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TECHNOLOGY BASE RESEARCH PROJECT FOR ELECTROCHEMICAL ENERGY STORAGE

REPORT FOR 1982

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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May 13, 1983

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TABLE OF CONTENTS

	page
i. EXECUTIVE SUMMARY	i
I. INTRODUCTION	1
II. ELECTROCHEMICAL SYSTEMS RESEARCH	3
A. New Systems	
1. Intermediate-Temperature Cells	3
a. Sodium/Alkali Nitrate Cells	3
b. Study of High Energy Cathodes for Molten Salt Batteries	4
2. Ambient-Temperature Cells	
a. All-Inorganic Ambient-Temperature Lithium Battery	5
b. Sulfolanes as Electrolytic Solvents for Rechargeable Lithium Batteries	7
B. Metal/Air Systems	
1. Iron/Air Battery Research and Development	9
a. Iron/Air Battery Development	9
b. Bifunctional Air Electrode Research	12
2. Aluminum/Air Power Cell Research and Development	15
a. Cell Configuration and Process Development	15
b. Battery Hardware Development	18
c. Air Cathode Research and Development	20
d. Crystallizer Process Research and Development	22
e. Investigation of Alloys Containing Manganese	24
III. SUPPORTING RESEARCH	26
A. Alkaline Cells	
a. Battery Electrode Studies	26
b. Reaction Profiles in Porous Electrodes	29
c. Nickel Electrode Research	30
d. Development of a High-Rate, Insoluble Zinc Electrode for Alkaline Batteries	31
e. Supported Liquid-Membrane Battery Separators	32

page

f. Temperature Limitations of Secondary Alkaline Battery Electrodes 33

g. Thermodynamic Framework for Estimating the Efficiencies of Alkaline Batteries 34

h. An Electrochemical and Morphological Study of the Restructuring and Loss of Capacity of Alkaline Battery Electrodes 36

B. Zinc/Halogen Cells

a. Surface Morphology of Metals in Electrodeposition 37

b. Dendritic Zinc Deposition in Flow Batteries 39

c. Zinc Electrode Morphology in Acid Electrolytes 41

d. Transport in Aqueous Battery Systems 42

C. Molten Salt Cells

a. Molten Salt Battery Research 44

b. Physical Chemistry of Molten Salt Batteries 45

c. Thermal Management of Battery Systems 46

d. New Battery Materials 47

e. Molten Salt Cell Research 51

D. Solid Electrolytes for Alkali/Sulfur Cells

a. Electrochemical Properties of Solid Electrolytes 55

b. Improved β''-Al_2O_3 Electrolyte Through Transformation Toughening 60

c. Research on the Principles of Superionic Conduction 61

d. Electrical Conduction and Corrosion Processes in Fast Lithium Ion Conducting Glasses 63

e. Glass Electrolytes and Advanced Cell Concepts 64

E. Components for Ambient-Temperature Lithium

a. Surface Layers on Battery Materials 66

b. Metal Couples in Nonaqueous Electrolytes 68

c. Polymeric Electrodes for Ambient-Temperature Lithium Batteries 69

d. Research on Novel Membranes for Lithium Batteries 71

e. Electrochemistry of the Sulfide/Polysulfide Couple 72

F. Cross-Cutting Research

a. Bibliography of Convective Transport Correlations 73

b. Annotated Bibliography of Battery Evaluations 73

page

c. Transition Metal-Oxide Coated Titanium Electrodes for Redox Batteries 74
d. Analysis and Simulation of Electrochemical Systems 75
e. Engineering Analysis of Electrochemical Gas Evolution 77
f. Modeling of Current Distribution with Active-Passive Kinetics 78

IV. ELECTROCHEMICAL PROCESSES 80

A. Membranes
a. Multicomponent Transport Data for Concentrated Electrolytes 80
b. Development of a Multicomponent Transport Theory and Transport Data for Concentrated Electrolytes 81
c. Synthesis and Development of Novel Fluorocarbon Phosphoric Acid Polymers for Ion Exchange Membranes 82
B. Air Electrodes
a. Transition Metal Macrocyclic and Related Complexes as Catalysts for Oxygen Electrodes 83
b. Electrode Kinetics and Electrocatalysis 85
c. Oxygen Cathodes for Energy Conservation and Storage 88
C. Corrosion
a. Polysulfide Containment Materials 90
D. Metal Reduction
a. Development and Testing of the Mathematical Model for the Hall-Heroult Cell 91
b. Transport Phenomena in an Improved Electrochemical Cell Design for the Production of Mangesium 95
E. Miscellaneous
a. Continuous Organic Electrochemical Synthesis 96
b. Electrochemistry Applied to Thermal Conversion 98
c. Fuels and Chemical from Depolarized Water Electrolysis 98

page

V. FUEL CELLS FOR VEHICLES 100

a. Fuel Cells for Vehicles 100

b. Advanced Chemistry and Materials for Fuel Cells 112

VI. APPENDICES 115

A. Financial Information 115

B. Management Activities 117

C. Acknowledgement 118

i. EXECUTIVE SUMMARY

The Lawrence Berkeley Laboratory (LBL) is the Lead Center for management of the Technology Base Research (TBR) Project, which is supported by DOE's Office of Energy Systems Research. The purpose of this project is to provide the research base which supports DOE efforts to develop electrochemical technology for electric vehicle and stationary energy storage applications.

The general objective of the TBR project is to help provide advanced electrochemical systems that can satisfy stringent performance and economic requirements for electric vehicle and stationary energy storage applications. The specific goal of the project is to identify the most promising electrochemical technologies and transfer them to industry and/or another DOE program for further development and scale-up.

General problem areas addressed by the project include identification of new electrochemical couples for advanced batteries, determination of technical feasibility of the new couples, improvements in battery components and materials, establishment of engineering principles applicable to electrochemical energy storage and conversion, and the assessment of fuel cell technology for transportation applications. Major emphasis is given to applied research which will lead to superior performance and lower life-cycle costs.

The TBR project is divided into four major project elements: Electrochemical Systems Research, Supporting Research, Electrochemical Processes, and Fuel Cells for Vehicles. This report describes the research, financial, and management activities relevant to the TBR project in CY 1982.

Electrochemical Systems Research

The objectives of this project element are to identify, evaluate and initiate development of new electrochemical couples with the potential to meet or exceed advanced battery and electrochemical system performance goals. Research projects were conducted on advanced intermediate-temperature battery systems, ambient temperature lithium

cells, and metal/air batteries, including aluminum/air and iron/air. Highlights of this project element follow:

- A positive electrode consisting of equimolar $LiNO_3$-$LiNO_2$ diluted by about 25 mol% $NaNO_3$ was identified as a suitable composition for a sodium/alkali nitrate cell at 200°C.

- A $LiClO_4$ electrolyte yielded cycling efficiencies superior to that obtained with $LiAsF_6$ when employed in Li/sulfolane/Li test cells. Initial cycling tests using sulfolane at 50°C showed cycling efficiency was slightly increased and cell polarization markedly decreased. These results indicate that sulfolane electrolytes may be useful at elevated temperatures.

- Encouraging results were obtained on the cycle life of an inorganic rechargeable lithium cell. A cell with a solid positive electrode and a new electrolyte was tested for over 150 cycles without significant loss of its original capacity during cycling between cutoff voltages of 2.6 V and 4.1 V.

- Program management responsibility for iron/air research was transferred from Lawrence Livermore National Laboratory (LLNL) to LBL. LLNL will continue technical management of aluminum/air projects.

- Major achievements of the aluminum/air program include:

  - The operation of six-cell and two-cell stacks without degradation of performance compared to laboratory baseline cells.

  - Redesign of solution-side current collection grid and successful application to wedge-shaped cells on an engineering scale (600 cm^2). The ability of such cells to operate with continuous anode feed and rapid refueling was demonstrated.

  - Fabrication and testing of air electrodes catalyzed with certain macrocyclic complexes. Cycle life was extended to above 1000 standard drive cycles (comparable to SAE J227AD drive cycle) using non-noble metal catalysts.

  - The influence of minor electrolyte additions and precipitated $Al(OH)_3$ on air electrode life was determined.

  - Development of a comprehensive mathematical model of aluminum trihydroxide precipitation under battery conditions.

Supporting Research

The objectives of this project element are to provide and establish scientific and engineering principles applicable to batteries and electrochemical systems; and to identify, characterize

and improve materials and components for use in batteries and electrochemical systems. Projects in this program provide research that supports a wide range of battery systems -- alkaline, flow, molten salt, non-aqueous, and solid electrolyte. Other projects are directed at research on improving the understanding of electrochemical engineering principles, surface analysis of electrodes, and electrocatalysis. Highlights of this project element follow:

- A zinc halide electrolyte composition was identified in which the cross-term diffusion coefficients are significant. This result is markedly different from previous measurements, which had indicated small cross-term diffusion coefficients. This result suggests that extreme care must be taken to accurately model transport processes in zinc/halogen cells.

- A specially-designed high temperature calorimeter was employed to measure the heat generation rates of a LiAl/FeS cell. The measured results showed excellent agreement with predicted values of cell heat generation based on previous thermodynamic calculations.

- Testing of Li/FeS_2 cells containing various Li-alloy negative electrodes continues. Laboratory-scale cell tests were initiated on ternary negative electrode alloys (Li_5Al_5Fe, $Li_5Al_5Fe_2$ and $Li_4Al_4Fe_2$) which offer the possibility of a higher average discharge voltage and higher specific power. These ternary alloys resulted in a voltage about 200 mV higher than that for the Li-Al system due to the presence of Li_3Al_2.

- Physicochemical measurements continue to provide useful data for analysis of Li/FeS_2 cells. The emf vs. temperature values for the $3Li + 2FeS_2 \rightarrow Li_3Fe_2S_4$ transition and the $Li_3Fe_2S_4 \rightarrow Li_{2+x}Fe_{1-x}S_2+Fe_{1-x}S$ transition were determined. An analysis of the data resulted in the following equations, $E(V) = 1.5558 + 0.0004785T$ (^oC) and $E(V) = 1.3867 + 0.00065T$ (^oC), respectively.

- Investigations are underway to understand the behavior and to enhance the cycle life of Zn/NiOOH alkaline batteries. Cycle-life tests of cells with liquid membrane separators showed encouraging results. Thermodynamic data were used to obtain a better understanding of the voltage efficiency of alkaline batteries.

- Efforts to synthesize novel block copolymers continues. Procedures have been developed that appear to yield polymers that are useful for testing in electrochemical cells with lithium electrodes.

- The structural study and evaluation of Nasicon electrolyte for Na/S batteries were completed. Further development work on this electrolyte was terminated because of its degradation in hot sodium.

- A novel micromosaic electrode was fabricated using semi-conductor technology. The effect of gas bubbles on mass transport processes is being investigated.

Electrochemical Processes

The objectives of this project element are to identify, evaluate and initiate development of efficient electrochemical energy conversion technology. Research projects involved investigation of ion transport in membranes, electrocatalysis to improve the performance of electrochemical systems, electrorefining of metals, electroorganic synthesis, water electrolysis, and thermally-regenerative cells. Highlights of this project element follow:

- The paper "A Mathematical Model for Prediction of Currents, Magnetic Fields, Melt Velocities, Melt Topography and Current Efficiency in Hall-Heroult Cells," authored by Y. Zundelvich, D. Sharma, and J. Evans, was selected to receive the 1983 Extractive Metallurgy Science Award.

- Experimental studies have provided a better understanding of ion transport in Nafion membranes. Parameters such as membrane fixed ion concentration, anion concentration in the membrane, wet membrane density, and ion transference member have been measured.

- Research on non-noble metal electrocatalysts for O_2 reduction was directed at studies of transition metal macrocyclics (TMM). Electrochemical measurements showed that heat treatment of TMM's improved their electrocatalytic activity in air electrodes.

Fuel Cells for Vehicles

The objectives of this project element are to identify, evaluate and initiate development of fuel cell technology for transportation applications. This effort involves basic research to improve the performance of fuel cell systems for use in transportation applications and applied research to establish proof-of-concept. Highlights of this project element follow:

- The rate of oxygen reduction was measured on a rotating platinum disc electrode in trifluoromethanesulfonic (TFMSA), phosphoric, perchloric, and sulfuric acids (all at pH = 0) and in potassium hydroxide (at pH = 14). Tafel plots, which were independent of rotation speed (400 to 3600 rpm), indicated that the overall reduction of oxygen is controlled by the first charge transfer step under Langmuir adsorption conditions. In the potential region of interest, the current density followed the sequence KOH > H_2SO_4 ≅ TFMSA >

H_3PO_4 > $HClO_4$. Mechanistic considerations indicated that oxygen reduced predominantly (80 to 97%) to water through a 4-e transfer reaction. The results did not substantiate claims that more H_2O_2 is formed in alkaline media. However, in acid media, anion adsorption appears to promote the formation of H_2O_2.

- Electrode characterization using ion beam techniques was continued. Platinum distribution in a postcatalyzed electrode was found to be quite nonuniform, leading to inefficient catalyst use. Analysis of new and used electrodes with PtV electrocatalyst at the cathode showed that under operating conditions the PtV electrocatalyst is not stable; vanadium dissolves in the electrolyte and is transported through the matrix to the anode. These results are consistent with the observed performance degradation of the fuel cell.

- The structure, transport, and stability of solid polymer electrolytes (SPE) were investigated. Proton nuclear magnetic resonance studies showed that cations coupled to the ion-exchange sites were solvated with different quantities of water, depending upon the specific cation involved. Electron microprobe and scanning electron microscope analyses were made with new and used Nafion membranes and electrode assemblies. No attack of the carbon-sulfur bonds was evident during operation.

- A single cell, which was designed for investigation of fuel cell performance under simulated vehicle operating conditions, was operated continuously for 4000 hours with hydrogen and air as the reactants. The power density showed very little variation over this period of time.

- Preliminary analyses of chemical and thermal fluxes of a fuel cell system were carried out. Calculations of heat generation and consumption rates indicated that the thermal energy available from the fuel cell stack is sufficient to meet thermal requirements for the fuel conditioning step under various load requirements.

- System studies were performed for selected heavy-duty transportation systems, consumer vehicles, and buses using the Los Alamos fuel cell vehicle simulation program developed at Los Alamos National Laboratory. The heavy-duty transportation studies were done to determine the feasibility of using fuel cell power plants in locomotives and river tow boats. The locomotive application appeared promising. Additional consumer vehicle simulations were performed to provide data for planning the 20-kW phosphoric acid base line power plant test. Bus simulations with SPE fuel cell systems were performed for comparison with the bus system studies previously done with phosphoric acid fuel cells.

- The reduction of oxygen on tetrasulfonated metal phthalocyanines (M-TSPs) of Fe, Co, Ni, and Mn in 0.1 N TFMSA was measured. The activities of the M-TSPs for oxygen reduction decreased in the order Fe > Co > Mn > Ni. No activity was found for carbon monoxide or formic acid oxidation.

- A cell for maintaining a reproducible SPE/electrode interface was made. Preliminary studies using cyclic voltammetry in inert atmospheres, oxygen reduction, and hydrogen oxidation were made on the Nafion 1200/platinum interface. Many features of the voltammograms are very similar to those found in purified TFMSA electrolytes. Tafel slopes of RT/F and RF/2F were obtained for oxygen reduction and hydrogen oxidation, respectively, at the Nafion/platinum interface.

Planned Activities in 1983

New research projects planned include:

1. Selection of an industrial prime subcontractor for development of aluminum/air battery.

2. Research on separators for alkaline batteries.

3. Development of a thermally-regenerative electrochemical system using sodium.

4. Investigation of alloy electrocatalysts for the phosphoric acid fuel cell.

5. Development of a solid polymer electrolyte fuel cell and testing of a phosphoric acid fuel cell for electric vehicle applications.

I. INTRODUCTION

This report summarizes the activities for the Technology Base Research (TBR) project for Electrochemical Energy Storage in calender year 1982. The objective of the TBR project, which is sponsored by the Department of Energy (DOE) and managed by Lawrence Berkeley Laboratory (LBL), is to identify electrochemical technologies that can satisfy stringent performance and economic requirements for electric vehicles and stationary energy storage applications. The ultimate goal is to transfer the most promising electrochemical technologies to industry or another DOE project for further development and scale-up.

Besides LBL, which has overall responsibility for the TBR project, technical management of several projects is shared with Lawrence Livermore National Laboratory (LLNL) and Los Alamos National Laboratory (LANL). Brookhaven National Laboratory (BNL) and Argonne National Laboratory (ANL) participate in the TBR project by providing research support in several of the project elements.

The TBR project consists of the four major project elements listed in Table 1. The objectives of each project element and the specific battery and electrochemical systems addressed are also summarized in Table 1.

This report is sub-divided into the four major project elements and includes technical summaries for the various research projects. Financial information that relates to the various projects is presented in Appendix A. The management activities for the TBR project are described in Appendix B.

Table 1. Summary of the Technology Base Research Project.

Project Elements	Objectives	Battery Systems/Project Areas
Electrochemical Systems Research	o Identify, evaluate, and initiate development of new electrochemical couples with the potential to meet or exceed advanced battery and electrochemical systems performance goals.	o Advanced systems (Na/SCl_4, Na/NO_3), ambient temp. Li (Li/SO_2, Li/sulfolane), metal/air (Al/air, Fe/air)
Supporting Research	o Provide and establish scientific and engineering principles applicable to batteries and electrochemical systems o Identify, characterize, and improve materials and electrochemical systems.	o Alkaline (Zn/NiOOH, Fe/NiOOH), flow (Zn/halogen) molten-salt (Li/metal sulfide), non-aqueous (propylene carbonate), solid electrolyte (Na/S, Li/S), materials for high temperature batteries, polymer electrodes, novel membranes and separators, electrochemical-engineering studies, surface analysis of electrodes, electrocatalysis
Electrochemical Processes	o Identify, evaluate, and initiate development of efficient electrochemical energy conversion technology.	o Ion transport in and development of membranes, electrocatalysts for electrochemical systems, electrochemical production of Mg and organic chemicals, water electrolysis, thermally-regenerative cells, corrosion phenomena
Fuel Cells For Vehicles	o Identify, evaluate, and initiate development of fuel cell technology for transportation applications.	o Phosphoric acid and solid polymer electrolyte fuel cells, alternative fuel cell electrolytes

II. ELECTROCHEMICAL SYSTEMS RESEARCH

The major thrust of this project element is to investigate promising electrochemical couples for advanced batteries and metal/air batteries for electric vehicles. Projects on the metal/air systems, aluminum/air and iron/air, were managed by LLNL, while the projects on new electrochemical systems such as the ambient-temperature Li cells and intermediate-temperature (150-300°C) cells, Na/SCl_4 and $Na/NaNO_3$, were managed by LBL.

A. NEW SYSTEMS

1. INTERMEDIATE-TEMPERATURE CELLS

Sodium/Alkali Nitrate Cells

(M.F. Roche, Argonne National Laboratory)

The objective of this study is to evaluate sodium/β''-Al_2O_3/alkali-nitrate secondary cells as an intermediate temperature alternative to the Na/S battery. These cells may operate at about 200°C, which is 150°C lower than the operating temperature of sodium/β''-Al_2O_3/sulfur cells. The expected benefits of a lower operating temperature are improved cell life through lower corrosion rates and improved energy efficiency through lower heat losses.

The investigations of the molten alkali-nitrate electrodes have consisted of potentiometric titrations, cyclic voltammetry, cycling tests of small (1-3 Ah) cells, and phase studies using X-ray diffraction, metallography, and scanning electron microscopy. The molten alkali nitrates employed to date in these studies have been $NaNO_3$ (mp 307°C), $LiNO_3$ (mp 256°C), and the $LiNO_3$-$NaNO_3$ eutectic (mp 196°C).

Cells with molten $NaNO_3$ as the electrode material and nickel as the current collector have been operated at 330°C for 500 h (20 cycles) with an electrode utilization of 60%. The X-ray diffraction analyses and potentiometric titrations have shown that the $Na/NaNO_3$ cell reaction is $2Na + NaNO_3 \rightarrow Na_3NO_3$ (sodium orthonitrate) with an emf of 1.55V (630 Wh/kg). The mixtures of $NaNO_3$ and Na_3NO_3 generated during cell

operation cause severe oxidation of the nickel current collector and also etch the β''-Al_2O_3. Chemical tests and X-ray diffraction analyses have shown the nickel oxidation product to be the black solid, $NaNiO_2$. The product of the β''-Al_2O_3 reaction is Na_5AlO_4, which has a significant solubility in the electrode material (2400 ppm Al).

Cells with molten $LiNO_3$ as the electrode material and nickel as the current collector failed to operate more than one cycle at 275°C because of fracture of the β''-Al_2O_3. Ion microprobe profiles indicated a doubling of the Li:Na ratio in the fracture zone. The X-ray diffraction analyses and potentiometric titrations have shown that the $LiNO_3$ electrode reaction is:

$$4Na + 2LiNO_3 \rightarrow Li_2O + Na_3NO_3 + NaNO_2.$$

There are two voltage plateaus at 2.25 V and 1.45 V, each representing 50% of the theoretical capacity, and the theoretical specific energy is 860 Wh/kg. Chemical tests have indicated that the combination of $LiNO_3$ and its discharge products is not as corrosive as the $NaNO_3$ - Na_3NO_3 mixture. Nickel showed only a minor surface oxidation and the solubility of alumina was reduced by a factor of six.

Cells with molten $LiNO_3$ - $NaNO_3$ eutectic as the electrode material and nickel as the current collector have been operated at 260°C for 700 h (14 cycles) with an electrode utilization of 25%. A thin, protective oxide layer formed on the nickel current collector in these cells, and the β''-Al_2O_3 appeared to be unaffected by the electrode material. These preliminary tests indicate that the $LiNO_3$ - $NaNO_3$ mixtures are superior to either $LiNO_3$ or $NaNO_3$ alone.

Study of High Energy Cathodes for Molten Salt Batteries

(G. Mamantov, University of Tennessee)

The objective of this program is to investigate the electrochemical and chemical processes of the rechargeable low-temperature molten salt cell Na/β''-alumina/SCl_3^+ in molten chloraluminates. This cell, which operates at 180-250°C and has an open circuit voltage of 4.2V, is being

evaluated as an intermediate-temperature alternative to the Na/S battery.

Studies during the past year have involved the development of a laboratory cell to improve both the specific energy density and specific power of this cell. A significant improvement in the power density has been achieved. For one of the cells, a specific power of 430 mW/cm^2 (231 W/Kg) using a current density of 200 mA/cm^2 at 250°C has been obtained with a tungsten current collector in the positive electrode compartment. For another cell equipped with a Reticulated Vitreous Carbon current collector, a specific power of 627 mW/cm^2 (337 W/kg) at 350 mA/cm^2 has been reached.

Additional studies of the polarization phenomena at the molten salt β"-alumina interface, Raman spectroscopic and electron spin resonance experiments on sulfur-containing species in molten chloraluminates, and examination of used β-alumina tubes were also performed.

Publications

1. K. Tanemoto, R. Marassi, C.B. Mamantov, Y. Ogata, M. Matsunaga, J.P. Wiaux, and G. Mamantov, "Oxidation of Sulfur in Chloro-aluminate Melts of Intermediate pCl," J. Electrochem. Soc., 129, 2237 (1982).

2. G. Mamantov, R. Marassi and K. Tanemoto, "The Chemistry of the Rechargeable Low Temperature Molten Salt Cell Na/β"-Alumina/SCl_3^+ in $AlCl_3$-NaCl," Extended Abstracts, Fall Meeting of the Electrochemical Society, Detroit, MI., October 1982.

2. AMBIENT-TEMPERATURE CELLS

All-Inorganic Ambient-Temperature Rechargeable Lithium Battery

(A.N. Dey, Duracell, Inc.)

The objectives of this project are to evaluate the all-inorganic Li/SO_2 rechargeable battery for energy storage applications, to investigate alternative cathode materials, and to search for alternative electrolytes lower in cost than the $Li_2B_{10}Cl_{10}$-SO_2 presently used. A cost-shared joint program with the Department of Energy has been established

to develop a rechargeable system capable of 100 to 200 cycles at 50% to 80% depth of discharge. The ultimate goal is to develop a battery with a life of 500 to 800 deep-discharge cycles for electric vehicle and/or stationary energy storage applications.

Previously, a cycle life of 50-100 cycles at 10-20% depth of discharge was achieved with Li/SO_2 "D" cells using porous carbon as the positive electrode and SO_2 as the active depolarizer. Both the $Li_2B_{10}Cl_{10}$ and a less expensive salt, to be referred to as EX1, were evaluated and showed similar cell performance. The Li/SO_2 cells delivered only 20-30 cycles at 100% depth of discharge due to degradation of the porous carbon electrode. Solid lithium dithionite formed within the porous carbon electrode on discharge, which in turn generated large internal stress and made the electrode brittle. The repeated structure change on charge/discharge caused irreversible damage to the carbon electrode.

A new solid positive electrode material, to be referred to as CX1 has been developed. The CX1 material is compatible with the inorganic SO_2 electrolyte. In the Li/CX1 system, SO_2 is not directly involved in the cell reaction during operation. The new system has a specific energy of 1100 Wh/kg, which is comparable to that of the Li/SO_2 system. It has significantly better cycle life on deep discharge than the Li/SO_2 system; over 100 cycles on deep discharge to 2.6V was obtained in cells with EX1 electrolyte. A practical Li/CX1 battery is expected to deliver more than 4 times the specific energy of a lead-acid battery.

Other exploratory experiments have led to the discovery of a new salt, to be referred to as EX2. The EX2 electrolyte has high electrical conductivity; about 1×10^{-1} ohm^{-1} cm^{-1} at ambient temperature and 6×10^{-2} ohm^{-1} cm^{-1} at 0^oC, which is significantly better than that of the other organic electrolytes used in rechargeable lithium batteries. Thermal expansion of the electrolyte is only about 1% per 10^oC increase in temperature. An average lithium cycling efficiency of over 97% is obtained in this new electrolyte. Morphology study has shown that the lithium deposited at 1 or 2 mA/cm^2 is not dendritic. The EX2 electrolyte also has good stability toward oxidation, which allows the use of

positive electrode of high potential vs. lithium such as CX1. Experimental Li/CX1 cells operating with the new EX2 electrolyte have demonstrated 200-300 deep cycles at 1 to 2 mA/cm^2 discharge/charge rate between the cutoff voltage of 2.6V and 4.1V. The CX1 positive electrode can deliver only about 50% of its theoretical capacity to 2.6V cutoff. Further discharge to 2.0V to obtain more capacity has shown an adverse effect on cell cycle life. The performance of the CX1 cathode is strongly dependent on the electrode composition and fabrication process. Extensive efforts are currently concentrated on the improvement of the CX1 electrode capacity utilization and cycle life. The Li/EX2/CX1 system has also been found to tolerate overcharge without damaging the cell performance, which makes the system far superior to other rechargeable lithium systems presently under development.

A study of cells containing multiple electrodes has also been initiated recently and preliminary results are encouraging. No serious problem is expected in scaling-up of the new Li/EX2/CX1 system. More studies on cells with multiple electrodes and of various designs are planned.

Sulfolanes as Electrolytic Solvents for Rechargeable Lithium Batteries

(J.S. Foos and S.B. Brummer, EIC Laboratories, Inc.)

The purpose of this research is to investigate the use of sulfolane electrolytes in rechargeable Li batteries. The critical parameters are: conductivity, stability, and ability to cycle Li.

Sulfolane has commonly been selected for use as a solvent because of its resistance to oxidation, and many purification schemes are tailored for this applications. For rechargeable battery application, it is appropriate to develop a purification scheme for the removal of reducible impurities. A variety of purification techniques have been explored. A preferred sequence includes vacuum distillation, distillation at atmospheric pressure, and treatment with alumina. Sulfolane thus purified is nearly transparent in the UV to 220 nm and has a melting range of less than 0.5°C.

It appears that 3-methylsulfolane (f.p. $0^{o}C$) has little or no advantage over sulfolane. The commercial solvent contains more impurities than sulfolane. The conductivity of its $LiAsF_6$ solution is lower than and its viscosity is nearly equal to that of sulfolane at $30^{o}C$. The freezing point difference may be of secondary importance because electrolyte solutions in sulfolane are liquid at ambient temperature.

In storage tests, sulfolane electrolytes were observed to be stable to Li metal for months at $70^{o}C$, whereas sulfolane reacts rapidly and completely with Na/K alloy. Electrolyte solutions in sulfolane have conductivities similar to solutions in 2Me-THF. In blends with relatively polar ethers, synergistic conductivity effects are observed. The type and magnitude of these effects varies with the ether.

An important accomplishment in this work is the development of a laboratory half cell for testing Li cycling efficiency, which is shown to have some predictive value for full-cell behavior. Li in electrolytes consisting of $LiCLO_4$ in purified sulfolane was cycled with up to 80% efficiency at $30^{o}C$ in this test cell.

The effect of temperatures up to $90^{o}C$ on Li cycling efficiencies has been evaluated. It was observed that at $90^{o}C$ the Li cycling efficiencies in sulfolane approach those of ethers at room temperature. This indicates that Li cycling in sulfolane is not limited by the reactivity of sulfolane with Li. If this reactivity affected cycling adversely, it would be expected that the extent of reaction would increase at elevated temperatures and would thereby decrease cycling efficiency. The opposite is actually observed.

Sulfolane has been shown to provide electrolytes stable to Li metal and capable of cycling Li at moderate efficiency. These electrolytes have a highly positive anodic cutoff, are thermally stable, and would be expected to be safe due to the low volatility of the relatively nontoxic sulfolane.

B. METAL/AIR SYSTEMS

1. IRON/AIR BATTERY RESEARCH AND DEVELOPMENT

The overall objective of this program is to develop an electrically-rechargeable iron/air battery that has the potential to provide low-cost electric vehicles with a range of about 160 km. The present critical technical problem is the development of a reliable, low-cost air electrode. Thus, the major effort of this program is directed to research and development of an air electrode, while continuing a low-level effort in cell testing and development. This program is conducted at the Research Laboratory of the Westinghouse Electric Corporation (WEC) and at Case Western Reserve University (CWRU). In this cooperative research, WEC fabricates and tests air-electrodes, supplies materials and samples to CWRU for testing, and evaluates new electrode structures and catalysts developed by CWRU. The role of CWRU is to determine the factors controlling electrode lifetime and develop stable and innovative catalysts and structures suitable for the iron/air battery.

Iron/Air Battery Development

(E.S. Buzzelli, Westinghouse Electric Corporation)

The objective of this project is to develop an iron-air battery as an automotive energy source that provides low-cost transportation for specific vehicle applications such as commuting and urban delivery. In addition to the continued program of performance testing and life-cycle testing of air electrodes, research was conducted in the following areas.

1. Evaluation of new materials to replace the present catalyst system composed of Ag, NiS, $FeWO_4$, and WC-12%Co.

2. Studies of the relationship of structural materials and processing techniques to electrode performance and lifetime.

3. Investigation of factors influencing cell operation and life, including electrolyte flow rate, interelectrode gap, separator material, and the configuration of current collectors.

Three electrodes (10 cm^2) cut from a large sheet were tested at three different temperatures (25, 45, and 60°C) in a synthetic O_2-N_2 humidified gas mixture. A cycling routine of 50 min. discharge at 50 mA/cm^2, a 10 min. open-circuit period, followed by a 5 hr. charge at 12.5 mA/cm^2 was used. Results through 100 cycles indicated a decreased break-in period with increasing temperature for the oxygen-reduction mode and a decrease in the time of onset of discharge-potential deterioration. No definite break-in period was associated with the oxygen-evolution mode at any temperature although deterioration in the oxygen-evolution potential was noted at approximately cycle 45 for the 60°C test.

A series of electrodes were fabricated to evaluate the effects of Teflon binder loading, carbon/Teflon agglomerate size, carbon/Teflon working time, and dispersion/wetting agents on electrode performance. Cathodic polarization increased dramatically when the Teflon content was less than 2% or greater than 9%. Open circuit potentials were more positive when Teflon content was less than 2% and reached a maximum at around 8-10% Teflon. Agglomerate-size studies revealed that, within the size range examined (200-1500 microns), a smaller size leads to lower overpotentials for both oxygen reduction and oxygen evolution. Results from the Teflon working-time studies showed that short working times lead to low oxygen evolution overpotentials. A 1-hour working time has been identified as optimal from the discharge standpoint. The Teflon dispersion agent caused an undesired variability in electrode performance. Little effect on oxygen evolution potentials was observed over the range of loading levels investigated.

Results of tests of an electrode incorporating a steam-treated acetylene black carbon support in lieu of the conventional Shawinigan acetylene black has revealed electrical performance to be in the same range of conventional substrate electrodes. It remains to be established if electrode lifetimes are enhanced. (Steam treated acetylene is more resistant to carbon oxidation, thought to be a large contributing factor to electrode failure).

Two air electrodes were fabricated with platinum replacing the silver catalyst. Poor performance of about -0.200V vs. Hg/HgO was obtained for 100 cycles, at which point the cells were taken off test. The charging mode was not studied because the high potential damages the performance during discharge. Floating-electrode tests with platinized electrodes showed that these electrodes do not perform better than the silverized electrodes.

The search for an oxygen-evolution catalyst was continued. Half-cell tests of electrodes incorporating additives, which were suggested by voltammetry of Ni powder/additive mixes, have identified promising candidates. Cr_3C_2 + Cr_2S_3 in silverized carbon performed particularly well in discharge (-0.118V vs. Hg/HgO at 25 mA/cm^2). NiS + 316 stainless steel on silverized carbon was both efficient and long-lived for oxygen evolution (0.499V at 12.5 mA/cm^2).

The floating-electrode method was used to screen prospective catalysts. Electrodes made from silver-loaded carbon, stainless steel powder and NiS exhibited second-order rate constants better than those for Ag alone (5.6×10^4 vs. 4.6×10^4 $m^{-1}s^{-1}$). Peroxide decomposition rate constants were evaluated for various stainless steels, Cr, and the traditional additives (NiS, WC-12%Co, $FeWO_4$). An air electrode employing 316 stainless steel displayed stable performance in both operational modes, rivaling that of the best electrodes made with the conventional additive package, however, Cr dissolved into the electrolyte. Follow-up experiments involving the cycling of sintered iron electrodes (10 cm^2) in KOH + K_2CrO_4 indicated deleterious effects of the Cr on observed capacity. Consequently, Cr-free Ni-Fe additives are being pursued. Pseudo-Tafel curves obtained on various steel wool and nickel-plated steel wool current-collecting grids showed a reactively sintered Fe-Ni grid was beneficial for oxygen generation (highest O_2 evolution current at 0.550V vs. Hg/HgO).

Testing of subscale iron-air cells was performed. For 100 cm^2 cells, stable cell voltages in the range of 0.65 to 0.70 volts along with stable cell capacities of 75-80% of their first-cycle values were routinely achieved over extended cycling. Some cell voltages in excess

of 0.72 volts were attained. Interelectrode gap variations, modified cell configurations, and alternative cell separators were examined. Tabbing of the iron electrode periphery was found to increase cell structural integrity but experiments with alternative separator materials were not successful in extending cell leakage-free cycle life.

In-cell probe measurements of 100 cm^2 cells revealed up to 30mV disparity compared to the electrode voltages obtained with reservoir probes. A series of experiments with air-electrode tabbing using 10 cm^2 four-layer electrodes showed an unexpected variation of polarization resistance with nickel tab length and little correlation with the tabbed length/electrode width ratio. Studies have now been initiated with 100 cm^2 cells to determine the effects of air electrode current collector tabbing configuration on performance. Both total and IR (ohmic) polarization resistance is being monitored as a function of cycle, the latter using current-interruption techniques.

A test on the effect of low level vibration was performed to simulate road operations. A 40 cm^2 cell was vibrated at 60 cycles/sec. No effect was detected through fifty cycles.

Bifunctional Air Electrode Research

(E.B. Yeager, Case Western Reserve University)

The objectives of this project are (1) to established the chemistry and physical structure of the state-of-the art bifunctional electrode (Westinghouse formulation) to understand the catalytic function and factors that control cycle life, and (2) to optimize the electrode structure and catalysts for bifunctional electrode operation. Research during 1982 was conducted on:

1. Characterization of bifunctional electrodes obtained from Westinghouse Corporation.

2. Carbon support studies.

3. Identification of more-active catalysts offering promise for bifunctional O_2 electrode application.

4. Fundamental research on O_2 electrocatalysis with special emphasis on the transition-metal macrocyclics and various oxide catalysts.

Ten identical electrodes cycled at Westinghouse for various lengths of time were examined using x-ray energy dispersive spectroscopy (XEDS), x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The electrodes were fabricating using silver-catalyzed Shawinigan acetylene black, Teflon, NiS, $FeWO_4$, and WC-12 wt.% Co in a structure consisting of four active layers and one hydrophobic backing layer.

The analyses indicate that a rapid release of tungstate, a slow release of sulfate, and the formation of hydrated oxides of Fe, Co, and Ni in a high state of dispersion occurred during the break-in period. The amount of Ag, Fe, Co, and Ni remained fairly constant throughout the cycle test. The oxygen/carbon and fluorine/carbon ratios increased significantly during cycling which indicated oxidation of carbon or loss of carbon by other means has occurred. Simple measurement of weight loss indicated a loss of carbon of at least 30% during 420 8-h cycles. Scanning electron microscopy of cycled vs. uncycled electrodes also showed morphological changes indicative of carbon loss. From these studies, it was concluded that the losses of Ag, Fe, Co and Ni are not large and that the oxidation and loss of carbon are the major causes of electrode failure.

A series of gas-fed electrodes was fabricated and tested under both cycling conditions and steady-state polarization to determine the chemical species that are the most critical for O_2 reduction and generation. For cycled electrodes without Ag, the findings were: (1) Co is active as a peroxide elimination catalyst, and (2) NiS and FeS or $FeWO_4$ form an effective O_2 generation catalyst. For cycled electrodes containing Ag the conclusions were: (1) Co, NiS, and FeS (or $FeWO_4$) in various combinations do not lead to substantial improvements in the cathodic polarization exhibited by Ag-catalyzed Shawinigan acetylene black alone; (2) the combination of NiS and FeS leads to very good anodic polarization; and (3) the combination of Ag, $Ni(OH)_2$ and $Fe(OH)_3$ had better anodic and cathodic polarizations. The overall conclusions were that (1) O_2 reduction to peroxide occurs mainly on the carbon; (2) a form of hydrated cobalt oxide is a good peroxide eliminator; (3) Ag is a good peroxide

eliminator whose activity can be maintained by the presence of $Ni(OH)_2$; and (4) Ni and Fe hydroxides are critical catalysts for O_2 generation, possibly through the formation during cycling of the hydrated spinel $Ni_xFe_{3-x}O_4$.

There was a continuing effort to test catalysts which appeared promising for O_2 reduction, generation or both. Electrodes were made using carbon and three representative catalyst systems: molybdenum naphthalocyanine (MoNc, obtained from Dr. Michel Savy, CNRS, Bellevue, France) plus inorganic compounds, lead ruthenate and lanthanum strontium cobaltate (a perovskite made by the freeze-dry method). For O_2 reduction the macrocyclic system was superior at moderate to high current densities, and for O_2 generation it was superior at all current densities. The presence of cobalt or its oxidation products markedly enhanced the O_2 reduction and generation activity of MoNc after cycling, and the short-term stability of the O_2 reduction activity was much enhanced. There was also a small gain in cathodic activity and a large gain in anodic activity with the addition of NiS and FeS.

Fundamental studies on the macrocyclics, such as Co and Fe (tetramethoxyphenylporphyrin) and phthalocyanine, are in progress using principally surface enhanced Raman and Mossbauer spectroscopy in both in-situ and ex-situ measurements together with electrochemical measurements to establish the state of the macrocyclic on the electrode surface. Work was initiated on macrocyclics pyrolyzed at temperatures up to 900°C. While the structures were drastically modified, these materials have exhibited good catalytic activity for O_2 reduction and long life in the reduction mode.

Because of the importance of carbon oxidation in the failure process, work was recently initiated to examine carbons and graphites which may have oxidation resistance superior to Shawinigan black. A graphitized carbon black obtained from Professor A. Scaroni, Penn State University, and ExCO, a highly ordered carbon produced pyrolytically from CO (obtained from Dr. Michael Savy of the CNRS, Bellevue, France) have both exhibited lower electrochemical oxidation rates in preliminary tests than Shawnigan black. These results tend to confirm previous work

by other workers that a high degree of structural order can lead to improved oxidation resistance.

2. ALUMINUM/AIR POWER CELL RESEARCH AND DEVELOPMENT

The objectives of this program are to develop an aluminum/air battery as an automotive energy source for general-purpose vehicles and to evaluate its ability to provide vehicles with the range, acceleration performance, and rapid refueling capability of current internal-combustion-engine vehicles. The aluminum/air program, which was conducted at LLNL and at several industrial companies under subcontract, focused on the following research areas: (1) experimental investigation of alternative cell configurations, (2) testing of specific configurations in multicell stacks, (3) long-term testing of air electrodes under simulated vehicle duty cycles, (4) determination of kinetics of aluminum trihydroxide crystallization under candidate battery operating conditions, and (5) studies of anode behavior of alloys containing minor impurities such as iron, manganese, gallium, and phosphorus.

Cell Configuration and Process Development

(E. Behrin and J.F. Cooper, Lawrence Livermore National Laboratory)

Development and Testing of a Six-Cell Stack: The purpose of these experiments was to investigate the behavior of aluminum/air cells in an integrated, engineering-scale stack designed for rapid removal and replacement in both electrodes. The stack uses a parallel-plate design (M1-LLNL) described earlier.[1,2] Although successful scale-up to 1000 cm^2 anodes was achieved, the six-cell stack was constructed on the more convenient scale of a 167 cm^2 cell. The cells were constructed of laminated-fiber-filled epoxy sheets to minimize fabrication costs.

The cell stack contains anodes that are attached to a sheet of copper-clad fiber-filled epoxy, electronic circuit board. This sheet supports the anode and provides for anode current collection by means of soldered joint. The interelectrode gap is maintained with a non-conducting ribbed separator (thickness 0.32 cm). The cathode and

separator are attached to a flexible PVC diaphragm and are advanced pneumatically toward the anode during dissolution by the cathode air stream overpressure. The airflow is from top to bottom, and air streams are connected in parallel. The electrolyte flow is from top to bottom. The electrolyte enters through ports at the top of each cathode module and flows down the back side of the air electrode module of the adjacent cell. Electrolyte flow is thus in series for groups of three cells. The cells are connected electrically in series.

Polarization data were obtained over a range of: aluminate concentration of 1-3 molar, current density of 0-8 kA/m^2, electrolyte-flow Reynolds number of 125-1000, airflow of 2-6 times stoichiometric at 6 kA/m^2, operating temperature of 60-70°C, and experimental times of 3.5 and 5 hours.

The major conclusions of these tests were as follows. (1) Stack performance showed no degradation relative to single cell performance for the same pair of electrodes (a 20% improvement in peak power resulted from modifications of the air distribution in the cathode cassette). (2) Losses in cell voltage at high aluminate concentrations can be offset by increasing operating temperature: e.g., peak power above 5 kW/m^2 at 70°C for 2 M $Al(OH)_4^-$. (3) The increased anode polarization encountered at 5-6 kA/m^2 (for Re = 500-1000 in 2.2 M $Al(OH)_4^-$) was probably indicative of limiting solution-side mass transport. (4) Dissolution was uniform over the electrode surface between the ribs until anode exhaustion was reached. (5) The maximum deviation of individual cell voltage in the stack was less than 5%.

<u>Experiments with Cells of Wedge Geometry</u>: A series of experiments were performed with $Al(Sn)H_2O$ and Al/Air cells of a wedge geometry. This configuration is intended to provide: (1) full anode utilization, (2) simple, rapid refueling by the addition of rectangular slabs of aluminum to a dry chamber above the cell, (3) continuous gravity feed of the anode into the cell, and (4) partial recharge capability for purposes of cell capacity equalization ("topping off").

Experimentation was begun with an engineering-scale cell that contained two replaceable cathode cassettes (each 300 cm^2) positioned at an angle about a central wedge-shaped anode. Anode current collection is provided by parallel triangular tracks of copper in the interelectrode gap which define the interelectrode spacing while making a knife-edge contact with the anode at the aluminum-electrolyte interface. Continuous anode feed and current collector less than 2% of cell voltage were observed. Interruptions in the continuity of feed were observed in some cases where the cells had been inadvertently distorted during assembly. Near the rib/anode interface, the anode profile evolved a ridge (height, 0.6 mm; width, 2-4 mm) due to the non-uniform primary current distribution. In some cases, the anode showed a long-term evolution of shape, which reduced the effective area of the electrode. While the continuous anode feed has been demonstrated, it was apparent that sufficient deviations from the planar geometry and non-uniformities of current distribution resulting from any cause may impair operation of the cell. These effects will be investigated both by mathematical modeling and operation of cells with well-characterized geometries.

Crystal Production and Handling: Uncertainties in design parameters for crystal production and handling account for the largest potential error in overall battery mass and volume estimates. The rate at which aluminate is removed is a function of the total area of crystallizing seed surface, aluminate concentration, and slurry temperature. Several possible concepts for providing a maximum of crystallizing area and minimum component mass were investigated.

An earlier design by the Aluminum Company of America used cyclone separators to clarify electrolyte as it emerged from a slurry storage tank. A derivative of this design was examined which incorporated the cyclonic action directly in the slurry storage vessel. An unreasonable amount of pumping power was required to achieve suitable seed densities (0.45 kg/liter).

Another crystallizer design concept was explored in which incoming electrolyte flow enters a cylindrical container from a perforated tube that runs along its central axis. The electrolyte flows radially

outward through a dense slurry and then through a polypropylene cloth at the cylinder wall. A cake is allowed to build up to promote agglomeration of fine particles. Clarified electrolyte is gathered in the annulus between the filter support deck and the outer cannister and sent back to the cell module. Within the filter drum, a slow-moving set of paddles and scrapers (like those used in ice cream freezers) continuously breaks up the filter cake and repulps the seed.

A recent analysis found that the overall mass, volume, and costs fell steadily as the design aluminate concentration was raised up to the limit of the cell performance data. This points out the need for additional cell testing at elevated aluminate concentration (about 2.4 M up to and above 3.0 M).

Battery Hardware Development

(E.L. Littauer, Lockheed Missiles and Space Corporation)

The primary purpose of this work is to investigate the refuelable power cell concept through the development and operation of rapidly-refuelable, full-scale aluminum-air multicell hardware. Efforts were focused on the optimization of the anode solution-side current collector (SSCC) design and the development and operation of a refuelable, six-celled module.

Optimization of Solution Side Current Collector: The M1-1-LMSC bicell was fitted for current and potential mapping by substituting a 200 cm^2 copper plate for the anode, and imposing a 50 A current between the anode and the terminal. The cathode (Eltech/Electromedia) was left in place and the tests were run without electrolyte.

The location of current takeoffs in the cell were changed to the side of the cell to minimize current collector IR losses. A major loss in cell voltage occurring in previous tests was attributed to the corrosion of the beryllium-copper SSCC near the point of contact with the aluminum. This problem was alleviated by silver-plating all components prior to assembly by silver-soldering and nickel-plating the assembled current collector and solder joints. A vexar barrier was introduced

between the air electrode and the SSCC, resulting in a total cell thickness of 2 mm. Cell power output was observed to be 4.29 kW/m^2 at a cell potential of 0.79 volts. This is a 19 to 34% improvement over Lockheed's previously observed power densities of 3.2 to 3.6 kW/m^2.

Analysis of cathode polarization indicated a slope of 190 $mV/kA\text{-}m^{-2}$, which may be compared to previous studies (with the same cathodes mounted in nickel frames with top tab current collection) demonstrating polarization slopes of 174 and 190 $mV/kA\text{-}m^{-2}$. Analysis of anodic polarization indicates a slope of 9 $mV/kA\text{-}m^{-2}$ which is comparable to prior first-time usage observations of the SSCC.

Cell Testing: Two SSCC designs were evaluated in single cells of the M1-1-LMSC design. (In this design, 200 cm^2 anode plates are pneumatically advanced toward the cathodes by an air bladder.) The first SSCC design utilized parallel ribs of 2 mm nickel-coated copper wire for anode current collection, and the ribs were insulated from the cathode by a polypropylene screen. Two tests were prematurely terminated due to mechanical design problems. The second design provided for substitution of nickel-toothed ribs for the nickel-plated beryllium copper (BeCu). A gradual increase in anode polarization was thought to be due to wear of the protective nickel from the contact tip and subsequent erosion of BeCu. Comparison of anodic performance indicates no additional voltage loss due to the all-nickel construction. This configuration was adopted for subsequent 6-cell testing.

Anode utilization tests show that the residual fragments from 200 cm^2 anodes weigh less than 2 g. A 3.2 mm thick anode was tested without edge or back protection to determine total anode consumption. Anode depletion was evidenced by a gradual decay in power output. Residual anode fragments, found primarily along the electrolyte outlet, weighed 1.92 g.

Initial tests with a nickel coating for edge and backside protection showed that a 33-micron coating is too thick. Prior testing of anodes with no edge or back protection revealed that 99% anode utilization was achieved before current flow ceased. However, parasitic corrosion of the edges and backside occurred despite backside contact with the air

bladder. An adherent 33 micron, (6.85 g) nickel coating was electroplated on the edges and back of the 3.2 mm thick anode. It was planned that the anode would be completely consumed, and the nickel would fragment and be washed away. Tests showed that the nickel was indeed adherent and protective, but it was too thick and ductile to fragment. The 25.3 g of residual aluminum represented 15% of the original anode. The anode appearance showed preferential dissolution in the central region and less dissolution beneath the SSCC contacts (as previously observed).

Anode/Cathode Evaluations: The nickel-coated anode described above was consumed during three tests in which coulombic efficiency was 78-86%, peak power density was 2.98-3.06 kW/m^2 and specific energy was 2.2-2.4 kWH/kg (vs. 8.13 theoretical). The current and energy yields were a function of the test cycle which included 30 min. at 1.25 kA/m^2, 30 min. at 2.5 kA/m^2, and 60 min. at 3.75 kA/m^2. The relatively-constant peak power resulted from substituting stable nickel for the normally corroded Be-Cu SSCC. The DSC cathode contained 1.2 mg Pt/cm^2.

Initial tests of cobalt-catalyzed (10% Co-PC and 10% Co-TMPP) cathodes showed peak power and cathode polarization comparable to those for platinum-catalyzed cathodes. All tests utilized the same 3.2 mm "RX808" anode in electrolyte containing 4 M Na, 1 M Al, and 0.06 M Sn at 60° C.

Air Cathode Research and Development

(I. Malkin, Diamond Shamrock Corporation)

The objective of this work is to develop high quality, long lived air electrodes for use in Al/air batteries. Emphasis was directed at evaluating and testing air electrodes containing new catalysts and structures.

Experimental cathodes catalyzed with platinum have shown excellent initial performance, but progressively poorer performance on subsequent intermittent operation. A series of tests were run with platinized RBDA air cathodes to determine the catalyst loss as a function of lifetime.

The platinum content values were obtained by analyzing tested electrodes against a calibration curve established using Source Excited Fluorescence Analysis (SEFA) and a set of standard electrodes with Pt loadings of 0-1.2 mg/cm^2. The virgin air cathode samples had only 0.8-0.9 mg/cm^2 Pt instead of the 1.2 mg/cm^2 expected. After 100 cycles of operation, 50% of the platinum was lost. A relatively stable value of 0.3 mg/cm^2 Pt (70% loss) was reached by 250 cycles of operation.

Cathodes catalyzed with CoTMPP (cobalt tetramethoxyphenylporphyrin) demonstrated drive-cycle performance equivalent to that for platinum catalyzed electrodes through 600 cycles. One air cathode, which was catalyzed with a combination polymeric cobalt phthalocyanine $(CoPC)_n$/spinel catalyst, achieved slightly over 1000 cycles of operation before failure. Initial voltages were below those of platinum-catalyzed electrodes at all current densities, but this difference can be partially compensated by the use of pore former in the active layer. Alternate cobalt macrocyclic catalysts, cobalt meso-tetra-pentafluorophenylporphyrin (CoTFPP), on RB carbon showed performance inferior to that of CoTMPP.

Short term compatibility with air cathodes has been demonstrated for three aluminum alloys. Anode materials prepared at Ohio State University were first dissolved at 200 mA/cm^2 in full cells under anticipated battery operating conditions. Cathode polarization curves were then recorded after anode dissolution, in approximately 24 hour intervals. No significant effect on cathode polarization was found.

Electrodes constructed with thicker conductive hydrophobic layers were evaluated, but the thicker layer did not lead to increased cycle life in tests using the CoTMPP catalyst. However the cathode potential was not adversely affected, so there may be some value in the increased strength of the thicker layer. A coat of PVA paint on platinum catalyzed RB electrodes had previously yielded improved cathode bubble pressure without any loss in electrical performance. This was not the case with a CoTMPP catalyzed cathode. Electrical performance was reduced and the bubble pressure increased, but was still below the LLNL specification of 6.9 kPa (2.3 ft. H_2O).

Different active layer carbon materials were screened. Ammonia-treated RB carbon showed better electrical performance than non-treated RB carbon, but a more rapid voltage decay than CoTMPP-catalyzed RB. Tests with Ketjenblack-EC active layers did not give promising results. However, combining it with UB-104 carbon yielded an active layer (CoTMPP-catalyzed) that showed less voltage loss and longer life than the unmixed Ketjenblack.

Crystallizer Process Research and Development

(F.S. Williams, Aluminum Company of America)

Physical property data on density, viscosity, and electrical conductivity were developed and reduced to correlation form for synthetic electrolytes containing (nominally) 7 g/l Sn and 0.20 g/l Ga in 3, 4, 5, and 6 M NaOH. Concentrations of $Al(OH)_4^-$ were selected at six levels for each NaOH concentration and ranged from 0 to as high as 4 M $Al(OH)_4^-$ at 6 M NaOH. Measurements of each property were made at 25, 40, 60, and 80°C. The effect of the Sn and Ga impurities was to increase density by a relatively small percentage, increase viscosity by a significant percentage, and decrease electrical conductance by a significant percentage.

Isothermal, batch-precipitation experiments at 40, 60, and 80°C were utilized to obtain data to develop kinetic and solubility correlations as a function of electrolyte and system parameters.

The precipitation rate equation formulated is:

$$-\frac{dC}{dt} = \frac{K_o EXP^{-E/RT} A_t (C_t - C^*)^2}{(C_{Na-free})^2}$$

where dC/dt = moles Al/min.

$K_o = 1.923 \times 10^5$ (EXP(-8.735 C_{Sn})) moles/m^2-min.

$E = 12.4 \pm 1.1$ Kcal/g mole

C_{Sn} = [Sn] (molar)

$C_t - C^*$ = Al supersaturation (molar)

A_t = Seed surface area (m^2/l clear liquor)

$C_{Na\text{-}free}$ = Free caustic concentration (M), i.e., the difference between total sodium and aluminate concentrations.

The aluminate solubility equation that was derived is:

$$\ln C_{Al}^* = -2.6964 + 0.01824\ T + 0.36185\ C_{Na} + 0.75575\ C_{Sn} + 14.811\ C_{Ga}$$

where:

C_{Al}^* = Al (molar)

C_{Na} = NaOH (molar)

C_{Sn} = Sn (molar)

C_{Ga} = Ga (molar)

T = Temperature (^oC)

The precipitation-rate equation is of the same form as one derived earlier at LLNL.[3] Precipitation rate was negatively affected by tin in solution, with a 40% reduction in the rate constant being attributed to 0.06 M Sn. Both Sn and Ga co-precipitated with the $Al(OH)_3$ to an extent strongly dependent on temperature. Very high precipitation rates resulted in Na levels in the product exceeding the target level of 0.24% Na (on a hydrate basis). The incorporation of Na in the product was also a strong function of temperature. Based on computer simulations of a single-stage, continuous precipitator, it was projected that the maximum production rate specification of 0.042 moles Al/sec (6 m^2 battery anode area and a total Al dissolution rate of 0.2 A/cm^2, as appropriate for a 40 kW battery) could be met at 4 M NaOH, a 40-50 litre system volume, and 60-70^oC, provided the relative saturation and seed area were driven to levels well above those normally used in industrial, Bayer precipitation. The region of feasible operation with respect to meeting the aluminate production specification was delineated.

A full-scale precipitator of a hydrocyclone design was operated in a continuous mode to assess production rate, population changes with time, and hardware aspects. A digester was used to drive $Al(OH)_3$ into solution. It was found that the required production of $Al(OH)_3$ could be attained at the high relative saturations indicated by computer simulations. The cyclone system for solid-liquid separation and classification did not function satisfactorily.

Investigation of Alloys Containing Manganese

(N.E. Richards, Reynolds Metals Company)

Previous work (1981) indicated that acceptable voltage and coulombic efficiency could be achieved with aluminum of commercial purity (0.04-0.06% Fe) if additions of manganese were made. The additions form intermetallic compounds with iron to reduce the activity of the latter for hydrogen evolution. This study was extended to the investigation of the nominal composition, Al-0.04Fe-0.04Ga-0.08Mg-0.04Mn. Magnesium was excluded from most of the samples based on the (mistaken) belief that it was electrochemically inactive and served only to strengthen the alloys. Alloys without Mg and various ratios of Fe/Mn were constructed and subjected to alternative heat-treatment and coldworking techniques. Electrochemical tests included simultaneous measurements of electrode potential and coulombic efficiency.

The following conclusions were reached: (1) 0.8% Mg greatly improves coulombic efficiency, reducing hydrogen evolution by a factor of 5. (2) Coulombic efficiency increases with manganese additions to the 0.04% Fe alloys. (3) Fabrication processes (particularly heat-treatment duration and temperature) have a profound effect on electrode coulombic efficiency.

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III. SUPPORTING RESEARCH

This project element is directed at studies on a wide variety of battery systems, which are summarized in Table 1, as well as projects on fundamental studies in electrochemical engineering, surface analysis and electrocatalysis that support the development of electrochemical energy-storage systems; and research on battery components such as electrodes, separators, electrolytes, and cell containers. Several projects in this project element provide support for a range of electrochemical technologies; their summaries are presented in a separate sub-section called Cross-Cutting Research. Note that the LBL research efforts (listed as "Electrochemical Energy Storage" in Appendix A) are divided between the generic battery technologies to which they apply.

A. ALKALINE CELLS

Battery Electrode Studies

(E.J. Cairns and F.R. McLarnon, Lawrence Berkeley Laboratory)

The purpose of this research is to study the behavior of electrodes used in secondary batteries and to investigate practical means for improving their performance and lifetime. Investigations have centered on the zinc electrode, which exhibits satisfactory performance in rechargeable alkaline cells (Zn/NiOOH, Zn/Air, $Zn/Fe(CN)_6^{-3}$), but has an inadequate cycle life. The short lifetime and continual capacity loss of the zinc electrode are closely related to a phenomenon known as shape change, the redistribution of active material over the face of the electrode as the cell is cycled. The approach used in this investigation is to study life- and performance-limiting phenomena under realistic cell operating conditions.

A computer-controlled test system has been designed and constructed to allow the simultaneous and continuous cycling of 16 or more electrochemical cells. The system offers resolution and stability within 0.025% of full scale, and response times are typically 1 ms. A wide variety of charge and discharge regimes, including pulsed charge and power discharge profiles, have been implemented through various computer algorithms.

The test system has been employed to investigate the effects of constant-current and various pulsed-current charging modes on the cycle life and capacity retention of Zn/NiOOH cells cycled at 100% depth-of-discharge. Test results included cell voltages, potentials of the NiOOH and Zn electrodes versus Hg/HgO reference electrodes, coulombs, watt-hours, average voltages, and associated efficiencies. Post-mortem tests included Zn electrode X-ray studies. A 30ms-ON/90ms-OFF pulse profile, with a 15mA/cm^2 peak current density, improved the operating conditions of the cells by minimizing the overpotentials on the Zn and NiOOH electrodes. In contrast to all other charge profiles tested, it eliminated cell shorting (for at least 100 cycles) and slowed the loss of ZnO reserve, thereby preventing rapid cell capacity decline.

A series of electrolytes formulated with low hydroxide-ion concentration have been tested in 1.35 Ah tri-electrode Zn/NiOOH cells to assess their ability to reduce zinc redistribution rates. A 3.5 M OH^- electrolyte and a 3.5 M OH^--3.4 M F^- electrolyte were tested along with a caustic-borate electrolyte. These electrolytes were chosen to exhibit ZnO solubilities approximately 25% that of "standard" 7.4 M KOH electrolyte. Zinc redistribution rates were found to be lower for electrolytes with reduced ZnO solubility, and zinc penetration of the separator was non-existent, even when overpotentials approached 130 mV when charging the Zn electrode in the borate electrolyte and 290 mV in the fluoride electrolyte. The high overpotentials were found to occur even when substantial amounts of ZnO remained in the electrode. Less than 2% inactive zinc was found in the zinc electrodes cycled in the fluoride and borate electrolytes, and a similar low amount was present in electrodes cycled in the 3.5 M and 7.4 M OH^- electrolytes.

The high solubility of the zincate ion in Zn/NiOOH battery electrolytes may be decreased by adding a less-polar solvent, such as an alcohol, to the electrolyte while maintaining a high KOH concentration. ZnO solubilities were measured in KOH-water-methanol and KOH-water-ethanol electrolytes to determine the extent of the Zn species solubility suppression.

An electrochemical cell has been designed and built to study the behavior of a model zinc electrode pore in alkaline electrolyte. The cell design permits in-situ microscopic observation of the electrode surface, and multiple zinc reference microelectrodes provide simultaneous measurements of local electrochemical potentials. The reference microelectrodes are fabricated using semiconductor processing techniques, including vacuum metal deposition and photolithography. The effects of varying pore diameters, electrolyte formulations, and electrode area/electrolyte volume ratios on zinc electrode discharge behavior are being studied.

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Reaction Profile in Porous Electrodes

(T. Katan, Lockheed Missiles and Space Corporation)

The objective of this program is to determine the governing processes within the confines of typical pores in porous zinc electrodes. The identification and evaluation of microscopic phenomena are sought to accurately ascertain the origin of the shape change observed during prolonged cycling. Data from this work will be useful for developers of alkaline-zinc electrodes and, eventually, batteries for electric vehicles.

The experimental approach was to construct a simulated zinc pore having dimensions comparable to those of real pores, about 20 microns in diameter. In-situ viewing with a microscope was accomplished via a transparent epoxy window on one side of the pore, and potential was monitored with a series of microscopic zinc threads embedded in the window and measured at intermittent closed- and open-circuit potentials.

Evolution of the transient current-density distribution was characterized by a "reaction front" that moved into the pore, followed by a zone of relatively lower reaction rate. This lower-rate region corresponded to the appearance and movement of a white ZnO layer. Precipitated ZnO then caused blockage, masking the pore surface and forcing

the front inwards, to about 2 mm at most.

Concentration profiles were obtained from the potentials of the microreference electrodes at open circuit. At the pore mouth, the OH^- concentration gradually increased above its initial concentration as OH^- was released from the $Zn(OH)_4^=$ species precipitating as ZnO. These concentration gradients are sufficient to form concentration cells with zinc dissolution and deposition at rates of about 0.8 mA/cm^2 of geometrical electrode area. The magnitude of this effect can easily account for shape change caused by the non-uniform current density distribution associated with electrode-edge effects.

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Nickel Electrode Research

(J. Newman, Lawrence Berkeley Laboratory)

Porous nickel electrodes for high-energy batteries are currently prepared by electroprecipitation of $Ni(OH)_2$. The objective of this experimental research program is to develop a fundamental understanding of the precipitation of nickel hydroxide by the electrochemical reduction of nitrate ions, which changes the pH. This type of electrode is used as the positive in a number of practical or promising systems (those with negative electrodes of hydrogen, zinc, iron, and cadmium). Polarization characteristics of some nickel nitrate solutions were determined with a rotating-disk-electrode apparatus. Ring/disk electrode experiments indicated the irreversibility of the electrode processes.

Development of a High Rate Insoluble Zinc Electrode For Alkaline Batteries

(A. Charkey, Energy Research Corporation)

The objective of this program is to investigate the benefits of using an insoluble Zn electrode to improve the lifetime of the Zn/NiOOH battery. The major tasks consisted of (1) preparation of activated or partially insoluble zinc oxides, (2) determination of solubility of prepared materials in aqueous KOH solutions, and (3) electrochemical evaluation and full-scale testing of these materials.

Activated ZnO samples were formulated which singly, or in combination with dilute electrolyte formulations, resulted in partially insoluble discharge products. Activated ZnO, prepared by alloy vaporization or by thermally accelerated diffusion of metallic dopants into the ZnO lattice proved to be less soluble than pure ZnO, but also proved to be less electrochemically active. This resulted in reduced efficiency, higher degrees of polarization and passivation, and decreased conductivity. These effects are known to be detrimental to the performance of secondary zinc-nickel oxide batteries, and this approach was abandoned.

A more workable approach has been to use pure ZnO in conjunction with other materials, which after initial hydration and charging, form a highly conductive and insoluble matrix. Electrodes prepared from these materials are expected to exhibit improved performance in two ways. First, there is an even distribution of permanent, highly-conductive nucleation sites along the apparent electrode surface, providing for even Zn deposition and distribution during charging. Second, the resulting increase in effective surface area decreases actual current densities, thereby decreasing overvoltages. This should decrease dendrite formation and gas evolution in addition to allowing for use of higher current densities.

Problems posed by the development of this type of electrode material are largely material selection problems. Materials must be chosen carefully, not only to fulfill their function within the electrode system, but also to provide for minimal counter-productive interaction with each other. Electrochemical evaluations of these types of materials showed

generally favorable behavior.

Supported Liquid Membrane Battery Separators

(J.P. Pemsler, Castle Technology Corporation)

The program objective is to develop supported liquid membrane separators to improve the cycle life of the Zn/NiOOH battery. In particular, a separator that will both prevent zinc dendrite growth and alleviate capacity loss due to zinc shape changes is being sought.

Supported liquid membrane separators use highly-specific organic transport reagents, which are contained in a microporous structure, to transport hydroxyl ions during cell operation. Earlier work on this contract demonstrated selective transport of hydroxyl ions, zincate ion rejection, and stability in 25 wt% KOH at 50°C. A number of ion-exchange reagents/solvent/modifier systems were developed with separator resistances in the range of 15-600 ohm cm^2.

During calendar year 1982, Zn/NiOOH test cells with supported liquid-membrane separators were assembled and cycled at two-hour discharge and four-hour charge rates with current densities in the range of 7-10 mA/cm^2. These cells, which contained a single 1 mil thick microporous substrate supported liquid membrane, performed successfully for over 200 cycles to 60% of original capacity. Under identical conditions, a single layer of microporous separator without the liquid ion-exchange reagents failed by zinc dendrite shorting after only a few cycles. A control cell containing three layers of the microporous separator without the supported liquid membrane achieved 375 cycles before falling to the 60% capacity level.

All cells were dismantled and examined for failure mode. Cells incorporating supported liquid membranes revealed that cell life may have been limited by excess pressure on the electrode package. This caused the zinc electrode wick to dry out and also exposed the supported liquid membrane to localized heating. Simple steps taken to alleviate this problem resulted in improved cycling behavior, but a new test cell design is required to optimize the incorporation of supported liquid-

membrane separators.

A major accomplishment has been the development of supported liquid membrane separators with low resistance. Values substantially less than 1 ohm cm^2 have been achieved in 5M KOH. Cells can now be routinely prepared and cycled with membrane resistances of 1 ohm cm^2, and efforts are underway to solve engineering problems associated with membranes exhibiting resistances in the 0.1-1.0 ohm cm^2 range. With this development it may be possible to use multiple layer supported liquid membranes, which might significantly improve cell cycling behavior (as demonstrated with the control cell with three layers of the microporous separator).

Additional studies of fundamental transport mechanisms, membrane supports and stability are being conducted.

Temperature Limitations of Alkaline Battery Electrodes

(M. McKubre and M. Madou, SRI International)

The objective of this project is to determine the effects of temperature variations in the range 0 to 100°C on charge and discharge processes at iron, zinc, and nickel-oxide electrodes in concentrated KOH solutions. Particular attention has been focused in this study on changes in the mechanisms or kinetics of charge and discharge reactions that may impose limitations on battery usage under extreme operating conditions. In addition, the anomalous effect of zincate concentration on the discharge of zinc, and the beneficial effect of lithia on the charge and discharge of nickel-oxide electrodes were investigated.

Results of AC impedance and rotating ring disk studies indicate that the discharge of zinc is an autocatalytic process, the rate increasing with increasing concentration of the product species (zincate). Other experiments have been performed to study the influence of electrolyte composition and temperature on the passivation of zinc, which occurs in two stages. A detailed model has been proposed for the discharge of zinc in KOH, involving the important elements of autocatalysis, mass transport limitation of species moving to and from the electrode, and

partial and complete passivation. This model provides a plausible mechanism for "shape change" of zinc electrodes, and it can be applied in a quantitative way to improve the modeling work of others.

Experimental results show that oxidation and subsequent reduction of iron electrodes is largely impeded by migration and diffusion processes within the oxide film. Thus, discharge- and charge-acceptance rates might well be improved by modifying the film structure, possibly by the addition of suitable dopant ions. Detailed mechanisms have been proposed for the charge and discharge of iron in KOH at low and high temperatures. These models account for dissolved intermediate species that are observable experimentally.

Experiments have been directed toward understanding the beneficial effect of lithium hydroxide on the capacity, potential, and life of the nickel oxide electrode. The nickel electrode in both the discharged and charged states was observed to behave like a semiconductor, and the benefits of Li may be ascribed to a doping effect. Depending on the potential, an n-type or p-type semiconducting oxide can be present, giving rise to anodic or cathodic photocurrents under illumination. AC impedance results indicated that a solid-state diffusional process, presumably of protons through the oxide film, dominated the impedance behavior for the charged electrode. A semiconductor/electrochemical model has been developed which is able to give a clearer understanding of the mechanisms of charge and discharge of the nickel oxide positive electrode, both in the presence and absence of lithium ion.

Thermodynamic Framework for Estimating Efficiencies of Alkaline Batteries

(D. Macdonald, Ohio State University)

The objective of this study is to determine the thermodynamic properties of Fe, Ni, Zn, Al, and Li in concentrated LiOH, NaOH, and KOH solutions as a function of temperature (-10 to 120°C) and concentration (1-8 mol kg^{-1}). These data are useful for determining the thermodynamic stability and electrochemical performance of battery electrodes and for selecting the optimum conditions under which various battery systems

should operate. Activity coefficients for the solute in concentrated LiOH, NaOH, and KOH solutions have been obtained at various concentrations and temperatures. The activity of water is found to decrease markedly as the stoichiometric concentration increases, and the effect is most pronounced at lower temperatures. In general, the activity coefficients decrease with increasing temperature, but their dependence on concentration varies with the identity of the cation (Li^+, Na^+, K^+).

The pH of concentrated hydroxide solutions was calculated and plotted as a function of concentration and temperature. While the pH exhibits a steady increase with concentration for each hydroxide, the effect is less marked for LiOH. It is also observed that the pH decreases along the series KOH>NaOH>LiOH for any given stoichiometric concentration.

A computer program has been prepared to calculate potential-pH relations. The program contains facilities for computing the activity of water and pH of the medium for any given system, and hence for calculating the equilibrium potentials for each reaction at various stoichiometric concentrations of alkali hydroxide. The program is also capable of handling mixed metal oxidation products, such as $NiFe_2O_4$, which may form because of transport of soluble products from one electrode to another. Using computed data, metal/air cell potentials were obtained for each concentration and temperature. Cell potentials for Al/air and Zn/air were found to increase with concentration, and the magnitude of the increase follow the order KOH>NaOH>LiOH. In contrast, at each concentration the cell potentials decrease as the temperature increases. Potentials for Li/air and Fe/air cells exhibit the opposite behavior. In the case of Li, the potentials decrease with increasing concentration largely because the Li anodic reaction ($Li \rightarrow Li^+ + e^-$) is independent of pH. The decrease in cell potential for Fe/air is due to a greater shift in the potential of the oxygen reduction with concentration compared with that of the anodic reaction.

Cell potentials have been compiled also for the Fe/NiOOH cell. The dependence of these potentials on concentration and temperature differs from the two groups above; an increase in either parameter results in a

decrease in cell potential. The concentration effect, which is small, arises simply from the decrease in the activity of water.

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An Electrochemical and Morphological Study of the Restructuring and Loss of Capacity of Alkaline Battery Electrodes

(D. Macdonald, Ohio State University)

The objective of this project is to investigate the degradation processes of porous $Ni(OH)_2$ electrodes in alkaline solution during charge/discharge cycling at temperatures from 0 to 100°C. The aim is to obtain a better understanding of capacity losses in Zn/NiOOH and Fe/NiOOH batteries.

A transmission-line model has been adopted to represent a porous electrode. The model does not specify the form of the solution/pore wall and solution/backing plate interfacial impedances. Experimental AC impedance data for a planar nickel specimen have therefore been used to determine an equivalent circuit for the interfacial impedance in the model. The equivalent circuit used in the present study is appropriate over the potential range from 0 to 500 mV vs. Hg/HgO/8 M KOH and for temperatures from 0 to 100°C.

The components of the equivalent circuit are:

R_1 = solution resistance between reference and Ni electrodes.

C = double layer capacitance at film/solution interface.

R = charge transfer resistance (Ni/Ni^{2+} at low potentials and possibly Ni^{3+}/Ni^{4+} at 500 mV).

W = Warburg diffusion impedance of an ionic species involved in the film-growth process.

In this equivalent circuit, the series combination of R and W is in parallel with C; these three components are in series with the solution resistance, R_1.

A curve-fitting computer program has been developed to determine a combination of resistances, capacitances, and Warburg coefficient in the equivalent circuit that agrees with experimental data. Experimental impedances for planar Ni electrodes have been accurately reproduced with the best-fit values in the theoretical impedance expression derived for the equivalent circuit.

In addition to impedance studies, cyclic voltammograms for a planar Ni specimen have been recorded at various temperatures and sweep rates. The potential for $Ni(OH)_2$ oxidation to NiOOH has been determined in relation to oxygen evolution. Above ambient temperature, there is evidence that incomplete NiOOH reduction on the cathodic sweeps eventually causes the oxygen evolution process to progressively reduce porous $Ni(OH)_2$ electrode charging efficiencies during cycling. Two other kinetic features were evident. First, $Ni(OH)_2$ oxidation to NiOOH is not diffusion-controlled in 8 M KOH, and second, $Ni(OH)_2$ reduction is not possible over the temperature and potential ranges employed.

B. ZINC/HALOGEN CELLS

Surface Morphology of Metals in Electrodeposition

(C.W. Tobias, Lawrence Berkeley Laboratory)

The objective of this project is to develop a pragmatic understanding of the partial processes governing the macrocrystallization of metals. This understanding is necessary for the design and optimization of rechargeable galvanic cells such as the zinc/halogen systems. Current projects include: (1) The effect of hydrodynamic flow on the surface morphology of zinc, (2) dynamic modeling of surface profiles in electrodeposition and dissolution, and (3) mass-transport effects in the

deposition of alloys.

The macromorphology of zinc obtained by electrodeposition from acidic zinc salt solutions was studied under a wide range of process conditions and electrolyte properties. The influences of current density, pH, hydrodynamic conditions, time of deposition, and zinc salt composition were investigated to evaluate the importance of each one's contribution to the nature and quality of the deposit. Under certain conditions the morphology of the deposit reflects the fluid motion over the surface of the electrode. Zinc has a tendency to form grooved deposits in both laminar and turbulent flow and under conditions when mass-transfer is not controlling, i.e., well below the limiting current.

To verify the transport conditions, mass-transfer limiting currents of zinc deposition in acidic $ZnCl_2$ and $ZnSO_4$ solutions have been determined by potential-sweep voltammetry using a rotating disk electrode. Various zinc concentrations, rotational speeds, and potential-sweep rates were used in obtaining the cathodic polarization curves. High sweep rates (100, 200 mV/s) and low concentrations (0.05 M, 0.10 M) of zinc in well-supported electrolyte solutions give distinct limiting-current plateaus for all rotational speeds. In 0.05 M $ZnCl_2$ + M KCl solution, only the 200 mV/s sweep rate and the lower rotational speeds (200, 400 rpm) give limiting-current plateaus. Zinc diffusion coefficients obtained from the limiting currents are: 0.98×10^{-5} cm^2/s in 0.05 M $ZnCl_2$ + M KCl and 0.78×10^{-5} cm^2/s in 0.05 M $ZnSO_4$ + M Na_2SO_4, in reasonable agreement with literature values.[1,2] The zinc surface area increases too rapidly at slower potential sweep rates, and also at higher zinc concentration, to permit the development of distinct limiting current plateaus.

The morphology of electrodeposited zinc was investigated under galvanostatic conditions in a channel-flow cell with a Pt cathode and Zn anodes, using in situ time-lapse motion picture photography. In the absence of mass-transfer control, zinc forms grooved deposits in a certain current density range (5-80 mA/cm^2) reflecting the fluid motion in both laminar and turbulent flow situations (Re 1600-9000); smooth deposits develop at higher current densities, most likely because of higher

nucleation rates. Time-lapse motion picture experiments permitted study of the sequence of events occurring in the development of zinc deposit morphology.[3,4] Within a few seconds after the start of Zn deposition, a Pt substrate becomes fully covered. At low current densities (hence, low overpotentials) the deposit contains a large range of growing, protruding crystals. Because of ohmic advantage and also because of improved mass transfer, the large protrusions tend to grow faster than smaller ones. Better mixing in the wake of large protrusions tends to cause rapid nucleation and formation of ridges. Eventually the secondary flow patterns stabilize, resulting in the formation of well-defined, quite evenly-spaced ridges in the metal deposit. At high current densities the nucleation is more dense, the size distribution of crystallites is narrow, therefore protrusions, and hence striations do not form.

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Dendritic Zinc Deposition in Flow Batteries

(J.R. Selman, Illinois Institute of Technology)

The objectives of this project are to clarify the solution-side transport processes involved in zinc deposition from acidified halide electrolytes and to investigate the interaction of transport processes with the dendritic micro-profiles. In addition, this investigation seeks to clarify the role of hydrogen co-deposition on zinc deposition and dendrite initiation.

Diffusivities of zinc in highly-concentrated zinc halide solution, which are needed for the optimization of cell design, were measured by the polarographic method. Extensive data were obtained at 25°C for both

$ZnCl_2$ and $ZnBr_2$ solutions (0.1-3 M zinc halide) with 3 M KCl as supporting electrolyte. To gain more insight into the significance of these data for comparison with literature data, the following factors were further explored using dilute solutions of zinc halide: (1) effect of pH on the polarization curve and current plateau and (2) mercury flow-rate and drop time.

To interpret these effective diffusion coefficients, the effect of migration was assessed in a preliminary way by assuming dilute-solution transport equations, including reversible complexation. This transport analysis was applied for different reacting species and for a range of values of the complexation constant. The variation in the complexation constant was related to the degree of hydration of the ions in solution, according to Skou, et al. (Electrochimica Acta 22, 169 (1977)).

The ionic distribution diagrams for the $ZnCl_2$-H_2O and ZnCl-KCl-H_2O systems were calculated using the hydration model of ion activity. For the range of zinc concentrations used in zinc/halogen batteries (1-3 M $ZnCl_2$), the analysis indicated that three species are present. These are Zn^{2+}, $ZnCl^+$, and $ZnCl_3^-$ in the binary $ZnCl_2$ solutions, while $ZnCl_3^-$ is the dominant species in supported $ZnCl_2$ solutions (3 M KCl).

Binary diffusion coefficients, which are needed in the analyses of concentrated solution, have been derived for $ZnCl_2$-H_2O from the transport data of Agnew and Paterson (J. Chem. Soc. Farad. Trans. I 74, 7896 (1981)). The results appear to reflect increasing complexation. Consequently, a concentrated solution transport model in terms of four ionic species only (K^+, Cl^-, Zn^{2+}, and $ZnCl_3^-$) has been adopted for further work.

Experimental investigations of the growth of dendritic zinc in these electrolytes were conducted using a cell with concentric inner rotating-cylinder electrode. The cell allowed *in situ* optical observation of deposit morphology during electrodeposition under conditions of uniform current distribution and controlled convection. The systematic analyses of the effects of current, convection, concentration, and pH are in progress.

Zinc Electrode Morphology in Acid Electrolytes

(J. McBreen, Brookhaven National Laboratory)

The zinc electrode is common to both zinc/chlorine and zinc/bromine flow batteries. Although considerable progress has been made in engineering these batteries, there are still problems with the zinc electrode. The objective of this work is to elucidate the mechanism of zinc deposition in acid electrolytes and to devise methods to control zinc-electrode morphology. In 1982, work focused on obtaining baseline data on the initial stages of electrocrystallization in ultra pure zinc chloride and zinc bromide electrolytes. In addition, the effects of modified charging methods, organic surfactants, inorganic additives, and substrates were investigated.

High-purity 3 M $ZnCl_2$ and 3 M $ZnBr_2$ electrolytes were prepared by the reaction of 99.9999% zinc with the distilled azeotrope of HCl and 99.998% bromine under triply-distilled water, respectively. The initial stages of zinc deposition on glassy carbon were investigated using the potential step method. In the present study, most of the results could be fitted to a model for instantaneous nucleation of three-dimensional centers followed by growth under kinetic control.

From the electrochemical measurements and the model, the rate constants for crystal growth in the direction perpendicular (k^1) and parallel (k^2) to the substrate were obtained. The following values were obtained for the rate constants for zinc deposition on glassy carbon in 3 M $ZnCl_2$, pH=2.8. N_o is the instantaneous nucleation rate.

Overvoltage (mV)	zFk^1 (mA/cm^2)	k^2N_o ($moles^2\ cm^{-6}s^{-2}$)
23	15.84	1.42×10^{-5}
25	32.59	4.13×10^{-5}
27	45.27	9.75×10^{-5}
30	75.14	4.04×10^{-4}

On glassy carbon the nucleation overvoltage for zinc deposition from 3 M $ZnCl_2$ is ~17mV. In 3 M $ZnBr_2$ of similar pH the nucleation overvoltage is ~12 mV. In $ZnBr_2$ the rate constants are about an order of magnitude higher.

Small additions (10^{-4} M) of Pb^{++} or Bi^{+++} ions decrease the rate constants by as much as two orders of magnitude. Additions of fluorinated surfactants slow down the kinetics considerably and in some cases lead to progressive nucleation of three-dimensional centers.

Deposition of zinc on zinc occurs via a mechanism consisting of simultaneous two-dimensional layer growth and the nucleation of three-dimensional centers. On silver and copper there is underpotential deposition of a zinc monolayer, alloy formation and subsequent deposition of zinc via a two-dimensional layer mechanism with negligible nucleation overvoltage.

Superimposition of square wave potential pulses increase the nucleation rate and modifies the orientation of the zinc deposit.

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Transport in Aqueous Battery Systems

(D.G. Miller, Lawrence Livermore National Laboratory)

The objective of this project is to provide diffusion data for multicomponent solutions in zinc/halogen batteries. Experimental measurements of the diffusion coefficients of the $ZnCl_2$-KCl-H_2O system were undertaken to provide information that would be useful in modeling and

optimizing zinc/halogen battery systems.

Measurements for $ZnCl_2$-KCl concentrations (in mol-dm^{-3}) of (0.5, 2) (1.5, 2), and (2.5, 2) showed that the main-term diffusion coefficients, D_{ii}, changed size relative to one another, but cross-term coefficients, D_{ij}, were small. This year, a higher concentration of KCl was used. Contrary to expectation, the term D_{21} for the composition (0.5, 4) was large and negative. Large cross terms will complicate modeling procedures, so it was desirable to examine the effect of varying the KCl concentration for $ZnCl_2$ fixed at 0.5. To characterize this curve, KCl concentrations of 0.5, 1.25, and 4.0 (2.0 had been measured previously) were used. The new results are presented in Table 1.

The $ZnCl_2$ used in previous experiments was of poor quality. This did not affect the mixtures, because the added KCl swamped the impurities. However, the data for the $ZnCl_2$-H_2O were expected to be affected. Redetermination of D_v for several compositions of very high purity $ZnCl_2$ gave results about 0.0-0.5% lower than the previous ones. This is in the direction expected from the absence of alkali metal impurities. The new results are still significantly above the earlier measurements of Agnew and Paterson[1] at low concentrations.

Densities have been measured on pure aqueous $ZnCl_2$ from 0.04 to 5.69 mol-dm^{-3} because of discrepancies in the literature. Densities were also determined on the ternary systems at 8-14 points around each average composition.

Table 1. Diffusion Coefficients of $ZnCl_2$-KCl-H_2O at 25°C[a]

c_1	c_2	10^5D_{11}	10^5D_{12}	10^5D_{22}	10^5D_{21}
0.49994	0.50003	0.9347	0.0172	0.1607	1.5553
±.00003	±.00002	±.0046	±.0004	±.0032	±.0056
0.50001	1.2499	0.9354	0.0393	0.1633	1.4826
±.00005	±.0001	±.0085	±.0005	±.0044	±.0103
0.49992	3.9994	0.9172	0.0275	-0.6439	1.9999
±.00002	±.0001	±.0029	±.0012	±.0029	±.0062

[a] 1 denotes $ZnCl_2$, 2 denotes KCl; ± values denote 1 standard deviation; concentration units are mol-dm^{-3}; diffusion coefficient units are cm^2-s^{-1}.

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C. MOLTEN SALT CELLS

Molten-Salt Battery Research

(J. Newman, Lawrence Berkeley Laboratory)

The Li-Al/FeS_x battery and the Na/S battery are candidates for electric vehicle propulsion and stationary energy storage applications. Many aspects of their behavior, however, are poorly understood. The objectives of this theoretical study are to examine important system parameters, and suggests experiments that provide information needed to improve the design and operation of the battery.

An improved method for approximating the conductivity of heterogeneous porous electrodes is being developed. The method currently used in the mathematical model of the LiAl/FeS cell overestimates electrode conductivity. An extension of the classical result of Maxwell was applied and resulted in effective conductivities as much as an order of magnitude smaller than those obtained by the previous method. This method will later be extended to develop a mathematical model of the LiAl/FeS_2 cell.

The performance of Na/S secondary cells is strongly influenced by the diffusion of anions and cations through the polysulfide melt. Thus, optimal design of sulfur electrodes will depend upon the availability and accuracy of diffusion-coefficient data for polysulfide melts. An

experimental apparatus has been built to measure the diffusion coefficient of sodium ions in melts of sodium polysulfides, using the method of restricted diffusion. Some preliminary experiments have been performed with this apparatus, and work is currently under way to perfect the design of the apparatus. In addition, binary interaction parameters for sodium polysulfide melts, assuming a pseudo-binary melt, have been calculated using transport data obtained from the open literature.

Invited Talk

1. John Newman, "Mathematical Model of the Li-Al/FeS Molten Salt Battery," Sandia National Laboratories, Albuqerque, NM, Materials Science Seminar, June 18, 1982.

Physical Chemistry of Molten-Salt Batteries

(J. Braunstein, Oak Ridge National Laboratory)

Although current-induced precipitation in the electrolyte within porous electrodes may affect adversely the utilization of reactants and overall battery performance, there has been no direct measurement of this effect in a molten-salt battery.(1) The objective of this study is to obtain measurements of composition shifts that could occur during discharge of a Li-Al negative electrode in a LiAl/LiCl-KCl/FeS battery.

SEM/EDX analysis of anolyte composition showed regions in the front part of the electrode where pure lithium chloride precipitated during electrolysis. The distribution of LiCl composition on an axially-cut anode section is nonuniform. The regions of solid precipitation accentuate the nonuniformity of current distribution, indicated by adjacent regions with no composition change. Cathodic reaction indicated by an increase in the KCl concentration was observed primarily near the cell walls. Calculations with a one-dimensional model also predicted cathodic reaction at the collector in the back of the electrode. Such inhomogeneities could lead to swelling and increased ohmic resistance.

Behavior in actual battery electrodes similar to those observed in the present study remains to be demonstrated. Nevertheless, more accurate measurements of electrolyte composition, together with precise analysis of the alloy phases in the Li-Al electrode, would be desirable

for more detailed understanding of this system.

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1. R. Pollard and J. Newman, "Applied Battery and Electrochemical Research Program for Fiscal Year 1980," LBL-12514, E. Cairns, ed., p. 48.

Thermal Management of Battery Systems

(H.F. Gibbard, Gould, Inc.)

The objectives of this project are to determine heat generation rates, measure temperature distributions, analyze heat-transfer rates, and to evaluate thermal management strategies for Li/Metal Sulfide batteries.

A high-temperature calorimeter for measuring cell heat generation was modified for extended operation at temperatures of 450°C or more. The operating ranges of temperature and heat flow are room temperature to 500°C and 0 to 50 W, and the detection limit is 1 mW. The temperature coefficient of emf of LiAl/FeS cells was measured and found to be a complicated function of temperature, state of charge, and electrolyte composition.

The rate of thermal-energy generation was calculated from a thermodynamic equation. The results were in good agreement with the heat flow measured with the high-temperature calorimeter.

The cell reaction of FeS to J-phase and J- to X-phase during discharge was noted in calorimetric measurements for cells containing LiCl-KCl-LiF electrolyte. The effect of varying electrolyte composition on cell heat generation was investigated. For cells containing no potassium ion, in which the formation of J-phase is impossible, the endothermic effect associated with the J-to-X transition is not observed.

A cell containing the LiCl-LiBr-LiF electrolyte was fabricated with a type-K ungrounded thermocouple embedded in the middle of a central negative electrode. The change in the internal temperature of the cell was monitored during various rates of discharge. The cell capacities were 168, 162, 128, and 113 Ah for 40, 60, 80, and 100 A constant-current discharge, respectively. The internal temperature of the cell increased 44°C, 45°C, 39°C, and 39°C at the end of 40, 60, 80, and 100 A discharge. If the temperature increase during discharge is approximated as linear, the rates of internal temperature increase are 34.5, 24.4, 16.7, and 10.5°C/hour for 100, 80, 60, and 40 A discharge, respectively.

The rate of thermal energy generation in a cell containing an all lithium-cation electrolyte was calculated from the measured values of emf, temperature coefficients, and cell polarization. The average rates of heat generation were 8.7, 16.4, 25.6, and 33.2 W for 40, 60, 80, and 100 A discharge, respectively. These values are relatively higher than the cell with LiCl-KCl-LiF electrolyte because the latter contains potassium ion, and the endothermic reaction of J- to X-phase reduced the total heat generation in the cell. The result also indicates that for a practical EV application, a cooling system is necessary for the battery system during high-rate discharge.

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New Battery Materials

(R.A. Huggins, Stanford University)

The objectives of this research program are to evaluate the structural, thermodynamic, and kinetic parameters of materials for use as electrode and electrolyte components in high-temperature lithium-based secondary storage batteries and to develop new materials based on

principles derived from this evaluation. The approach places emphasis on the relationships between fundamental thermodynamic and kinetic parameters, e.g., phase equilibria, Gibbs free energy values, equilibrium potentials, chemical diffusion within solid phases, etc., and the microscopic and macroscopic electrochemical phenomena. The microscopic structural basis for the observed properties is also given attention.

Ternary lithium-transition metal oxides have been investigated as possible positive-electrode reactants in high-temperature lithium-based systems. These oxides have a significant potential advantage over metal sulfides with regard to container, seal, and current-collector corrosion problems. Progress has also been made on the prediction of the potentials of binary oxides as positive electrodes, as well as the composition-dependence in mixed-conductor electrodes in terms of the thermodynamic properties of the ions and conduction electrons. Several new mixed-alkali materials with "propped" cubic and layer-type crystal structures have been synthesized which have greatly enhanced diffusion kinetics for lithium, as well as appreciable solubilities.

Also under evaluation is a new molten salt electrolyte that can be used in the presence of elemental lithium at intermediate temperatures. It appears that this salt can be used at temperatures as low as 135°C and with positive electrodes with very low lithium activities, and thus high voltages. This electrolyte, based on lithium nitrate, is highly oxidizing and causes the formation of a very thin layer of lithium oxide on the surface of the lithium. This layer has the fortunate property of being a good solid electrolyte for lithium ions, has a very low electronic conductivity, and is relatively insoluble in the molten salt. As a result, lithium can be passed through it in either direction, making it possible to produce reversible solid lithium electrodes. The thermodynamic basis for the stable operating limits of these nitrate salts is now understood, and quantitative measurements have been made of the growth and properties of the solid electrolyte protective layer. These salts have also been shown to function as redox reaction hosts.

Work has also been done on negative electrode materials, including the demonstration of all-solid high-rate electrode structures using a mixed-conducting solid matrix surrounding dispersed fine particles of the reactant phase. Experiments have been performed to evaluate the properties of binary lithium alloys at temperatures around 150°C. The higher melting points of such compounds makes them much safer to use than elemental lithium in highly-oxidizing intermediate-temperature molten salt electrolytes. Investigations have also begun on several ternary lithium-alloy systems to determine both the potential and capacity of such alloy electrodes.

Studies on lithium-conducting solid electrolytes have involved measurements of the stability range and electronic leakage, as well as compositional effects upon the ionic conductivity in several families of solids containing tetrahedral anionic groups. One of the phases in the lithium-zirconium-oxide system has been studied and found to be thermodynamically stable in the presence of elemental lithium, as well as having high lithium conductivity.

Publications

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2. Robert A. Huggins, "Use of Molten Salt Electrochemical Cells to Determine Thermodynamic and Kinetic Properties of Solids," in Chemical Metallurgy - A Tribute to Carl Wagner, N.A. Gokcen, ed., AIME, New York, p. 149 (1982).

3. Anita J. Mark, "The Electrochemical Insertion of Lithium into Cubic Tungsten Bronze," Master's Thesis, Stanford University (July 1982).

4. Robert A. Huggins, "Solid Electrolytes," in Electrochemistry in Industry - New Directions, U. Landau, E. Yeager and D. Kortan, eds., Plenum Press, p. 195 (1982).

5. Ian D. Raistrick and Robert A. Huggins, "The Transient Electrical Response of Electrochemical Systems Containing Insertion Reaction Electrodes," Solid State Ionics 7, 213 (1982).

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2. Ian D. Raistrick, N.A. Godshall and Robert A. Huggins, "Ternary Compound Electrode for Lithium Cells," U.S. Patent 4,340,652, July 20, 1982.

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2. Robert A. Huggins, "Ionic Mobility in Li-Conducting Crystalline Electrolytes," presented at the International Meeting on Lithium Batteries, Rome, Italy, April 1982.

3. R.F. Aspandiar, Ian D. Raistrick and Robert A. Huggins, "Structure and Lithium Ionic Conductivity of Compounds with Tetrahedral Anionic Groups," presented at the American Ceramic Society Meeting, Cincinnati, May 1982.

4. Anita J. Mark, Ian D. Raistrick and Robert A. Huggins, "A Study of the Electrochemical Insertion of Lithium into Cubic Sodium Tungsten Bronze," presented at the Electrochemical Society Meeting, Montreal, May 1982.

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6. R.F. Aspandiar, "Lithium-Conducting Oxide Solid Electrolytes," presented at the 1982 Department of Materials Science and Engineering Industrial Affiliates Meeting, Stanford University, May 1982.

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8. J.P. Doench and Robert A. Huggins, "Study of Lithium Alloy Electrodes in the Intermediate Temperature $LiNO_3$-KNO_3 Molten Salts," presented at the Electrochemical Society Meeting, Detroit, October 1982.

9. Ian D. Raistrick and Robert A. Huggins, "Kinetics of Lithium Insertion into Transition Metal Oxide Solid-Solution Positive Electrode Materials," presented at the Electrochemical Society Meeting, Detroit, October 1982.

10. Ian D. Raistrick, "The Application of AC and Transient Techniques to the Study of the Kinetics of Lithium Insertion into Oxide Solid Solution Electrodes," presented at the Symposium on "In-Situ Methods for Characterizing Electrodes and Electrochemical Processes," AIChE Meeting, Los Angeles, November 1982.

11. Robert A. Huggins, "Bewegliche Ionen und Transduktor-Effekte in Festkoerpern," presented at the Festkolloquium anlaesslich des 60, Geburtstages von Prof. Dr. Albrecht Rabenau, Stuttgart, Germany, November 1982.

Molten-Salt Cell Research

(R.K. Steunenberg, Argonne National Laboratory)

The primary objective of this project is to conduct the research required to develop cells for an advanced electric-vehicle battery that has very high specific energy and power, long cycle life, and an acceptable cost. This project consists of tasks on cell modeling and electrochemical engineering, research on positive and negative electrodes, and materials research and development.

The primary focus of the electrochemical engineering and cell design studies was the development and testing of a computer program to predict the performance of full-scale battery cells of varying theoretical capacities and energy-to-power ratios. This program was developed using (1) data from the testing of light-weight experimental (25 or 35 Ah capacity) Li-Al/FeS cells having a design of the type used in full-size cells and (2) earlier test data from full-size (>150 Ah) Li-Al/FeS cells. Design variations with regard to active materials and electrolyte composition, type of separator, type of current collector, and cell shape can be input to the program; specific energy, specific power, and voltage losses across all of the current-carrying elements of the cell (including the electrode current collectors, interelectrode connectors, and cell terminals) can then be predicted. These design variables can be changed by simply replacing a data pack in the program.

A research effort was conducted to identify electrodes suitable for advanced high performance battery cells. The approach is to evaluate the thermodynamic and kinetic properties (performance) of the electrodes and the effects that various parameters have on such properties. The

experimental designs used in carrying out the kinetic study included a small one-dimensional electrode (0.7 cm^2 in area) operated in a suitable open cell and a sealed, compact monocell. The working-electrode designs in both cells used current collectors that were essentially resistance-free; consequently, electrode voltage losses were confined to the electrode beds and the electrode current distribution was nearly one-dimensional. Reference electrodes were used to measure the working electrode potential.

The area specific resistance for a 15-s potential relaxation (ASR_{15}) was obtained for two open cells with Li-Si one-dimensional electrode (Li-Si counter electrode). Under the conditions of the study, the Li-Si electrode has three voltage plateaus at compositions of $Li_{3.25}Si$-$Li_{2.33}Si$, $Li_{2.33}Si$-$Li_{1.71}Si$, and $Li_{1.71}Si$-Si. The ASR_{15} values increase on the three Li-Si plateaus as lithium is discharged from the electrode, but drop sharply as the discharge reaction shifts from one plateau to the next. Pulse-current studies for three Li-Si electrode compositions indicate good power characteristics on all but the $Li_{1.71}Si$-Si plateau.

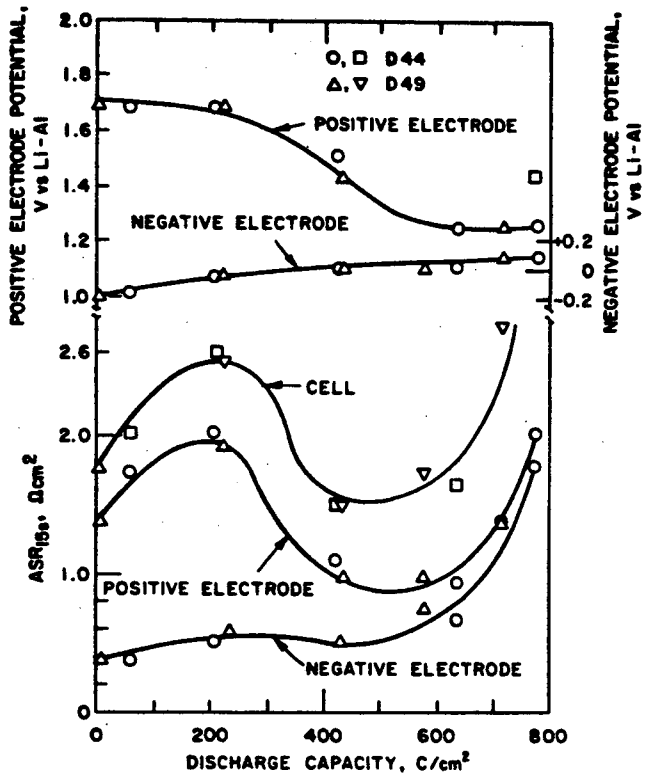

Fig. 1. Discharge Characteristics of Sealed Test Cell (discharge current density, 37 mA/cm^2

The performance of the Li-Si and FeS_2 electrodes was evaluated using a sealed cell, where the Li-Si electrode was 0.5-cm thick with a capacity density of 1.01 Ah/cm^3, and the FeS_2 electrode was 0.3-cm thick with a capacity density of 1.1 Ah/cm^3. Characteristic electrode potentials and ASR_{15} values for the Li-Si and FeS_2 electrodes of this cell are shown in Figure 1. The reproducibility of these values was excellent. The figure shows that significant ASR_{15} values develop in the FeS_2 electrodes in the $FeS_2 \rightarrow Li_3Fe_2S_4$ transition region. Moreover, it was found that the ASR_{15} values observed for the Li-Si electrode in the sealed cell are similar to those observed in the one-dimensional Li-Si electrode.

Earlier Li/FeS cells with a Li-Al-Fe negative electrode have shown a discharge voltage about 0.2 V higher than the usual LiAl/FeS cell. An investigation of the phases and phase relations in the Li-Al-Fe system was undertaken to identify the reason for this higher discharge voltage.

Compositions with the nominal stoichiometries Li_5Al_5Fe, $Li_5Al_5Fe_2$ and $Li_4Al_4Fe_2$ were prepared and analyzed by metallography, X-ray diffraction and chemical analysis. From these data, a partial phase diagram for the Li-Al-Fe system was constructed. A number of three-phase fields were identified, the most important being one bounded by the phases Li_3Al_2, FeAl and $FeAl_2$. These phase relations indicate that a negative electrode having a composition of $Li_4Al_4Fe_2$ or $Li_5Al_5Fe_2$ would discharge primarily at a potential established by Li_3Al_2, which is about 0.2 V higher than the potential for LiAl.

In the thermodynamic investigations, emf measurements have been made on the $3Li\text{-}Al + 2FeS_2 \rightarrow Li_3Fe_2S_4 + 3Al$ transition. Emf data were obtained at various states of discharge over the temperature range 382-455°C. A linear regression analysis of these data yielded the following emf for this transition:

$$E = 1.5558 + 0.0004785T(^{o}C)$$

The correlation coefficient for the data represented by this equation is 0.996. The emf measurement was found to be independent of state of discharge.

Using a sensitive, in-situ analytical technique based on the Nernstian response characteristics of the Ni/Ni_3S_2 half-cell couple to dissolved Li_2S, the solubility of Li_2S in LiCl-KCl eutectic was found to be 780 and 980 ppm at 400 and 450°C, respectively. The concentrations of Li_2S found for Li_2FeS_2 were $2.06 \pm 0.14 \times 10^{-2}$ mol/l at 400°C and $2.28 \pm 0.16 \times 10^{-2}$ mol/l at 450°C. The above values agree well with those obtained earlier using a cyclic-voltammetric procedure. Analytical data obtained for Li_2FeS_2 were used to calculate the free energy (δG) for the reaction

$$Li_2S + FeS \rightarrow Li_2FeS_2$$

For 400 and 450°C, values of -1.5 ± 1.0 and -2.6 ± 1.0 kJ, respectively, were obtained. These calculated Gibbs free energy values are in very good agreement with those obtained earlier in this laboratory using emf data.

Efforts in materials research were directed toward the determination of the kinetics and rate-controlling mechanisms in the reaction of aluminum with current-collector materials (e.g., low-carbon steel, nickel and Type 304 stainless steel) in Li-Al negative electrodes. This reaction results in the formation of a brittle, intermetallic layer, which can reduce the conductivity of the current collector. In addition, candidate coating materials for arresting diffusion between the aluminum and the hardware material were evaluated. The deposition and diffusion rates of aluminum were measured in separate experiments to determine the rate-controlling mechanisms. The deposition rate was determined using an electronic couple between aluminum and low-carbon steel in LiCl-KCl electrolyte and measuring the steady-state current. The diffusion rate was determined using standard diffusion couples between aluminum and the test metals (low-carbon steel or nickel). The results of these experiments indicated that the rate-controlling step for the overall aluminum reaction shifts from galvanic deposition to diffusion with time. The diffusion coefficients were 3.4×10^{-11} and 2.7×10^{-11} cm^2/s for nickel and low-carbon steel, respectively.

Selected coating materials (e.g., TiN, TiC, Cr, Mo) were evaluated for resistance to the aluminum reaction using diffusion couples at 450°C for 1000 h. These tests identified chemical-vapor-deposited TiC and electroplated chromium as the most promising candidates.

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3. A.K. Fischer and D.R. Vissers, "Microscopy of Electrodes Operating in Molten Salts," Proc. of the Symp. on Transport Processes in Electrochemical Systems, R.S. Yeo, T. Katan, and D. Chin, eds., Vol. 82-10, The Electrochemical Society, Pennington, NJ p. 141 (1982).

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D. SOLID ELECTROLYTES FOR ALKALI/SULFUR CELLS

Electrochemical Properties of Solid Electrolytes

(L.C. De Jonghe, Lawrence Berkeley Laboratory)

The objective of this work is to study the chemical and electrochem-

ical stability of sodium beta and beta" alumina towards molten sodium under conditions of electrolysis. In such solid electrolytes, rapid and slow degradation can take place. The aim is to clarify the degradation mechanisms and to provide guidelines for prolonged operation of sodium/sulfur cells.

A thermodynamically-based model was used to assess the effects of the formation of a layer of lowered ionic conductivity and increased electronic conductivity on the applied voltage at which solid electrolyte failure is to be expected. Such a layer can result from electrolyte contamination with electrode impurities. It is found that when a significant increase in electrolyte resistivity is produced, electrolyte failure can be initiated by deposition of sodium internally in the solid electrolyte. The results stress the necessity of operating solid electrolyte cells, such as Na/S, in a manner that minimizes electrode contamination.

Sodium beta alumina solid electrolytes containing some very large grains were subjected to a unidirectional sodium-ion current. The exit surface of the sodium ions was then examined, and it was found that degradation has been initiated at the boundaries of very large grains (Fig. 2). The grain junctions are marked at 1 and 2. There is degradation at the junction of the two grains at 1, but none at the junction of the grains at 2; they are two different types of boundaries [Fig. 2(b) and 2(c)]. This observation suggests that the long, faceted sides of the large grains are mechanically weak. These facets correspond to 00.1 planes. Further evidence of the low bonding strength along 00.1 faceted grain boundaries can be seen in Fig. 3, which shows a fracture along a partial 00.1 faceted grain boundary. In the region where the grain boundary deviated from an exact 00.1 facet, the spinel-spinel block bonding, arrowed in Fig. 3, survived. The fractured path shows directly that grain boundary strength depends on grain boundary structure.

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5. L. C. De Jonghe, "Degradation Mechanisms of Sodium Beta Aluminas," LBL-14365.

6. A. Buechele, L. C. De Jonghe, and D. Hitchcock, "Degradation of Sodium Beta Alumina: Effect of Microstructure," LBL-13188.

7. L. C. De Jonghe, A. Buechele, and K. H. Yoon, "Grain Boundaries and Solid Electrolyte Degradation," LBL-14150.

Invited Talks

1. Lutgard C. De Jonghe, "Solid State Electrochemistry and Batteries," Institute of Physics and Chemistry, University of Sao Paulo, Sao Carlos, Brazil, August 1982.

2. Lutgard C. De Jonghe, "Materials Problems in Energy Storage," Department of Materials Science, Federal University of Sao Carlos, Brazil, August 1982.

3. Lutgard C. De Jonghe, "Solid Electrolyte Properties," Institute of Physics, Federal University of Minas Gerais, Belo Horizonte, Brazil, September 1982.

4. Lutgard C. De Jonghe, "Solid Electrolyte Batteries," Institute of Nuclear Energy Research, University of Sao Paulo, Sao Paulo, Brazil, September 1982.

5. Lutgard C. De Jonghe, "Electrochemical Energy Storage," Energy Company of Sao Paulo (CESP), Sao Paulo, Brazil, September 1982.

6. Lutgard C. De Jonghe, "Microstructure and Properties of Sodium Beta Aluminas," RUCA, Antwerp, Belgium, June 1982.

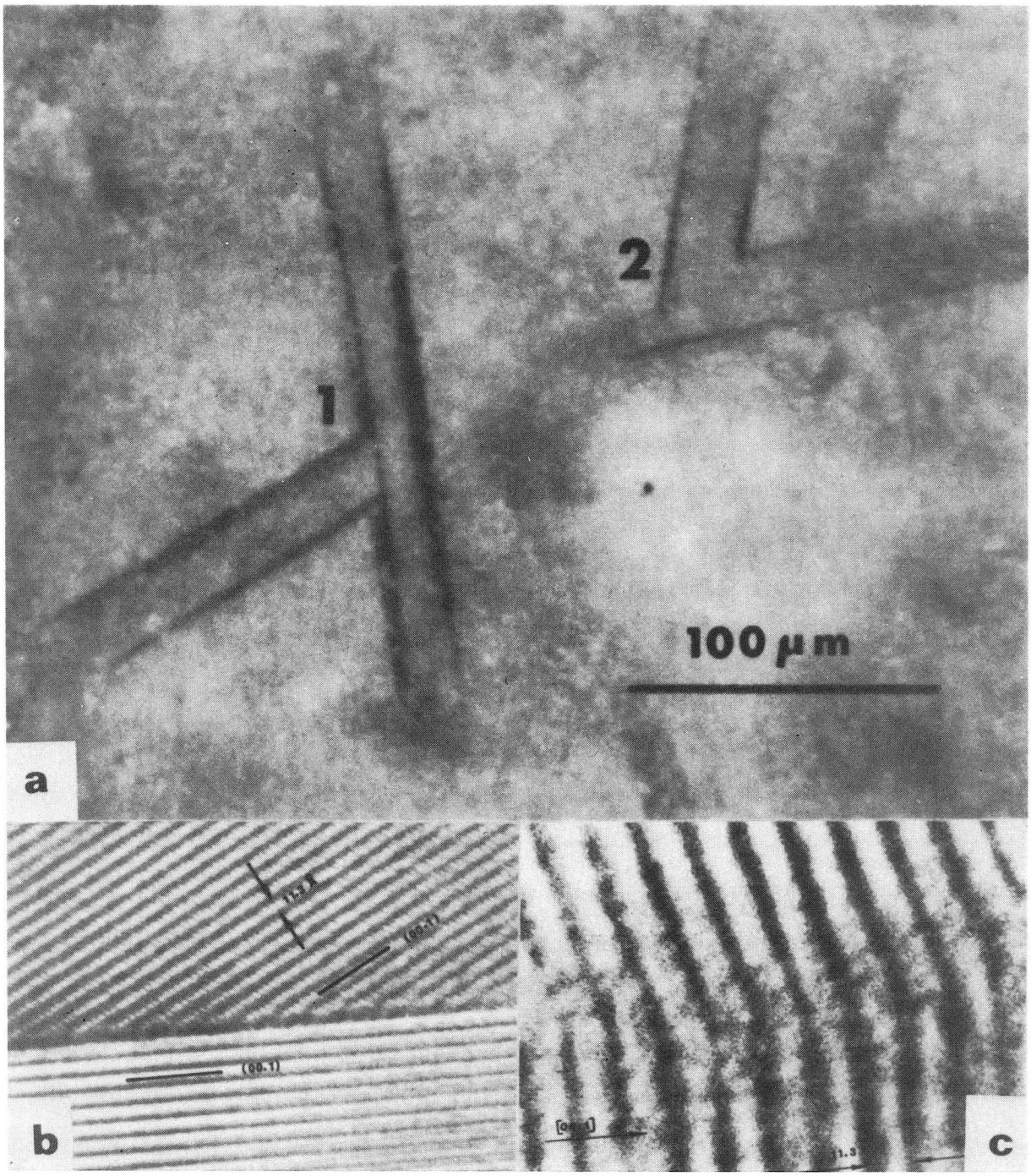

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Fig. 2. (a) Optical micrograph of silver- stained sodium exit surface for electrolyte subjected to unidirectional current flow of 50 mA/cm^2, in a Na/Na cell, at 300^oC. The two configurations of Mode I initiation have been labeled. (b) Lattice image of a grain boundary structure corresponding to 1 in (a). (c) Lattice image of a grain boundary structure corresponding to 2 in (a).

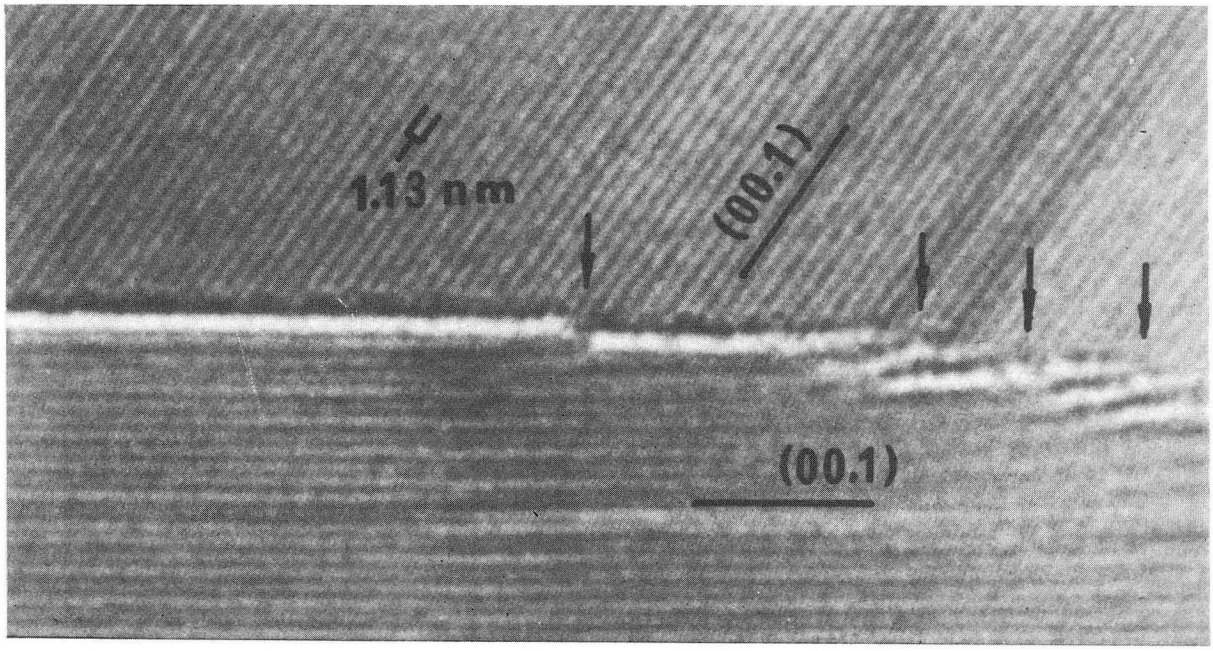

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Fig. 3. Fracture at a grain boundary partially faceted along 00.1 planes. Where the grain boundary deviates from an exact 00.1 facet, as in Fig. 2(c) direct spinel-spinel block bonds (arrowed) have survived. This demonstrates directly that the grain boundary strength depends on its structure.

Improved Beta"-Aluminum Oxide Through Transformation Toughening

(F. Lange, Rockwell International Science Center)

The objectives of this research program are to improve the fracture toughness and strength of the sodium-ion conducting electrolyte, β"-Al_2O_3, by incorporating zirconia as a second phase and to optimize these mechanical properties with the properties required for use of the electrolyte in advanced storage batteries.

The initial phase of this work has emphasized the fabrication of microstructures in which the zirconia is well dispersed and has a grain size ≤ 1 μm. The route chosen is based on dispersing ultrafine powders of β"-Al_2O_3 and zirconia in an alcohol, such as 1-butanol.

These dispersions are stable and electrophoretic measurements have shown that both powders are positively charged, with zeta potentials in the range 30 to 60 mV. Green ceramic bodies are then produced by filtration of the suspensions using a plaster of paris or powder mold. Thus, the presence of agglomerates (weak forces) that occur in dry consolidation routes are avoided, and moreover, the second phase is expected to be well-dispersed. After careful drying, the composite materials are densified by normal techniques, though it was found that densification (> 97% theoretical) could be accomplished at slightly lower temperatures, i.e., 1535°C for the composites and 1480°C for single-phase β"-Al_2O_3. β"-Al_2O_3/zirconia composites containing up to 20 vol% zirconia have been fabricated using commercial powders. The starting powders were found to contain hard agglomerates (> 2 μm) that could not be dispersed with alcohols. Milling of the dispersions can be used to break up the agglomerates, but this was found to lead to contamination (lowers ionic conductivity) and microstructural defects. An improved technique using an ultrasonic probe and sedimentation was therefore introduced.

Observation of the fired microstructures showed that the zirconia was well dispersed with an average grain size of ~1 μm. X-ray diffraction confirmed that the zirconia was retained in its tetragonal state and that β"-Al_2O_3 was the other primary phase. The presence of the zirconia second phase also eliminated the tendency for exaggerated grain

growth that occurs in single-phase materials. This was found to eliminate failures from large grains and is expected to be beneficial in the use of these materials as electrolytes.

Measurement of the mechanical properties of the composite materials has shown that the strength can be increased by a factor of two to three compared with the single-phase material. In addition, tetragonal ZrO_2 led to increases in strength greater than those expected by transformation toughening by eliminating failures from large grains of β''-Al_2O_3 (decreases critical flaw size). Currently, failures in the composites are occurring from identifiable processing defects, such as voids, which indicates the potential for higher strengths. Preliminary measurements of ionic resistivity indicate that for up to 15 vol % ZrO_2, the strength/ionic resistivity increases compared with single phase β''-Al_2O_3.

Principles of Superionic Conduction

(B.J. Wuensch, Massachusetts Institute of Technology)

Alkali-ion conductors of relevance to battery systems and other solid-electrolyte applications have been examined in the present program in an attempt to gain insight into the principles which govern fast-ion conduction. The program has two main tasks:

(1) Perform exploratory syntheses, characterization, and conductivity measurements of possible new fast-ion conductors.

(2) Determine crystal structures, using x-ray or neutron scattering, of materials of high conductivity and in which a marked variation of property with structure and chemistry is apparent.

The ionic electrical conductivity of solid solutions in the NASICON solid solution system, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, increases to a maximum (0.2 $ohm^{-1}cm^{-1}$ at 300°C) at x=2.3, a value four orders of magnitude larger than the conductivity of the end-members of the system. The increase in conductivity seemed closely connected to structural change as one lattice constant and the unit cell volume of the solid solutions pass

through a maximum near the same composition. Detailed structural analyses of a series of solid solutions extending across the NASICON system [x=1.0 and 2.5 (hexagonal, $R\bar{3}c$) and x=1.6 and 2.0 (monoclinic, C 2/c)] have been completed in the past year. Of two available sites for the mobile Na ions, the first site, which is fully occupied at x=0, was found to remain fully occupied at all compositions. The second site, Na(2), which is fully occupied at x=3, fills progressively with increasing x. In the monoclinic phases, Na(2) splits into two sets of symmetry-independent sites which are not equally occupied. The Si and P ions were found to be ordered (but not fully) in both monoclinic phases.

A procedure for calculation of the position and maximum radius of the sphere which can just pass through a non-coplanar assemblage of rigid equal spheres was developed and used to evaluate the size of the "window" at the saddlepoint for jumps along likely Na-diffusion paths in the structure. It is found that the rotation of the tetrahedral units in NASICON causes the windows to increase to a maximum size, close to the radius of Na^+, near x=2, the composition of maximum conductivity.

The probable diffusion path which is responsible for the high ionic conductivity of NASICON is likely a jump between Na(2) sites. The ionic conductivity of solid solutions in the NASICON system therefore reaches a maximum for intermediate compositions because the concentration of Na ions and the window size along the diffusion path <u>both</u> reach optimum values near the same composition.

The relevance of these results toward the development of improved battery materials is that information on the diffusion mechanism, as well as the window size and Na concentration necessary for optimum conduction, have now been established. Accordingly, it should be possible on this basis to use known interionic distances to tailor new compositions with similar structural parameters including some, perhaps, which might be free of the phosphorus component which has been suggested as the origin of degradation of NASICON in the presence of molten sodium.

Publications

1. I. Kohatsu, A.K. Ekholm and B.J. Wuensch, "Electrical Conductivity of Some NASICON-Related Solid Solution Systems," Bull. Am. Ceram. Soc. 61 419 (1982).

2. L.J. Schioler, B.J. Wuensch and E. Prince, "Structural Changes in the NASICON Solid Solution System," Bull. Am. Ceram. Soc. 61, 805 (1982).

Electrical Conduction and Corrosion Processes in Fast Lithium Ion Conducting Glasses

(H. Tuller, Massachusetts Institute of Technology)

The objectives of this project are to relate glass composition and structure to fast ion transport and chemical durability; and to identify glasses, which have optimized alkali-ion transport rates, chemical durability and thermal stability, for use as an electrolyte in Li/S cells.

Experiments were conducted to obtain an improved understanding of how glass composition and structure correlate with fast ion transport and durability in glasses. The electrical conductivity of two crystalline phases in the lithium borate system, lithium metaborate ($Li_2O \cdot B_2O_3$) and lithium diborate ($Li_2O \cdot 2B_2O_3$), were measured. Specimens were prepared by isostatic pressing of sintered powders of both 98 and 99.999% purity to achieve relative densities of approximately 80%. Specimen microstructures were examined then by scanning electron microscopy. The metaborate exhibited a fibrous structure while the diborate exhibited an equi-axed microstructure with grain-size of ~5μm.

Electrical conductivity measurements were performed as a function of temperature by an ac complex impedance technique which permitted distinction between grain- and grain-boundary resistivity. Activation energies of ~1 eV at temperatures above 500°C and somewhat lower values at reduced temperatures were obtained. Both the magnitude of resistivity and activation energy were found to be considerably higher than in the glassy counterparts, suggesting different mechanisms of transport. Ion exchange studies were initiated to examine the potential effect on fast Li ion transport in glasses of composition 0.3 Li_2O-0.7 B_2O_3 that were annealed in $NaNO_3/LiNO_3$ melts. The results suggested

that Li^+-Na^+ association occurred in this glass.

Measurements were performed on electrochemical cells of the form "LiAl"/glass electrolyte/Li and "LiAl"/glass electrolyte/"LiSn"/glass electrolyte/"LiAl." The electrolyte was a fast ion conducting glass in the system Li_2O-LiCl-B_2O_3. In the first cell, near theoretical open circuit potentials at 180-200°C were obtained, which indicated that the glass electrolyte (0.3 Li_2O-0.7 B_2O_3) retained an ionic transference number of unity even in contact with molten Li. Degradation nevertheless occurred, by formation of reaction layers that ultimately led to cracking at elevated temperatures. The second configuration, which included a working and a reference cell, was used to vary the a_{Li} in the initially-pure Sn "inner" electrode by titration from one of the "LiAl" electrodes. In this way, the electrolytic characteristics of the glass could be examined over an extended range of a_{Li} while in contact with a liquid electrode of $a_{Li} < 1$. Upon continued titration, a series of steps were obtained in a plot of cell potential vs Li/Sn ratio, corresponding to the successive formation of intermediate Li-Sn compounds. These results suggest that the glass electrolyte examined here appears to behave in a near-ideal fashion over an extensive lithium-activity range.

Publications

1. D.P. Button, R. Tandon, C. King, M.H. Velez, H.L. Tuller and D.R. Uhlmann, "Insights into the Structure of Alkali Borate Glasses," Journal of Non-Crystalline Solids 49, 129 (1982).

2. M.H. Velez, H.L. Tuller, and D.R. Uhlmann, "Chemical Durability of Lithium Borate Glasses," Journal of Non-Crystalline Solids 49, 351 (1982).

Glass Electrolyte and Advanced Cell Concepts

(S. Susman, Argonne National Laboratory)

The objective of this research is to develop a high-conductivity glass electrolyte for the Na/S battery. This glass electrolyte, termed NASIGLAS (for Na^+ Super Ionic Glass), has several inherent advantages over the β''-Al_2O_3 ceramic electrolytes presently used in Na/S batteries. The most significant of these is ease of fabrication and associated low

cost of the glass-electrolyte tubes which can be cast directly from the molten glass.

NASIGLAS analogs of a NASICON ceramic, $Na_{1+x}Zr_{2-x/3}Si_xP_{3-x}O_{12-2x/3}$,[1] were prepared, and their properties were investigated. These NASIGLAS analogs have been prepared over the composition range $2.25 \leq x \leq 3$. Evidence of phase separation and crystallization became more apparent at the higher phosphate compositions; optical microscopy and X-ray diffraction studies indicated trace quantities of γ-Na_3PO_4 at $x \leq 2.5$. For x=3, the glass transformation and crystallization temperatures were 722°C and 977°C, respectively, in DTA measurements at 25°C/min. The ionic conductivity of the glasses was measured by the complex admittance method. Values are shown in Table 1.

Table 1. Ionic Conductivity and Activation Energy for Various NASIGLAS Compositions

X	σ 300°C ($ohm^{-1}cm^{-1}$)	E_{act} (eV)
2.25	1.55×10^{-3}	0.60
2.50	1.08×10^{-3}	0.61
2.75	1.93×10^{-3}	0.55
3.00	1.23×10^{-3}	0.55
3.25	1.60×10^{-3}	0.55

The conductivity at 300°C for the end member (x=3.00) is the same as that of the corresponding NASICON. The conductivities shown in Table 1 are about 50 times higher than those of the borate glass developed by the Dow Chemical Company for use in Na/S cells.[2]

The NASIGLAS samples have been tested for compatibility with both reactor-grade sodium and purified sulfur in one-week exposures at 300°C. The samples were unaffected by the sulfur, but they exhibited a color change from clear to yellow-tan in the sodium. This type of color

change has been observed in silicate glasses, and may be suppressed by increasing the soda-to-silica ratio.[3] Studies are currently underway to optimize the glass composition for conductivity and chemical resistance.

References

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2. C.A. Levine, "Development of a Sodium-Sulfur Battery Suitable for use by Electric Utilities and for Vehicular Propulsion," Final Report for the Period March 1979 - May 10, 1981, DOE/ET/25103-T1.

3. C.A. Elyard and H. Rawson, "The Resistance of Glasses of Simple Composition to Attack by Sodium Vapor at Elevated Temperatures," pp. 270-286, Advances in Glass Technology, Plenum Press, New York, 1962.

E. COMPONENTS FOR AMBIENT-TEMPERATURE LITHIUM

Surface Layers on Battery Materials

(R.H. Muller, Lawrence Berkeley Laboratory)

The purpose of this work is to provide direct experimental information about formation and properties of surface layers on battery electrode materials. Present studies are focused on lithium in nonaqueous solutions. Surface layers of improved ionic conductivity are necessary for the deposition of lithium from nonaqueous solutions in rechargeable batteries. These surface layers should also be self-healing and inhibit corrosion reactions. Two approaches are being taken to identify appropriate surface layers: control of composition and microstructure. To those ends, improved means to form lithium nitride films and disordered oxygen and hydrogen-doped nitrides are under study.

Lithium can be used in different ambient-temperature nonaqueous electrolytes primarily because of the formation of surface layers which prevent the spontaneous reaction of the metal with solvents and solutes. However, these surface layers hinder efficient metal deposition from solution during recharge. The present measurements were conducted in order to determine film properties not affected by damage possibly inflicted in previous pulse measurements,[1] to investigate an approach

to improve film conductivity, and to clarify discrepancies between ellipsometrically and electrochemically determined film thicknesses. Lithium nitride was investigated as a protective surface layer because of reported high ionic conductivity.[2]

Simultaneous ac-impedance and ellipsometer measurements were conducted. Real and imaginary parts of the complex impedance were derived from Lissajous figures of current and potential displayed on an oscilloscope. The ellipsometer was of the self-compensating type in the polarizer-quarter wave plate-sample-analyzer configuration with a mercury arc (546 nm) or argon ion laser (514 nm) light source. Nitride films were formed by different exposures to gaseous nitrogen.

Film resistances derived from the low-frequency intercepts of complex impedance plots are in good agreement with pulse measurements. The previous interpretation that differences in film thickness between optical and electrical measurements are caused by inhomogeneous film structure, therefore remains valid. The highest film resistance was obtained for films formed in $LiClO_4$ solutions of propylene carbonate (PC), the lowest in pure solvent. Nitride layers showed intermediate film resistances. The protective properties of these layers were still evident after 250 h exposure to 1 M $LiClO_4$ at open circuit. The formation of the nitride layer was found to be strongly inhibited by trace amounts of oxide. Ellipsometer measurements during polarization of lithium in 1 M $LiClO_4$/PC showed a large difference between anodic and cathodic processes: metal dissolution appears to occur through the oxide layer with roughening of the substrate, but metal deposition occurs primarily on top of the oxide in the form of islands.

To further investigate the validity of the conclusion[1] that the protective surface layer formed on lithium in propylene carbonate-lithium perchlorate electrolyte was an oxide resulting from reaction with residual water rather than lithium carbonate, as conventionally accepted,[3] two experimental approaches are being taken: electrolyte of extremely low water content, prepared by treatment with lithium amalgam, is being used, and freshly-cut lithium electrodes are brought in contact with a very small volume of electrolyte in a new thin-layer cell.

Infrared spectroscopy has shown that the precipitate formed on lithium amalgam is not lithium carbonate but probably a polymerization product of the solvent.

References

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Publications

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2. F. J. Schwager and R. H. Muller, "Impedance and Ellipsometer Measurements of Lithium Electrodes in Propylene Carbonate Solutions," Extended Abstract No. 295, Electrochemical Society Meeting, Detroit, MI, October 17-21, 1982; LBL-13618.

Metal Couples in Nonaqueous Electrolytes

(C.W. Tobias, Lawrence Berkeley Laboratory)

The objective of this project is to develop practical alternatives to aqueous or high-temperature molten-salt systems for advanced batteries and the efficient electrochemical reduction and oxidation of reactive metals. Current work with propylene carbonate is aimed at improving solvent preparation techniques, increasing solvent stability, and identifying the mechanisms by which co-solvents improve solubility and conductivity. Knowledge of the solubility of inorganic salts in organic solvents is needed to gain better understanding of solvation in organic media and to guide the development of organic electrolyte solutions for electrochemical applications. In contrast to the relative abundance of data on other properties of these solute-solvent systems (e.g., conductivity, heats of solution, transport numbers), there is a paucity of data on solubility.

The solubilities and solution densities of five potassium salts (KCl, KBr, KI, KSCN, $KClO_4$) are under study in five aprotic organic solvents: ethylene carbonate, propylene carbonate, butyrolactone, dimethylformamide, dimethoxyethane, and mixtures of these solvents. The solvents and salts used were commercially-available, reagent-grade. Solvents were dried with molecular sieves (Linde 4A), and the salts stored under vacuum over P_2O_5. Saturated solutions were prepared by adding an excess of the dried salt to the dried solvents in a capped vial. The vials were stored in a dessicator for at least a week and briefly shaken daily. The ethylene carbonate solutions were stored at 40°C. The other solutions were stored at room temperature (22-24°C). Solubility was determined by atomic absorption spectrometry.

The results obtained in this work compare favorably with literature values. The K_{sp} of KBr in DMF calculated from the solubility obtained in this work is 2.37. A value of 2.4 is reported by Parker.[1] The solubilities of several potassium salts reported by Harris[2] are up to 40% higher than those obtained in this work. Because Harris determined solubility by solvent evaporation, incomplete removal of the solvent could be responsible for the high solubility values.

References

1. A.J. Parker, J. Amer. Chem. Soc., 89, 3703 (1967).

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Polymeric Electrodes for Ambient-Temperature Lithium Batteries

(G.C. Farrington, University of Pennsylvania)

The objective of this project is to investigate the properties of intrinsically-conductive polyacetylene to determine its feasibility for use as electrodes in ambient-temperature rechargeable lithium batteries. Investigations of the electrochemical reactions and chemical stability of oxidized and reduced polyacetylene films were carried out using cyclic voltammetry, controlled-potential electrolysis, chronopotentiometry, resistivity measurements, thermogravimetric analysis, and differential-scanning calorimetry. Electrochemical measurements were

performed with propylene carbonate electrolytes containing $LiClO_4$ and $LiAsF_6$. The stability of unreacted polyacetylene as well as materials that had been oxidized chemically with bromine and iodine and electrochemically with AsF_6^- as the anion was also investigated.

Both virgin polyacetylene and samples that have been oxidized to the conducting state react readily with oxygen. At room temperature, the reaction irreversibly degrades the polymer, presumably by interrupting the conjugated double bond network essential for its high electronic conductivity. The reaction proceeds even more rapidly at elevated temperatures. Any technological application of polyacetylene must consider its rapid degradation upon exposure to air and moisture.

Polyacetylene $(CHX_y)_x$ was electrochemically oxidized to a composition of y=0.10 and subsequently reduced with an overall coulombic efficiency of 85-95%, but only if the electrolyte was highly purified and present in minimal quantity. At an oxidation level of 0.10, the potential of a polyacetylene electrode was about 3.9 V vs. Li/Li^+ in a $LiClO_4$-propylene carbonate solution. Further oxidation to higher levels was increasingly inefficient because of competing oxidation of the electrolyte.

When polyacetylene that has been oxidized was reduced at a current density of 0.5 mA/cm^2, about 50% of the stored charge was extracted before the electrode potential reached 2.5 V vs. Li/Li^+. The remainder of the charge was recovered at a slower rate during controlled-potential reduction at 2.5 V. Lower constant-current levels did not significantly increase the charge which could be recovered in the initial reduction step.

These results do not suggest that polyacetylene is a cathode material with extraordinarily high specific energy or power. What is not known is whether the limits observed here are intrinsic or due to the particular morphology of the samples that were used. If the maximum oxidation level could be increased to 0.20 or 0.30, the prospects for the use of polyacetylene cathodes in high specific energy non-aqueous cells might be considerably improved.

Publications

1. R. Huq, D. Frydrych, and G.C. Farrington, "Electrochemical Studies of the Polyacetylenes for Lithium Battery Applications," Extended Abstracts, Abstract No. 311, Fall Meeting of the Electrochemical Society, Detroit, MI October 1982.

Novel Membranes for Lithium Batteries

(M. Litt, Case Western Reserve University)

The objective of this project is to synthesize and characterize polymeric membranes for use in ambient-temperature rechargeable lithium batteries. Several synthesis routes were taken to produce membrane films of homopolymers and multiblock copolymers.

Pure polyethylene-glycol tosylate containing two tosyl ends per chain was prepared. Using this as initiator, an ABA triblock copolymer was made (A=5000, B=3500). The membrane was brittle and could not be oriented by stretching. Therefore, attention was focused on synthesizing multiblock copolymers of the type $(AB)_x$ which would have good mechanical properties. It was decided to prepare homopolymers containing two active ends and link the active ends using suitable coupling agents in order to obtain multiblock copolymers. Ethylene glycol bis triflate 2-isobutyl oxazoline adduct was prepared and used as an initiator to produce homopolymers with two active ends and narrow molecular-weight distribution.

Homopolymers of ethyl oxazoline were made and experiments to couple with benzimidazole were only partially successful, because reaction occurred only on one end. Hence, no molecular weight increase could be observed. However, all of the benzimidazole reacted. Coupling was observed and molecular weights increased as coupling progressed, with the following coupling agents: (1) Na salt of benzimidazole, (2) 4,4-diaminodiphenyl methane, (3) hexamethylene bis-aniline, and (4) triethylene glycol bis-aniline. However, the coupling reactions stopped before complete conversion with (2), (3) and (4). A triblock polymer, ethyl oxazoline-isobutyl oxazoline-ethyl oxazoline, containing active ends was reacted with hexamethylene bis-aniline; coupling occurred and an increase in molecular weight was observed. However, degradation of

the coupled product was observed while attempting to drive the reaction to higher conversions by continued heating. Pentablock copolymers were prepared by sequential addition of monomers, isobutyl oxazoline and ethyl oxazoline. Films from these polymers were found to have better mechanical strength than the triblock polymers. The propanoyl groups in these block copolymers were hydrolyzable by 4.7 M HCl.

2-isobutyl oxazoline was synthesized (procedure available in literature). Polymers made from this monomer melt crystallized very well, even when cooled very rapidly from the melt.

Efforts continue to synthesize $(AB)_x$ multiblock copolymer. The present effort is to convert the active end of the homopolymer of isobutyloxazoline into an amine end quantitatively and then react the homopolymer with polyethylene glycol tosylate.

Electrochemistry of the Sulfide/Polysulfide Couple

(R.J. Remick, Institute of Gas Technology)

The objective of this study is to obtain fundamental data on the redox behavior of solutions containing sodium sulfide and sodium polysulfide using a platinum-wire electrode. The experimental measurements showed that the equilibrium potential of the sulfide/polysulfide redox couple has a pH sensitive component. Experimental results indicate that platinum is not a good electrocatalyst for this couple, but upon anodization, a layer is formed on the surface of the platinum which imparts a reasonable catalytic activity to the electrode. A mechanism is proposed based on present results and past literature which accounts for most, if not all, of the observed phenomena.

F. CROSS-CUTTING RESEARCH

Bibliography of Convective Transport Correlations

(J.R. Selman, Illinois Institute of Technology)

The objectives of this project are (1) to search the scientific and technical literature for references on experimentally-established convective mass-transfer and heat-transfer correlations and (2) to abstract, index, review, and publish essential information as a bibliography useful for the detailed analysis of convective transport phenomena in energy storage systems.

A search of prominent electrochemical and chemical engineering journals from 1970 to 1982 was conducted. The computer search system DIALOGUE was used to aid the literature search. A total of 360 correlations were collected including those recorded in previous surveys of mass transfer correlations. (e.g., J.R. Selman and C.W. Tobias, Adv. Chem. Eng. 10, 211 (1978)). All mass-transfer correlations were classified according to a nine-digit number that reflected the flow and electrode characteristics of the mass transfer system.

The MIDAS system of Prime Computer, Inc., was adopted for data storage and retrieval. The MIDAS data file was created with Prime-supplied subroutines CREAK and KBUILD.

Annotated Bibliography of Battery Evaluations

(W.J. Walsh, Argonne National Laboratory)

This project focused on the preparation of an annotated bibliography of over 450 battery publications covering the period 1976 to 1982. The objective of this document was to summarize and place into perspective the principal battery evaluations published during this period. The compilation concentrated on systems studies, comparative evaluations, and assessments of battery technology. It is intended that this bibliography will facilitate the transfer of battery knowledge acquired during this period of intensive research and development.

A draft version of the bibliography was completed in 1982 and submitted to members of the battery community for review. Based on the reviewers' comments and suggestions, a final version of the bibliography was completed. A first printing of 100 copies is scheduled for early 1983.

Transition Metal-Oxide Coated Titanium Electrodes for Redox Batteries
(R.F. Savinell, University of Akron)

The objective of this research program was to investigate the electrocatalytic activity of transition-metal oxides for use as long life electrodes in redox batteries. A primary motivation for this work was to produce porous electrodes (of titanium) with reproducible surface activity for experiments to corroborate predictions of porous electrode theory. An additional goal of this research program was to ascertain if a simple one-step outer-sphere electron transfer mechanism applies to the ferric-ferrous redox reaction at high reactant/product concentrations in a strong acid chloride medium.

Low-overpotential exchange current densities of the ferric-ferrous couple were measured in concentrated solution (0.5 M Fe^{2+}, 0.5 M Fe^{3+}, 1 M HCl) on rotating-disk electrodes of Pt, RuO_2, and IrO_2. Significant corrections to the overpotential were necessary for ohmic effects, mass-transfer effects, and nonuniform current distribution. The data show that the electrocatalytic activity of RuO_2 (ks=1.92 x 10^{-3} cm/s) is comparable to that of Pt (ks=1.42 x 10^{-3} cm/s) while the activity of IrO_2 (ks=1.21 x 10^{-4} cm/s) is approximately an order of magnitude less than Pt. Since the measured free energy of activation was similar for all three substrates (5.4-5.8 Kcal/mole), a non-binding interaction between the redox couple and the electrode surface is suggested (i.e. outer-sphere transfer mechanism). The variation in exchange currents for the different substrates can be attributed to some extent on double layer effects but primarily to crystal structure differences.

Analysis and Simulation of Electrochemical Systems

(J. Newman, Lawrence Berkeley Laboratory)

The objective of this program is to improve the performance of electrochemical cells used in the inter-conversion of electrical and chemical energy. Experiments and mathematical models are designed to identify the physical phenomena that govern these systems. The phenomena involved may include hydrodynamics, convective- and diffusive-mass transfer, ohmic potential drop, charge transfer, and heterogeneous and homogeneous kinetics. A thorough understanding of the interactions among the phenomena governing a given system leads to mathematical models that agree with experiment and predict system behavior. The models are then useful in the identification of important parameters, and eventually aid in the design and scale-up of electrochemical systems.

Quantitative design and scale-up criteria are needed for battery systems. Presently, parametric or empirical studies are done to determine the effect of design variables on battery performance. A computer model that utilizes fundamental small cell data (or micromodeling data) is being developed that predicts the energy and power performance of a scaled-up battery. The model is general and may be applied to many types of battery systems. The battery can be optimized for maximum energy or power, or a compromise design may be selected. Inherent limitations of battery performance or specific areas of development requiring attention can be identified. In general, voltage and weight penalties of the current collectors, interconnecting bus and post, electrolyte, positive and negative active material, and cell container are taken into account. Subject to variation or prediction are the number of positive electrodes per cell, length of the bus and post, area of electrodes, current-collector weight, and total delivered capacity. These results are based on a correlation of dimensionless resistance vs plate area. This figure is curve fit and is used to generate the combined resistance of the electrochemical cell and current collecting grids as a function of depth of discharge. Accuracy to within 3 to 5% of a more sophisticated method is typically obtained.

Channel flow of electrolyte between two plane parallel electrodes is used in redox batteries and industrial processes such as metal refining and electroorganic synthesis. A mathematical model is being developed to predict the current and potential distribution in a channel-flow cell with an interelectrode gap on the order of, or thinner than, the diffusion layer thickness. That is, a product from one electrode reaches and reacts at the other electrode. One of the preliminary results of the model was a criterion to determine whether or not the thin-diffusion-layer approximation may be applied to a given channel flow cell. The model can take into account an arbitrary number of species and multiple reactions at the electrodes.

Experiments have been conducted to study the passivation behavior of iron electrodes. Experimental results obtained with a rotating-disk electrode revealed an anodic limiting current in aqueous acidic media. In an electrolytic solution of a given composition, the limiting current was found to be proportional to the square root of the disk rotation speed. For a given rotation speed, the limiting-current decreased with increasing electrolyte pH. Current oscillations have been observed within certain potential ranges on the limiting current plateau. The frequency of these oscillations has been found to be proportional to the square root of the disk rotation speed. Subharmonic current oscillations have also been observed under certain voltage and rotation speed conditions. Work is currently under way to develop a model describing the oscillatory phenomena. Physical phenomena judged to be important include iron dissolution kinetics, salt-film formation and dissolution, potential distribution, concentration profiles in the electrolyte, hydrodynamics, and the dependence of the passivation potential on surface conditions. The model will include a stability analysis using techniques involving limit cycles and bifurcation analysis.

An alternating-current impedance method is being used to study the anodic electrodissolution of a rotating zinc disk in an acidic chloride medium. Initially, the corrosion process must be characterized by establishing the dc polarization behavior. A model has been developed to analyze experimentally-obtained kinetic data. The model also determines the corrosion potential and current for a wide range of electrolyte compositions. Finally, the ac behavior must be studied. An ac impedance

experimental procedure, applicable over a wide frequency domain, is currently being developed. Information about the capacitive double-layer, along with the faradaic electron-transfer reaction will be obtained and analyzed.

Publications

1. Peter S. Fedkiw and John Newman, "Mass-Transfer Coefficients in Packed Beds at Very Low Reynolds Numbers," Intern. J. Heat Mass Transfer 25, 935 (1982).

Engineering Analysis of Electrochemical Gas Evolution

(C.W. Tobias, Lawrence Berkeley Laboratory)

Gas evolution is among the most common reactions in advanced rechargeable batteries and in electrolysis. The objective of this project is to establish the influence of electrode geometry and surface morphology, and of electrolyte composition, on bubble size and residence time, and to elucidate the role of free and forced convection as it affects overpotential behavior and ohmic resistance in electrochemical gas-evolution processes. A thorough understanding of the physical processes involved in the liberation and movement of gases at electrodes and in the electrolyte should lead to improved energy efficiency in rechargeable batteries and other electrochemical systems.

At a gas evolving electrode, surface molecules are produced and diffuse into the electrolyte, forming a supersaturated layer near the electrode. Bubbles are then nucleated and grow through coalescence and diffusion until they disengage from the surface and rise, causing a microscopic flow of electrolyte, thereby enhancing the transport of reacting ions and product species. A micromosaic electrode capable of generating individual bubbles and measuring their effect on transport processes has been developed in this laboratory. The utility of the device to record changes in the rate of mass transfer during a single bubble disengagement has already been demonstrated. However, the micromosaic electrode has been found to be susceptible to mechanical degradation and chemical corrosion, despite the special protective safeguards designed into the device. The degradation of the electrode, which is quite apparent from

an examination with an optical microscope, severely limits the useful lifetime of an electrode and makes it necessary to acquire the maximum amount of information from each experiment. To make this possible, a data acquisition system has been designed and built, and a program developed, for the on-line control of the mosaic electrode. The computer not only controls the input/output of data but it also has the capability of monitoring and controlling the growth of bubbles during experiments. The micromosaic electrode coupled to the data acquisition system was used to obtain more detailed information on changes in mass transfer rates resulting from a single bubble-disengagement event.

Publication

1. C.W. Tobias and Dennis Dees, "A Micro-Mosaic Electrode for the Study of Transport Phenomena at Gas Evolving Surfaces," Extended Abstracts No. 11-C-19, Vol I, p. 468. 33rd Meeting of the International Society of Electrochemistry, Lyon, France, September 10-15, 1982.

Modeling of Current Distribution with Active-Passive Kinetics

(C.W. Tobias, Lawrence Berkeley Laboratory)

Fundamental electrochemical-engineering data for the distribution of current is important in improving the efficiency and design of batteries and electrochemical systems. The present work is designed to extend the scope of current distribution modeling to encompass systems that involve active-passive kinetics. A case of special interest is the coexistence of distinct active and passive regions side by side on the same electrode. A finite-element model has been developed for cells that exhibit this phenomenon. As in previous models, the potential obeys Laplace's equation, but in this case the boundary condition at the anodes comprises an idealized active-passive, current-voltage characteristic.

For experimental verification of the model, a rotating-cylinder cell was designed and built. The highly asymmetric electrode arrangement promotes the coexistence of separate active and passive regions on an anode that is segmented to allow determination of currents by weight loss. Results for the dissolution of a Ni anode in 2.0 M H_2SO_4 + 1.0 M $NiSO_4$ electrolyte were obtained. The location of the active-passive boundary

was found to be stable, and the character of the current distribution followed expectations. The prediction from the model, using kinetic-overpotential data and conductivities appropriate to the experimental system, showed good agreement with the experimental current distribution.

Publications

1. C.W. Tobias and G.A. Prentice, "A Survey of Numerical Methods and Solutions for Current Distribution Problems," J. Electrochem. Soc., 129, 72 (1982), LBL-12191.

2. C.W. Tobias and G.A. Prentice, "Simulation of Changing Electrode Profiles," J. Electrochem. Soc., 129, 78 (1982), LBL-12192.

3. C.W. Tobias and G.A. Prentice, "Deposition and Dissolution on Sinusoidal Electrodes," J. Electrochem. Soc., 129, 316 (1982), LBL-12167.

4. C.W. Tobias and G.A. Prentice, "Finite Difference Calculation of Current Distributions at Polarized Electrodes," AIChE Journal, 28, 3 (1982), LBL-11058.

IV. ELECTROCHEMICAL PROCESSES

This project element has the objective to provide research to develop energy-efficient electrochemical conversion technologies. Several approaches to achieve this objective are considered in the TBR project. These include projects to (a) improve components for electrochemical systems such as separators (membranes), electrodes, and cell containers, and (b) research to improve the materials utilization and efficiency of electrochemical processes such as metal reduction, electroorganic synthesis, and water electrolysis. Efforts in area (b) have been phased-out of the TBR Project during 1982.

A. MEMBRANES

Multicomponent Transport Data for Concentrated Electrolytes

(T.R. Beck, Electrochemical Technology Corp.)

The objective of this work is to investigate general aspects of transport theory as well as to provide new data on mass transfer in Nafion membranes. The information obtained in this study will be useful for the optimum utilization of membranes in industrial electrochemical processes.

The phenomenological transport theory has been used to interpret the results of experiments using radiotracer ions. Self-permeability coefficients of sodium and chloride ions were determined for a Nafion 7-1100 membrane immersed in 1.0 N NaCl at 23°C. The flux of each radiotracer was also determined while a current was being passed. The results of these low-current-density experiments suggested that the transport properties of the Nafion membrane had changed at the moment current flow began. Furthermore, the transference numbers calculated from these experiments did not agree with those obtained by other means, under different experimental conditions.[1,2] Previous investigations of the dependence of transference number on current density have concluded that the principal effect is caused by concentration changes within the boundary layers at the membrane-solution interfaces.[3,4] Experimental results and calculations indicated that this type of "polarization"

effect was not the cause of the results observed with the present experiments conducted at low current densities. In order to investigate the hypothesis that transference numbers depend on current density and to extend the experiments to higher current density, a new apparatus was designed and constructed. The new cell is capable of operating with current densities of up to 1 A/cm^2 without exhibiting membrane polarization phenomenon, so long as the sodium chloride concentration exceeds 0.1 N.

Ion solubility coefficients have been determineed for sodium and chloride ions in Nafion. The results are within a few percent of previously reported data[1] but the "fixed ion" concentration appears to increase slightly as a result of membrane aging.

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Development of Multicomponent Transport Theory and Transport Data for Concentrated Electrolytes

(D.N. Bennion, Brigham Young University)

The objective of this project is to conduct mass-transport measurements with Nafion membranes using dialysis, high-pressure reverse osmosis, and conductivity cells. Measurements of the equilibrium data have been accomplished for $NaOH-H_2O$-Nafion membrane system. The data for 1, 4, 8, and 12 M NaOH at temperatures of 28°C, 50°C, 70°C, and 90°C were obtained by a combination of soaking, blotting, weighing, and analysis techniques. The parameters determined were (1) membrane anion concentration, (2) membrane water concentration, (3) membrane fixed ion concentration, and (4) wet membrane density. The water concentration in

the membrane decreased with the external NaOH concentration at a given temperature whereas the other parameters increased. At a particular external NaOH concentration, the water content increased with temperature. Electrodialysis and dialysis measurements have also been made at room temperature using a cell similar to one used by Pintauro.[1] However, the main problem was gassing of the electrode which made it extremely difficult to measure the volumetric flow through the membrane. Nickel and cadmium porous electrodes were tried unsuccessfully. On the porous Ni electrode, the gassing was not as great as that observed with Cd electrodes. The concentration difference and the volumetric flow rate through the membrane were measured. Using this information, the transference number was calculated, and the trend in the data was similar to that observed by Yeager.[2] There were slight leaks in the cell due to gassing; to overcome this problem, a weighing technique is now used.

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The Synthesis and Development of Novel Fluorocarbon Phosphoric Acid Polymers for Ion Exchange Membranes

(R.J. Lagow, University of Texas)

The objectives of this project are to investigate the synthesis and development of novel fluorocarbon-phosphoric acid polymers for cost-effective ion-selective membranes. The synthesis procedure

involves the direct fluorination of hydrocarbon polymers containing phosphonate functional groups.

A wide range of functionalized copolymers of bis(beta-chloroethyl)vinyl phosphonate and vinyl chloride have been successfully synthesized using a modified procedure of Gallagher and Hwa (J. Polym. Sci., Polym. Symp., 64, 329 (1978)). Using THF as a solvent, 6 mil thick cast films were obtained which contained approximately 30 percent bis-beta and 70 percent vinyl chloride. A glass transition temperature of 313 ^{o}K was observed.

Preliminary fluorination studies to determine the stability of the carbon-phosphorus bond were performed on the monomeric species, dimethylphosphonate. Some degradation was observed and milder fluorination conditions are now being used which will preserve the carbon-phosphorus bond. Experimental methods for determining the survival of functional groups in the cast polymer films indicates a high degree of functionality remaining.

The use of electron-beam radiation for cross-linking has also been investigated. Preliminary results indicate that the competing degradation reaction must be minimized.

B. AIR ELECTRODES

Transition Metal Macrocycles and Related Complexes as Catalysts for Oxygen Electrodes

(E. Yeager, Case Western Reserve University)

The objective of this research is to develop high-activity, stable catalysts for O_2 reduction in acid electrolytes using transition-metal macrocyclics and related complexes. The research involves a fundamental study of the kinetics of the O_2 reduction on the catalysts and to identify the most promising candidates for application in fuel cells.

The 4-electron reduction of O_2 without solution-phase peroxide as an intermediate depends on the particular transition metal and its redox characteristics, as well as steric factors including the possibility of dioxygen bridging. While various complexes have substantial catalytic activity in acid and alkaline electrolytes, they generally lack stability, particularly at elevated temperatures in concentrated acids. Sources of instability are under study and include demetallization, irreversible oxidation of the ligand, and slow loss of the adsorbed complex into the solution. Attempts were made to increase the stability by partial fluorination of the ligand but with little success. Currently various polymeric forms of the macrocyclic catalysts are being tried for increased stability.

An important development towards achieving long-term stability has been the partial pyrolysis of transition-metal macrocyclics. Some of the most active O_2 electrocatalysts have been prepared by heat-treatment of such complexes as the μ-oxo-iron(III) meso-tetra-p-methoxyphenylporphyrin $(Fe\text{-}TMPP)_2O$ (800°C), cobalt meso-tetra-p-methoxyphenylporphyrin, (Co-TMPP) (450°C), and polymeric iron-pthalo-cyanine $(FePc)_n$ (450°C) on a high-area carbon (e.g., RB carbon of the Pittsburgh Carbon Co.) for two hours in a N_2 atmosphere. So far, only short-term polarization measurements have been carried out with gas-fed electrodes. These show comparable or better activity for O_2 reduction (particularly with $(Fe\text{-}TMPP)_2O$ on de-ashed RB carbon) in 85% H_3PO_4 at 100°C and also 4-10 M NaOH at 40-100°C, as compared with high-area platinum-catalyzed carbon cathodes (e.g., Prototech).

Mossbauer and voltammetric studies have indicated major chemical and structural changes associated with such heat-treated samples. Other spectroscopic techniques (ESCA and ESR) as well as magnetic susceptibility will be used in the near future to assess chemical and structural changes in the pyrolyzed material. Pyrolysis of the metal-free macrocyclic without a transition metal present on the carbon surface does not lead to molecules with significant catalytic activity. The transition metal, however, need not be in the complex but can be added either as a separate salt or present in the high-

surface area carbon support during the pyrolysis.

The present view is that the heat treatment up to 900°C produces a nitrogen-containing pyropolymer with the transition metal acting as a catalyst for the pyrolysis. Some of the transition metal may also be adsorbed on the pyropolymer surface through nitrogen coordination and continue to function as a catalyst for the O_2 reduction.

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Electrode Kinetics and Electrocatalysis

(P.N. Ross, Lawrence Berkeley Laboratory)

The objectives of this project are to provide a fundamental understanding of electrocatalysis at metal electrodes and to conduct research to support the development of a bifunctional air electrode for metal/air systems. This research involves the study of Pt electrode surfaces by surface-analysis techniques and the measurement of corrosion rates of carbon blacks in alkaline solution.

The platinum/platinum oxide system is of special fundamental importance at present because of persistent speculation in the literature that cycling platinum electrodes through metal-oxide transformation disorders the metallic state[1,2] and creates an activated state of platinum.[3] LEED patterns were obtained for a

UHV-prepared Pt(100) surface that was contacted with 0.3 M HF at 0.4 V RHE, swept ten times at 100 mV/s between 0.02 and 0.82 V RHE and separated from the electrolyte while potentiostated at 0.4 V. Detailed analysis of LEED patterns of a Pt(100) surface that was cycled 10 times through the surface-oxide phase showed a vertically-dislocated terrace structure with a mean terrace width of 1.5 nm. The step dislocation density was ca. 3×10^{14} sites/cm^2, and the ordered (100) site density was 12×10^{14} sites/cm^2, i.e., about one atom in four is associated with a dislocation. A Pt(100) surface cycled only within the metallic potential region had a longer range order, with a dislocation density less than 5×10^{13} sites/cm^2, i.e. only one atom in twenty is associated with a dislocation. The effect of cycling into the oxide-formation potential region on the LEED pattern at the beam energy of 134 eV was examined. Cycling through the oxide phase introduced a significant concentration of high coordination sites into the low-index surface that could activate the surface for structure-sensitive reactions. However, oxygen reduction is not a structure sensitive reaction,[4] thus cycling Pt(100) does not activate the surface for this reaction.

Carbon black is used as a basic structural and current collecting material in a number of battery and fuel cell applications. In both the composite Ni electrode (e.g. Zn/NiOOH battery) and the bifunctional air electrode (e.g. Zn/air or Fe/air), the carbon black is at oxygen-evolution potentials during the charge cycle. The oxygen-evolution potential is nearly one volt anodic to the corrosion potential for carbon (graphite), and it is expected that the corrosion of the carbon black material in these electrodes would be a fundamental life-limiting factor.

Carbon-corrosion studies have been conducted using two different carbon-black precursors, acetylene black, and an HAF type furnace black (ASTM N330). TEM indicated heat treatment at 2700°C had little effect on the microstructure of acetylene black, which has a very heterogeneous structure that defies simple characterization. Heat treatment of the HAF furnace black resulted in dramatic

conversion from turbostratic to micrographitic, with little apparent loss of surface area (ca. 70 m^2/g). All four carbon materials had the same nominal BET surface area, but the corrosion rate varied significantly indicating as expected that microstructure is an important fundamental property. Considerable effort has been devoted to define an acceptable rate of corrosion of the carbon black material for battery application. No single clearly-defined rate has been established, but some qualitative guidelines have been established. Using the qualitative guidelines developed in this program, it seems clear that acetylene black is unacceptable for use in bifunctional air electrodes. Heat-treated HAF furnace black appears to have promising corrosion resistance that encourages further exploration of its use.

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Oxygen Cathodes for Energy Conservation and Storage

(L.J. Gestaut, Diamond Shamrock Corporation)

The objective of this project is to develop a cost-effective air electrode for use in chlor-alkali cells. Recent effort has been concentrated on the development of new, more chemically stable carbons prior to their fabrication into electrodes, and electrode testing in alkali electrolytes.

Experiments were conducted to determine the electrode failure mechanism. It was determined that the electrochemical isolation of carbon/catalyst aggregates was limiting the performance of the electrodes. This was manifested as a loss of the available carbon and catalyst areas for the oxygen reduction. The carbons used for the fabrication of the electrodes and the method of fabrication were both altered to control this phenomenon.

Early electrode life was poor, seldom extending beyond a few months. Due to the use of alternate carbons and the development of electrode structures to control the effects of electrochemical isolation, the electrode life increased. Through adaptation and expansion of the existing cell technology, the electrodes were operated in bench scale chlor-alkali cells. With these cells, it was determined that gas and electrolyte leakage could be controlled, that the peroxide levels generated within the catholyte could be accommodated by various changes, that the membrane could tolerate the catholyte, and that the cathode could operate in sodium hydroxide. This demonstrated the technical feasibility of air cathodes in chlor-alkali cells.

From this study it was concluded that the air cathode has been demonstrated as a feasible technology for the production of chlorine and caustic from chlor-alkali membrane cells. The use of the air cathode in these systems has been demonstrated to reduce cell electrical power consumption by approximately 25%. The electrodes utilized in these systems are satisfactory for initiation of the technology, but suffer from a gradual performance deterioration which eventually requires their replacement. Investigation of a variety of available carbons suggests that material that combines the necessary high activity with resistance to deterioration is not yet available. Such a material would greatly facilitate the further development of low-cost alkaline air cathode technology.

C. CORROSION

Polysulfide Containment Materials

(J. Battles, Argonne National Laboratory)

The objective of this task is to develop new alloys for positive-side current collectors and containment materials in Na/S and Li/FeS_2 cells, or other cells with high sulfur activity and high electrical potential at the positive electrode.

Initial investigation has focused on the corrosion in sodium polysulfide environments. For these experiments, in-house synthesis of high-purity sodium polysulfides (Na_2S_3, Na_2S_4, Na_2S_5) has been carried out. The synthesis procedure involves the slow addition of high-purity sulfur to reactor-grade sodium contained in a molybdenum crucible in the furnace well of an inert-atmosphere glovebox. The first stages of the reaction (up to about Na_2S_2) are extremely exothermic, and the temperature of the reaction is kept between 100-200°C by regulating the rate of addition of the sulfur. A final heating at about 280-290°C ensures a homogeneous product. Chemical analysis shows the product to be single-phase and greater than 99% pure.

The corrosion kinetics of AISI-1008 steel (a low-carbon, low-impurity iron) have been studied in various sodium polysulfides and pure sulfur. The kinetics follow a parabolic rate law in sulfur with a rate constant of 5.7×10^{-12} cm^2/sec. However, in the sodium polysulfides, the corrosion rate at any particular time is higher than in sulfur -- the rate increases as the value of x in Na_2S_x decreases. For example, after 20 hours, the corrosion rate is about twice as fast in Na_2S_4 as in pure sulfur, 3.5×10^{-7} cm/sec vs. 1.8×10^{-7} cm/sec. There is also an apparent mechanistic change in the corrosion reaction so that the kinetics no longer obey the parabolic rate law. The order of the rate law decreases as x decreases with the kinetics being apparently first-order in Na_2S_4 with a rate constant of 1.8×10^{-8} sec^{-1}.

D. METAL REDUCTION

Development and Testing of the Mathematical Model for the Hall-Heroult Cell

(J.W. Evans, Lawrence Berkeley Laboratory)

The purpose of this investigation is to reduce the energy consumed in the electrochemical production of aluminum. A mathematical model for the Hall-Heroult cell has been developed that computes the current distribution in the cell, the magnetic field, the electromagnetic stirring forces, the velocity field of the electrolyte and aluminum, the bowing of the interface, and the current efficiency.

Figure 1 depicts the conductors in and around six 185-kA cells forming part of two adjacent rows of cells (three cells shown in each row). The computed current efficiency for one of the cells is also given in the figure. The computed interface shape for the cell shown arrowed in Fig. 4 is depicted in Fig 5. The computed current efficiency and interface trough to peak distance are consistent with observations on actual cells.

During 1982 the mathematical model was used to predict the effect of design changes on cell performance. It was predicted that separating the rows of cells by a greater distance would be beneficial, but that increasing the separation between cells in a row would have little effect. The model successfully predicted the well-known inferior performance of cells at the end of rows. An interesting prediction was that the electrolyte/aluminum interface could be flattened considerably in a design in which current is removed through the bottom of the cell, rather than the sides (which is the present practice). Bowing of the interface is reduced by a factor of five for a cell of this nature.

Details of the mathematical model and the computer programs have been requested by three aluminum companies (Alcoa, Reynolds, and Martin Marietta) and have been transferred to them.

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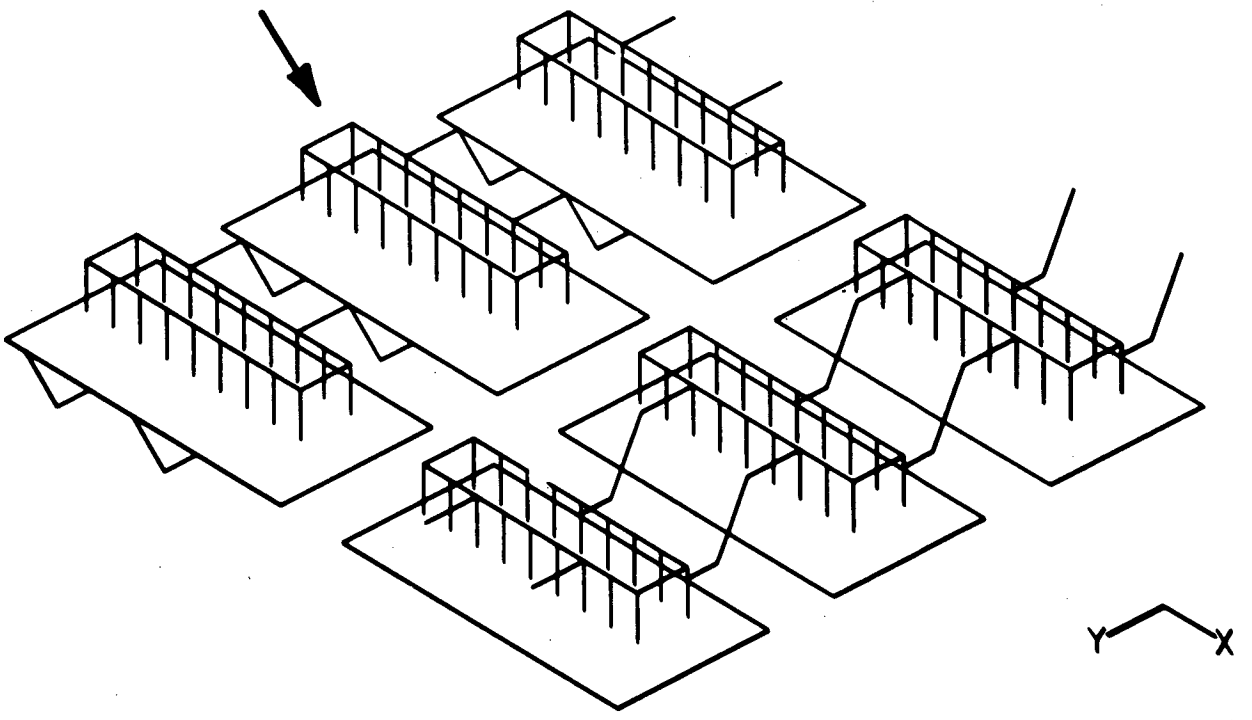

Fig. 4. Six 185 kA quarter riser cells in two potlines. Only the anode and cathode bus, risers, and anode rods for each cell are shown. Subsequent calculations are for the cell marked with an arrow and take account of the currents in all the conductors shown.

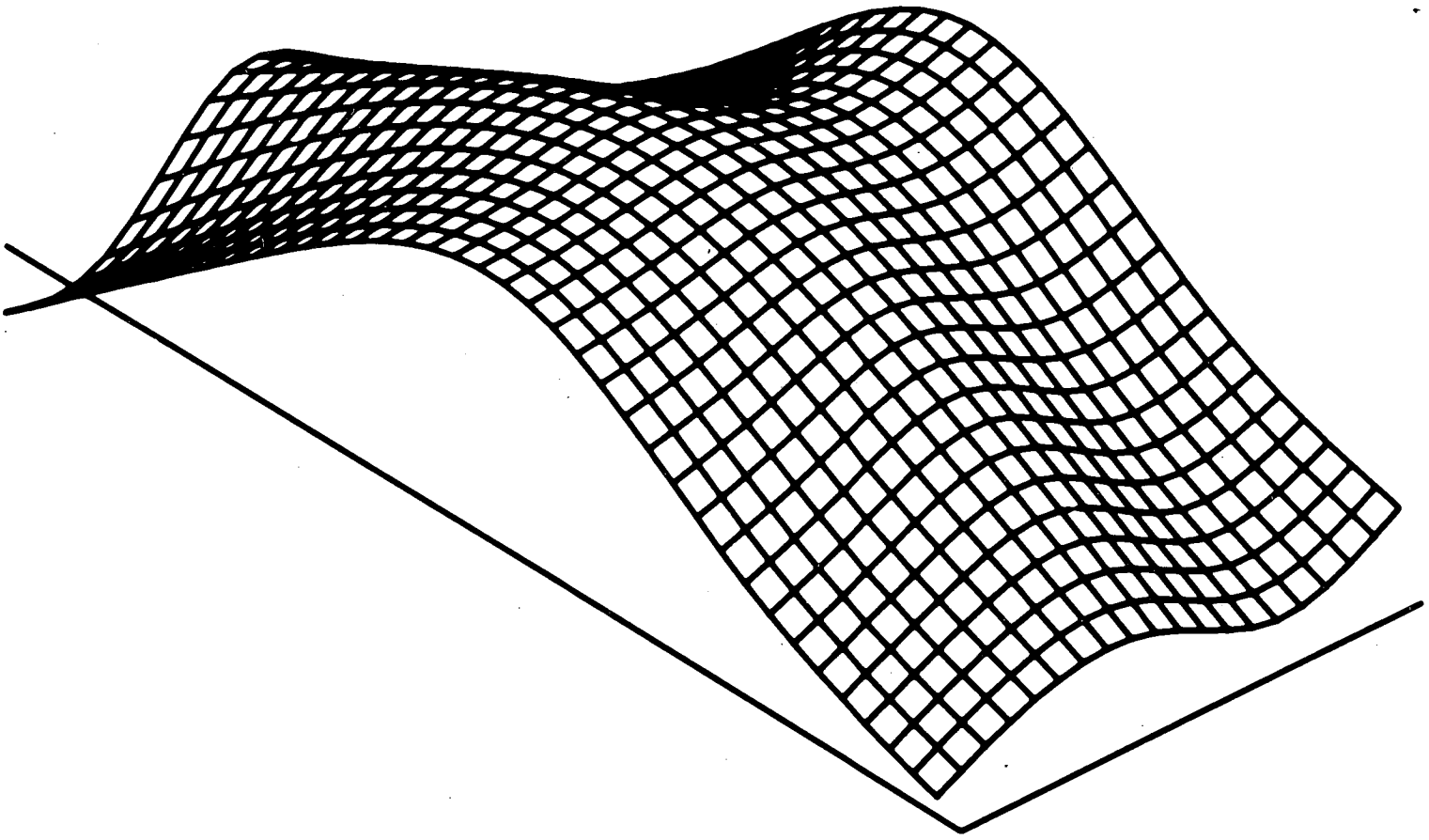

Fig. 5. The interface between aluminum and cryolite computed for the cell indicated in Fig. 4. Straight lines indicate a horizontal plane. The vertical scale is exaggerated by a factor of 40. Current flow in the potline is from upper right to lower left. The trough-peak distance is 8.8 cm.

Transport Phenomena in an Improved Electrochemical Cell Design for the Production of Magnesium

(D.R. Sadoway, Massachussetts Institute of Technology)

As part of a research program in fluid-flow phenomena in magnesium electroreduction cells, the effects of electrolyte contamination by both boron and sulfate were studied. Both contaminants decrease the current efficiency of the electrolysis cell and, thus, increase the specific energy requirements of the product magnesium metal. It is not clear how this happens, so the objective of the current research was to determine the mechanism of degradation of cell performance.

A laboratory-scale electrolysis cell that is representative of industrial conditions was constructed to permit visual observation within. Electrolysis experiments were conducted using an electrolyte with the composition of 10% $MgCl_2$, 10% $CaCl_2$, 20% KCl, and 60% NaCl at current densities of 5.55, 27.75, and 83.25 mA/cm^2. The effects of electrolyte contamination by 0.05% boron and 0.5% sulfur were studied by repeating the electrolyses with the addition of B_2O_3 and $MgSO_4$, respectively. The cathodic films deposited under these conditions were analyzed to determine how these impurities degrade cell performance.

Electrolysis was conducted galvanostatically. The cathode was low carbon steel, and the anode was graphite. Table I summarizes the cell performance data.

Table I. Cell Performance Data

Current Density (mA/cm^2)	Voltage with respect to Chlorine Electrode (V)		
	(a)	(b)	(c)
5.55	2.6	0.6	0.65
27.75	2.9	0.9	1.10
83.25	2.9	-	-

(a) uncontaminated electrolyte: 10% $MgCl_2$, 10% $CaCl_2$, 20% KCl, 60% NaCl.
(b) electrolyte (a) with B_2O_3 added to give 0.5% boron.
(c) electrolyte (a) with $MgSO_4$ added to give 0.5% sulfur.

For the uncontaminated electrolyte (column a), the results are in excellent agreement with industrial practice. The laboratory-scale appears to be representative of industrial-scale operations.

For the contaminated electrolytes (column b and c), cell voltages are too low to produce magnesium metal. With both contaminants, nonmetallic deposits were formed. The deposit produced from electrolyte containing 0.05% boron was found to consist of magnesium, boron, sodium, chlorine, and oxygen. This deposit, which consisted of many layers that easily peeled off, covered the entire cathode surface. The relative amounts of the elements identified suggest that MgB_x, MgO, Na_2O, $MgO_xH_yCl_z$, and $MgNa_yB_z$ could be present. The sodium levels are high enough to be consistent with possible codeposition of sodium. The deposit produced from the electrolyte containing 0.5% sulfur showed sulfur levels 13 times that in the electrolyte. Again, high levels of sodium were found in the deposit, which was extremely thin and fragile, and appeared to consist of MgO and MgS.

E. MISCELLANEOUS

Paired Organic Electrochemical Synthesis in Continuous Flow Cells

(M.M. Baizer, University of California at Los Angeles)

Conducting paired reactions in an undivided flow cell, in which reactions at both electrodes contribute usefully to the formation of final product(s), should be more energy-efficient than using two separate cells, one to prepare the cathodic product (with accompanying "sacrificial" anodic reaction) and one to prepare an anodic product (with accompanying "sacrificial" cathodic reaction). The objective of this project was to evaluate this concept by investigating a model system, the oxidation of glucose to gluconic acid and the reduction of glucose to sorbitol. Each of these processes has been separately practiced on an industrial scale.

It was established early in this program that in a mixture of glucose and the primary reduction product (sorbitol), the former is preferentially oxidized. Likewise the oxidation product (gluconic acid) is not reduced while glucose is being reduced at the cathode. Some anticipated problems were solved, e.g., choice of optimum pH and flow cell configuration, whereas others are currently being examined, e.g. a δ-gluconolactone/glucose redox cycle.

Three types of flow cells have been used in this study: a parallel-plate flow cell and two packed-bed flow cells, one with parallel current and electrolyte flow, the other with the current perpendicular to the solution flow. The optimum results obtained to date are shown in Table 1. The results indicate that the paired synthesis is feasible and can be conducted with minimal formation of by-products. The anodic current efficiencies and the yields of the oxidation product, gluconic acid, are very good. However, the cathodic current efficiencies and yields (sorbitol) are not yet as good as desired. Further improvements and the design of sensible separation methods for the products are being devised.

Table 1. Present Optimum Operating Conditions for the Glucose Paired Synthesis, Parallel Packed Bed Flow Cell

Cathode:	Zn(Hg)
Anode:	Graphite
Electrolyte:	0.8 M NaBr and 0.8 M Glucose
Applied Potential:	-2.1 V vs. SCE; Current density: 10 mA/cm^2
pH:	7.0
Temperature:	25^oC
Electrolyte Flow Rate:	0.8 l/min.
Current Efficiencies at 0.4 F/mole:	Sorbitol 20%, Gluconic Acid 65%
Product Yields at 0.4 F/mole:	Sorbitol 78%; Gluconic Acid 95%

Electrochemistry Applied to Thermal Conversion

(H. Chum, Solar Energy Research Institute)

The objective of this project is to evaluate thermally regenerative electrochemical systems (TRES) and to carry out research to define systems that might be applicable for conversion of low-grade heat to electricity. One task involved the organization of a specialists' workshop on TRES which included a thorough critical review of past and present work on TRES. Existing heat engines and those in development were reviewed for comparison. Even though electrochemical heat engines have been researched for at most 25 years, the workshop was successful in identifying some promising types of TRES. The papers and discussions presented at the workshop were published in a report (see below).

In the other task, electrochemical reactions with a reversal of potential near room temperature and which have large, opposite isothermal-temperature coefficients of the electrode potential were investigated. Regeneration by both heating and cooling were considered. Twelve redox couples of iron and copper and a variety of ligands were investigated in aqueous media. Several of the reactions investigated displayed large and opposite isothermal temperature coefficients, but in most of the couples investigated, the final TRES configuration would require a separator. Several of the redox couples could be used for electrochemical energy storage in redox regenerative batteries.

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Fuels and Chemical from Biomass Depolarized Water Electrolysis

(M. St. John, Institute of Gas Technology)

The principal objective of the program was to identify anode depolarizers, derived from biomass sources, that are capable of reducing the overall cell voltage for electrochemical hydrogen generation by replacing the oxygen evolution reaction with a thermodynamically more-

favorable electrooxidation of biomass materials. A secondary objective was to determine the reaction products from the anodic oxidation of the biomass materials. Two beneficial outcomes of the biomass electrooxidation were envisioned: (1) the synthesis of a desirable organic chemical from a biomass feedstock, and (2) the complete electrooxidation of the biomass to CO_2 which could have utility as a method of removal of unwanted or waste biomass from water. These beneficial anodic reactions would, of course, be occurring along with a desirable cathodic reaction, such as hydrogen generation at the counter electrode.

The biomass-derivable materials for anode depolarizers were selected from the two most abundant biomass materials groups, carbohydrates and lignins. In particular, glucose, its derivatives and its polymers were selected from the carbohydrate group. Lignins selected were those derived from the two principal pulping processes (sulfite and kraft). These biomass materials were surveyed for electrooxidative activity at varying experimental conditions of electrolyte (pH), anode material, and temperature. This variation in experimental conditions resulted in a great diversity of electrochemical behavior for the biomass materials selected, thus making generalizations difficult. However, all the biomass materials examined showed some anodic activity under some experimental conditions and potentials prior to oxygen evolution. The electrooxidations were always irreversible, and several reactions were often detected at potentials ranging from +200 to +1200 mV versus RHE and current densities from a few microamperes to hundreds of milliamperes per cm^2. Analysis of reaction products for the electrooxidation of glucose on Pt and lead ruthenate anodes showed that oxidation to CO_2 occurred. The highest electrochemical activity was obtained in alkaline electrolytes, followed by acid, and then neutral electrolytes. The greatest effect on the biomass electrochemical activity was observed by changing the anode material, thus indicating the catalytic nature of the reactions. The largest current densities for the electrooxidation of carbohydrates were obtained with Pd, Ni and lead ruthenate anodes, on the order of 200 mA/cm^2, making them likely electrode candidates for anode depolarizers. The short-term data suggest that cells generating hydrogen which employed carbohydrate or lignin for anode depolarizers could operate in the range of 600 to 1100 mV.

V. FUEL CELLS FOR VEHICLES

The objective of this project element is to evaluate the potential of fuel cell systems for use in transportation applications. Two major systems, the phosphoric acid fuel cell and the solid polymer electrolyte (SPE) fuel cell, are being evaluated. In addition, fundamental research to support these two fuel cell technologies is also being conducted at LANL and BNL. LANL has technical responsibility for the R&D effort and LBL has responsibility for overall program management.

a. Fuel Cells for Vehicles

(J. Huff and S. Srinivasan, Los Alamos National Laboratory)

The objectives of this program are (1) to conduct basic research in electrochemistry to explore and improve the potential of fuel-cell systems for use in transportation application; and (2) to conduct applied research necessary to bring fuel-cell technology to an established proof-of-concept level. Research efforts were directed at electrode kinetics and electrocatalysis of fuel cell reactions, characterization of electrodes, physicochemical characterization of electrolytes, evaluation of electrode and fuel cell performance under simulated vehicle operating conditions, and fuel cell system simulations.

Electrode Kinetics and Electrocatalysis

The effects of electrolytes such as trifluoromethanesulfonic (TFMSA), phosphoric, perchloric, and sulfuric acids (all at pH = 0) and potassium hydroxide (at pH = 14) on oxygen reduction kinetics at 25 ± 1°C at platinum using the rotating ring-disc electrode technique were investigated. Figure 6 shows the mass transfer corrected Tafel plots, which are independent of rotation speed in the 400- to 3600-rpm range. In the region from 0.6 to 0.8 V for acid and 0.75 to 0.9 V for alkaline media, the Tafel slope is 120 mV. This result has also been obtained by other authors[1,2] and indicates that the overall reduction of oxygen is controlled by the first charge-transfer step under Langmuir adsorption conditions. For potentials lower than 0.5 V, the current seems to reach a limiting value. However, this region was not investigated more

closely because the potential lies outside the range of interest for fuel cells. In the potential region where the Tafel slopes are 120 mV, the current density is higher in the alkaline electrolyte than in the acid electrolytes and follows the sequence KOH > H_2SO_4 ≅ TFMSA > H_3PO_4 > $HClO_4$.

Mechanistic studies of oxygen reduction indicated that oxygen reduced predominantly (80 to 97%) to water through the 4-e transfer reaction. However, the results of this work did not substantiate the claims that more H_2O_2 is formed in alkaline media.[2]

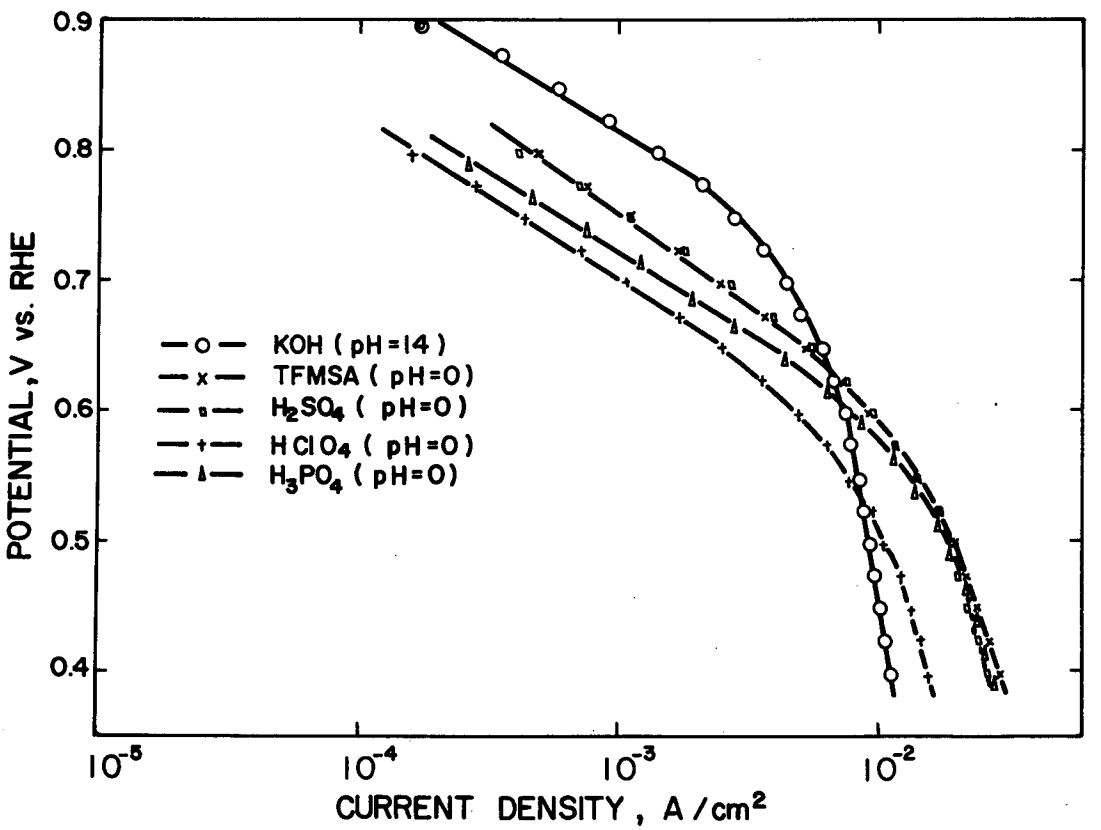

Figure 6. Mass transfer-corrected Tafel plots for oxygen reduction on platinum at 25°C.

Characterization of Electrodes

The ion-beam analysis technique was developed for measuring the platinum distribution in new and used fuel cell electrodes.[3] Using the ion microprobe, it was possible to measure the platinum and other component distribution with 5-μm spatial and 2-μm depth resolution.

Experimental data demonstrated that it is possible to profile the platinum concentration throughout the active region of the electrode. Therefore, it was decided to examine the platinum distribution in a postcatalyzed electrode using the Rutherford backscattering technique. The Rutherford backscattering measurement showed a surface peak and increasing concentration with depth (Figure 7). By taking data points 50 μm apart along the surface of the electrode, the platinum concentration vs depth vs linear position was determined. Figure 8 represents an isometric view of this data. The platinum distribution is quite nonuniform, indicating that such post-catalyzed electrodes do not use platinum efficiently.

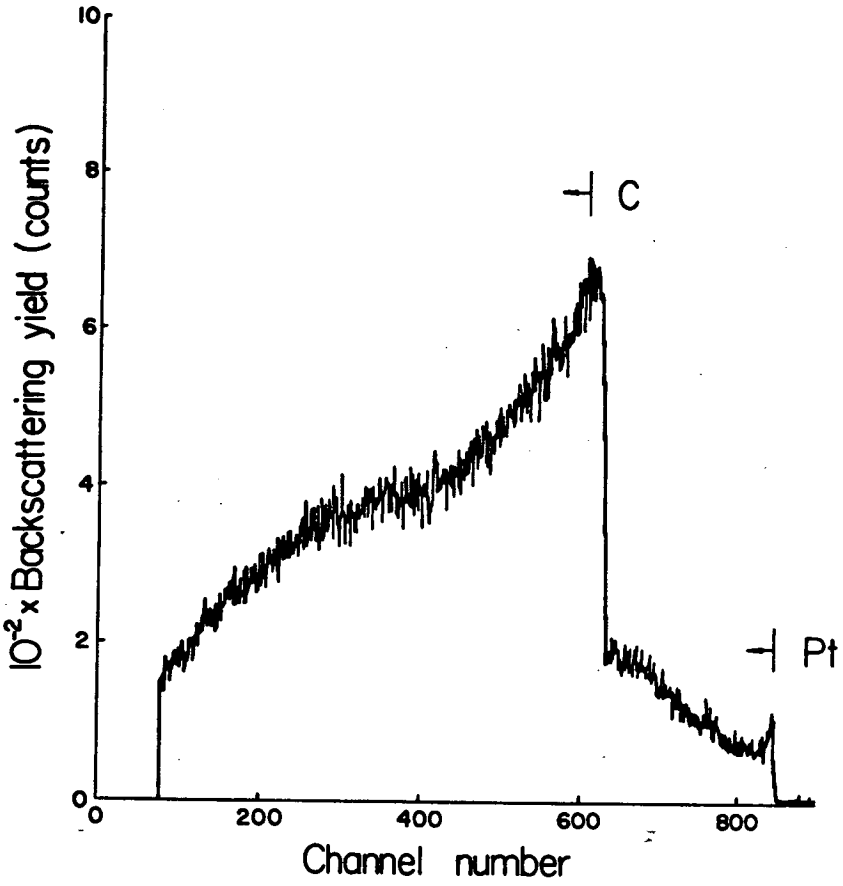

Figure 7. Rutherford backscattering spectrum for a postcatalyzed cell electrode.

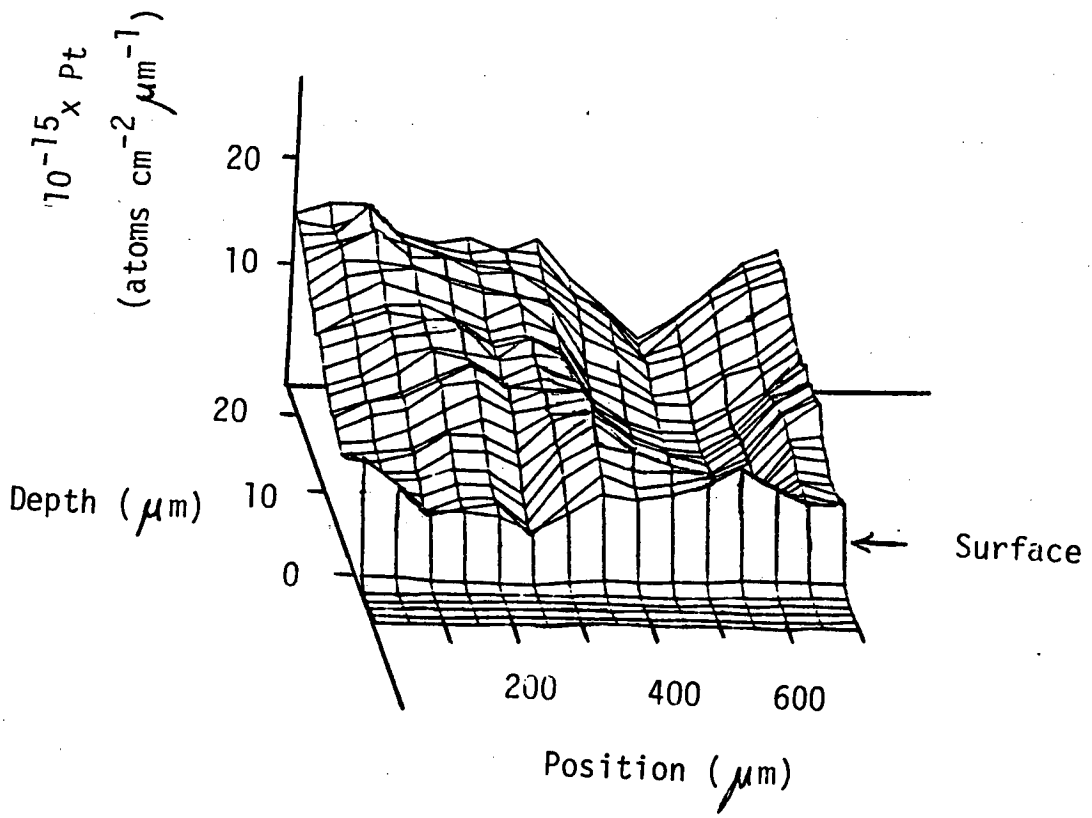

Figure 8. Isometric view of the platinum distribution in a postcatalyzed fuel cell electrode.

This technique was also used to measure the depth distribution of two different mass elements simultaneously. Intermetallic catalysts such as PtV were examined for stability under operating conditions within the electrode. New and used fuel cell anodes and cathodes containing PtV electrocatalyst and platinum electrocatalyst, respectively, were obtained from Energy Research Corporation. The results for a new electrode and for one used 3000 h in a fuel cell showed that, in the used electrode, no vanadium was found in the cathode; instead, it was found in the matrix very close to the anode. Apparently the PtV electrocatalyst is not stable under operating conditions; vanadium dissolves in the electrolyte and is transported through the matrix to the anode. These results are consistent with the observed performance degradation of the fuel cell.

Physicochemical Characterization of SPE Membranes

Proton nuclear-magnetic resonance was used to explore water parameters within Nafion membranes. A section of EW-1200 Nafion was cut into strips 8.1 cm x 0.63 cm x 0.025 cm (dry weight of 0.250 g). The samples were boiled in distilled water for 2 hours and then immersed in 1.0 M HCl, 1.0 M KCl or 1.0 M NaCl for 2 hours at room temperature. The individual strips were surface dried and then tightly coiled for insertion into standard NMR tubes. By suitable manipulation, either a single coil or two coils could be positioned in the instrument's measurement zone. Relaxation-time measurements were made using the method of pulse decay, where the time-averaged signal-intensity is measured at fixed periods following the introduction of the perturbing pulse. Then the signal intensity function is plotted as a function of the delay time. Alternatively, the long relaxation times of the three bulk solutions were measured by the null method, a more useful method for long relaxation times.

Each Nafion polymer strip contained 2.1×10^{-4} moles of ions. These ions, a cation coupled to the SO_3^- group, are solvated with different quantities of water at each exchange site, somewhat higher than previous literature values. Less water is incorporated for sodium- and potassium-containing solutions. Using empirical parameters (Dupont), calculations show that Na^+ ions involve a 13:1 water molecules per site

ratio while K^+ ion results in a ratio of 9:1. These values are only approximate because actual moisture content is not easily determined and because the empirical constants are written in terms of volume and not mass. Although one polymer sample strip gave sufficient NMR signal intensity for the H^+ solution, two were required for Na^+ and K^+, reflecting the lesser amounts of water held within the latter polymer samples.

Relaxation data showed that the relaxation times for H^+, Na^+, and K^+ are 93, 318, and 296 ms, respectively. (Replicate measurements suggest an error of ±5%.) These initial results indicate that water incorporated in Nafion is widely dispersed through the polymer system and that water relaxation times are influenced by particular cations, with protons giving extremely short values. Variation of water content, caused by either a change in temperature or by alteration of the polymer structure, results in significant changes in the effective solvation number. These preliminary experiments demonstrate that NMR measurements are useful for probing water parameters within SPE membranes.

The electron microprobe and scanning electron microscopy were used to study samples (supplied by General Electric) of a freshly-prepared membrane and electrode assembly and one that had been used in fuel cell operation (with hydrogen-oxygen gases) for 2000 hours. The electron microprobe was also used to map the sulfur profiles through these Nafion samples by moving the electron beam between the two platinum-carbon electrocatalytic layers. It was thought that chemical degradation, either from peroxide attack (generated in trace amounts at the cathode) or from localized heating, might result in attack at either the carbon-oxygen (ether) or carbon-sulfur bonds. In either case, soluble short-chain aliphatic sulfonic acids would result, leading to a decrease in sulfur content. Although these data showed considerable scatter, resulting in part from electron beam heating of the low thermal conductivity polymeric matrix, no apparent alteration in sulfur content was apparent in the two samples when the sulfur map was reviewed.

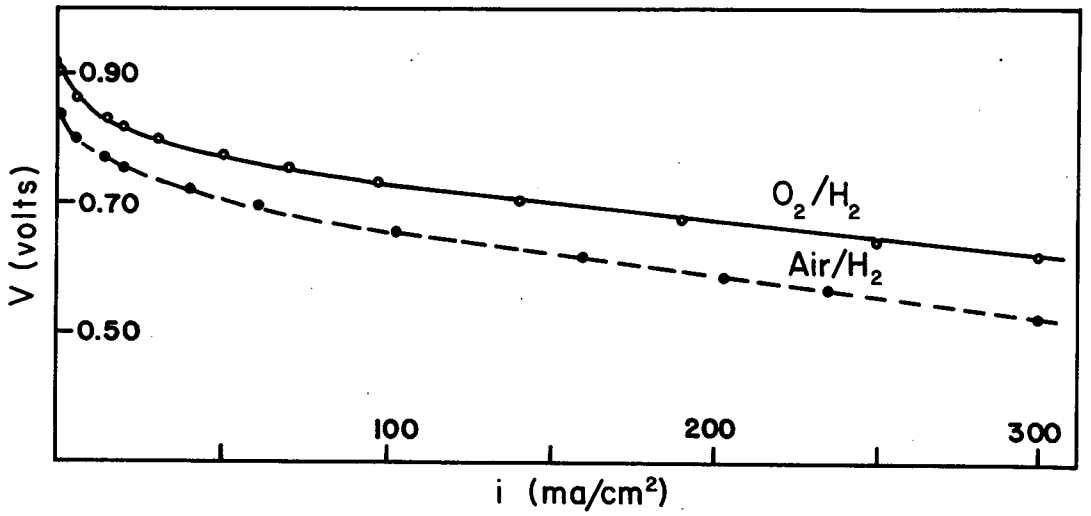

Figure 9. Single cell potential-current density curves after 4 months of continuous operation.

Fuel Cell Testing

Efforts were made to develop single cells that will exhibit stable performance during long term operation (about 3 to 4 months) under constant load for use in investigations of fuel cell performance under simulated vehicle operating conditions. The cell design that evolved incorporated an electrolyte reservoir and electrolyte presaturators.

A single cell assembled with electrodes and a Kynol matrix (Energy Research Corporation) operated continuously with hydrogen and air as the reactants for 4000 hours. The potential-current density relation of this cell after 4-month operation on hydrogen and air is shown in Figure 9. During the first 800 hours of operation, the power density showed a slight increase with time. Thereafter, the power density shows hardly any variation with time. The power density was 130 mW/cm^2 with hydrogen and air as reactants. On switching from air to oxygen, the corresponding power density was 170 mW/cm^2.

Fuel Cell Systems Analysis

A steady-state calculation was completed that provides the heat and mass flows for an indirect methanol fuel cell. A constant methanol-water premixed feed enters an evaporator, where the liquid mixture is converted to the gaseous state, then to a reformer operating at 200°C, and finally to the anode compartment of the fuel cell stack. The fuel cell operates at a constant 20-kW level, supplying a combined constant load of traction motors (through a power conditioning set) and secondary batteries (if necessary for start-up or acceleration). Waste heat is discharged from the stack in two forms, chemical energy contained in exhausted hydrogen (the "anode vent") and thermal energy removed from the operating stack through a combination of excess air and the stack cooling system. This secondary heat is discharged at the operating temperature of the fuel-cell stack, 200°C for the phosphoric-acid system, 104°C for the SPE assembly, and approximately 85°C for the TFMSA system.

Although the anode waste heat stream is low in energy content, combustion with a stoichiometric amount of ambient-temperature air generates useful temperatures for auxiliary processing. Assuming that a typical anode exit stream consists of 59% H_2O, 11% H_2, and 30% CO_2 at a temperature of 104°C, combustion of the mixture with oxygen results in a temperature (adiabatic) of 750°C. This temperature is sharply dependent upon flow rates and heat-exchanger geometry; however, it is assumed that the anode stream can provide energy to drive the reformer at 200°C even when the fuel cell system is operating at lower temperatures, such as the 104°C SPE case described above.

The calculation of heat generation and consumption rates for a constant output of 20 kW shows that the total heat generated by the fuel cell increases sharply with current density. The thermal energy contained in the anode vent increases as well because, as the current density increases, a higher mass flux of hydrogen is required, and the code assumed that a constant fraction of that gas was utilized within the stack.

The calculation showed that thermal energy generated by anode vent combustion is generally sufficient to meet thermal requirements for the fuel-conditioning step under all anticipated load requirements. This is not true if the vaporization step is included in the fuel conditioner energy balance. However, methanol vaporization at 65°C (1 atm) with a high heat of vaporization (9.37 kcal/gm mol) can be driven with waste heat even from the 85°C TFMSA fuel cell stack. Of course, a premixed fuel cannot be reliably vaporized with such low-temperature heat. In such cases, some methanol will have to be burned to drive the fuel vaporization step. Methanol utilized in this way decreases system efficiency. This analysis suggests that the two forms of waste heat are best utilized separately, first to vaporize the fuel streams and then (the anode vent) to supply process heat for the reforming step. In this way, the fuel cell stack provides the required thermal energy for onboard reforming of methanol.

The efficiency of the integrated system decreases linearly with increasing current density from 200 to 600 mA/cm^2. These calculations do not include parasitic losses such as cooling fan motors; at these decreased efficiency levels, cooling power must be increased. These parasitic losses, when included in these calculations, will exacerbate the efficiency decrease. Using the above assumptions, higher efficiencies (approximately 50%) result only at modest operating current densities regardless of the fuel cell system. If a 100 mV improvement in fuel cell potential is attainable, the calculations indicate that system efficiency will increase approximately 10% uniformly through the operating range, approaching 60% thermal efficiency at lower values of current density. Continued improvements reach a limiting situation because eventually insufficient heat is generated to drive the fuel processing system, and direct methanol combustion is again required to drive this initial chemical step.

Fuel Cell Vehicle System Simulations

System simulations were performed for selected heavy-duty transportation systems, consumer vehicles, and buses using the Los Alamos fuel cell vehicle simulation program. The heavy-duty transportation studies

were done to determine the feasibility of using fuel cell power plants in locomotives and river tow boats. Additional consumer vehicle simulations were performed to provide data for planning the 20-kW phosphoric acid base line power plant test. Bus simulations with SPE fuel cell systems were performed for comparison with the bus systems studies previously done with phosphoric acid fuel cells.

The fuel cell power plants considered for the heavy-duty applications were an advanced phosphoric acid system and an SPE system. Two types of trains were simulated, each with both fuel cell systems.[4] A five-locomotive expedited freight train pulling 4000 gross (2750 net) tons in 50 cars at 70 mph and a two-locomotive slow freight pulling 8000 gross (6000 net) tons in 80 cars at 45 mph were considered. Comparison of train energy consumption (Btu/net ton-mile) for the two fuel cell power plants with diesel energy consumption yielded energy savings of 100% for the slow freight and 50% for the expedited freight. Thus, the two fuel cell power plant systems appear promising for use in locomotive applications.

The push-tow boat was simulated for operation from Pittsburgh to New Orleans on the Ohio and Mississippi Rivers. Average energy consumption for upstream and downstream operation was determined. When compared to diesel operation, there was no apparent advantage to using fuel cells as power plants for the push-tow boat.

Consumer vehicle systems using a 20-kW phosphoric acid fuel cell were simulated to help define requirements for a 20-kW power plant test. One facet of these studies was to determine if it would be feasible to use enough batteries to provide acceleration peaking for a small pickup truck, a heavier vehicle than the X-car used in earlier simulations. It had been established in previous simulation studies that the addition of batteries for peaking leads to a system in which the batteries naturally also provide a larger proportion of the cruising power. This suggests that a pure fuel cell power plant, using batteries only for start-up, is the optimum approach to fuel-cell electric-vehicle propulsion. The truck results were typical for systems with a large battery complement and indicated that it would not be profitable to attempt to run the

vehicle with a hybrid system using a substantial battery contribution.

Two SPE fuel cell systems in a city bus were simulated for comparison with phosphoric acid systems simulated previously. One SPE system used reformed methanol as the fuel, and the other used hydrogen. The simulations were run over a modified composite Department of Transportation drive cycle that has been used to measure diesel fuel consumption. The fuel consumption in miles per gallon of diesel fuel equivalent that was obtained in this analysis are:

System	mpg Diesel
Diesel (measured)	3.92
Target PAFC[a]	5.52
Advanced PAFC[a]	7.28
SPE, methanol	6.99
SPE, hydrogen	7.39

[a] Phosphoric acid fuel cell.

Methanol Reformer Analysis

A 2-kW methanol reformer was studied to evaluate reformer requirements for transportation applications. There was considerable difficulty in reliably initiating automatic combustion and maintaining catalyst temperature. Several modifications were made to the reformer in an attempt to remedy these problems. They included replacing the burner nozzle with one designed to atomize water at fuel rates and pressures closer to vehicle requirements, relocating the glow-plug igniter, and repositioning the burner nozzle to prevent vapor lock. Although these modifications did improve the ability to dependably ignite the fuel mixture, there remained considerable difficulty in controlling and sustaining combustion and, therefore, in controlling catalyst temperature in the reactor portion of the reformer. Because it is essential that the fuel processing system start and perform reliably and efficiently, the reformer will be fully instrumented and studies of its strengths and weaknesses in both steady-state and transient operation

carried out. Data obtained will be used to guide future reformer designs for vehicular applications.

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4. J.R. Huff and H.S. Murray, "Feasibility of Fuel Cells for Selected Heavy-Duty Transportation Systems," Los Alamos National Laboratory Report LA-9488-MS (October 1982).

Publications

1. H. Olender, J. McBreen, W.E. O'Grady, S. Srinivasan, and K.V. Kordesch, "Design of a Fuel Cell for Electrode Kinetic Investigation of Fuel Cell Reactions," J. Electrochem. Soc. 129, 135 (1982).

2. J.R. Huff, J.B. McCormick, D.K. Lynn, R.E. Bobbett, G.R. Dooley, C.R. Derouin, H.S. Murray, and S. Srinivasan, "Application of Fuel Cells to Highway and Nonhighway Transportation," Symposium Proceedings of the IGT Fuel Cells Technology Status and Applications Meeting, Chicago, Illinois, November 16-18, 1981 (Institute of Gas Technology, Chicago, May 1982).

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4. E.R. Gonzalez and S. Srinivasan, "Electrochemistry of Fuel Cells for Transportation Applications," Proceedings of the World Hydrogen Energy Conference IV, Pasadena, California, June 13-17, 1982.

5. C.J. Maggiore, "The Nuclear Microprobe - Investigating Surface with Ions," Los Alamos Science 3-2, 27-45 (Summer 1982).

6. D.K. Lynn, J.B. McCormick, R.E. Bobbett, and J.R. Huff, "Acid Fuel Cell Technologies for Vehicular Power Plants," Proceedings of the 17th Intersociety Energy Conversion Engineering Conference, Los Angeles, California, August 8-13, 1982.

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8. J.R. Huff and H.S. Murray, "Feasibility of Fuel Cells for Selected Heavy-Duty Transportation Systems," Los Alamos National Laboratory Report LA-9488-MS (October 1982).

9. E.R. Gonzalez and S. Srinivasan, "The Adsorption of Trifluoromethanesulfonate Anions on the Mercury/Electrolyte Interface," Electrochim. Acta 27, 1425 (1982).

b. Advanced Chemistry and Materials for Fuel Cells

(J. McBreen, Brookhaven National Laboratory)

The objectives of this work are to evaluate electrocatalysts that minimize or eliminate the need for noble metal catalysts in fuel cells and to investigate the enhancement in the kinetics of oxygen reduction and the kinetics of oxidation of hydrogen/carbon monoxide mixtures in alternative acid electrolytes. The efforts were focused on the measurement of the kinetics of oxygen reduction, the preparation and characterization of metal phthalocyanine electrocatalysts, and the examination of the solid polymer electrolyte (SPE)/platinum interface.

In this program a careful study was made of the reaction order with respect to pH for the reduction of oxygen in H_3PO_4, $HClO_4$ and CF_3SO_3H. It was found that the correct value of the reaction order is 1. In H_3PO_4, the main difficulty in determining the mechanism is the apparent variation of the transfer coefficient with temperature.

Several tetrasulfonated metal phthalocyanines (M-TSP) were prepared employing the metals Fe, Co, Ni, Mn, Ir and Rh. Synthesis was carried out using the template reaction scheme where sulfothalic acid and the metal salt were reacted together with a molybdenum catalyst in nitrobenzene at elevated temperature for 5-7 hours to form the compound. The first-row transition metals Mn, Fe, Co, and Cu all reacted and formed the desired compounds in high yields. In the case of Ir and Rh, only a small yield was achieved, and the synthesis had to be modified. Extraction of the final product was extremely difficult and was achieved only using paper chromotography techniques. Synthesis of the Ru compound, was unsuccessful. The tetrasulfonated phthalocyanines were soluble in water. Monolayer coverages with the M-TSP on a current collector could be achieved by dipping a pyrolytic graphite disc electrode in a M-TSP

solution. The result was an adherent and stable layer of the phthalocyanine on the graphite. The oxygen reduction activities of the M-TSP in 0.1 N TFMSA was found to decrease in the order Fe > Co > Mn > Ni. In the case of CO and HCOOH oxidation, no activity was found for any of the first-row complexes. In preliminary runs, some initial activity was found for CO oxidation on Ir-TSP. However, when further purified, no activity was observed. No measurements were made on the Rh-TSP because of problems in purifying the compound. The initial work on phthalocyanines has shown considerable promise. Work is now devoted to improving the synthesis and purification techniques. A sublimation apparatus for electrode preparation has been set up.

A cell for maintaining reproducible electrode/electrolyte contact was made to investigate the SPE/electrode interface. Provisions were made for reference electrode measurements, and the cell also had special provisions for pre-humidification of gases and could be operated at temperatures up to 120°C and pressures up to 10 atmospheres. Preliminary studies were made on the Nafion 1200/platinum interface. These investigations included cyclic voltammetry in inert atmospheres, oxygen reduction and hydrogen oxidation. Typical cyclic voltammograms on platinum in contact with a Nafion 1200 membrane showed many features similar to those found in purified TFMSA electrolytes. At elevated temperatures (~70°C) there is an adsorption process on the platinum in the potential region where oxygen reduction normally occurs (~0.6V NHE). In addition, elevated temperature affects the formation of oxides on platinum. There is little temperature effect in the hydrogen adsorption region, other than a shift of the adsorption peaks.

The Tafel slope for oxygen reduction at the SPE/platinum interface at 70°C is ~RT/F. The reaction order with respect to oxygen pressure is unity. Thus, the oxygen reduction mechanism at the SPE/platinum interface is quite different from that in H_3PO_4. This presumably is due to the absence of anion adsorption on the platinum. The kinetics for hydrogen oxidation at the SPE/platinum interface are much faster than that found for oxygen. The Tafel slope is ~RT/2F. The reaction order with respect to hydrogen pressure is one half.

Publications

1. H. Olender, J. McBreen, W.E. O'Grady, S. Srinivasan and K.V. Kordesch, "Design of a Cell for Electrode Kinetic Investigations of Fuel Cell Reactions," J. Electrochem. Soc. 129, 135 (1982).

2. H. Olender, W.E. O'Grady, H.S. Isaacs, S. Srinivasan, and A.C.C. Tseung, "Electrochemical Methods for In Situ Regeneration of Active Surfaces Area of Aged Fuel Cell Type Electrodes," J. Applied Electrochem. 12, 135 (1982).

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Subcontractor Financial Data - CY 1982

Subcontractor	Principal Investigator	Project	Contract Value (K$)	Duration (months)	Expiration Date
ELECTROCHEMICAL SYSTEMS					
New Systems					
ANL	M. Roche	$Na/NaNO_3$	250	12	9-82
University of Tennessee	G. Mamantov	$Na/SCl_4(NaCl-AlCl_3)$	85	16	1-83
Duracell Internatinal, Inc.	A. Dey	Li/SO_2	1500	39	12-84
EIC Laboratories, Inc.	B. Brummer	$Li/Sulfolane/TiS_2$	97	12	3-83
Metal/Air					
Westinghouse Company	E. Buzzelli	Fe/Air	1175	37	2-83
Case Western Reserve University	E. Yeager	Bifunctional Air Electrode	367	28	2-83
LLNL	E. Behrin/J. Cooper	Al/Air R&D	820	12	9-82
Lockheed Missiles and Space Co.	E. Littauer	Al/Air Hardware	223	11	3-83
Diamond Shamrock Corporation	I. Malkin	Air Cathode	200	14	12-82
Aluminum Company of America	F. Williams	Electrolyte Control R&D	272	24	12-82
Reynolds Metal	D. Scott	Al Anodes	24	2	5-82
SUPPORTING RESEARCH					
LBL	E. Cairns, L. DeJonghe, J. Evans, R. Muller, J. Newman, P. Ross, and C. Tobias	Electrochem. Energy Storage	1000	12	9-82
Alkaline					
Lockheed Missiles and Space Co.	T. Katan	Reaction Profiles	65	17	9-83
Energy Research Corporation	A. Charkey	Insoluble Zn Electrode	102	12	4-82
Castle Technology, Inc.	J. P. Pemsler	Liquid Membranes	65	12	3-83
SRI International	M. McKubre	Electrode Kinetics	46	12	2-82
Ohio State University	D. Macdonald	Cell Thermodynamics	36	15	3-83
Ohio State University	D. Macdonald	Electrode Restructuring	53	12	12-83
Zinc/Halogen					
Illinois Institute of Technology	J. R. Selman	Zn Deposition	94	29	8-83
BNL	J. McBreen	Zn Morphology	100	12	3-83
LLNL	D. Miller	Transport Properties	55	12	12-82
Molten-salt					
ORNL	J. Braunstein	Li/FeS Composition Profiles	50	12	9-82
Gould, Incorporated	H. F. Gibbard	Li/FeS_2 Thermal Management	100	12	6-83

Subcontractor Financial Data - CY 1982

Subcontractor	Principal Investigator	Project	Contract Value (K$)	Duration (months)	Expiration Date
Stanford University	R. Huggins	New Battery Materials	334	14	11-82
ANL	R. Steunenberg	Molten Salt Cell Research	750	13	11-82
Solid Electrolytes					
Rockwell International, Inc.	F. Lange	Improved $\beta''Al_2O_3$	120	12	4-83
Massachusetts Institute of Technology	B. Wuench	Superionic Conductors	66	12	3-83
Massachusetts Institute of Technology	H. Tuller	Li Conducting Glasses	88	12	10-82
ANL	S. Susman	Na Conducting Glasses	80	12	11-82
Ambient-Temperature Lithium					
University of Pennsylvania	G. Farrington	Polymeric Electrolytes	107	12	1-83
Case Western Reserve University	M. Litt	Polymeric Electrolytes	82	17	12-82
Institute of Gas Technology	R. Remick	Polysulfide Electrocatalysis	39	12	10-83
Cross-Cutting					
Illinois Institute of Technology	J. R. Selman	Transport Correlations	36	18	8-83
ANL	W. Walsh	Battery Assessment	60	12	9-82
University of Akron	R. Savinell	Titanium Electrodes	31	12	9-82
ELECTROCHEMICAL PROCESSES					
Membranes					
Electrochemical Technology Company	T. Beck	Ion Transport in Nafion	30	12	5-83
Brigham Young University	D. Bennion	Ion Transport in Nafion	30	12	4-83
University of Texas	R. Lagow	Fluoropolymer Membranes	65	12	5-82
Air Electrodes					
Case Western Reserve University	E. Yeager	Macrocyclic Catalysts	115	12	5-83
Diamond Shamrock Corporation	L. Gestaut	Air Cathodes	399	20	5-82
Metal Reduction					
Massachusetts Institute of Technology	D. Sadoway	Mg Electrorefining	28	9	9-83
Miscellaneous					
University of California at Los Angeles	M. Baizer	Electroorganic Synthesis	94	12	9-83
SERI	H. Chum	Thermal Conversion	74	12	9-82
Institute of Gas Technology	M. St. John	Water Electrolysis	90	12	9-82
FUEL CELLS FOR TRANSPORTATION					
LANL	J. Huff/S. Srinivasan	Fuel Cell R&D	875	12	9-82
BNL	J. McBreen	Fuel Cell Research	250	12	9-82

B. MANAGEMENT ACTIVITIES

LBL assumed management responsibility as the Lead Center for the DOE-sponsored TBR project in 1982. In this role, LBL is responsible for the overall management of the four project elements in the TBR project:

Electrochemical Systems Research
Supporting Research
Electrochemical Processes
Fuel Cells for Vehicles

The aluminum/air program (part of the Electrochemical Systems Research Project Element), will be managed by LLNL, and the Fuel Cells for Vehicles program will be managed by LANL.

During 1982 LBL managed 40 subcontracts and conducted a vigorous research program in Electrochemical Energy Storage. LBL staff members attended project review meetings, made site visits to subcontractors, and participated in technical management of various TBR projects. LBL staff members participated in the following management activities:

- Overviews of the Technology Base Research Project presented to John Brogan on April 12, 1982 and Jan Mares on June 2, 1982, both at LBL.
- Review of the Technology Base Research Project held at LBL on June 2-3, 1982. This meeting focused on the LBL in-house research program, the LLNL metal/air program, and the LANL/BNL fuel cell programs.
- Overview of the Technology Base Research Project presented at a meeting of the Interagency Advanced Power Group in Cleveland, Ohio on May 6-7, 1982.
- Second International Workshop on Reactive Metal-Air Batteries held at the Lockheed Laboratories in Palo Alto, California, on May 17-18, 1982.
- Research Assistance Task Force Meeting that addressed corrosion problems in electrochemical energy/storage conversion devices held in Columbia, Maryland on July 13-14, 1982. This meeting was jointly sponsored with DOE's Division of Materials Sciences, Office of Energy Research.

- Lithium/Metal Sulfide Battery Workshop held at ANL on August 26-27, 1982. LiAl/FeS development programs and ANL's Molten-Salt Cell Research Program were reviewed.

- "Fuel Cells for Transportation Advisory Committee Meeting," held in Los Alamos, NM, November 9-10, 1982.

- Comprehensive review of the Chromium/Iron Redox program held at Allied Chemical, Syracuse, NY, November 23-24, 1982.

- National Fuel Cell Seminar held in Newport Beach, CA, November 15-16, 1982.

- 5th DOE Battery and Electrochemical Contractors' Conference, held in Crystal City, Virginia, December 7-9, 1982.

Milestones accomplished in 1982 by the TBR project include:

- Development of Nasicon ceramic electrolyte was terminated because of degradation in sodium/sulfur cells.

- The fabrication of subscale aluminum-air multicell modules was completed and testing was initiated.

- A "Fuel Cell for Transportation Program Plan" on the development of fuel cells for transportation application was completed.

- Industrial participation in the development of the sodium/sulfur chloraluminate technology was sought but no commitments were made by industry. The decision was made to continue a low-level research effort to maintain some visibility to the industrial community.

- An air cathode for chlor-alkali cells has achieved one-year life with a power saving of greater than 25%.

- A study was completed that concluded solid polymer electrolyte fuel cells are feasible to consider for transportation applications.

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