport Data," Lawrence Berkeley Laboratory Report, LBL-16556, April 1983.

REFERENCES

23. Ruggeri, R.T. and T.R. Beck, "Development of Multicomponent Transport Theory and Transport Data for Membranes in Concentrated Electrolytes" Lawrence Berkeley Laboratory Report, IBL-16557, July 1983.
24. Madou, M.J. and M.C.H. McKubre, J. Electrochem. Soc. 130, 1056, (1983).
25. Madou, M.J., "A Semiconductor Electro-chemistry Approach to the Study of Oxide Films on Nickel, Iron, Zinc, and Cadmium Electrodes" Annual Report SRI International, SRI Project 5703, June 1984.
26. Lee, J, C.C. Christianson, and N.P. Yao, Extended Abstracts of Battery Division, The Electrochemical Society, Inc., Washington, D.C., p. 20-21, October 9-14, 1983.
27. Lee, J, K. W. Choi, C.C. Christianson, and N.P. Yao, Extended Abstracts Electrochemical Society Mtg., Detroit MI, Vol. 82-2, p. 5-6 (1982).
28. Berk, L.B. and C.T. Liu, J. Electrochem. Soc. 131, 952 (1984).
29. Ross, P.N., "Corrosion of Carbon in Gas Evolving Electrodes" International Society of Electrochemistry 35th Meeting, Extended Abstracts, p. 48, August 5-10, 1984.
30. Cooper, J.F., "Aluminum-Air Power Cell Research and Development Progress Report", Lawrence Livermore Laboratory Report, UCRL-90465 (Preprint) dated Feb. 22, 1984.
31. Cooper, J.F., "Estimate of the Consumer Cost of Aluminum Feed for Electric Vehicles" Lawrence Livermore Laboratory Report, UCRL-90468 (Preprint) dated Feb. 22, 1984.
32. Bellows, R.J., C. Elspass, H. Einstein, P. Grimes, E. Kantner, P. Malechesky and K. Newby, "Zinc-Bromine Batteries for Bulk Energy Storage" 18th Intersociety Energy Conversion Engineering Conference, IECEC paper no. 839278. August 21-26, 1983, p. 1696.
33. Bellows, R.J., P. Grimes, H. Einstein, E. Kantner, P. Malachesky, and K. Newby, IEEE Transactions on Vehicular Technology, VT-32, 26 (1983).

REFERENCES

34. (a) Barton, J.L. and J. OM Bockris, Proc. Roy. Soc., 268A, 485 (1962). (b) Diggle, J.W., A.R. Despic, and J. O'M.Bockris, J. Electrochem. Soc., 116, 1503 (1969).
35. Landau, U., "Zinc Electrodeposition and Dendrite Growth from Zinc Halide Electrolytes" Final Report EPRI Em-2393, Case Western Reserve University, Cleveland, Ohio, May 1982.
36. Hsie, W.C. and J.R. Selman, "Zinc Electrodes in Flowing Acidic Electrolytes" International Society of Electrochemistry 35th Meeting, Extended Abstracts, p. 211, August 5-10, 1984.
37. Foos, J.S. and L.M. Rembetsy, "Sulfolane Electrolytes for Secondary Cells", International Society of Electrochemistry, 35th Meeting, Extended Abstracts, p. 237, August 5-10, 1984.
38. Farrington, G.C., B. Scrosati, D. Frydrych, and J. DeNuzzio, J. Electrochem. Soc. 131, 7 (1984).
39. Nazri, G. and R.H. Muller, "Effect of Residual Water in Propylene Carbonate on Films Formed on Lithium," Extended Abstracts of Battery Division, The Electrochemical Society, Inc., Fall Meeting, Washington, D.C., p. 98, October 9-14, 1983.
40. Hanson, K.J., M. Matlosz, C.W. Tobias, and J. Newman, "Theory of Cyclic Voltammetry for Reactions Having Complex Stoichiometry," International Society of Electrochemistry, 35th Meeting, Extended Abstracts, p. 950, August 5-10, 1984.
41. Mark, A.J., I.D. Raistrick, and R.A. Huggins, J. Electrochem. Soc., 130, 776 (1983).
42. Raistrick, I.D. and R.A. Huggins, "Electrochemical Studies of Lithium Insertion Reactions of Vanadium Oxide Bronzes" Extended Abstracts of Battery Division, The Electrochemical Society, Inc., Fall Meeting, Washington, D.C., p. 115, October 9-14, 1983.
43. Barney, D.L., R.K. Steunenberg, A.A. Chilenkas, E.C. Gay, and J.E. Battles, "Lithium/Iron Sulfide Batteries for Electric-Vehicle Propulsion and Other Applications", Argonne National Laboratory, Report No. ANL 83-62, dated September 1983.
44. Gay, E.C., J.E. Battles, and W.E. Miller, J. Electrochem. Soc. 130, 1646, (1983).

REFERENCES

45. Chen, D.M. and H.F. Gibbard, J. Electrochem Soc. 130, 1975 (1983).
46. Redey, L. and D.R. Vissers, J. Electrochem Soc. 130, 231 (1983).
47. Maroni, V.A. and Z. Tomczuk, J. Electrochem. Soc. 130, 864 (1983).
48. Preto, S.K., Z. Tomczuk, S. von Winbush, and M.F. Roche, J. Electrochem. Soc. 130, 264, (1983).
49. Redey, L. and D.R. Vissers, "Electrochemical Performance of Porous Nickel Sulfide Electrodes", International Society of Electrochemistry, 35th Meeting, Extended Abstracts, p. 78, August 5-10, 1984.
50. Godshall, N.A., I.D. Raistrick, and R.A. Huggins, J. Electrochem. Soc. 131, 543, (1984).
51. Buechele, A.C., L. C. de Jonghe, and D. Hitchcock, J. Electrochem. Soc. 130, 1043 (1983).
52. de Jonghe, L.C., "Degradation of Solid Electrolytes" International Society of Electrochemistry, 35th Meeting, Extended Abstracts, p. 14, August 5-10, 1984.
53. Feldman, L., and L.C. de Jonghe, J. Mat. Sci., 17, 517 (1982).
54. Wroblowa, H.S., V. Markovac, R.P. Tischer, and G.M. Crosbie, "Corrosion of Materials in Sodium Sulfur Cells", International Society of Electrochemistry, 35th Meeting, Extended Abstracts, p. 252, August 5-10, 1984.
55. EXXON Enterprises, U.S.-Pat. 4060412 (1977); W.L. Winterbottom, R.P. Tischer, and H.S. Wroblowa, Patent pending. (as cited in reference 54).
56. Wuensch, B.J., L.J. Schioler, and E. Prince "Relation Between Structure and Conductivity in the NASICON Solid Solution System". Proceedings of the Conference on High Temperature Solid Oxide Electrolytes, Vol II-Cation Conductors. Brookhaven National Laboratory BNL-51728, p. 55, October 1983.

REFERENCES

58. Ross, P. and F. Wagner, "The Application of Surface Physics Techniques to the Study of Electrochemical Systems", Adv. in Electrochem. and Electrochem. Eng., C. Tobias and H. Gerischer eds., J. Wiley and Sons, New York (1984) pp. 69-112.
59. Wagner, F., and P. Ross, J. Electroanal. Chem., 150, 141, (1983).
58. Andricacos, P., and P. Ross, J. Electrochem. Soc., 130, 1340 (1983); 130, 1353 (1983); 131, 1531, (1984).
59. Andricacos, P., and P. Ross, J. Electroanal. Chem., 167, 301, (1984).
60. Dees, D.W. and C.W. Tobias, "Development of a Data Acquisition and Control System for the Study of Mass Transfer Phenomena on a Micro-Mosaic Electrode," Electrochemical Society Extended Abstracts, vol 83-1, Extended Abstract 469, May 8-13, 1983.
61. Dees, D.W. and C.W. Tobias, "A Micro-Mosaic Electrode for the Study of Transport Phenomena at Gas Evolving Surfaces," International Society of Electrochemistry, 33rd Meeting, Extended Abstracts, p. 456, Sept. 5-10, 1982.
62. Dees, D.W. and C.W. Tobias, "Experimental Observations of Free Convection Mass Transfer to a Horizontal Surface with a Micro-Mosaic Electrode," Electrochemical Society Extended Abstracts, Vol 84-1, Extended Abstract 394, May 6-11, 1984.

APPENDIX A

ABBREVIATIONS

For the reader's convenience, this appendix lists acronyms and abbreviations that appear in the text. The abbreviations have been subdivided into three categories, the first covering organizations and programs, the second technical terms, and the third physical units.

Organizations and Programs

AMB	Aqueous Mobile Battery Project
ANL	Argonne National Laboratory
BCT	Battery Components Technology (ANL)
BECC	Battery and Electrochemical Contractor's Conference
BEST	Battery Energy Storage Test
BNL	Brookhaven National Laboratory
CWRU	Case Western Reserve University
DOE	Department of Energy
EC	Office of Energy Conservation (DOE)
ECS	Electrochemical Energy Storage Branch (DOE)
EDA	Energy Development Associates, a Gulf+Western Co.
EES	Electrical Energy Systems Program (DOE)
EHV	Electric and Hybrid Vehicle Program (DOE)
EP	Eagle Picher
EPRI	Electric Power Research Institute
ESR	Energy Systems Research (DOE)
ETD	Exploratory Technology Development and Testing (SNL)
ETV-1	Electric Test Vehicle - 1
EV	Electric Vehicle
FC	Fuel Cell
FY	Fiscal Year
G.E.	General Electric Co.
HNEI	Hawaii Natural Energy Institute
IIT	Illinois Institute of Technology
JPL	Jet Propulsion Laboratory
LANL	Los Alamos National Laboratory
LBL	Lawrence Berkeley Laboratory
LLNL	Lawrence Livermore National Laboratory
NBTL	National Battery Test Laboratory (ANL)
PSE&G	Public Service Gas and Electric
RE	Renewable Energy Program (DOE)
SE	Solar Energy Program (DOE)
SNL	Sandia National Laboratories
SOHIO	Standard Oil of Ohio
STOR	Energy Storage Technology Division (DOE)
TBR	Technology Base Research (LBL)
TSD	Technology and Systems Development Branch (DOE)
TVA	Tennessee Valley Authority

Organizations and Programs (continued)

UAH	University of Alabama, Huntsville
UTC	United Technologies Corporation

Technical Terms

ac	alternating current
ASR	Area specific resistance
BET	Brunauer, Emmett, Teller
BOP	Balance of plant
CIPR	Current interruption electrode potential relaxation
CoTAA	Cobalt tetraazaannulene
CoTMPP	Cobalt tetrameso-p-methoxy phenyl porphyrin
dc	direct current
DoD	Depth of discharge
EDAX	Electron dispersive x-ray spectroscopy
EHV	Electric hybrid vehicle
ESCA	Electron scanning chemical analysis
ETV-1	Electric test vehicle - 1
ETX	Electric motor (ac) and transaxle
EV	Electric vehicle
EVEM	Electrical vehicle engineering model (Ford Na/S battery test vehicle)
FC	Fuel cell
FeTMPP	Iron tetramethoxy phenyl porphyrin
FePC	Iron phthalocyanine
FeTPPA	Iron (II)-tetra-3,4-pyridinoporphyrizine
FeTSPC	Iron tetrasulfonated phthalocyanine
FPE	Fluorinated polyethylene
FUDS	Federal urban driving cycle
H ₂ TMPP	Tetramethoxyphenyl porphyrin
HREELS	High resolution electron energy loss spectra
ICE	Internal combustion engine
ISOA	Improved state-of-the-art
LEED	Low energy electron diffraction
MO	Molecular orbital
MTSP	Metalated tetrasulfonated phthalocyanine
NMR	Nuclear magnetic resonance
PAM	Positive active material
PC	Propylene carbonate
PI	Power indicator
PTFE	Polytetrafluoroethylene (Teflon ^R)
PVC	Polyvinylchloride
RCCE	Rotating concentric cylinder electrode
RHE	Reversible hydrogen electrode
RRDE	Rotating ring disc electrode
SB	Shawinigan Black
SEM	Scanning electron microscope

Technical Terms (continued)

SERS	Surface enhanced Raman spectroscopy
SLM	Supported liquid membrane
SOA	State-of-the-art
TAA	Tetraazaannulene
TFEDSA	Tetrafluoroethane 1,2 disulfonic acid
TFMSA	Trifluoromethyl sulfonic acid
TMPP	Tetramethoxy phenyl porphyrin
WEBS	Wind energy battery system
XAFS	X-ray absorption fine structure

Physical Units

A	ampere
cc	cubic centimeter
cm	centimeter
Emf	electromotive force, V
g	grams
h, hrs	hour (s)
Hz	Herz (cycles/sec)
kg	kilograms
km	kilometers
kPa	kilopascals (1.01×10^2 kPa = 1 atm)
kV	kilovolts
kW	kilowatts
kWh	kilowatt hours
l	liter
m	meter
M	molar
ma	milliampere
mah	milliampere hours
mi	mile
ml	milliliter
m/o	mole percent
mph	miles per hour
mW	milliwatts
MW	megawatts
MWh	megawatt hours
nm	nanometer
rpm	revolutions per minute
sp. gr.	specific gravity
V	volts
v/o	volume percent
W	watts
Wh	watt hours
w/o	weight percent
μ	micron
μ g	microgram

DISTRIBUTION

<u>No. of Copies</u>		<u>No. of Copies</u>	
	<u>OFFSITE</u>		Dr. E. Cairns Lawrence Berkeley Laboratory Energy and Environment Division One Cyclotron Road Building 90, 3rd Floor Berkeley, CA 94720
10	Mr. J. Quinn U.S. Department of Energy Forrestal Building, Rm 6A049 1000 Independence Ave., SW Washington, DC 20585		Dr. R. P. Clark Sandia National Laboratories PO Box 5800 Albuquerque, NM 87185
10	Dr. A. R. Landgrebe U.S. Department of Energy Electrochemical Energy Storage CE-141, MS 5 E-036 Forrestal Building 1000 Independence Ave., SW Washington, DC 20585		Dr. T. Farrell U.S. Department of Energy Electrochemical Energy Storage Forrestal Building CE-141, MS S E-036 1000 Independence Ave., SW Washington, DC 20585
30	DOE Technical Information Center Dr. J. Birk Electric Power Research Institute 3412 Hillview Ave. PO Box 10412 Palo Alto, CA 94303		Mr. M. Chiogigio U.S. Department of Energy Forrestal Building, Rm 6A049 1000 Independence Ave., SW Washington, DC 20585
	Mr. J. Brogan U.S. Department of Energy Office of Energy Systems Research Forrestal Building, Rm 5E-052 1000 Independence Ave., SW Washington, DC 20585		Mr. K. Grothaus Sandia National Laboratory Kirtland Air Force Base PO Box 5800 Albuquerque, NM 87185
	Mr. P. Brown U.S. Department of Energy Forrestal Building 1000 Independence Ave., SW Washington, DC 20585		Mr. F. R. Kalhammer Electric Power Research Institute 3412 Hillview Ave. PO Box 10412 Palo Alto, CA 94303

No. of
Copies

ONSITE

Dr. K. Kinoshita
Lawrence Berkeley Laboratory
Energy and Environment Division
Building 90, 3rd Floor Rm 3026
Berkeley, CA 94720

Mr. R. Kirk
U.S. Department of Energy
Office of Vehicle and
Engineering R&D
1000 Independence Ave., SW
Washington, DC 20585

Dr. F. McLarnon
Lawrence Berkeley Laboratory
Building 90, Room 3026
Berkeley, CA 94720

Dr. N. J. Magnani
Sandia National Laboratories
PO Box 5800
Albuquerque, NM 87185

Mr. R. Matsumoto
Ceramatec, Inc.
163 West 1700 South
Salt Lake City, UT 84115

Dr. R. Meredith
U.S. Department of Energy
Electrochemical Energy Storage
Forrestal Building
CE-141, MS 5 E-036
1000 Independence Ave., SW
Washington, DC 20585

Dr. E. Brooman
505 King Avenue
Columbus, OH 43201

DOE - Richland Operations

H. E. Ransom

283 Pacific Northwest Laboratory

W. B. Ashton
D. R. Brown
R. M. Fleischman
C. J. Hostick
J. Hurwitch
C. H. Imhoff (271)
Publishing Coordination (2)
Technical Information (5)