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TECHNOLOGY BASE RESEARCH PROJECT FOR ELECTROCHEMICAL
ENERGY STORAGE
REPORT FOR 1981

Frank McLarnon

June 1982

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TECHNOLOGY BASE RESEARCH PROJECT FOR ELECTROCHEMICAL ENERGY STORAGE
REPORT FOR 1981

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Berkeley, California 94720

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June 1, 1982

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CONTENTS

1. Introduction and Summary	1
Electrochemical Systems Research (Chapters 2 and 3)	1
Supporting Research (Chapters 4 and 5)	2
Electrochemical Processes (Chapter 6)	4
Fuel Cells for Transportation (Chapter 7)	4
2. New Electrochemical Systems	5
Ambient-Temperature Systems	5
Intermediate-Temperature Systems	8
High-Temperature Systems	9
3. Metal-Air Systems	11
Iron-Air Battery Research and Development	11
Aluminum-Air Power Cell Research and Development	18
Vehicle Applications and Engineering Analysis	30
4. Engineering-Science Research	35
Lithium/Metal Sulfide Cells	35
Alkaline Cells	41
Flow Systems	48
Cross-Cutting Research	54
Photoelectrochemical Cells for Energy Storage	57
5. Materials Research	62
Sodium/Sulfur High-Temperature Cells	62
Lithium-Sulfur High-Temperature Cells	64
Ambient-Temperature Lithium Cells	67
6. Electrochemical Processes	69
Air Electrodes	69
Membranes for Electrochemical Processes	70
Electrochemical Reduction of Metals	72
Electrolysis	77
7. Fuel Cells for Transportation Applications	81
Subcontractor Activities	82
Characteristics of an NH_3 -Air Alkaline Fuel Cell in a Vehicle	
Application	86
Los Alamos Research and Development	86

CHAPTER 1 INTRODUCTION AND SUMMARY

The Technology Base Research (TBR) Project provides the applied research base that supports all Department of Energy (DOE) electrochemical energy storage applications: electric vehicles, electric load-leveling, storage of solar electricity, and energy and resource conservation. The goal of the TBR project is to identify electrochemical technologies having the greatest potential to satisfy stringent performance and economic requirements and transfer them to industry or another DOE project for further development and scale-up.

In October 1981, the Lawrence Berkeley Laboratory (LBL) was assigned lead center responsibility for management of the TBR project. LBL reports to DOE headquarters and oversees the activities of several Technology Centers that participate in the project.

The TBR project consists of four major elements: electrochemical systems research, supporting research, electrochemical processes, and fuel cells for transportation. A summary of activities in these four project elements during 1981 is provided in the following paragraphs.

ELECTROCHEMICAL SYSTEMS RESEARCH (CHAPTERS 2 AND 3)

This element includes efforts to identify, evaluate, and initiate development of promising electrochemical couples. It is divided into two parts: New Electrochemical Systems and Metal/Air Systems. The work is done at two Technology Centers. LBL is responsible for new electrochemical systems, and the Lawrence Livermore National Laboratory (LLNL) manages metal/air R & D activities.

A summary of 1981 activities managed by the New Electrochemical Systems Technology Center (LBL) appears as Chapter 2 of this document. Major highlights are:

1. Management responsibility for the ambient-temperature Zn/NaOH/Fe(CN)_6 hybrid redox system was transferred to the Exploratory Technology Development (ETD) Project, managed by the Lead Center at Sandia National Laboratories, for further development and scale-up. Recent activities are described in the ETD 1981 annual report.

2. The high-temperature Ca/molten salt/ FeS_2 system was shown to have adequate (but not superior) performance, and no further development work is planned at this time.
3. Exploration of the new intermediate-temperature $\text{Na}/\beta''\text{-Al}_2\text{O}_3/\text{NaNO}_3$ system was initiated.

Metal/air R & D activities are presently focused on the iron/air and aluminum/air systems, and a summary is included as Chapter 3. Major accomplishments in the iron/air program are:

1. The characterization and increase in understanding of the catalytic activity and failure modes of Westinghouse iron and air electrodes.
2. The fabrication of bifunctional air electrodes that now exhibit lifetimes in the neighborhood of 500 test cycles.
3. The development of a technique to measure low rates of carbon corrosion.

Major achievements of the aluminum/air program in 1981 are:

1. Mechanical refuelability of a full-scale (0.1 m^2) aluminum-air bicell was demonstrated.
2. Solution-side current collection was investigated in half- and full-cell configurations, and performance and scale-up parameters were obtained.
3. The addition of manganese to iron-containing aluminum in order to reduce parasitic corrosion was established as a route to the production of a low-cost fuel plate of high efficiency.
4. Life tests of air cathodes in battery electrolytes under stimulated vehicle duty cycles was initiated, and degradation rates were correlated with modes of operation.

SUPPORTING RESEARCH (CHAPTERS 4 AND 5)

LBL is the Technology Center for the Supporting Research Project Element, the goal of which is to develop an electrochemical scientific and engineering base to facilitate improvements in secondary batteries and other electrochemical energy conversion devices. Activities include research and development efforts that speed the introduction of electrochemical systems into the marketplace, long-term research into generic problems, and investigations of new materials. Progress is summarized in Chapter 4 (Engineering-Science

Research) and Chapter 5 (Materials Research). Highlights of engineering-science research efforts include the following:

1. Structural, optical, thermodynamic, and electrical studies of battery electrodes in ambient-temperature alkaline systems and high-temperature molten-salt systems provided improved understanding of the phenomena governing cell performance and lifetime.
2. Investigations of new electrode/electrolyte formulations and novel separators for the Zn/NiOOH battery continued.
3. Studies of transport processes and measurements of transport properties in Zn/halogen flow systems were initiated.
4. Calorimetry provided extremely accurate measurements of thermal energy generation rates in high-temperature Li/FeS cells.
5. Measurements of composition profiles in Li/FeS and Zn/NiOOH systems lacked sufficient accuracy to warrant continuing efforts.
6. Investigations of new components for photoelectrochemical energy storage cells were initiated. Amorphous boron photoelectrodes, photo-intercalation compounds, and antimony redox couples are being studied.

Major accomplishments in materials research in 1981 were:

1. NASICON ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$) ceramic electrolyte was shown to be unstable in molten Na at 300°C, and no further development work for high-temperature applications is planned. Rather, efforts will be focused on materials research and electrochemical compatibility of new compositions.
2. A novel technique to fabricate thin-walled $\beta''\text{-Al}_2\text{O}_3$ tubes by a tape-wrapping process was shown to be feasible and potentially competitive with conventional methods.
3. Electrical properties of fast Li-ion-conducting glasses ($\sigma_{300} \approx 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$) in the system $\text{Li}_2\text{O}-(\text{LiCl})_2\text{-B}_2\text{O}_3$ have been measured and correlated with glass composition and structure.
4. New ceramic systems, including several NASICON-like structures, have been found to display fast ion conduction.
5. It was demonstrated that the polymer film polyethylene oxide-lithium trifluoroacetate is, in fact, a solid electrolyte that conducts Li ions ($\sigma_{140} \approx 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$). Small quantities of water vapor absorbed by the films increase their conductivities by 2 orders of magnitude to values in agreement with prior measurements.

ELECTROCHEMICAL PROCESSES (CHAPTER 6)

LBL is the Technology Center for the Electrochemical Processes Project Element. The objective of this element is to develop energy-efficient electrochemical technology for use in fuel cells, industrial applications, and galvanic cell processes. Major achievements in 1981 were:

1. Air-cathode technology for improved chlor-alkali cell efficiency was transferred to the private sector.
2. Hydrogen anodes were shown to provide marked energy savings in the electrowinning of zinc, and the technology was transferred to the private sector.
3. Mathematical modeling studies identified novel cell designs for improved energy efficiency of the Hall-Héroult process for aluminum reduction.
4. The Al_2S_3 process was investigated as an attractive alternative to the conventional Al_2O_3 process for aluminum reduction.

FUEL CELLS FOR TRANSPORTATION (CHAPTER 7)

Los Alamos National Laboratory (LANL) is the Technology Center for the Fuel Cells for Transportation Project Element. The objective of this effort is to explore the potential use of fuel cell systems as mobile power plants. Highlights of activities in 1981 include:

1. Assessments of phosphoric acid electrolyte fuel cells and solid polymer electrolyte fuel cells indicated the technical feasibility of employing these technologies in vehicular applications.
2. Adsorption studies on cathodes in acid electrolytes confirmed that, in order to improve fuel cell oxygen electrode performance, neutral or anionic species must not be allowed to adsorb.

CHAPTER 2 NEW ELECTROCHEMICAL SYSTEMS

AMBIENT-TEMPERATURE SYSTEMS

Two programs on lithium ambient-temperature systems were conducted during 1981: one in Li/SO_2 at Duracell International, Inc., and another in organic-based electrolyte at Electrochimica Co. The work at Electrochimica was directed toward the study of Li cyclability in different organic electrolytes and the examination of experimental methods for determining anodic stripping efficiency. Selected results were:

1. For morphological studies with scanning electron microscopy (SEM), a nickel substrate is undesirable (compared to a solid lithium or aluminum substrate) since it leads to nonuniform and nonadherent deposition of smaller crystallites, often accompanied by codeposition of gels, polymers, and other materials that have nothing to do with metallic lithium.
2. For stripping efficiency studies, an aluminum substrate was found to be reliable and reproducible and to provide significantly higher efficiency than nickel under the same conditions.
3. It was found that meaningful stripping efficiency studies should be conducted in the range of $2\text{--}5 \text{ coulomb}/\text{cm}^2$ for the deposition step and that a number of cycles should be performed to first remove water impurities and then to observe the effect of cycling on the resulting stripping efficiency.
4. Of the two anions so far studied, both perchlorate and AsF_6^- can operate (although perchlorate shows a greater dendritic growth tendency). The results of obtained stripping efficiencies, SEM observations, and safety considerations make the AsF_6^- anion more desirable.
5. Of the solvents studied, propylene carbonate with cosolvents has been found to be totally undesirable, 2 Me-THF was undesirable from the point of view of stripping efficiencies, and dioxolane with 30% dimethyl ether yielded the best overall results.
6. Adding SO_2 to the electrolyte at the 3-molar level to protect freshly deposited lithium from solvent attack resulted in improved stripping efficiency. The concept may have merit, but lower concentrations of SO_2 or other additives could be more desirable.

7. In summary, the $\text{AsF}_6^-/\text{dioxolane}$ electrolyte system (with and without cosolvents) offers the most adherent, crystalline deposits and is a good point of departure for future development.

The Li/SO_2 system is commercially available in a number of cell sizes as a primary battery system. These cells deliver a specific energy of 330 Wh/kg and specific power of 380/836 W/kg. The Li/SO_2 primary system consists of a Li foil anode, a porous carbon-PTFE catalytic current collector, and a catholyte consisting of acetonitrile, SO_2 , and LiBr supporting salt. The postulated cell reactions are:

Discharge:

Recharge:

The discharge reaction product lithium dithionite, $\text{Li}_2\text{S}_2\text{O}_4$, is an insoluble solid that precipitates in the porous carbon cathode, blocking further reduction of SO_2 . During storage and discharge, the lithium anode is protected from chemical reaction with SO_2 by formation of a protective film of $\text{Li}_2\text{S}_2\text{O}_4$. The reversibility of the cell reactions is known. However, the cycle life is limited by the irreversible reaction of electro-deposited lithium with the acetonitrile organic cosolvent forming lithium cyanide, methane, and other more complex organic compounds that cannot be reoxidized back to soluble lithium salts. These lithium-solvent reactions lead to an irreversible loss of lithium. There are preliminary indications that the problem can be eliminated by using the salt $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, which is soluble in SO_2 and provides a highly conducting solution. In a completely inorganic system, comprised of a Li anode, porous carbon cathode, inert cathode material, and SO_2 solvent with $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ electrolyte salt, the only reaction occurring is dithionite formation, which is straightforward and reversible.

The salt $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ is a member of the class of polyhedral borane anions and is known to be extremely stable. There is some evidence that the $\text{B}_{10}\text{Cl}_{10}^{2-}$ anion may be oxidized during charging to form a stable, soluble species. This oxidation of $\text{B}_{10}\text{Cl}_{10}^{2-}$ is important for providing overcharge protection of individual cells to balance the cells in a multicell battery.

During 1981, a program was initiated at Duracell to examine more thoroughly the chemistry of the cell reactions in the all-inorganic $\text{SO}_2/\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ electrolyte. Coulometry and quantitative analysis of the discharge product indicated that dithionite is the only discharge product (within experimental error of about 2%). Overcharge of $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ was observed to oxidize the $\text{B}_{10}\text{Cl}_{10}^{2-}$ to $\text{B}_{10}\text{Cl}_{10}^{2-}$ at 3.6 V, providing desirable overdischarge protection (the one-electron reaction is very reversible).

To augment this work with ambient-temperature lithium, proposals addressing both the organic and inorganic electrolyte were solicited in August 1981. Fifteen were received and reviewed, and the single proposal chosen was from EIC Laboratories for a study on the feasibility of sulfolanes as electrolytes for rechargeable Li batteries. Also, at the start of FY 1982, Lawrence Berkeley Laboratory assumed management responsibility for a Li/SO_2 battery development effort initiated in the Office of Energy Research and conducted by Duracell International, Inc. A replacement for the very expensive $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$ salt is being pursued, along with fundamental studies on the mechanism of degradation of the porous carbon positive electrode. After complete discharge, the carbon electrode expands and becomes hard and brittle due to saturation with the insoluble product $\text{Li}_2\text{S}_2\text{O}_4$. After recharge, the carbon electrode returns to a flexible condition, but the large internal stresses generated on discharge breaks electrical contact from some portion of the electrode material. Repeated flexation with cycling causes the electrode to deteriorate; this appears to be the principal cycle-limiting process at present. Recent work has led to new candidate materials for both the salt and the positive electrode material. The lower cost electrolyte exhibits about the same cycling performance as $\text{Li}_2\text{B}_{10}\text{Cl}_{10}$, and the new positive electrode material has increased the cycle life in 1 Ah cells to 180 at 2 mA/cm^2 . Further study of these new materials is in progress.

INTERMEDIATE-TEMPERATURE SYSTEMS

Two systems are under investigation in the intermediate (150-300°C) temperature regime. The cell system $\text{Na}/\text{Na}^+\beta''\text{-Al}_2\text{O}_3/\text{SCl}_4$ ($\text{AlCl}_3\text{-NaCl}$) at 180-250°C has been studied extensively at the University of Tennessee and has reached a point where a decision with regard to transition into engineering-oriented cell design and testing should be made. An interesting feature is the relatively high open-circuit voltage of 4.2 V. A number of cells were run this past year to investigate: (1) carbon as a current-collector material in the positive electrode; (2) operation on the "second plateau," corresponding to the reduction of elemental sulfur to sulfide; and (3) operation of cells with metal (as opposed to glass) cases. Laboratory feasibility has been shown in all of these areas, with varying degrees of success.

A new program was started in 1982 at Argonne National Laboratory on sodium/alkali nitrate cells for temperatures of 200°-250°C. The cells employ molten sodium negative electrodes, β'' -alumina electrolytes (Ceramatec), and molten alkali-nitrate positive electrodes. The overall cell reaction can be represented as:

where MNO_3 is the alkali nitrate and MNO_2 is the corresponding nitrate. Argonne National Laboratory has conducted preliminary cycling tests, with MNO_3 being NaNO_3 (mp 307°C), LiNO_3 (mp 256°C), or the NaNO_3 - LiNO_3 eutectic (mp 196°C).

For example, the NaNO_3 electrode has been cycled at 330°C for 14 cycles (500 h) with an average utilization of about 40% per cycle. The type 304 stainless steel current collector in this 1.75-V cell was severely corroded; Na_3CrO_4 and Na_4CrO_4 were detected by X-ray diffraction of the NaNO_3 after this cycling test. Similarly, the NaNO_3 - LiNO_3 eutectic electrode was cycled at 206°C for 14 cycles (700 h) with an average utilization of about 25% per cycle. The nickel screen current collector in this 1.62-V cell was oxidized to some extent, but it continued to function well. The LiNO_3 electrodes, using the Ni screen current collector and a temperature of 260°C, generally failed within one cycle because the β'' tubes fractured. Ion microprobe profiles revealed a significant increase in the ratio of lithium to sodium in the fracture areas of these failed tubes. These preliminary tests

have demonstrated the rechargeability of certain alkali nitrate electrodes, but they have also indicated the need for detailed fundamental studies directed toward optimization of the alkali nitrate mixture and the current collector.

HIGH-TEMPERATURE SYSTEMS

Two systems are under investigation in the high ($>300^{\circ}\text{C}$) temperature regime. Argonne National Laboratory is investigating a calcium-metal sulfide concept that should, in principle, offer a lower cost alternative to the lithium/metal sulfide battery. This effort has nearly completed its development at the laboratory level. The calcium/iron disulfide cell employs $\text{CaAl}_{1.2}\text{Si}_{0.4}$ negatives electrodes, $\text{Fe}_{0.93}\text{Co}_{0.07}\text{S}_2$ positive electrodes, and $\text{LiCl-NaCl-CaCl}_2\text{-BaCl}_2$ (mp 383°C) electrolyte. The electrodes are separated by layers of BN felt and the current collectors are iron (negative electrode) and molybdenum (positive electrode). This cell, which is operated at 475°C , has been shown to be capable of high specific energy and power, e.g., multi-plate cells containing 33 wt% active material will yield over 120 Wh/kg and 170 W/kg. However, declining coulombic efficiency presently limits the cell cycle life to about 300 cycles (one-half year of accelerated testing). This coulombic efficiency problem is caused by contamination of the BN felt separator by the electrode materials, which become very finely divided (less than 10 microns in diameter) during extended cycling. To retain such materials in the electrodes, a separator with a less open structure than the BN felt currently available must be developed. Powder separators such as MgO are one possible solution.

The Li alloy/ $\text{LiI}(\text{Al}_2\text{O}_3)$ /metal sulfide system is a totally solid-state, high-temperature battery which was being developed under joint sponsorship with Duracell International, Inc. A totally solid-state battery could circumvent many of the problems associated with Li high-temperature batteries, e.g., simple construction, low self-discharge rate, and high energy efficiency. The components can be assembled in a bipolar stack and consolidated with conventional powder processing techniques at relatively low cost. Since the inception of the program in 1978, the system has undergone significant development and improvement. Early performance levels were 50-100 cycles at 40% capacity utilization at C/10 rate (5 mA/cm^2); recently, 300-400 cycles at C/5 rate and 50-60% capacity utilization were achieved. A number of Li alloy negatives and metal sulfide positives were examined and the optimal combinations selected for further study. Positive-electrode limited cells of 1 Ah

capacity have produced 500 deep-discharge cycles at 50-65% of stoichiometric capacity with high (99-100%) coulombic efficiency and high (84-87%) energy efficiency at 5 mA/cm² (C/10 rate). Negative electrode modification recently improved the C/5 rate capacity utilization to 45-55%. Peak specific power observed in this latest system was 220-340 W/kg (without packaging) at full charge and 100-200 W/kg at half charge. The capacity utilization at high rate and the peak power appeared to be limited by high interfacial impedance at both electrodes (more so at the negative electrode).

CHAPTER 3 METAL-AIR SYSTEMS

The principal objective of metal-air R & D is to develop a refuelable battery as an automotive energy source for general-purpose electric vehicles and to conduct engineering demonstrations of its ability to provide vehicles with the range, acceleration, and rapid refueling capability of current internal-combustion automobiles. A second objective is to develop an electrically rechargeable battery for specialized electric vehicles, such as commuter vehicles, for low-cost transportation.

To fulfill the principal objective, an aluminum-air battery research and development project is underway. It is intended to develop (1) a mechanically rechargeable aluminum-air power cell, (2) cost-effective anode and cathode materials and structures to demonstrate the reliability and economic feasibility of this technology, and (3) an integrated propulsion system utilizing the power cell.

To fulfill the second objective, an iron-air electrically rechargeable battery is being developed. This work is presently directed at developing a low-cost, long-lived air electrode, the critical component of the battery. Upon successful completion of this phase of the program, battery hardware development will be initiated.

IRON-AIR BATTERY RESEARCH AND DEVELOPMENT

Background

An iron-air secondary battery is being developed for specialized vehicles. This room-temperature, electrically rechargeable battery has the potential to provide low-cost vehicles with a range of 160 km and a service life of 160,000 km. The present critical technical issue is the development of a reliable, low-cost bifunctional air electrode.

The program pursues air-electrode R & D testing while keeping a low-level effort in cell testing and development. This research is carried on as a multi-year program involving the Westinghouse Research Laboratory (WRL), Case Western Reserve University (CWRU), and the Lawrence Berkeley Laboratory (LBL). This joint effort was initiated in FY 1981 to improve the performance and cycle life of the bifunctional air electrode. In this cooperative research, WRL fabricates and tests air electrodes, supplies materials and samples to CWRU and LBL for testing, and evaluates new structures and catalysts developed by CWRU and LBL. The role of CWRU and LBL is to determine the factors controlling

electrode lifetime and to develop stable and innovative catalysts and structures suitable for the Fe-air system.

The basic iron-air cell being developed consists of a high-surface-area iron anode, a bifunctional (used for both charge and discharge) air electrode, and an electrolyte consisting principally of a 25% solution of potassium hydroxide. During discharge, the air electrode reduces free oxygen in the air to form hydroxyl ions, and the iron electrode discharges to its first oxidation state. The net cell reaction is:

In the charge mode, the air electrode continuously evolves oxygen, and Fe(OH)_2 is reduced to elemental iron. Discharge voltages of approximately 0.82 V at 25 mA/cm^2 and charge voltages of approximately 1.55 V at 12.5 mA/cm^2 are achieved.

The sintered iron electrode has traditionally been known to have long life with stable performance. The iron structures developed at WRL are well understood, and fabrication parameters have been carefully documented. The relationships between electrode performance and structural parameters such as particle size, pore size, and density have been modeled with good experimental agreement. Current anodes have demonstrated a mass utilization of greater than 0.4 Ah/g (theoretical maximum is 0.96 Ah/g) and lifetimes greater than 10^3 deep-discharge cycles.

The cycle life of iron-air cells is currently limited by the stability of the bifunctional air electrode. In principle, separate unifunctional air electrodes could be employed in each of the charge and discharge modes with increased reliability, but weight and volume considerations favor a single bifunctional electrode. Bifunctional electrodes must be stable over the potential range required by both reactions (0.6-1.7 V vs NHE); this puts a formidable strain on materials stability. The bifunctional air electrode developed by WRL survives for 250 charge/discharge cycles with reasonably good characteristics under both oxygen-reduction and oxygen-evolution conditions. Single electrodes have been successfully operated for over 500 cycles.

The Westinghouse-made air electrodes typically are composed of various carbons and Teflon with a nickel or nickel-coated current collector. Catalyst

additives include Ag, WC-12%Co, FeWO_4 , and NiS. The electrodes weigh approximately 0.2 g/cm^2 and have a silver content of less than 1 mg/cm^2 .

Iron-Air Battery Development

Research at Westinghouse Research Laboratory during this period has been directed almost exclusively toward fundamental and applied studies of the bifunctional air electrode. Besides the continuing program of life-cycle testing of air electrodes, studies have included: (1) the optimization of electrode fabrication and processing techniques, (2) the measurement of silver migration during electrode operation, (3) the measurement and control of surface current density variations, and (4) the screening and testing of new O_2 -reduction and O_2 -evolution catalysts.

Electrode testing. Electrodes are normally cycled in a 25% KOH aqueous solution at 25°C against a Ni sheet counter electrode. These half-cells are run using unscrubbed ambient air. The electrolyte level within each cell is maintained via a solenoid-activated water level sensor. Potentials are measured relative to a Hg/HgO reference electrode. During discharge (O_2 reduction), electrodes are operated at a current density of 25 mA/cm^2 for 4 hours. Charging is accomplished at a current density of 12.5 mA/cm^2 , also over 4 hours. Once a week, electrodes are polarized in both operating modes over a current density range of $25\text{--}125 \text{ mA/cm}^2$ (discharge) and $12.5\text{--}62.5 \text{ mA/cm}^2$ (charge) to obtain polarization resistance.

Some 4-ply air electrodes exhibited lifetimes in the neighborhood of 600 test cycles with little or no structural degradation. During testing, charge potentials did not significantly deteriorate while discharge potential gradually increased from the initial 160 mV below Hg/HgO to 200 mV and beyond.

Electrodes were made using alternative processing techniques amenable to low-cost, high-rate production. Testing indicated that electrodes fabricated by furnace heat treatment followed by rolling possess performance and lifetimes similar to those of normal hot-pressed electrodes.

Prototype-size 400-cm^2 air electrodes were fabricated and tested to establish the mechanical properties and integrity of these larger units. Testing was also performed using electrodes containing various abrasive materials to enhance Teflon fibrillation.

Electrodes with various combinations of size-graded active materials were also fabricated and tested to find a combination of particle sizes that will produce the optimum morphological structure for the air electrode.

An electrode designated LIU-135 has been one of the most stable air electrodes ever observed in this program. After passing its break-in period, it had a discharge potential that remained within 0.005 V at -0.135 V (vs Hg/HgO) for over 200 cycles. Charge potential fluctuated only slightly more than the discharge potential and remains around +0.525 V over virtually the entire cycle life.

Catalyst evaluation and testing. A voltammetric screening program was conducted to find new additives principally to improve oxygen-evolution characteristics, but with a few possible oxygen-reduction catalysts also being examined. Additives were screened by examining their threshold potentials, correlated to O_2 -evolution potential. The most promising ($Cr_{23}C_6$, $CuWO_4$, B_4Si , $CoCrO_4$, Bi_2S_3 , $PbTiO_3$) were used as additives in two-ply air electrodes cycled in half-cells. Other electrodes were made and tested using $Cr_3C_2 + PbTiO_3$, $Cr_3C_2 + NiS$, and $Cr_3C_2 + FeS$. Only $PbTiO_3$ showed good performance as a single additive.

Research into possible material additives to replace NiS , $FeWO_4$, and/or WC-12%Co was undertaken. An electrode incorporating an Fe powder-Ni hydrate mixture has yielded a promising O_2 -evolution potential of +0.542 V and a reduction potential of -0.169 V, during its first 100 cycles of operation.

Cyclic voltammetry and electron microscopy have been used to determine the degree of Ag migration in cycled bifunctional air electrodes. Up to 3000 Ah in both single mode and charge/discharge cycling has induced no detectable Ag migration to Ni current collectors, electrolyte, or Ni sheet counter electrodes. By monitoring the $Ag^1 \rightarrow Ag^0$ peak, it was shown that electrodes fabricated without the additives NiS , $FeWO_4$, or WC-12%Co lose silver within 330 sweep cycles. Those electrodes with the additives run the equivalent of thousands of cycles with no apparent silver loss.

Iron-air cell testing. Testing of 100-cm² iron-air cells were undertaken. Emphasis has been placed on the design of a lightweight cell case and the attainment of long-term cyclic voltage stability in the range of 0.75-0.80 V. Voltage stability has been demonstrated in the range of 0.65-0.70 V, following an initial break-in cycle. These cells typically exhibit capacities of 0.3 Ah/g-Fe. In an effort to increase cell voltage, an ultra-thin cell casing design has been developed, making possible inter-electrode gaps as low as 0.01 in.

An operational test of an iron electrode opposite a two-ply air electrode showed that certain areas of the air electrode produce higher than normal current density and cause greater discharge of the opposing area of the iron electrode. This nonuniform discharge has a detrimental effect on total iron capacity and is thought to be due to variable wetting of the air electrode. Such nonuniformities are related to electrode fabrication, particularly Teflon fibrillation.

A method of fabricating iron electrodes that do not require LiOH in the electrolyte for charge capacity retention was sought. The elimination of LiOH could benefit the air electrode, which appears to degrade in the presence of this additive.

Bifunctional Air-Electrode Research

The overall goal of this research at Case Western Reserve University is to improve the bifunctional air electrode by lowering the anodic and cathodic polarization and increasing the cycle life. The objectives are: (1) to establish the chemistry and physical structure of the present Westinghouse bifunctional air electrode with emphasis on understanding the catalytic function and factors controlling cycle life, and (2) to optimize the electrode structures and catalysts for bifunctional operation.

Most of the work done at CWRU has focused on understanding the catalytic activity and failure modes of WRL electrodes. The role of electrode components were examined using cyclic voltammetry, rotating-disk and ring-disk measurements, and floating electrode techniques. Comparisons of new and failed electrodes were made using chemical analysis, scanning electron microscopy, secondary ion mass spectrometry, and X-ray diffraction.

Analytical work was done on Westinghouse electrodes removed after varying numbers of cycles up to 420. X-ray energy dispersive and ESCA analysis of the active layer, together with elemental analysis of the electrolyte, show that WS becomes almost completely depleted from the electrode, while Ag, Co, and Se are depleted at a slower rate. The Ni level in the electrode and electrolyte tends to rise after 300 cycles, indicating possible large Ni corrosion. Scanning electron microscopy showed a change in morphology with active-layer wetting. This change is thought to indicate carbon oxidation.

Rotating disk and ring-disk measurements have shown directly that (1) carbons such as Shawinigan black (SB) and Ketjen black have activity for a

two-electron O_2 reduction but not for peroxide decomposition; (2) silver-catalyzed SB seems able to decompose peroxide but has diminished ability to perform the two-electron O_2 reduction; and (3) silver is easily lost from porous carbon electrodes when they are set at potentials positive of +300 mV vs Hg/HgO.

Gas-fed electrodes were subjected to rapid cycles for extended periods to monitor break-in processes so that more meaningful polarization data could be obtained. Electrodes containing Ag, C, NiS, $FeWO_4$, and WC/Co had better polarization characteristics both anodically and cathodically than an electrode containing silver/Shawinigan black, which in turn had better characteristics than an electrode containing SB only. From other evidence, it was seen that electrodes containing Ag-SB and Ag-SB plus additives eliminated peroxide effectively.

Various combinations of the additives used by WRL were used in floating-type electrodes and subjected to cathodic break-in, cycling, steady-state polarization measurements, and cyclic voltammetry in addition to the new open-circuit potential decay measurements. It was concluded that: (1) silver-catalyzed Shawinigan black (Ag-SB) decomposed peroxide effectively, but may have lower overall activity for O_2 reduction; (2) the additives $FeWO_4$, NiS, and WC/Co reactivate the Ag-SB for O_2 reduction (two-electron process on carbon); (3) WC/Co increases the peroxide decomposing activity of the Ag-SB, (4) Co is an effective peroxide decomposer; and (5) after electrochemical cycling, combinations of additives containing Ni, Fe, and Co have catalytic activity for O_2 generation.

In work using the standard CWRU gas-fed electrode technique with Co, Ni and Fe-based additives, the following conclusions were reached: (1) Co metal after anodic-cathodic cycling becomes a good peroxide eliminator, (2) the Co catalytic activity is inhibited by the presence of Fe, (3) low anodic polarization is associated with the presence of Ni and Fe, (4) this O_2 generation catalytic activity is inhibited by the presence of Co, and (5) the presence of W has little effect in either O_2 reduction or generation catalysis.

Research continues on alternative catalyst systems that appear attractive for either the cathodic or anodic functions and, in a few cases, both. Besides high catalytic activity, trace constituents in the electrolyte derived from these catalysts must not interfere with the operation of the iron negative

electrode. This restriction may eliminate some otherwise promising O_2 electrocatalysts.

Research at LBL pursued three parallel tasks:

1. Investigating the dynamic structure of metal oxide-TFE/carbon layers under oxygen evolution conditions.
2. Studying the kinetics of corrosion of acetylene black at oxygen evolution potentials using ^{14}C tracer techniques.
3. Developing new bifunctional electrode concepts.

A variety of transition metal oxides were impregnated into Shawinigan acetylene black and tested as oxygen-reduction catalysts in 30% KOH at 20-45°C. Uncatalyzed acetylene black was observed to have relatively poor activity for oxygen reduction. Oxides of Fe, Ni, Co, and Ru were studied in considerable detail. Stoichiometries and structures of the oxides were determined by X-ray diffraction and transmission electron microscopy. The stoichiometries found to be most stable over the potential region ± 200 mV vs Hg/HgO were Co_3O_4 , Fe_2O_3 , NiO, and RuO_2 . Crystallite sizes observed in transmission electron microscopy were generally 10-20 nm except in the case of RuO_2 where crystallites of 5-10 nm were observed. Kinetic studies of oxygen reduction indicated Co_3O_4 was the most active material, with the ordering

These four metal oxides were examined as oxygen evolution catalysts. The materials were prepared as coatings on Ta Exmet screens fired at temperatures above 500°C to eliminate large variations in surface area. Stoichiometries determined by X-ray diffraction were RuO_2 , Co_3O_4 , Fe_2O_3 , and NiO of crystallite size above 100 nm. Porosimetry indicated roughness factors of ca. 50-100. For continuous electrolysis at 10 mA/cm^2 , the relative activities were $RuO_2 \approx NiO > Co_3O_4 \gg Fe_2O_3$. However, the NiO was adversely affected by potential cycling ± 200 mV vs Hg/HgO; and the relative activities for cycled electrodes were $RuO_2 > Co_3O_4 \approx NiO \gg Fe_2O_3$.

Carbon-14 acetylene black, prepared in a retort by incomplete combustion of $^{14}C_2H_2$, was used to determine the corrosion rate of this carbon black at oxygen evolution potentials (450-600 mV vs Hg/HgO). The corrosion rate exhibited a potential dependence of 130 ± 10 mV per decade and an activation energy of 23 ± 3 kcal/mole. The primary corrosion product was not CO_2/CO_3^{2-}

but hydrocarbons at least partially soluble in KOH. Spectrophotometry indicated the product is a mixture of materials with absorption bands in UV (230 nm) and the visible (400-500 nm). Corrosion of other types of carbon blacks, e.g., channel and furnace blacks, produced products with the same UV-visible spectra. The corrosion rate of acetylene black appears unacceptable for use in bifunctional air electrodes. Graphitized furnace blacks have sufficiently low rates of corrosion at 500-550 mV vs Hg/HgO at 25°C to last 1000 eight-hour charging cycles.

ALUMINUM-AIR POWER CELL RESEARCH AND DEVELOPMENT

Background

The aluminum-air power cell R & D program¹ pursues in parallel the development of system hardware and cost-effective electrodes. Hardware development makes use of model electrodes (Reynolds alloy RX808 and the Diamond Shamrock standard air electrodes) for development and testing of the battery system through each level of complexity. The levels of system development are identified as follows: M0 (a full-scale single cell); M1 (a refuelable single cell); M2 (refuelable, integrated multicell module); M3 (multicell module integrated with electrolyte composition and thermal control subsystems); M4 (laboratory prototype battery). Calendar year 1981 emphasized experimental studies of alternative designs of refuelable cells (M1 series) and stackable bicells (M2).

Electrode development efforts are motivated by prospects for improved efficiency and were directed toward (1) obtaining a fundamental understanding of the electrochemical behavior of pure and alloyed aluminum; (2) identification and segregation of undesirable materials (principally Fe) in low-cost aluminum primary mill products; and (3) experimental evaluation of cathodes containing low levels of noble-metal catalysts, catalysts of non-noble metals, and alternative electrode structures of improved mechanical integrity and bubble pressure.

Efforts at Lawrence Livermore National Laboratory (LLNL) are aimed at experimental evaluation of basic cell configurations and cell/crystallizer processes, as well as electrochemical studies of pure and alloyed aluminum. Continental Group Inc. (CGI) and the Lockheed Missiles and Space Co. (LMSC) are tasked with the reduction of such configurations and processes into practical, fully-engineered hardware. Reynolds Aluminum Co. supplied model anodes (RX808) and developed an alloy of improved cost effectiveness. Reynolds also estimated

the cost of alternative routes to alloy production and fabrication of candidate fuel plates.

Diamond Shamrock Corporation (DSC) supplied model cathodes and investigated degradation and failure modes of electrodes subjected to various duty cycles simulating road use; it also evaluated alternative structures and catalysts.

Research at Lawrence Livermore National Laboratory

Cell/stack configurations and battery process development

M0 series. The M0 experimental cycle consisted of seven experiments with a full-scale (0.1 m^2) Al-air cell,² the last of which employed an external crystallizer to control electrolyte composition via hydrargillite precipitation. Experiments were begun in 1980, with data reduction, analysis, and reporting completed in 1981. The purpose of this cycle was to investigate the behavior of the aluminum-air cell on the scale and in the range of operating conditions anticipated for vehicular operation, and to verify the applicability of the kinetic equations derived for hydrargillite precipitation by jointly operating the M0 cell with a fluidized-bed crystallizer.

The M0 cell, jointly designed by LLNL and LMSC, features a fixed cathode and an anode ($25 \text{ cm} \times 40 \text{ cm} \times 0.6 \text{ cm}$) supported on a flexible diaphragm. A constant interelectrode gap (3.2 mm) was achieved by advancing the anode during dissolution against a ribbed polypropylene separator. Using the RX808 alloy ($0.07\% \text{ Ga}$, $0.8\% \text{ Mg}$) and the DSC standard electrode ($1.2 \text{ mg/cm}^2\text{-Pt}$), polarization curves were obtained under various combinations of electrolyte composition ($4\text{M NaOH} + 1\text{-}2.7\text{M Al(OH)}_{3,\text{aq}} + 0.06\text{M Na}_2\text{Sn(OH)}_6$), flow rate ($\text{Re} = 500\text{-}1000$), air flow ($1.4\text{-}14$ times stoichiometric requirements), and current density ($0\text{-}5.8 \text{ kA/m}^2$), at a fixed temperature of 60°C . As the equilibrium concentration for $\text{Al(OH)}_{3,\text{aq}}$ is 0.96M , all experiments were conducted under supersaturated conditions.

At an electrolyte flow rate of 0.22 l/s ($\text{Re} = 1000$), the pressure drop across the cell was $2\text{-}3 \text{ kPa}$ ($0.3\text{-}0.4 \text{ psi}$), indicating a total resistance to electrolyte flow in the interelectrode gap and manifold plena of 0.5 W . At 4 times stoichiometric air-flow rates (0.3 l/s at 2 kA/m^2) and a hydrostatic head of 2.8 kPa (25 cm of electrolyte), the resistance to air flow is 0.9 W . When corrected for efficiencies of pumps and motor, these quantities indicate auxiliary pumping requirements of less than 2% of the nominal gross power of the cell, 225 W . The comparison of voltage and power as a function of current density is shown for various experimental systems in Fig. 1.

Fig. 1. Power density, cell, and electrode potentials (uncorrected for IR losses) in various experimental systems using the DSC standard air electrode (1.2 mg-Pt/cm^2) and RX808 ($0.07\% \text{ Ga}$, $0.1\% \text{ Mg}$) in $4\text{M NaOH} + 1\text{M Na Al(OH)}_4 + 0.6\text{M Sn(IV)}$ at 60°C . The M2-6 cell (a six-cell stack) was designed and constructed in 1981 and discharged in early 1982.

M0/crystallizer experiment. A 0.1-m^2 cell was operated with and without exchange of electrolyte between the cell and a fluidized-bed crystallizer containing an initial seed charge of 0.72 kg. Concentration of aluminate was controlled at 2.6M for 120 minutes, at 60°C and 4M NaOH. The kinetic expression derived earlier proved to be reasonably accurate in designing a crystallizer of proper scale, but uncertainties exist in seed surface area determination, in the distribution of the precipitation reaction and the seed area between crystallizer and cell electrolyte circuits, in evolution of the particle size distribution, and in the amount of secondary nucleation, agglomeration, or fracture of seed particles. This work established the feasibility of controlling electrolyte composition by the precipitation of hydrargillite under conditions of sustained vehicular operation, using a crystallizer of reasonable size. The work was not continued with M0 because of a more extensive study planned by Alcoa.

Rapidly refuelable cells and cell stacks, M1 and M2 series. The purpose of these experiments was to evaluate a cell configuration allowing rapid removal and replacement of an anode module and to provide a low-cost module for subsequent investigations of processes occurring in joint operation of a multicell stack and crystallizer. Following successful scale-up to 1000-cm^2 size, the M1-LLNL and M2-LLNL units were constructed on the more convenient 167-cm^2 experimental scale.

The rapidly refuelable 167-cm^2 single cell³ (M1-LLNL) was the first of three refuelable aluminum-air cell configurations to be tested in 1981. The cell reproduced the polarization curves of the 25-cm^2 reference Al-air cell and yielded a maximum power of 4.2 kW/m^2 , or 97% of that obtained with the reference cell. The M1 cell makes use of a fixed anode (soldered to a copper-clad circuit board) and a moving cathode/separator module suspended on a flexible diaphragm. The internal manifolding of electrolyte in this design results in a minimum pressure drop. The cell is constructed of sheared, fiber-filled epoxy.

The cell was modified and two-celled stacks were assembled and tested in parallel and series flow. Results replicated the characteristics of baseline 25-cm^2 cells up to a current density of 6 kA/m^2 . The test apparatus was modified for a 6-cell stack (M2-LLNL) to be tested in early 1982.

In the M0, M1, and M2 series experiments, the DSC standard electrode was used (1.2 mg-Pt/cm^2) and exhibited polarizations (IR free) in the range

0.48-0.70 ohm-cm². This value is somewhat higher than that found in small-scale half-cell polarization tests of the same electrodes at DSC (0.3-0.4 ohm-cm²). The discrepancies may result from differences in electrolyte impurities, current collection techniques, start-up procedures, or air distribution between the experimental systems.

Experimental Evaluation of Solution-Side Current Collection (SSCC)

An Al/H₂O(Ni) cell was equipped with dry-side and solution-side anode current collectors such that the mode of current collection could be rapidly switched in situ, leaving the interelectrode geometry and anode state essentially unchanged. This cell employed a 5.07 cm² aluminum anode disk and a nickel counter electrode, at which hydrogen was evolved during galvanostatic polarization of the cell. The SSCC was a right-angle knife edge 2.5 cm long and having an area of 0.3 cm² exposed to the electrolyte. At a current density of 2 kA/m², cell voltages decreased 16 mV with SSCC; hydrogen evolution remained the same to within experimental precision (± 60 A/m²). The linear resistivity of the knife-edge junction was found to be 0.042 ohm-cm and was independent of contact pressures over the range of 50-400 Nt/m. The unexpectedly small amount of hydrogen evolving from the exposed portions of the SSCC may be due to the formation of a scale of hydrated alumina on the SSCC near the contact point. Here, transport of dissolved aluminate is hindered in the restricted geometry, allowing high concentrations and spontaneous precipitation.

Wedge-Shaped Cells

LLNL proposed the application of solution-side current collection to a wedge-shaped cell design (invented by Despic in 1979) as a means of using wedge cells in caustic electrolytes. A design analysis was performed to evaluate the concept. The wedge-shaped cells with SSCC, to be tested in early 1982, provide for (1) continuous feed and complete anode utilization, (2) rapid refueling by the addition of rectangular plates to a compartment above the cell, (3) a dimensionally stable cell without moving parts, and (4) the possibility of partial recharge.

Anodic Dissolution of Aluminum and Aluminum Alloys

A parametric study of anode/electrolyte combinations using standard 25-cm² aluminum-air cells was conducted over the following range of operating conditions: temperature, 40-70°C; caustic concentration, 3-8M; aluminate concentration, 0.25-4M; electrolyte flow rate, Re = 1000-7000. The cathode

was a standard DSC air electrode (1.2 mg-Pt/cm^2). Both high-purity aluminum (99.999%) and RX808 alloy (0.07% Ga, 0.1% Mg) were investigated. For pure aluminum, the rate of water-reduction was a minimum (0.5 mA/cm^2) at 4M NaOH , $40\text{--}60^\circ\text{C}$, at a fixed electrode potential of -1.5 V vs Hg/HgO . The polarization of aluminum was greatly reduced by the addition of gallium; the RX808 showed 3 times the surface power density of pure aluminum under conditions of peak energy yield. The parasitic corrosion of the RX808 was concentrated at grain boundaries, making surface characterization critical to the evaluation of these alloys.

Survey of electrochemical behavior of aluminum alloys. As part of the Reynolds activity in the development of alloys for use in the vehicle, LLNL has routinely determined the properties of alloys fabricated by Reynolds. Approximately 60 compositions have been surveyed. In these studies, electrode potential and the hydrogen gas evolution rate are simultaneously measured for various current densities, galvanostatically controlled. Data are reduced to plots of the partial current densities for aluminum dissolution and water reduction against electrode potential. The anode is macrophotographed following each experiment to record surface topography. The anodes studied represent (1) pure aluminum/electrolyte combinations in which minor alloy constituents are varied parametrically, (3) alloy/electrolyte combinations in which the heat treatment of the sample is an experimental parameter, and (4) alloy/electrolytes in which the composition of the electrolyte is altered, including surveys of corrosion inhibitors. This work is nearing completion and will be reported in 1982.

Hardware Development and Electrode Studies

The cost of this subcontract was shared with Continental Group, Inc. (CGI) in return for foreground patent rights. Research was carried out both at the CGI Energy Systems Laboratory⁴ in Cupertino, California, and at Lockheed Missiles and Space Company (LMSC) in Palo Alto, California, under subcontract to CGI. The primary purpose of this research is to verify the power cell concept through the development and demonstration of rapidly refuelable, full-scale, aluminum-air multicell hardware adaptable to practical application in a vehicular propulsion system. The demonstration of a full-scale (0.1 m^2 anode), rapidly refuelable bicell was a critical-path milestone for the aluminum-air program in FY 1981. This work was performed at LMSC. A secondary purpose of this contract is to investigate the behavior of aluminum and of

some alloys in caustic electrolytes, with particular attention to the active/passive transitions found under certain conditions. This work was undertaken at CGI.

Power-cell studies. The practicality of solution-side current collection (SSCC) in aluminum-air cells has been established. This technique (invented by LMSC in 1980) achieves anode current collection by pressing metal contacts to the anode at the aluminum/electrolyte interface. The technique obviates making mechanical or soldered connections to the anode prior to loading into the cell, and eliminates the need for isolating such connections from the electrolyte to prevent corrosion. SSCC allows rapid refueling using anode plates having minimum fabrication steps and wide dimensional tolerances. Lockheed reports a loss of voltage of 40 mV (relative to dry-side current collection) and 97% anode utilization in a 50-cm² test cell. Subsequent tests in an improved 200-cm² cell revealed anode polarization curves and hydrogen evolution rates differing little from those obtained with dry-side current collection under the same experimental conditions.

Solution-side current collection was used in three rapidly-refuelable test bicells: The M1-1 system featured two 200-cm² anodes advanced against a central cathode module by air-filled rubber bladders. The M1-3 system was the full-scale (0.1 m² anode) version of the M1-1 and is shown in Fig. 2. The M1-2 system used a single aluminum anode fixed between two movable air cathodes, which advance under pneumatic pressure during the dissolution of the anode.

The M1-1 bicell was employed extensively in parametric testing in 1981, using an automatic data acquisition system to record data, compute results, and characterize cell performance in both tabular and graphic formats. Parameters were changed up to 6 times during each of 24 tests. The best performance was 3.66 kW/m² peak power density at 0.89 V and 98.4% coulombic efficiency. Current density was 4.1 and 5.2 kA/m², for anode and cathode, respectively. Anodic and cathodic polarization was 1 and -147 mV/kA-m⁻², respectively.

Anode polarization was small and predominantly in the 10-20 mV/kA-m⁻² range. There was some tendency for the polarization to increase with time. SSCC/anode contact was stable in M1-1 when bladder pressure exceeded cell electrolyte pressure. A peak coulombic efficiency of 98% was achieved by coating the nickel SSCC collector. The performance of the aluminum-air battery is primarily dependent upon polarization of the air cathode since the aluminum

Fig. 2. The rapidly refuelable, full-scale (0.1 m^2) bicell, M1-3-LMSC. The cell uses an internal, permanent, solution-side current collector (SSCC) and obviates the necessity for making an electrical contact to the anode prior to its introduction into the cell.

anode has very little polarization loss. Very high cathode polarizations (greater than 125 mV/kA-m^{-2}) were observed, in contrast to results at DSC and LLNL. The cause of the discrepancy is not known.

A 16-cell module of the full-size M1-3 design was modeled to evaluate parallel and series electrolyte flows. Shunt current losses were low ($<1.5\%$) in both cases, and electrolyte flow through the cells in series must be at a high rate ($Re > 700$) to limit accumulated hydrogen gas to 20% (vol.) at 2 kA/m^2 . This flow would also limit temperature and aluminate increases to satisfactory levels. The need for a relatively complex pressure control system for air and electrolyte in each cell mitigates against the use of series electrolyte flow. Parallel flow of electrolyte into each cell appears preferable.

The major achievements in 1981 were the establishment of SSCC as a means of anode current collection and the demonstration of refuelability using SSCC in moving-anode and moving-cathode designs. While mechanical aspects of the full-scale M1-3 cell were satisfactorily demonstrated, optimization of the anode current collector design is necessary to overcome IR losses with SSCC on the 0.1-m^2 scale.

Unifunctional Air Electrode Development

The objectives of this work at Diamond Shamrock Corporation are to provide air electrodes suitable for development and testing of aluminum-air cells and to develop air electrodes for battery operating conditions. Thirty-nine $1,000 \text{ cm}^2$ and 44 smaller air electrodes were produced⁶ and delivered to LLNL, LMSC, and CGI.

A number of carbons and catalysts were tested that indicated the feasibility of meeting specification voltages with non-noble metal catalysis or with as little as 0.3 mg-Pt/cm^2 at high current density. Physical strength of electrodes was improved, overcoming delamination problems. It was shown that cathode bubble pressure can be increased.

An eight-cell life-test facility with computer control and data acquisition was constructed to evaluate air cathodes. Cathodes were cycled under simulated battery operating conditions with certain features of the drive cycle varied to determine their effect upon cathode life and performance. The study showed that extended periods of standby, in which the cathode stands at open circuit, greatly shorten cathode life. It was likewise found that the rate of decay in cathode potential is directly proportional to peak current density. Finally,

a linear relationship was found between cathode potential decay rate and duration of the current density steps in the drive cycle.

Life tests using the standard cycle (periods at 1-, 6-, and 2 kA/m² followed by 1 h standby) averaged 436 cycles to failure, although one life test resulted in twice this average (Fig. 3). Reduction of electrolyte flow rate increased electrode lifetimes to 998 standard test cycles.

Cathode failure is attributed to the combination of carbon corrosion and wetting of the active layer; there are indications that mechanical stresses caused by fluctuations in cathode differential pressure ultimately result in catastrophic failure of the cathodes.

Anode Development and Electrode Fabrication Studies

In addition to supplying standard anode alloys for testing of cell configurations at LLNL and CGI/LMSC, the objectives of this work conducted by Reynolds Aluminum Co. were to: (1) study the feasibility of producing battery anodes directly from Hall cell product, (2) investigate the recycling of battery reaction products, and (3) determine electrochemical properties of certain aluminum alloys.

The feasibility of producing aluminum anode plates for aluminum-air power cells directly from primary aluminum as produced in Hall cells was examined, and costs for these anode plates were estimated. A critical assumption was that aluminum anode plates of alloy composition, 0.4-0.8% Mn, 0.04% Fe, and 0.04% Ga, with minor impurities normally occurring in 5A and 6A grade primary aluminum, would be satisfactory for power cell application.

It was found feasible to produce this alloy from Hall cells in plants now producing high-purity metal and to go directly to 10- to 12-mm-thick anode slabs using a continuously moving mold caster. Gallium may be introduced into the metal by adding anhydrous dawsonite enriched in gallium oxide to the reduction cell. Manganese may be introduced into the metal in the reduction cell or in the holding/melting furnace. Unit cell size in the solidified alloy may be controlled by adding grain refiner just ahead of the caster. This alloy does not pose a problem to continuous casters and can be produced at nearly the same rate as commercial purity. Scrap anodes of appropriate purity could be recycled to the holding/melting furnace at the caster facility after cleaning and sorting.

The anodes produced by these processes would cost 33¢/kg over 3A grade molten aluminum costs (7.7¢/kg for premium purity, 5.3¢/kg for alloying agents,

Fig. 3. Preliminary testing of the Diamond-Shamrock, Inc. standard air electrode (PT loading, 1.2 mg/cm²) used in the development of battery hardware. Cycles consisted of 3 min at 1 kA/m², 0.5 min at 6kA/m², 10 min at 2 kA/m², and 2 h on open-circuit standby.

and 19.8¢/kg for casting and shearing). Anodes could also be produced with 0.03% Fe using Hall cell metal and continuous casting by the use of specially prepared aluminas, such as some chemical grade products. This would add another 22¢ to 33¢/kg to the 33¢/kg cost. It is not feasible to produce lower iron anodes directly from Hall cell metal.

The presence of 0.04%-0.06% Fe in the Hall-smelter product reduces coulombic efficiency at 2 kA/m² to 35% (cf. 90% for RX808 containing 0.01% Fe). It was determined that the addition of 0.04% Mn to an 0.04% Fe, 0.04% Ga, 0.8% Mg alloy improved the efficiency from 35% to 83%. The net energy yield of this alloy is 85% of that obtained from RX808 in standard cells. The alloy composition and preparation has not yet been optimized for use in the aluminum-air cell, but results indicate the potential for producing a cost-effective alloy directly from Hall-cell primary metal.

Aluminum Dissolution Research

The Institute of Electrochemistry, Belgrade, is investigating the electrochemical properties of aluminum alloys containing gallium and phosphorus in both saline (2M NaCl) and alkaline [4M NaOH + 1M Al(OH)₃ + 0.06M Na₂Sn(OH)₆] electrolytes. Forty-one alloys have been prepared with Ga ranging from 0% to 0.327%, either phosphorus-free or containing 0.1% phosphorus. These alloys have been analyzed for trace impurities, and detailed electrochemical analyses are proceeding.

Studies of Hydrargillite Precipitation

The objective of this Alcoa project is to develop and demonstrate processes for the control of aluminum-air battery electrolyte composition through the precipitation of aluminum trihydroxide. This involves two tasks:

- (1) determination of the physical properties of the caustic-aluminate electrolyte as a function of the chemical composition and temperature; and
- (2) determination of the hydrolysis reaction kinetics as a function of caustic level, degree of supersaturation, seed quantity and size, temperature, and gallium and tin impurity levels, and the operation of a complete precipitation system to determine changes in hydroxide seed population over time.

Task 1 was completed and resulted in data on density, viscosity, and electrical conductivity of electrolytes over a matrix of compositions ranging from 3M to 6M NaOH, and 0M to 4M Al(OH)₃, at temperatures of 25° to 80°C, and containing 7 g/l Sn and 0.2 g/l Ga.

Task 2 is nearing completion. Results of all kinetic experiments were analyzed and correlated in the following expression:

$$-dc/dt = K_o [e^{(-E/RT)} A_t (C - C^*)^2 / C_{Na}^2] \text{ mol/l-min} ,$$

where $K_o = [1.944 \times 10^7 \times \exp(-9.4321 C_{Sn})]$, $T = ^\circ K$, $E = 14.79 \text{ kcal/g mole}$, $R = \text{gas constant} = 1.9872 \text{ cal/g mole } ^\circ K$, $C_{Na} = \text{molar Na concentration}$, $C_{Sn} = \text{molar Sn concentration}$, $C - C^* = \text{molar Al supersaturation}$, and $A_t = \text{seed surface area m}^2/\text{l clear liquor}$. The negative effect of Sn is included in this expression, and test results were insensitive to Ga concentration in the range covered. An improved correlation with $(C_{Na} - C)^2$ replacing C_{Na} in the denominator has since been derived, which alters the rate at high aluminate concentrations.

VEHICLE APPLICATIONS AND ENGINEERING ANALYSIS

Background

A continuing part of the metal-air program is the analysis of battery and vehicle systems and their projected performance, cost, and energy consumption. Computer models, based on cell measurements and other laboratory experiments, are used to forecast battery and vehicle characteristics as well as transform vehicle requirements into development goals. These vehicle simulation and cost models were originally developed in 1977 and 1978 for the Department of Energy as part of a comparative analysis of energy storage devices for use in automobiles. Adaptations of these models along with newly developed battery simulation models are now employed in both the iron-air and aluminum-air programs.

The typical modeling procedure starts with a well-characterized internal combustion engine (ICE) vehicle. The model conceptually replaces the ICE propulsion systems (fuel, engine, transmission, etc.), with an electric propulsion system (battery, motor, motor controller, etc.). The new propulsion system provides both the energy and power required for the vehicle to meet previously specified values of range and acceleration. The result is an automobile having a predetermined range and acceleration capability, yet with

the same passenger-carrying capacity as the original ICE vehicle. The transformed automobile differs from the ICE vehicle in its mass, energy use, and cost.

Iron-Air Vehicle Analysis

A study by Westinghouse⁸ was completed analyzing the size and performance requirements of an iron-air battery propulsion system for various commuter-type electric vehicles. Battery characteristics were obtained from state-of-the-art and near-term iron and air electrodes and iron-air cell characteristics. Results were obtained for four defined levels of acceleration with varied vehicle passenger loadings and cruising ranges, with and without a regenerative braking capability. The results indicated the beneficial effects of regenerative braking in extending vehicle range and the existence of optimal power-to-mass ratios for each vehicle class. On the basis of this analysis, the iron-air battery system compares favorably with advanced secondary-battery propulsion systems in fulfilling vehicle missions for ranges of up to 240 km.

Aluminum-Air Vehicle Analysis

The performance characteristics of various electric propulsion systems based on the Al-air battery has previously been analyzed by Lawrence Livermore National Laboratory using the LLNL interactive vehicle model. In 1981, the Al-air performance and cost models were modified⁹ to reflect recent technical developments and changing economic conditions. The Al-air vehicle cost-estimating model, developed by Interplan Corp. in 1979, was updated to reflect 1981 costs and adapted to work with the new performance models residing in DOE's PDP-11 UNIX operating system.

A 5-passenger secondary-battery/Al-air battery hybrid vehicle has been analyzed. This vehicle uses high specific power secondary batteries for short trips, and the Al-air battery for range extension. Preliminary estimates show that the fuel cost (aluminum plus electric recharge) decreases from 10.3¢/mile for an Al-air vehicle to 6.6¢/mile for a hybrid vehicle, assuming an average yearly trip-length distribution profile.

Aluminum-Air Safety and Environmental Analysis

In December 1979, a contract between LLNL and the IWG Corporation of San Diego was enacted to perform a study¹⁰ of the health and safety impact of Al-air vehicles. This contract was successfully concluded, and a final

two-volume report (LLNL UCRL-15434) was published in November 1981. The conclusions of this study are summarized as follows:

1. The aluminum-air electric vehicle (AAEV) fuel cycle poses no serious health, safety, or environmental problems.
2. Air emissions for the AAEV fuel cycle are principally due to aluminum-reduction and fossil-fueled electricity generation, with these sources generally located outside critical air basins.
3. Fluorides are the most serious pollutants generated during aluminum smelting but are presently under strict control.
4. Lower hydrocarbon emissions associated with the AAEV are significant because of the presence of polycyclic aromatic hydrocarbons, some of which are carcinogenic.
5. Carbon dioxide and sulfur oxides are the largest emissions (by weight) of the aluminum industry and are presently unregulated.
6. Sulfur oxides and nitrogen oxides from Western coal are the major, significant emissions of concern in electrical generation.
7. Compared to coal-derived automotive fuel, the AAEV coal-based fuel cycle presently produces almost 18 times more sulfur oxides and almost 4 times more carbon dioxide emissions, but at least 8 times less hydrocarbon emissions.
8. Using hydroelectric or nuclear electricity generation, the AAEV fuel cycle can produce negligible amounts of nitrogen oxide emissions (aluminum is now produced using 41% hydro, 38% coal, 14% oil and gas, and 7% nuclear).
9. Sodium hydroxide represents the major hazard of the aluminum-air battery because of its corrosive nature.

The overall indications are that the proposed aluminum-air electric vehicles present no unusual environmental hazards and that the potential health and safety problems will be manageable.

Aluminum-Air Energy Use and Economic Cost

Lawrence Livermore National Laboratory has assessed Al-air energy consumptions and costs. The most potent factor determining vehicle fuel cost is the vehicular fuel efficiency, which is best expressed as the product of vehicle gross weight and fuel mileage, typically expressed in units of

ton-km/kg-Al. Vehicular fuel efficiency is determined by the computer integration of the characteristics of battery, motor, and motor controller over various drive cycles. Unoptimized model electrodes yield a fuel efficiency of 31 ton-km/kg-Al. The immediate goal, an optimized cell of 36 ton-km/kg-Al, is required for economic competitiveness, while 42 ton-km/kg-Al has been established as the long-term R&D goal of the alloy development phase of this project.

The cost of the anode plates depends strongly on the purity and alloying requirements, fabrication techniques, distributor and retail markups, and credit for returned hydrargillite. On the basis of the U.S. industry published price for delivered ingot plus additional costs for premium (low Fe) purity, plate fabrication, alloying agents, and retail markup, the cost for a hypothetical aluminum fuel plate was estimated to be \$1.74 per kg in 1981 dollars before taxes.

On the basis of this price and a vehicular fuel efficiency of 36-42 ton-km/kg-Al, the cost of fuel would be equivalent to a liquid fuel costing \$0.56-\$0.94/liter (\$2.12-\$3.54/gal) in advanced automobiles of fuel efficiencies in the range of 13.5-19.3 gross-ton-km/liter (35-50 gross-ton-miles/gal-fuel). Total primary energy consumption (assuming coal-based electricity) would range from 9%-66% more than an advanced automobile of the same weight and performance burning petroleum-derived gasoline, but would be comparable to the energy use of today's best gasoline- and diesel-fueled automobiles burning synthetic liquid fuels derived from coal. Therefore, a wide range of economic factors (external as well as direct), and not gross primary energy use, is likely to play the key role in the competitiveness of this vehicle in a petroleum-scarce world.

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CHAPTER 4 ENGINEERING-SCIENCE RESEARCH

This chapter describes much of the supporting research included in the Technology Base Research Project. The primary goal of the work is to establish scientific and engineering principles applicable to batteries and electrochemical systems. Projects include the application of advanced scientific tools to study electrode processes, mathematical modeling of battery systems, and battery assessment studies. These efforts cover all battery systems presently considered for energy storage, and projects are grouped according to the relevant generic electrochemical technology.

LITHIUM/METAL SULFIDE CELLS

Supporting research for the development of high-temperature lithium/metal sulfide cells includes fundamental studies of cell chemistry and engineering, mathematical modeling of cells, efforts to establish a workable thermal management strategy, and the measurement of composition profiles in working cells. An important aspect of these projects is the feedback and interaction between the various investigators.

Molten-Salt Cell Research

The scope of Argonne National Laboratory's program includes (1) studies of various lithium alloys used as the active material in negative electrodes, (2) investigations of FeS_2 and other transition-metal sulfides as the active material in positive electrodes, (3) evaluations of current-collector and separator materials, and (4) development of a computer model to predict the performance of full-scale cells.

Negative electrode research

Lithium-aluminum electrode morphology. An apparatus has been developed in which direct microscopic observations of a small electrochemical cell can be made at operating temperature (450°C) to study morphological changes of negative electrodes during charge and discharge. Features such as protrusion growth, powder formation, volumetric changes, and gas evolution can be observed. Several preliminary experiments conducted with Li-Al electrodes indicate that lithium can be charged into aluminum at rather high current densities. Some expansion of the aluminum electrode occurred during the charge, and subsequent charges and discharges resulted in the formation of some powdered LiAl reaction product. It is suspected that powder formation is related to the overpotentials associated with higher current densities.

Lithium-aluminum-iron electrode. The addition of finely divided iron to Li-Al electrodes has been found in preliminary tests to produce an electrode potential about 200-250 mV more negative than that of Li-Al alone in the ($\alpha+\beta$) region. Cyclic voltammograms for an electrode of the composition Al_5Fe_2 showed that 90% of the lithium capacity was obtained at about -225 mV vs. Li-Al.

Some preliminary cyclic voltammetry work shows a large peak at about -250 mV below the two-phase ($\alpha+\beta$)Li-Al region, but only a small peak is observed in the region where a β -LiAl reaction would be expected, and little evidence is seen of a solid solution reaction through the β -LiAl phase field. These findings may indicate the presence of a ternary phase, but other explanations for the voltammetry results are possible.

Lithium-aluminum-silicon electrode. Agglomeration in the Li-Al electrode may be related to the unusually high concentration of vacancies in the crystal lattice of β -LiAl, so the use of additives might control the agglomeration process by reducing vacancy concentrations. Earlier studies showed that the addition of cadmium or magnesium did not prevent agglomeration, but in similar experiments conducted with silicon additions of 0.5, 5.0, and 25.0 at.%, no agglomeration was found; however, none of the electrodes with silicon additives retained capacity as well as Li-Al electrodes. At the higher silicon levels, the capacity loss was not as pronounced. Severe agglomeration was found in a binary Li-Si electrode.

Earlier morphological studies of Li-Si and Li-Al-Si electrodes suggested that Li-Al and Li-Si may form ternary Li-Al-Si phases. Exploratory coulometric titrations, in which lithium was charged electrochemically into an Al-5.1 at.% Si electrode, showed voltage plateaus. These plateaus suggest that several three-phase composition regions were involved, some of which probably include ternary phases.

Lithium-silicon electrode. An exploratory experiment was conducted to charge lithium into a silicon powder bed at about 48 mA/cm^2 . The voltage plateaus agreed well with those reported by S. Lai¹ and could be related to electrode displacement and powder formation. The results indicate that the electrode behavior tends to be sluggish, at least for the -60, +100 mesh particle size silicon used in the electrode.

Positive electrode studies

Reference electrode development. Because electrolyte concentration shifts occur normally during cell operation, studies were conducted to determine the effects of both electrolyte concentration and temperature on the $\text{Ni/Ni}_3\text{S}_2$ reference electrode. Emf data for the electrode couple of $\text{Ni/Li-Al/LiCl-KCl, Li}_2\text{S}$ (saturated) $\text{LiCl-KCl/Ni}_3\text{S}_2/\text{Ni}$ show that the $\text{LiAl/Ni}_3\text{S}_2$ couple is significantly affected by temperature but relatively unaffected by electrolyte composition.

The response of the $\text{Ni/Ni}_3\text{S}_2$ electrode to various concentrations of Li_2S dissolved in LiCl-KCl eutectic electrolyte was also determined. The emf for this electrode showed a Nernstian response to S^{2-} concentration, in excellent agreement with that predicted theoretically for a two-electron reaction. This agreement, as well as the demonstrated stability of the electrode at very low levels of dissolved Li_2S (about 10^{-5} molal), indicates that this electrode could also function as an electroanalytical sensor for Li_2S in molten-salt systems.

To further improve the usefulness of the reference electrode system, a multifunctional sensor, which allows monitoring of both the cell temperature and the potential of the working electrodes, has been developed. The sensor consists of a chromel-alumel thermocouple combined with a $\text{Ni/Ni}_3\text{S}_2$ reference electrode. An important feature of the sensor is that it allows correction of the observed electrode potential for temperature variations in the cell.

Solubility studies. The FeS_2 electrode offers the potential of high performance but has been found to undergo rapid loss of capacity during cycling. Post-test metallographic examinations previously revealed the presence of iron and Li_2S deposits in the cell separator, suggesting that the capacity decline may be caused by the formation of soluble iron-sulfur species in the molten-salt electrolyte. The objective of this study is to determine the concentration, identity, and means of elimination of soluble electroactive iron and sulfur species that may be formed in the FeS_2 electrode during the operation of Li-Al/FeS_2 cells.

Preliminary voltammograms of electrolyte solutions saturated with FeS_2 showed a complicated electrochemistry; as a result, a study of the behavior of Li_2S in LiCl-KCl was carried out to assist in the understanding of the Li-Al/FeS_2 system. The results from this study indicate the following:

(1) the shape of the voltammogram is unaffected by Li_2S concentration; (2) the sequence of the anodic reaction is unaffected by increasing the temperature from 400° to 450°C , whereas the sequence of the cathodic reaction is affected by decreasing the temperature from 450° to 400°C ; and (3) the general features of the voltammogram are unaffected by changes in the composition of the electrolyte. Analysis of the voltammograms has made possible the tentative assignment of reactions to the peaks, from which proposals for the anodic-cathodic reaction sequences were made. The elucidation of the reaction sequence for the Li_2S phase will help to provide a further understanding of the FeS_2 electrode reactions.

Cyclic voltammetric techniques were also used to determine the solubility of Li_2S in the three compositions of LiCl-KCl electrolyte. The solubility of Li_2S was found to increase in LiCl -rich electrolyte and to decrease in KCl -rich electrolyte, when compared to that in LiCl-KCl eutectic. The diffusion coefficient of S^{2-} , obtained from plots of the normalized peak current densities, is $(5.2 \pm 1.0) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

In the case of FeS_2 , cyclic voltammetry at a glassy carbon electrode does not permit an accurate determination of the concentration of the sulfide ions in solution, since the solubility of FeS_2 appears to be relatively low. A voltammogram of a solution in which a crystal of FeS_2 was immersed for 335 h and then removed shows a main anodic peak at a potential ($E = 1.59 \text{ V}$) close to that of the first anodic peak of the voltammograms of Li_2S , which probably corresponds to the oxidation of S^{2-} to S^- . Since it was shown earlier that this peak can be used to determine Li_2S solubility, it was also used to estimate the concentration of S^{2-} : $(0.9 \pm 0.2) \times 10^{-2}$ moles/liter at 450°C in LiCl-KCl eutectic electrolyte.

A second experimental technique has also been developed to determine the concentration of S^{2-} in the electrolyte, by using a $\text{Ni/Ni}_3\text{S}_2$ electrode. The response of the electrode was first observed in electrolyte containing a known quantity of heat-treated, sulfur-free Li_2S . The emf measurements versus a $\text{LiAl} (\alpha+\beta)$ reference electrode were made 4 hours after each addition of Li_2S , and after a small recharge of the Ni_3S_2 electrode. The results showed a Nernstian response corresponding to a two-electron reaction. Emf measurements carried out when the solution was saturated with Li_2S gave values in good agreement with those obtained earlier. The break points of the potential-log C relationship define the saturation concentrations of Li_2S ,

and these saturation values are in reasonable agreement with the values obtained earlier from cyclic voltammetry.

The values of concentration or activity of S^{2-} ions in equilibrium with the X-phase that was measured were used to estimate the ΔG of the reaction $Li_2S + FeS \rightarrow Li_2FeS_2$. This resulted in values of ΔG of -1.5 ± 1.0 and -2.6 ± 1.0 kJ at 400° and $450^\circ C$, respectively. These calculated values agree well with those obtained earlier in this laboratory by Tomczuk et al.²

Emf measurements on disulfide electrodes. Efforts to determine the emf vs temperature curves for the various transitions of the FeS_2 and NiS_2 electrodes were continued. These data are necessary for a complete thermodynamic description of the $LiAl/FeS_2$ and $LiAl/NiS_2$ systems.

The experimental effort consisted of operating laboratory-scale cells (~ 5 Ah negative electrode capacity, ~ 1 Ah positive electrode capacity). However, the results obtained so far have been poor because of the formation of short circuits.

Spectroscopic studies. The objective here is to characterize the electroactive species present in the electrolyte zone of electrochemical cell systems employing metal sulfide electrodes. There is considerable evidence from prior spectroscopic and related physiochemical studies that sulfide species other than S^{2-} can form in molten salts when a portion of the sulfur is in an oxidation state higher than 2-minus (e.g., elemental sulfur, S_2^{2-}).

The systems chosen for initial study are MS_2 - Li_2S mixtures ($M = Co, Ni, Fe$) dissolved in alkali halides. A search was made of the pertinent literature, and some absorption spectrophotometric surveys were carried out on MS_2 - Li_2S solutions in $LiCl$ - KCl . On the basis of an analysis of published spectroscopic data and of results obtained in this work, a hypothetical correlation was developed between peak absorption frequency and the value of x in polysulfide species of the type S_x^{2-} . This correlation appears to offer a plausible description of polysulfide formation in terms of its dependence on $[S]/[S^{2-}]$ ratio. The correlation is reasonably consistent with most other experimental information on polysulfide-containing media.

Materials research

The galvanic deposition of aluminum from the Li - Al electrode and subsequent diffusion into the hardware components forms a brittle intermetallic reaction layer. Prolonged development of such reaction layers undermines the strength and lowers the conductivity of these components. Studies are in progress to

determine the aluminum deposition and diffusion rates for different substrate materials and to identify coatings that will prevent this reaction.

A third set of diffusion couples (nickel 200, low-carbon steel, and chromium-plated steel) were tested at 475°C for 100 h. The nickel specimens had diffusion layers consisting of NiAl_3 and Ni_2Al_3 zones. For both materials, diffusion followed a parabolic growth rate. The diffusion coefficients of $(34 \pm 2) \times 10^{-12}$ and $(27 \pm 3) \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for nickel and 1008 steel, respectively, are in good agreement with values estimated from the literature. Thickness measurements on the unaffected test metal were used to deduce the depth of penetration beyond the original interface and to determine the penetration coefficient. For both materials, approximately 25% of the diffusion layer growth occurred at the expense of the substrate.

The electroplated chromium layer on the steel substrate was effective in suppressing aluminum diffusion. Only a few 30- μm conical protrusions of a Cr-Al alloy developed after 100 h. However, prior tests have shown that both the number and dimensions of these protrusions increase with increasing test duration. Coatings of CVD-TiC were not tested for the 100-h interval, but this coating has successfully prevented deleterious aluminum diffusion at 475°C for more than 1000 h.

The galvanic deposition of aluminum onto steel substrates was investigated to temperatures as high as 535°C. Steady-state currents were used to calculate the aluminum deposition rates for the different test temperatures. These calculated rates were then compared to the experimental rates at 400 and 500°C, which were derived from actual aluminum weight gains in earlier immersion tests of 240-h duration. The temperature dependence of the deposition rate was shown to obey an Arrhenius relationship.

A similar study of the galvanic deposition of aluminum onto nickel was initiated, and incomplete data indicate that the deposition onto nickel is analogous to that on steel. This technique of monitoring the galvanic reaction appears to provide reliable estimates of aluminum deposition rates in a comparatively short time span.

Mathematical Modeling

Efforts at Lawrence Berkeley Laboratory^{3,4} have resulted in a sophisticated model of the composition changes expected in operating lithium/metal sulfide cells.

Thermal Management of Lithium-Aluminum/Iron Sulfide Cells

Experiments were performed at Gould, Inc. to study the rate of thermal energy generation in 200-Ah lithium-aluminum/iron sulfide cells.⁵ Two independent methods were used to determine the cell heat generation. The first is an indirect method that uses thermodynamic calculations based on precise measurements of cell potential; the second method directly measures heat generation with a new high-temperature battery calorimeter.⁶

The results for cell heat generation determined by the two independent methods are in excellent agreement. For a full-scale, 100-cell electric vehicle battery, total heat generation may reach 4 kW, which indicates the need for a cooling system to avoid excessive temperature rise. In 1982, Gould, Inc. plans to extend these studies to the lithium-silicon/iron disulfide system.

Measurement of Composition Profiles in Lithium-Aluminum/Iron Sulfide Cells

Basic studies at Oak Ridge National Laboratory have demonstrated the establishment of current-induced composition gradients in mixed molten-salt electrolytes. Composition shifts, if large enough, can produce significant deleterious effects, such as solid-phase precipitation in or near the electrodes of the LiAl/LiCl-KCl/FeS battery.

Composition profiles have been analyzed by atomic absorption (AA) and scanning electron microscopy/energy dispersive X-ray analyses (SEM/EDAX) and are summarized in Fig. 1. The data were analyzed by several methods to ascertain the accuracy with which the shape of the profile can be determined. These new results are the first quantitative measurements of the shape of the concentration profile in electrolyzed LiCl-KCl molten-salt eutectic.

ALKALINE CELLS

Supporting research for rechargeable batteries (Fe/NiOOH, Zn/NiOOH, Fe/Air, Zn/air, and Zn/Fe(CN)₆⁻³) is aimed at (1) improved understanding of the complex phenomena that limit the life and performance of zinc, nickel, and iron electrodes in alkaline electrolyte and (2) new electrode/electrolyte formulations and new separators for evaluation in test cells. A wide variety of modern scientific techniques is employed to measure and predict structural, chemical, and electrochemical changes in battery electrode materials, and the resulting information can be used by battery developers to optimize cell designs.

Fig. 1. Measured composition profiles in quenched electrolyzed LiCl-KCl.

- Atomic absorption and width of the analyzed section, SEM/EDAX and width of the moving window.
- Predicted profile.
- Least-squares quadratic fit to AA and SEM/EDAX data.

Several independent projects are being conducted to provide vital information and/or evaluate promising new avenues to improved electrode performance and lifetime.

Battery Electrode Studies

Lawrence Berkeley Laboratory is evaluating practical means for improving the lifetime and performance of the rechargeable zinc electrode. Zinc/nickel oxide cells are studied with a computer-controlled testing system designed specifically for cycle-life testing of battery electrodes. Eight modular-design current controllers were built and tested to verify independent control of up to eight channels from a single power supply. A variety of cycling regimes, including constant current, constant potential, constant power, and pulsed power, have been tested, and extensive data treatment and display capabilities are available. Experiments are being conducted to establish the effect of cell chemistry and various charging and discharging regimes on the behavior of Zn/NiOOH cells.

In related work at LBL, an electrochemical impregnation method of preparing porous Ni electrodes for high-energy battery applications is being investigated. An understanding of the present electroprecipitation method is necessary to develop an improved process for producing Ni battery electrodes. Preliminary experiments have shown that the $\text{Ni}(\text{OH})_2$ deposit becomes less adherent as the temperature of the acidic nickel nitrate bath decreases.

Basic Studies on Nickel-Zinc Batteries

A series of experiments was conducted at Lockheed, Inc. to establish governing processes in alkaline zinc/nickel oxide batteries. Specially designed microcells, acting as simulated pores, allowed in-situ access to the dimensional domain and internal area of pores in porous nickel and zinc electrodes. These model pores were made with Lucite windows for optical microscopic viewing and with multiple microreference electrodes for potential/position/time measurements.

The evolution of a 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 optically to the appearance and movement of a white ZnO layer. Precipitated ZnO then caused blockage of the second kind, masking the pore surface and forcing the front inwards.

Concentration profiles could be obtained from the potentials of the microreference electrodes at open circuit, as shown in Fig. 2. The ZnO front extended about 2 mm into the pore, where the OH^- concentration is increased above its initial concentration. The release of OH^- from $\text{Zn}(\text{OH})_4^{2-}$ during ZnO precipitation is evidently responsible for this concentration perturbation. Figure 2 also shows relaxation of the OH^- profile after 600 seconds at open circuit.

Development of a High-Rate Insoluble Zinc Electrode

The objective of this program at Energy Research Corporation is to investigate the insoluble zinc electrode as an approach to reducing capacity loss and shape change in rechargeable alkaline zinc batteries. Zinc oxide samples doped with 0.6 atom % Sn, Co, La, Bi, Al, Pb, Cd, Ce, and Fe were evaluated for solubility in 0-45% KOH and investigated as electrodes using cyclic voltammetry. In 20% KOH, the solubility of the doped ZnO samples (with the exception of ZnO + Pb) was 37-45% lower than for pure ZnO and only 12-25% higher than for the relatively insoluble calcium zincate.

A preliminary investigation has also been carried out to determine the solubilities of other zinc compounds in 35% KOH prior to evaluating their electrochemical behavior as zinc electrodes. Compounds identified as possessing an extremely low solubility include ZnF_2 (2 mg ZnO/ml), $\text{Zn}_2\text{B}_6\text{O}_{11}$ (11 mg ZnO/ml) and ZnTiO_3 (5 mg ZnO/ml). An electrolyte composition has also been found (26 wt% KOH + 8 wt% H_3BO_3 + 16 wt% KF) in which pure ZnO has a solubility of about 20 mg/ml.

The general current-potential behavior of sparingly soluble zinc oxide samples and doped zinc oxides is being studied for its dependence on repetitive potential sweeps and for its electrolyte composition, using cyclic voltammetry. Electrochemical performance of all doped materials tested, except for Sn-doped ZnO, was substantially poorer than for pure ZnO.

Sn-doped zinc oxide electrodes are being prepared for evaluation under cyclic conditions in Zn/Ni cells. The evaluation will also include the $\text{KOH}/\text{BO}_3^{3-}/\text{F}^-$ ternary electrolyte composition.

Supported Liquid Membrane Battery Separator

Castle Technology, Inc. is investigating the feasibility of supported liquid membranes as improved battery separators for the Zn/NiOOH secondary battery. Supported liquid membrane separators consist of active hydroxyl-ion transport agents dissolved in a suitable organic solvent and absorbed into the

Fig. 2. Open circuit potentials after 96 sec at 1 mA. Corresponding concentrations are indicated at the right.

pores of a microporous membrane. Several transport-agent/solvent combinations have been shown to permit rapid transport of hydroxyl ions but prevent intrusion of soluble zinc into the membrane.

Hydroxyl-ion and zincate-ion transport rates were measured for the series of supported liquid membranes in a two-compartment cell. The hydroxyl-ion transport rates were on the order of 10^{-9} mole $\text{cm}^{-2} \text{sec}^{-1}$. This flux is nearly as large as that through the microporous separator (Celgard 2500) alone, which transports hydroxyl ion at a rate of 3×10^{-8} mole $\text{cm}^{-2} \text{sec}^{-1}$. Transport of zinc species through the same cells with a zinc-saturated 35% KOH solution on one side of the membrane was below detectability limits, indicating a transport rate of less than 5×10^{-13} mole $\text{cm}^{-2} \text{sec}^{-1}$.

Resistivity measurements demonstrated the ability of the supported liquid membrane separators to transport hydroxyl ions specifically at a moderate rate.

Zinc/nickel oxide test cells have been assembled and tested, and current densities have exceeded 1 mA/cm^2 . Work is now directed at improving the solvent system to decrease membrane resistance so that the cell can be operated at $\sim 10 \text{ mA/cm}^2$.

Kinetic Limitation of Secondary Alkaline Battery Electrodes

SRI International has continued investigations into the mechanisms and kinetics of charge/discharge processes occurring at Ni, Fe, and Zn electrodes in KOH and LiOH/KOH electrolytes. Emphasis has been placed on the determination of possible failure modes induced by kinetic or thermodynamic effects at extremes of temperature.

Nickel: The principal temperature limitations of Ni(OH)_2 electrodes in KOH and LiOH are: (1) the evolution of the oxygen at high states of charge, which causes a substantial decrease in the electrode coulombic efficiency at elevated temperatures, and (2) an additional irreversible component observed following deep or prolonged discharge at the nickel positive. This second limitation is attributed to a slow equilibrium between α - and β - Ni(OH)_2 .

Iron: By combining cyclic voltammetric, rotating ring-disc electrode, and ac impedance studies with thermodynamic data, SRI has been able to deduce a detailed reaction sequence for iron in concentrated alkali. The high temperature and low temperature reaction sequences are found to be significantly different.

Zinc: The influence of hydrodynamic conditions and zincate concentrations on the dissolution of zinc have been examined extensively, in addition to the effects of KOH concentration and temperature.⁷

Thermodynamic Data for Alkaline Battery Electrode Reactions

Ohio State University's Fontana Corrosion Center is computing the thermodynamic properties⁸ of iron, nickel, zinc, aluminum, and lithium in concentrated lithium hydroxide, sodium hydroxide, and potassium hydroxide solutions. The objective of this project is to provide the detailed knowledge of thermodynamic properties necessary to compute voltage, coulombic, and thermal efficiencies of Fe/NiOOH, Zn/NiOOH, and metal/air battery systems.

Ohio State has reviewed and assessed the data in the literature for vapor pressure, activity coefficient, and other thermodynamic functions for concentrated LiOH, NaOH, and KOH solutions. Sufficient vapor pressure data are available over the desired concentrations (1-12 molal) and temperatures (-10°C to 120°C) for NaOH and KOH, but not for LiOH. An experimental apparatus has therefore been constructed to obtain vapor pressure data for concentrated LiOH solutions (1-10 mol kg⁻¹) at various temperatures between -20°C and 120°C.

Restructuring and Loss of Capacity of Alkaline Battery Electrodes

Ohio State University is conducting an electrochemical and morphological study of alkaline battery electrode restructuring.⁹ Restructuring of porous battery electrodes during cyclic charging and discharging is a principal mechanism of electrode capacity degradation and limits the performance of many alkaline battery systems. This research is aimed at developing an understanding of the restructuring mechanisms for porous iron and nickel electrodes over a temperature range of 0 to 100°C. The restructuring phenomena are studied with low-frequency ac impedance techniques to define the electrical and electrochemical properties of the porous electrode. Optical microscopy, scanning electron microscopy with EDAX, X-ray diffraction, and Auger electron spectroscopy are used to investigate the morphological, structural, and chemical properties of electrodes. Fundamental studies on the growth of oxide films on massive iron and nickel as a function of temperature are being carried out to provide additional information on the mechanisms involved.

A transmission-line model adopted to represent the porous electrode has been shown to reproduce the essential features of experimental impedance data. The impedance of rolled and bonded nickel electrodes has also been shown to increase with cycle number, and this feature is believed to be a direct result of porous electrode degradation.

Oxide film growth on planar nickel electrodes has been found to follow a logarithmic growth law, which can be explained by a point defect model for film growth.^{10,11} These studies provide valuable insight into the complex phenomena occurring in operating alkaline nickel electrodes.

This work will be extended to sintered nickel and iron electrodes.

Research on Alkaline Zinc Secondary Electrodes

Failure mechanisms for porous zinc secondary electrodes have been investigated both theoretically and experimentally.¹² The proposed model predicts hydroxyl-ion depletion in the zinc electrode chamber to be an important factor in electrode failure, and the objective of the project at Linfield Research Institute is to evaluate the model by measuring concentration changes in working cells.

In Fig. 3, the concentration data are compared with values predicted on the basis of simplified theory.¹² The observed depletion rate is considerably less than predicted; this difference may be due to a pressure difference neglected in the simplified theory. Even though observed K^+ and OH^- depletion rates are less than those predicted by the simplified theory, drastic OH^- depletion is observed, supporting the contention that such depletion contributes to decreased capacity of porous zinc electrodes.

FLOW SYSTEMS

Several flow systems (Zn/Br_2 , Zn/Cl_2 , and Cr/Fe) are being developed for energy storage applications. These efforts are hindered by incomplete understanding of the phenomena governing cell performance. For example, the zinc/halogen system energy capacity is dependent on the morphology of zinc electrodeposited from flowing electrolyte, and the initiation and propagation of undesirable forms of zinc deposits (dendrites, ridges) are poorly understood. Several research projects are focused on this and related problems.

The Influence of Lead Ions on the Macromorphology of Electrodeposited Zinc

The morphology of zinc as it is electrodeposited from acid solutions demonstrates a remarkable imprint of electrolyte flow conditions. Lawrence Berkeley Laboratory (LBL) has investigated the development of macromorphology of zinc deposits under galvanostatic conditions on a rotating platinum disk electrode.¹³ Logarithmic spiral markings, which reflect the hydrodynamic flow on a rotating disk, appear in a certain region of current density well below the limiting current density (Fig. 4). Morphological observations

Fig. 3. Graphical comparison of observed and predicted K^+ and OH^- concentrations as functions of time in cells with severely limited convective flow.

XBB 817-6215A

Fig. 4. The dotted line is an Archimedes spiral described by $\theta - \theta_0 = 0.0304 (r - r_0)$. The fine solid curve is a logarithmic spiral described by $\theta - \theta_0 = 1.25 \ln r/r_0$. Note that the Archimedes spiral deviates greatly from the striation.

revealed the major influence of trace lead ions on the amplification of surface roughness through coalescence and preferred growth of initial protrusions. Results obtained from ultrapure electrolyte suggest preferred crystal growth towards well-mixed regions of the concentration field caused by slight differences in crystallization overpotential.

Amplification of surface roughness has been shown to proceed sequentially: (1) nucleation and growth of nuclei, (2) coalescence of nuclei into larger protrusions, (3) preferential growth of larger protrusions, and (4) successive coalescence and consumption of smaller protrusions by larger ones.

The role of lead ions is to (1) decrease the number of initial nucleation sites for zinc, (2) poison the platinum surface for hydrogen evolution (hence, the whole surface can be covered by a thin layer of zinc-platinum alloy from the very beginning of deposition), (3) enhance successive coalescence and preferential growth of protrusions, and (4) deform the crystalline structure to a rounded shape.

H^+ ions do not seem to affect either the initial nucleation or the successive coalescence of protrusions, but they change the crystalline structure to a rounded shape with decreasing pH values.

The Morphology of Electrodeposited Copper

When a metal is electrodeposited, the developing surface morphology determines a variety of surface properties. LBL has investigated the surface morphology of copper produced under well-defined conditions of mass transfer and uniform current distribution,¹⁴ leading to three regimes: (1) dc deposition at the limiting current, (2) dc deposition below the limiting current, and (3) pulsed current deposition below the limiting current.

In regime 1, nodular powder deposits are due to transformation from a dendritic structure to a coherent one when the mass transfer boundary layer at the growing dendrite tip thins out. In regime 2, the roughness generated during electrodeposition results from the growth of a few large protruding crystals embedded in a very fine flat polycrystalline deposit resembling sand. Coverage by the "sandy" deposit gives the crystals a deceptively nodular and amorphous appearance (Fig. 5). In regime 3, the growth of the large crystals can be inhibited with pulsed current. The off-time between the pulses is demonstrated to be the cause of this phenomenon. It is proposed that during this period, passivation of crystal growth sites occurs.

9.59 MA/CM²

24.02 MA/CM²

40% I_L

90.25 MA/CM²

111 MA/CM²

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40% I_L

Fig. 5. Grain size of fine structure decreases with increasing current.

Dendritic Zinc Deposition in Flow Batteries

The Illinois Institute of Technology is attempting to clarify the effect of transport processes on zinc deposition from acidic electrolytes. The transport properties of zinc halide solutions, collected and correlated in an earlier research project,¹⁵ have been checked for consistency. Correlations for the $\text{ZnCl}_2\text{-H}_2\text{O}$ system have been used to derive multicomponent binary diffusivities that reflect basic simplifying assumptions about complexation in the electrolyte.

The migration contribution to the effective diffusivities has been calculated, and it is evident that complexation conditions have a strong effect on the apparent zinc diffusion flux. This explains in part the extreme concentration dependence of the effective diffusivity.

Transport Properties of Zinc Halide Electrolyte

Investigators at the Lawrence Livermore National Laboratory are measuring the four diffusion coefficients at each of three compositions of the $\text{ZnCl}_2\text{-KCl-H}_2\text{O}$ system. Preliminary results show surprisingly low values of the cross-term coefficients. These had been expected to be larger as a result of complex ion formation in zinc halide systems. This result, if found at other compositions, should simplify the equations for modeling battery systems.

Analysis and Simulation of Flow Systems

Lawrence Berkeley Laboratory is developing mathematical models^{16,17} to predict the behavior of various electrochemical flow systems and identify important process parameters. Experimental studies are employed when necessary to verify completeness and accuracy of the models.

A theoretical stability analysis is underway to examine the effects of additives, current density, flow hydrodynamics, and electrode materials on dendrite initiation and propagation. This work will provide a fundamental understanding of zinc dendrite growth in zinc/halogen batteries.

An alternating voltage impedance method will be used to study the anodic behavior of zinc in an acidic aqueous medium. This work should help prevent battery discharge due to the formation of pits within the electrodes. In this investigation, impedance measurements will be performed on both a rotating disk and a rotating hemispherical zinc electrode.

Many electrochemical systems use channel flow between two plane-parallel electrodes. For example, this configuration can be used in $\text{Fe}^0\text{-Fe}^2\text{-Fe}^{3+}$

redox energy storage cells or in electroorganic synthesis. A mathematical model is being developed to calculate the concentration, potential, and current distribution in a thin-gap flow cell. Previous models have assumed that the interelectrode gap is much larger than the diffusion boundary layer thickness, but the present model allows the gap to be thin enough for the diffusion boundary layers to interact. This model also can take into account multiple reactions at the electrodes.

Porous Titanium Electrodes for Redox Batteries

The University of Akron is investigating the electrolytic activity of RuO_2 , IrO_2 , and OsO_2 coatings on titanium substrates towards redox reactions. The goal is to develop electrodes possessing long-term stability and high activity.

Ruthenized titanium electrodes were prepared and characterized. Surface area values were low compared with commercial ruthenized titanium, probably because of less etching of the substrate.

An interesting comparison of a mixed oxide electrode ($\text{Ru}_x\text{Ti}_{1-x}\text{O}_2$ with 8.24 g Ru/m^2) and a ruthenized titanium electrode (17.3 g Ru/m^2) revealed an identical roughness factor of 150 for both electrodes. This result supports the view that less precious metal may be employed in the mixed oxide form with no decrease of true surface area.

The acquisition of kinetic data for the ferric/ferrous couple by the rotating disk electrode technique has begun.

CROSS-CUTTING RESEARCH

Several efforts in the Technology Base Research Project provide support for a range of electrochemical technologies. Application of sophisticated in situ experimental techniques, such as in situ ellipsometry and spectroscopy, to the study of surface layers on battery electrode materials can provide fundamental information about electrode processes that would be otherwise inaccessible to battery developers. Battery assessment studies and detailed bibliographies are useful to a wide segment of the electrochemical community.

Surface Layers on Battery Materials

Lawrence Berkeley Laboratory is employing advanced techniques to provide direct experimental information about formation and properties of surface layers on battery electrode materials.¹⁸ Both electrochemical and ellipsometric techniques have been used to study surface layers on lithium electrodes in propylene carbonate electrolyte.

The kinetic behavior of the Li electrodes has been found to be controlled by field-assisted ion conduction through an insulating surface layer. The thickness of this layer, as derived from capacitance measurements, increases with time according to a parabolic rate law, the rate increasing with water content of the solution. Measured reaction rates are consistent with the fast formation of a compact protective film by reaction with residual water. This layer acts as a solid ionic conductor, and a nonprotective porous overlayer has little electrical effect. Future efforts will be directed toward increasing the ionic conductivity of the compact surface layer.

An ellipsometric study¹⁹ was conducted in parallel with electrochemical measurements to provide independent optical data on the thickness, structure, and composition of surface layers formed on lithium in propylene carbonate solvent. Ellipsometry is particularly well suited for the in situ observation of electrochemical film formation because of its great sensitivity and minimum disturbance to the surface.

It was found that the growth of surface layers on lithium in propylene carbonate solutions can be followed by ellipsometry, although the refractive indices of many candidate film materials are close to those of the electrolyte. Film thickness calculated from ellipsometer measurements increase linearly over periods of several days at open circuit; thicknesses are several times larger than those derived from galvanostatic pulse measurements. Films are found to be inhomogeneous, with properties varying as a linear function of thickness; compact regions are located adjacent to the metal and porous regions adjacent to the solution. The compact region is responsible for the electrode capacitance; it can also be generated by reaction with water in the vapor phase. The porous region is primarily responsible for the ellipsometer measurements, and it may be formed by the precipitation of decomposition products of the solution.

Metal Couples in Nonaqueous Solvents

The objective of this project, conducted by Lawrence Berkeley Laboratory, is to develop practical alternatives to aqueous or high-temperature molten salt systems for the efficient electrochemical reduction and oxidation of reactive metals. Past accomplishments include the efficient reduction of potassium metal from KAlCl_4 in propylene carbonate.²⁰ Current work is focused on the use of a benzophenone/alkali metal ketal either as an effective drying agent

on nonaqueous electrolytes or, in combination with an inert electron collector, as an alkali metal electrode.

Current Distribution Studies

Recent LBL studies of the interaction of current density distribution with changing electrode surface profiles are well documented.²¹⁻²³ Now under development is a finite element model for characterizing electrodes that exhibit passivity. Of particular interest is the coexistence of active and passive regions on the same surface of a battery electrode. The finite element technique, relatively new to current-distribution modeling, is generally regarded as superior to the finite difference method for accommodating singularities and irregular geometries. To evaluate the validity of the assumptions made in setting up the model, the current distribution and the location of the "boundary" corresponding to active-passive transition will be measured on a rotating cylinder, using a segmented nickel anode.

In Situ Spectroscopic Study of Electrode Surface Layers

The University of Southampton is conducting in situ analyses of the interface between metal electrodes and aqueous and organic electrolytes. The methods of study are laser Raman vibrational spectroscopy, infrared vibrational spectroscopy, and a recently developed in situ X-ray diffraction system.

Initial studies on aluminum/aqueous electrolyte interfaces have employed laser Raman methods. Southampton has been able to confirm spectroscopic evidence indicating the presence of γ -like alumina on aluminum electrode surfaces. Initial experiments have been completed, and a detailed study is in hand on the nature of the oxide layers over alloys of aluminum.

Research on Lead/Acid Battery Electrodes

The Naval Research Laboratory (NRL) has conducted several investigations that elucidate important reactions or transformations occurring in lead/acid plate-active materials. Formation of electrochemically inactive PbO_2 is a substantial cause of positive plate capacity loss. Electrochemically active PbO_2 contains a proton species lacking in the inactive form, as revealed by NMR results at NRL, and a neutron/X-ray diffraction structure determination was undertaken to establish the proton lattice location. This has proved difficult and could not be completed in 1981.

Bibliography of Convective Transport Processes

The Illinois Institute of Technology is searching the scientific and technical literature for references on experimentally established convective

mass and heat transfer correlations with the aim of publishing a bibliography useful to battery researchers and developers. A preliminary search of the most prominent electrochemical and chemical engineering journals since 1970 has been made to supplement the available store of convective mass transfer correlations obtained by the limiting current method.²⁴ This search has resulted in 70 publications not previously recorded, and the information in the publications collected thus far has been stored on a computer disk file.

Battery Assessment Studies

Argonne National Laboratory is aiming to develop a logical and understandable method of establishing battery R & D goals that are optimum for DOE's energy storage applications. Efforts in 1981 were focused on the derivation of advanced battery performance goals for consumer electric vehicles. Cycle life/depth-of-discharge effects were analyzed, and an equation describing the interrelationship between specific energy, peak power, and cost was derived.

PHOTOELECTROCHEMICAL CELLS FOR ENERGY STORAGE

The goal of the work on photoelectrochemical cells is to identify components with performance, stability, and cost characteristics appropriate for a practical device to convert and store solar energy. Although several novel materials originally appeared to offer attractive properties, recent performance and stability data are discouraging.

Photoelectrochemical Storage Cell Based on Polycrystalline Silicon

SRI International has conducted theoretical and experimental investigations²⁵ on the performance of n- and p-type silicon in solution and has sought to identify redox couples capable of inducing maximum band bending (highest open circuit voltage) and to limit corrosion for both n- and p-type silicon.

The silicon electrode was shown to be subject to severe corrosion problems. This corrosion leads to highly insulating thin films of SiO_2 that block the photocurrent. Thus, the silicon electrode must be completely stabilized to realize high efficiency and acceptable cell life, but SRI's studies indicate that the required stability will probably not be achieved on a bare Si surface.

A promising method for stabilizing the Si is by application of thin metal films. However, the use of conducting surface films leads to a loss of open circuit voltage because of enhanced dark currents, and thick layers of conducting material block the incoming light. Further studies using less

active conducting polymer films might lead to new stable systems. At present, it appears that enhanced stability can be achieved only with a loss of efficiency.

Photointercalation Cells

EIC Laboratories, Inc. is investigating layered chalcogenides of general formula MX_2 for the storage of electrical energy generated by photoelectrochemical solar cells. These storage materials can be highly economical and have excellent volumetric energy densities, allowing direct incorporation into flat-plate photovoltaic modules. Two approaches are being evaluated:

(1) intercalation electrodes, such as Cu_nTiS_2 , that can be charged by a separate photoelectrochemical cell; and (2) "active" photointercalation/photodeintercalation cells in which the storage step is effected directly by irradiating a layered semiconducting photoelectrode.

A cell of the first kind consists of an n-GaAs photoelectrode and TiS_2 intercalation electrode. The intercalant was Cu in an acetonitrile-tetrabutylammonium chloride electrolyte. The major problem encountered in the cycling experiments was deterioration of the physical structure of the TiS_2 electrode, although the system itself appears to be chemically reversible between $0 < n < 0.6$.

Studies of "active" photointercalation devices were made on three single-crystal semiconducting layered dichalcogenides: HfS_2 , $ZeSe_2$, and ZrS_2 . HfS_2 and $ZrSe_2$ showed both p- and n-type photoresponse, indicative of nearly intrinsic, highly compensated type material, but no photoresponse was observed with the ZrS_2 crystals. Experiments to demonstrate complete photointercalation cells based on

are currently in progress.

Amorphous Hydrogenated Boron Thin Films

Amorphous hydrogenated boron (a-B:H) is a new semiconducting material whose optical band gap can be varied from 0.8 to 2.2 eV by controlling its hydrogen content during preparation.^{26,27} The objective of this program, conducted

by Giner, Inc., is to determine the suitability of a-B:H as an active electrode material in a photoelectrochemical cell.

Results to date indicate that a-B:H appears to be chemically stable in several redox electrolytes, including aqueous systems. However, low values of carrier mobility and photoconductivity appear to limit its usefulness as a photoelectrode.

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CHAPTER 5 MATERIALS RESEARCH

Materials research addresses problems impeding the development of advanced batteries. These problems include incompatibility of solid electrolytes with the electrodes, degradation of solid electrolytes during charge transfer, feasibility of mass production, and identification of new electrochemical couples and new electrolytes. Three main subjects are under investigation: sodium/sulfur high-temperature cells, lithium/sulfur high-temperature cells, and ambient lithium cells. All the high or intermediate temperature systems employ either ceramic or glassy electrolytes, with the exception of the intermediate-temperature molten-salt electrolyte proposed by Stanford University. Work on the ambient lithium cell focuses on identifying suitable polymeric separators.

SODIUM/SULFUR HIGH-TEMPERATURE CELLS

Electrochemical Properties of Ceramic Electrolytes

NASICONs have been identified as possible alternatives to sodium beta"-alumina solid electrolytes. Their advantage is that, while having ionic conductivities comparable to those of sodium beta"-alumina, they possess a much more isotropic conductivity so that certain grain boundary degradation phenomena, found in the beta aluminas, should not occur. At Lawrence Berkeley Laboratory, compatibility studies of several NASICONs with sodium showed that they are not chemically compatible with molten sodium above 300°C. The rate at which the degradation occurs depends on the chemical composition of the NASICON, the presence of impurities, and the temperature. Minor amounts of alumina cause the formation of a sodium alumino-silicate intergranular phase that leads to very rapid degradation. But even when such impurities are avoided, degradation takes place.

Since the rate of chemical attack decreases rapidly below 300°C, NASICONs might be used for extended periods below 200°C. This would require a different positive electrode mix, such as sodium nitrate/sodium nitrite. Static tests also showed that NASICONs appeared stable in saturated sodium chloride solutions and in sodium hydroxide solutions containing more than 30 wt% of sodium hydroxide. The apparent stability of NASICONs in contact with water-containing

electrodes extends their potential usefulness well beyond that of the sodium beta aluminas.

Fabrication of NASICON

Ceramatec, Inc. prepared NASICON powders by mixing various combinations of phosphates, silicates, zirconia, and carbonates. NASICON ceramics that were conventionally sintered contained small amounts of free zirconia. the densification of NASICON has to occur close to the melting point, 1275°C, where decomposition reactions become possible. Problems were encountered with the formation of free zirconia and the release of various amounts of sodium oxide and phosphorus pentoxide. The degree of decomposition is critically dependent upon the sintering temperature. This partial decomposition during densification is probably one reason sintered NASICON ceramics have poor mechanical properties and low corrosion resistance in liquid sodium. Although the corrosion resistance of NASICON ceramics and liquid sodium depends on the firing method, long-term stability above 300°C is difficult to project at this time. However, since NASICONs may be relatively stable in aqueous environments, their potential use in electrochemical systems was investigated. Static leaching studies in aqueous environments were conducted. The amounts of sodium and phosphorous that can be leached depend on conditions during fabrication. Higher sintering temperatures resulted in more leachable sodium and phosphorous. With the proper change of composition and the development of active powders that densify at lower temperatures, it is believed that ceramics can be developed that will be suitable for cells working at temperatures below 200°C and in applications with water-containing electrodes.

Fabrication of Beta Alumina Tubes

Sodium beta"-alumina tubes measuring 1 cm diameter and 10 cm long were prepared by Globe Union Division of Johnson Controls, Inc. by a tape-winding method. Wall thicknesses of 0.3 mm were fabricated by two-ply continuous winding from strips of cast ceramic tape, using commercial spiral-tube winding equipment. Essential parameters of the fabrication process were identified. Pinch closing of the tubes was accomplished by applying simultaneous heat and pressure. The finished tubes appear to have the necessary porosity, resistivity, and strength for sodium-sulfur battery applications. Problems that remain are partial delaminations at the joints between the wound strips and the difficulty of dimensional control for the thin-walled tubes.

This project has been terminated, and is now under consideration for transfer to the Exploratory Technology Development Project at Sandia National Laboratories.

Fundamental Studies of Superionic Conduction

The goal of this program at the Massachusetts Institute of Technology is to determine which crystal chemical characteristics are singularly responsible for the dramatically high alkali-ion conductivity of certain ceramic-ion conductors. For this purpose, a variety of compounds in the NASICON family have been fabricated. This family includes compounds with either sodium or potassium as the mobile ion, and with various chemical groups substituted for one another. The crystal chemistry of the framework and the concentration of alkali ions is closely connected with the conduction mechanism. This year's findings indicate that conductivity anomalies arise because of an interaction between the mobile ions and the crystal framework, rather than between the ions themselves. One compound, lithium titanium phosphate, was found to possess a NASICON-like structure and displayed ionic conductivity superior to that of lithium beta-alumina. These significant changes of properties with crystal chemistry will be examined in detail diffraction studies.

Strengthening of Beta Alumina

A program has been initiated at Rockwell International, Inc. to fabricate a stronger solid electrolyte by dispersing zirconia particles in it. When fracture is initiated, the zirconia particles immediately adjacent to the fracture will transform and hinder exact growth. Improving the fracture toughness of the ceramic electrolytes should increase their lifetime in Na/S cells.

LITHIUM/SULFUR HIGH-TEMPERATURE CELLS

New Battery Materials

Recent work on this program at Stanford University has introduced several new approaches that may have important practical as well as scientific consequences.

It has been found that a common and inexpensive molten-salt electrolyte can be used in the presence of elemental lithium with intermediate temperatures for both primary and secondary cells. It appears that this salt can be used at temperatures as low as 135°C and with both elemental lithium or high lithium activity negative electrodes and positive electrodes with very low lithium

activities, thus giving high voltages. This electrolyte, based upon lithium nitrate, is highly oxidizing and causes a very thin layer of lithium oxide to form on the surface of the lithium. This reaction layer acts as a good solid electrolyte for Li ions, and it is also relatively insoluble in the molten salt. As a result, lithium can be passed in either direction through it, making it possible to produce reversible solid lithium electrodes. Although the practical importance of this discovery has not yet been demonstrated, it does represent a major new direction for storage cells and could have substantial advantages over the higher-temperature electrolytes. Experimental work on the use of lithium alloys with melting points higher than lithium, employed to avoid the potential danger of lithium melting and rapid heat generation, have indicated that several alloys, including lithium-aluminum and lithium-silicon, also form solid electrolyte protective layers and exhibit the expected kinetic behavior.

The second development in this program is the introduction of a novel approach to an all-solid electrode structure that may have kinetic properties comparable to the traditional fine-particle, liquid electrolyte-permeated structure. The electrode is a composite microstructure containing finely dispersed reactant phases in a metallic matrix that has a very high chemical diffusion rate for the electrochemically active species, e.g., lithium. Several candidate matrix materials with the requisite thermodynamic and kinetic properties have been identified, and initial experiments indicate that such an electrode behaves as predicted. The concept is now being evaluated with electrodes to be used with the low-melting point molten-salt electrolytes.

Recent progress on positive electrode materials has involved the development of a thermodynamic basis for the quantitative understanding of the reactions and titration curves in ternary lithium/metal-oxide systems. A number of such oxide materials should be very interesting as positive electrode reactants, comparable in properties to the sulfides being pursued elsewhere, yet without the difficult sulfur-related corrosion problems. It has also been possible to predict the potentials of a series of binary oxides versus lithium from data such as electronegativities of the components and the position of the Fermi level (from the flat-band potential). In an attempt to improve the diffusion kinetics in mixed conducting electrode materials, the concept of synthesizing materials with "propped structure" has been introduced. As a model material of this type, two different, well-characterized alkali-metal

tungsten-bronze structures have been investigated. It was demonstrated that the diffusion kinetics for the insertion of a small ion, such as lithium, can be dramatically enhanced if the host oxide is "propped up" by the presence of another (relatively large) alkali metal ion.

Lithium-Conducting Glasses

This work at the Massachusetts Institute of Technology has focused on providing an improved understanding of how glass compositions and structures correlate with fast ion transport and chemical durability. Specifically, lithium-borate systems were systematically studied by adding chlorine and sulfate anionic species. Previously, the system lithium oxide-lithium chloride-boron oxide had been examined with 36.4 mole% Li_2Z ($\text{Z} = \text{O}, \text{Cl}_2$) in which the ratio ($\text{LiCl}/\text{Li}_2\text{Z}$) was varied from 0 to 0.5. In this program year, investigation was extended to include glasses with a composition of $\text{Li}_2\text{Z} \cdot 2\text{B}_2\text{O}_3$ (diborate) and $\text{Li}_2\text{Z} \cdot \text{B}_2\text{O}_3$ (metaborate) in order to investigate glasses in different regimes of network as a function of chloride additions. $\log \sigma$ (σ = conductivity) for the borates and metaborates exhibited a linear dependence on Cl for O substitution due to a complementary decrease in activation energy. Conductivities as high as $2 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 300°C were reached for a glass in the metaborate system with a corresponding activation energy of 0.46 eV. This falls within a factor of 5 of the lithium ion conductivity of Li_3N , often cited as the best crystalline ion conductor. Corresponding measurements of glass transition temperature and density performed on these same glasses demonstrated that, in contrast to conclusions based on spectroscopy, the glass structure is markedly affected by the substitution of lithium chloride for lithium oxide, even while maintaining a constant oxygen-to-boron ratio.

Specimens were exposed in the binary lithium-boron oxide to molten lithium at various temperatures and for various times. All specimens formed a thin black reaction layer whose thickness varied parabolically with time, supporting a model involving diffusion-controlled chemical attack. The studies were extended to examination of the corrosion of a large number of additional glasses in the ternary lithium oxide-lithium chloride-boron oxide family. The effect of lithium chloride additions differed in different composition regimes. For glasses with high boron oxide contents (larger than 70 mole%), the durability decreases with increasing chlorine concentration; for low boron oxide contents (less than 50 mole%), the addition of lithium increases the durability

of the glasses at modest temperatures. This last observation is particularly important since it suggests that glasses with both enhanced ionic conductivity and durability can be prepared by the proper choice of lithium chloride additive.

AMBIENT-TEMPERATURE LITHIUM CELLS

Polymeric Electrolyte for Ambient-Temperature Lithium Batteries

Investigations at the University of Pennsylvania were completed on the preparation and electrochemical properties of complexes formed between polyethylene oxide (PEO) and various alkali metals. Also, a start has been made on the study of the electrochemical behavior of various doped polyacetylenes. . These compounds have been proposed as potential anode and cathode materials for nonaqueous battery applications.

It was found that the PEO-LiTFA complexes were predominantly lithium-ion conductors. The films readily hydrate, and hydration increases their conductivity by as much as 3 orders of magnitude at 25°C. Above 100°C, the films melted to form extremely viscous liquids. They then slowly deform and begin to decompose over a period of several hours. The highest conductivities measured on the films were $3 \times 10^{-8} (\Omega\text{cm})^{-1}$ at 25°C and $1 \times 10^{-3} (\Omega\text{cm})^{-1}$ at 150°C.

Four aspects of the electrochemistry of polyacetylenes were examined: (1) chemical and thermal stability of doped and undoped films in contact with dry air, moist air, dry oxygen, and argon; (2) the oxidation of polyacetylene films in nonaqueous electrolytes consisting of propylene carbonate with dissolved LiAsF_6 ; (3) the reduction of polyacetylene films in a 90% diethyl ether/10% tetrahydrofuran electrolyte; and (4) reaction between polyacetylene doped with bromine and an undoped film in the absence of liquid electrolyte. It was found that polyacetylene films must be stored at very low temperature, preferably liquid nitrogen temperature in an inert gas, to prevent spontaneous reaction with oxygen. This reaction is accelerated by the presence of moisture. The oxidation of polyacetylene films was observed to be electrochemically faster than the reduction. Initial results suggest that the polyacetylene will be interesting cathodes, but it is unclear whether they will be attractive alternatives to the lithium anode. As cathodes, polyethylene may be capable of moderate energy densities and high power density. Whether they will accept charge efficiently is, however, uncertain. It

appears that a liquid electrolyte must be present to achieve rapid doping and undoping. The results so far indicate that considerably more work will be necessary to determine if polyacetylenes may revolutionize electrochemical energy storage technology as claimed by other workers.

Novel Membranes for Lithium Batteries

Work at Case Western Reserve University is aimed at developing new separators for ambient-temperature lithium cells, and it has now reached a point where materials of the desired structure can be made. The work can be divided into three topics:

1. Monomers and homopolymers. The poly-(p-toluyloethylene imine) was found to be inappropriate for the hard block since it could be crystallized from the melt. The monomer used subsequently was 2-isobutyloxazoline, whose polymer melts at 210°C. The use of O-dichlorobenzene as a solvent for all polymers was satisfactory. It could be purified in P_2O_5 .
2. Initiators. The glycol ester of trifluoromethane sulfonic acid made a suitable initiator after it was reacted with a monomer to make stable, crystalline 1,2-ethylene bisoxazolinium salts. All monomers reacted rapidly and quantitatively. Polymers made via this route have narrow molecular-weight distribution, which is desirable.
3. Coupling agents. The addition of several equivalents of toluyloxazoline to the previous fabrication schedule improved coupling with the di-amine, but further work will be necessary.

Block copolymers have been made from isobutyl oxazoline and ethyloxazoline, and the blocks have been coupled, both with and without having two equivalents of toluyloxazoline per end. These are the first polymers in the series that can be pressed into films at 220°C and also retain some mechanical integrity. The films made from polymer where no toluyloxazoline was added were brittle at room temperature, but could be handled after being softened in water. They are now under study.

CHAPTER 6 ELECTROCHEMICAL PROCESSES

The projects grouped here have the objective of increased energy efficiency and materials utilization in electrochemical energy conversion processes. Studies aimed at improving the efficiencies of chlor-alkali processes, metal electrowinning, fuel cells, and electroorganic synthesis are described.

AIR ELECTRODES

The use of an air cathode can reduce the operating voltage of chlor-alkali cells, leading to a substantial reduction of energy consumption. High-performance oxygen electrodes are also required for metal/air batteries (Chapter 3) and fuel cells (Chapter 7).

Oxygen Electrodes for Energy Conversion and Storage

A joint effort between Diamond Shamrock Corporation and Case Western Reserve University has shown definite promise of energy conservation. The chlor-alkali cell operating voltage can be reduced by 0.9 V when an air cathode is employed. This represents a 22% energy decrease when operated on air and 31% decrease on oxygen. Prototype fabrication of production-cell electrodes has been successful, and testing of a 100 cm² prototype cell has been initiated.

A broad array of catalytic materials is being investigated at Case Western Reserve University, and the results of studies of oxygen reduction on the various catalysts may be briefly summarized as follows:

1. Platinum and its alloys. These have the highest sustained overall activity on carbon supports (10^3 - 10^4 hours).
2. Silver. This is an attractive air electrode for intermediate performance, but it slowly goes into solution during extended operation.
3. Underpotential deposited metals. The adsorption of metal species, e.g., Tl and Pb, on metal catalysts, e.g., Pt and Au, increases the catalytic activity and offsets the inhibiting effects of some impurities.
4. Transition metal oxides. The spinels, e.g., Co_3O_4 and NiCO_2O_4 , are effective as hydrogen peroxide elimination catalysts and can be used to suppress peroxide in air cathodes catalyzed by Pt.
5. Perovskites. These, e.g., $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, have substantial activity for oxygen reduction as well as peroxide decomposition but show less overall activity than Pt.

6. Macrophyllic catalysts. Several transition metal macrocyclics, e.g., phthalocyanines and porphyrins, have short-term activity comparable to or greater than Pt.

The Case Western findings are being incorporated into test oxygen electrodes for evaluation in the chlor-alkali process by Diamond Shamrock Corporation.

Metal Oxide Doped Active Carbons as Oxygen Reduction Catalysts

It is well-known that activated carbon blacks and certain transition-metal oxides are catalysts for oxygen reduction. Lawrence Berkeley Laboratory is investigating¹ the possibility that the combination of a transition-metal oxide with an activated carbon support would give rise to a beneficial synergistic effect between the two.

An example of this synergism is shown in Fig. 1 for carbon black impregnated with Co_3O_4 . It is seen that $\text{Co}_3\text{O}_4/\text{EMC}$ carbon had 5 times the activity of $\text{Co}_3\text{O}_4/\text{acetylene}$ black in the potential region above -0.1 V (vs Hg/HgO), or about 3 times the specific activity of unsupported oxide of the same nominal surface area.

Bifunctional Air Electrode Studies

These studies at LBL provide supporting research in bifunctional air-electrode technology for DOE metal-air battery projects (Chapter 3). A number of metals and/or metal oxides have been examined for their stability and catalytic activity. With virtually every material examined, the polarization was greater in one direction than in the other. Qualitatively, the results were:

Unstable (dissolution): Ag, Pd, Fe_3O_4 , MnO_2

Reduction activity: Pt > Ru > $\text{Co}_3\text{O}_4 \approx \text{Rh} \approx \text{Ir} > \text{NiO}$

Evolution activity: Ir $\approx$ Ru > $\text{Co}_3\text{O}_4 > \text{NiO} > \text{Pt}$

Co_3O_4 was the most cost-effective catalyst of those studied so far and was very stable in the potential range of interest for air electrodes.

Corrosion of acetylene black in the potential region for oxygen evolution was studied using the ^{14}C tracer method. The corrosion rate showed a strong dependence on both potential and temperature, 140 mV per decade and 23 kcal/gmol, respectively.

MEMBRANES FOR ELECTROCHEMICAL PROCESSES

The goal of these studies is to provide fundamental data and new materials that will lead to the development of ion-selective membranes with superior performance and/or lower cost. The resulting technology will lead to more efficient fuel cell and electrolytic processes.

XBL 821-48

Fig. 1. Polarization curve for the reduction of pure O₂ with gas-diffusion electrodes using Co₃O₄ impregnated carbon black.

Multicomponent Transport Theory and Data for Concentrated Electrolytes

A joint effort by Electrochemical Technology Corporation and Brigham Young University will result in an improved multicomponent transport theory for Nafion ion-selective membranes. Transport data, such as ion fluxes, ion solubilities, osmotic characteristics, and transference numbers, are being collected, and the resulting information will guide the proper design and operation of various electrochemical processes that employ such membranes.

Novel Fluorocarbon Phosphoric Acid Polymers for Ion Exchange Membranes

The University of Texas is preparing fluorocarbon membranes by new synthetic methods that permit wide flexibility in the structure of the membrane. It is now possible to prepare functional fluoropolymers that result in highly conductive membranes, and the process should be much less costly than that presently employed to produce Nafion.

ELECTROCHEMICAL REDUCTION OF METALS

The following projects are aimed at identifying more energy-efficient routes for the electrochemical winning of metals.

Improvements in the Efficiency of Aluminum Reduction Cells

LBL has developed a mathematical model that predicts the performance of the aluminum-producing Hall-Héroult electrolytic cell. Rapid screening of alternative cell designs or operating practices can be carried out, promoting the development of cells consuming less electrical energy.

Two performance parameters of interest from an energy consumption viewpoint are the current efficiency of the cell and the flatness of the interface between the two liquid layers in the cell (molten aluminum and the molten salt electrolyte). Both parameters are primarily dependent on electromagnetic forces that arise within the cell from the interaction of cell currents with magnetic fields. The mathematical model 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 2, depicting the conductors for six cells, is typical of results recently generated by the model. These cells differ from the usual Hall-Héroult cell in that the current is taken out by conductors passing out through the bottom of the cell (the usual cell has conductors passing out through the side). The computed current efficiency is 93.1% versus a best computed current efficiency of 91.7% for a comparable cell of conventional

NOVEL CELL (50-50)

94.3% EFFICIENT

TROUGH-PEAK DISTANCE = 4.6 CM.
INTERFACE TOPOLOGY

XBL 823-8492

Fig. 2. A novel conductor arrangement for six Hall-Héroult cells and the current efficiency for such an arrangement. The lower half of the figure depicts the computed shape of the interface between molten metal and salt (vertical scale exaggerated for effect).

design. The computed aluminum/electrolyte interface for the novel cell is depicted in the lower half of Fig. 2 and is flatter than that of a comparable conventional cell (4.6 cm trough-to-peak distance versus 7.0 cm for the conventional cell). Refinement of the mathematical model is continuing.

Electrowinning of Aluminum

Argonne National Laboratory (ANL) is investigating an alternative to the Hall-Héroult process for aluminum reduction: the electrolysis of Al_2S_3 rather than of Al_2O_3 . Three reaction paths to Al_2S_3 were considered:

Experimental work on reactions (2) and (3) has focused on the effect of the flow rate of carbon disulfide and reaction time on the conversion of aluminum sulfate to the sulfide (reaction (2)). The percent conversion increased with the time of flow.

The results of the study of reaction (3) show that the conversion of Al_2O_3 to Al_2S_3 in the MgCl_2 - NaCl - KCl eutectic melt increased with the flow rate of the carbonyl sulfide (COS). The conversions were low, and the maximum final concentration was 0.39 wt% of Al_2S_3 in the melt. Separate measurements determined the solubility of Al_2S_3 in the melt to be 3 wt%, but the solubility could be increased to 7.5 wt% by the addition of 5 wt% aluminum chloride to the melt. The Al_2S_3 in the presence of AlCl_3 formed AlSCl in the melt.

Electrolysis experiments were conducted with three different Al_2S_3 concentrations. The electrolysis voltage was from 1.4 to 1.6 volts at current densities up to 200 mA/cm^2 for an Al_2S_3 concentration of 2 wt%, and the current efficiency was over 80%. In the MgCl_2 - NaCl - KCl eutectic that contained AlCl_3 , higher current densities could be used. A current efficiency of about 85% was obtained for the electrolysis of 5 wt% Al_2O_3 in AlCl_3 -containing eutectic at current densities ranging from 0.2 to 1.2 A/cm^2 . These results indicate the feasibility of the Al_2S_3 electrolysis method for preparing aluminum.

ANL has also initiated studies to improve the preparation of AlCl_3 , which is used in a new process for aluminum electrolysis. Studies are in progress on liquid-liquid extraction of AlCl_3 from an aqueous solution or from a suspension of aluminum hydroxide, $\text{Al}(\text{OH})_3$.

Electrowinning of Zinc

ANL has shown that the alkaline leach and electrolysis process is a lower energy route to zinc, in selected cases, than the commonly used sulfate process, but the realizable energy savings will probably be less than previous projected savings: 10% rather than 33%.³

The alkaline process is highly compatible with the lower-grade ores that will constitute a major source of the future U.S. zinc supply. Thus, if additional capacity should become necessary, the alkaline process represents a promising alternative.

Fuel Cell Electrode for Zinc Electrowinning

The Prototech Company has evaluated the use of a hydrogen anode to replace the oxygen-evolving lead anode in the electrolysis of zinc. The standard hydrogen electrode being used in these studies is a platinum-catalyzed gas diffusion anode containing 0.3 mg of Pt/cm². An energy saving of 1.69 kWh/kg of zinc (i.e., 50%) was obtained compared with the energy used when a standard lead anode is employed. Endurance tests of 1,000 hours have been carried out. Protech reports⁴ an overall energy saving from the H_2 process of about 40%. Combined amortization plus operating cost savings due to the H_2 process are 4.2-5.9¢/kg zinc.

Improved Electrochemical Cell Design for the Production of Magnesium

The Massachusetts Institute of Technology is assessing the effects of forced convection, applied electromagnetic fields, and cell configuration of Mg production rates. The aim of this project is to guide the design and operation of improved processes for Mg production.

Metal Recovery from Batteries

Castle Technology Corporation has investigated metal recovery from battery systems: zinc/nickel oxide, iron/nickel oxide, zinc/chlorine, zinc/bromine, sodium/sulfur, and lithium/aluminum iron sulfide. Estimated capital and operating costs for the recovery processes are listed in Table 1. The table indicates that the recovery of nickel yields the greatest economic benefit. Pilot plant evaluation of recovery processes would be premature prior to battery commercialization.

Table 1. Recycle process capital and operating costs for large electric vehicle battery plants.

Process	Product	Tons/yr	Capital cost (\$1,000)	Operating cost (\$1,000/yr)	Recycled material cost (\$/lb of product)	New material cost (\$/lb of product)
Zinc - acid leach	ZnO	5,282	4,830	7,300	69	45
Zinc - ammonia leach	ZnO	4,090	5,470	4,590	56	45
Zinc - pyrometallurgical	ZnO	4,090	4,770	2,800	34	45
Nickel solution - acid leach	NiSO ₄	9,929	4,670	5,590	28	103
Nickel solution - ammonia leach	NiSO ₄	9,930	5,010	6,270	32	103
Nickel powder - acid leach	Ni powder	8,107	11,310	9,190	57	250
Nickel powder - ammonia leach	Ni powder	8,780	11,050	9,870	56	250
Nickel powder - pyrometallurgical	Ni powder	8,167	6,440	3,940	24	250
Combined nickel and zinc - Acid leach	ZnO NiSO ₄	5,507 10,454	9,290	9,710	30	83
Combined nickel and zinc - ammonia leach	ZnO NiSO ₄	4,266 10,454	9,900	7,840	27	86
Zinc/chlorine	ZnCl ₂	8,423	1,620	2,330	14	25
Zinc bromine	ZrBr ₂	10,218	2,240	2,620	13	41
Sodium sulfur	Na ₂ S ₃	46,640	10,610	8,460	9	12
Lithium-aluminum/sulfide	Li ₂ S	8,560	7,830	9,190	54	125-155

ELECTROLYSIS

Gas evolution by electrolysis is one of the most common reaction types in electrosynthesis. Electrically rechargeable batteries also develop gases on charge. Improved understanding of the behavior of electrochemically generated gas-electrolyte emulsions should lead to improvements in the energy efficiency of gas-generating processes. Electroorganic syntheses and thermally regenerative cells are also included in this section.

Engineering Analysis of Gas Evolution in Electrolysis

Gas evolution is usually accompanied by two effects brought on by the bubbles: an increase in mass transfer rate and a rise in ohmic losses. Practical improvements in cell and electrode design have largely eliminated the resistance caused by bubbles in the bulk electrolyte, but the bubble layer (in the vicinity of the surface) remains a problem. The aim of this project, conducted by Lawrence Berkeley Laboratory (LBL), is to advance fundamental understanding⁵ of this bubble layer to stimulate improvement in cell performance.

To minimize the resistance of a gas-evolving cell, both the electrode coverage and the bubble layer thickness should be lowered. Studies at LBL show that strong coalescence achieves both of these desired effects. This leads to the conclusion that it is advantageous to operate under conditions in which coalescence occurs readily.

To obtain quantitative measurements of the effect of bubble dynamics on mass transport,⁶ a novel mosaic electrode has been produced jointly by LBL and the Hewlett-Packard Company. The electrode was prepared on a silicon chip by integrated circuit technology and consists of a 10 by 10 matrix of square platinum segments on 100-micron centers electrically isolated from each other (Fig. 3). The matrix is surrounded by 12 specially positioned segments and a relatively large buffer segment, all coated with platinum. The matrix simulates a continuous surface at the same time that it allows one to control and measure the current and/or potential for each segment. By careful control of such individual segment potentials, a single bubble can be nucleated and grown. Studies of the change in mass transfer when the bubble disengages are in progress.

Fuels and Chemicals from Depolarized Water Electrolysis

The Institute of Gas Technology is investigating the electrochemical oxidation of abundant materials derivable from biomass, and the aim is to

CBB 809-11046

Fig. 3. 10 x 10 matrix of electrically isolated platinum-coated segments on 100-micron centers, produced on a silicon wafer in collaboration with Hewlett-Packard Co.

identify suitable depolarizing agents that will decrease water electrolysis energy consumption. Various compounds, such as glucose, lignosulfates, and other wood-derivable materials are under investigation, and several appropriate electrocatalysts have been identified.

Continuous Organic Electrochemical Synthesis

The University of California at Los Angeles is investigating paired synthesis as a strategy to reduce energy consumption in electroorganic synthesis. In the glucose-paired reaction, it was found that improved efficiencies can be obtained in a packed bed cell if the electrodes are separated by a membrane. This indicates that a design of packed bed cells that prevents unwanted transport to the cathode is required. Such a cell with parallel current and electrolyte flow is now being built and tested.

Electrochemistry Applied to Thermal Conversion

The Solar Energy Research Institute has reviewed the literature on thermally regenerative electrochemical systems (TRES). The literature was divided into two broad classes: electrochemical engines regenerated by heat alone and those regenerated by combined input of heat and electricity. These classes were further separated into seven types of TRES whenever significant differences in the electrochemical cell or regenerator were found.

The experimental work addresses the utilization of low-grade heat sources through electrochemical systems such as Sn/Sn(II), Cr(III), Cr(II)/C. SERI is analyzing the scientific feasibility of analogous systems with materials that are abundant and inexpensive, such as the couples Cu/Cu(II) and Fe(III)/Fe(II) (on Pt or C). Voltage measurements as a function of temperature have been carried out.

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CHAPTER 7

FUEL CELLS FOR TRANSPORTATION APPLICATIONS

As a result of the significant progress made in fuel cell technology in recent years through the efforts of Department of Energy (DOE), the Electric Power Research Institute (EPRI), the Gas Research Institute (GRI), and the U.S. Army--all of which formed the basis for preliminary assessments--the fuel cell is considered a potential vehicular power plant for the future. Under the auspices of the DOE Offices of Energy Systems Research and Vehicle and Engine Research, the Fuel Cells for Transportation Applications program is carrying forward high-risk research and development that is necessary to bring fuel cell technology to an established proof-of-concept level, when it will become attractive for industry to undertake further development and scale-up for commercial transportation (buses, trucks) and individual vehicles (small vans, passenger cars).

The aim of this program is to make use of the high efficiency, low pollution (both air and noise), and nonpetroleum fuel sources of the fuel cell to develop a prototype vehicle power plant with the following characteristics:

1. Energy efficiency significantly better than internal combustion engines (ICE's).
2. Competitive with ICE vehicles in purchase cost and superior in maintenance cost.
3. Range, performance, and refueling time equivalent to ICE vehicles.
4. Utilization of methanol or other nonpetroleum fuel that can be easily distributed and stored.

At Los Alamos National Laboratory, the fuel cell technologies being assessed for potential vehicle use are phosphoric acid electrolyte (PAFC), solid polymer electrolyte (SPE), and super-acid electrolyte fuel cells. From these alternatives, one or two technologies will be selected for further electrochemical research emphasizing the requirements of vehicles. Verification will be closely coupled with the electrochemical basic research program as both applications and basic research have similar goals in cell improvement.

The technical feasibility of using the PAFC and SPE fuel cell systems in vehicles has been substantiated. Component production in both systems is amenable to mass production techniques, which should reduce the cost

projections of \$150-\$250/kW. These system designs must be verified and optimized, leading to the fabrication and testing of working prototypes. Success will require a strong research program aimed at improving electrocatalysis, electrolytes, and fuel processing to yield higher efficiencies and better performance. One problem is that, to improve oxygen electrode performance, neutral or anionic species must not be allowed to adsorb, as adsorption studies on cathodes in various acids have confirmed. Various means of preventing such adsorption are being explored.

SUBCONTRACTOR ACTIVITIES

In 1981, three design studies were undertaken between Los Alamos National Laboratory and United Technologies Corporation (UTC), Energy Research Corporation (ERC), and General Electric Company (GE) to assess the potential of PAFC, trifluoromethanesulfonic acid (TFMSA), and SPE fuel cell technologies, respectively, as related to the demands of a small consumer automobile (the General Motors X-car).

Since the vehicular requirements for the fuel cell and the system design tradeoffs for both the cell and vehicular systems are quite different from those of previous fuel cell applications, these studies provided the first opportunity for an in-depth assessment of fuel cell designs specifically for vehicles. Through computer simulation at Los Alamos, the advantages, limitations, and uncertainties of these technologies were investigated.

When the assessments began, the PAFC system, which has had most development, had reached a high level of performance and reliability in utility applications. Volume, weight, start-up time, and cost were perceived as features requiring special attention for vehicular application.

The SPE fuel cell system is also a mature technology, but mainly in aerospace applications where pure fuel and oxidant are used. In this technology, the concerns were the ability to use reformed fuel, water management, operating temperature limits, and cost.

The trifluoromethanesulfonic acid (TFMSA) system is currently an immature technology with data available only for single- and bi-cell operation, but it has the potential for improved fuel cell performance. Because of the lack of full-scale system experience, the assessment could not be based on actual operating power plant data and was subject to much more conjecture than the

other two systems. This same lack of information probably caused the assessment to indicate no significant performance advantage for this system over that of a phosphoric acid system.

The characteristics presented for the SPE and PAFC systems and the performance levels obtained from the computer simulation using these characteristics demonstrate emphatically that fuel cells are technically viable as vehicular power plants. These characteristics are compared to the target or projected system characteristics supplied by Los Alamos (based on 1980 PAFC power plant operational data) in Table 1.

It is important to note (Table 1) that the SPE fuel cell system weighs less than half of the target system and has approximately one-third the volume. The entire system can be easily placed under the hood of a GM X-car. The system's ability to produce power at ambient temperature allows for virtually instant start-up time. The PAFC system also falls well within specified values.

Table 1 also gives the operating points selected, the resulting electrode areas, the peak power capabilities, and the fuel cell system efficiencies at nominal load for the two fuel power plants. Both have efficiencies of over 50%, considerably better than the target system.

Using these values plus other necessary weight data, computer simulations were run to obtain performance data for a five-passenger vehicle (GM X-car). The stimulation results are shown in the last five lines of Table 1. In the phosphoric acid systems, batteries are required for immediate start-up. The 0-50 mph times are quite adequate when compared to today's compact passenger vehicles (Fig. 1). Of most interest are the gasoline-equivalent mileages, particularly the city values. Compared with the current GM X-car (22 mpg city, Environmental Protection Agency estimate), the two systems offer the energy equivalent of a 60-mpg ICE-driven vehicle for both city and highway driving.

Thus, the preliminary designs of the PAFC and SPE fuel cell systems for vehicles strongly support the technical feasibility of using fuel cells for transportation applications. Projected production costs for 100,000 units per year fall in the range of \$150-\$250/kW (1981 dollars) for both systems.

Achieving the performance projected in these assessments will require research in electrocatalysis, reforming, and electrolytes. In the PAFC system (discussed later), Los Alamos research experiments have substantiated the

Table 1. Characteristics of two 20-kW fuel cell systems.

	Previous Projections	GE SPE Fuel Cell	UTC Advanced PAFC
Weight (lb)	680	337	550
Volume ^a (ft ³)	12	4.1	7
Start-Up Time (min)	15	0	5
Operating Temp. Range (°C)	120-180	0-104	120-180
Nominal Op. Pts.			
Volts/Cell	0.6	0.72	0.853
Amps/ft ²	150	466	265
Watts/ft ²	90	335	226
Total Electrode Area (ft ²)	222	60	89
Peak Power (kW)	67	66	60
Fuel Cell System Efficiency at 20 kW ^b	40%	51%	57%
Vehicle Curb Wt. (lb)	3456	2760	3188
Battery Wt. (lb)	264	0	126
0-50 mph Time ^c (sec)	15.8	12.1	15.5
MPG of Methanol ^{c,d}			
City	21.5	27.4	33.3
Highway	24.2	29.7	33.6

^a Without packing factor.

^b Based on higher heating value of methanol.

^c Curb weight plus 300 lbs for passengers.

^d Multiply by 2 to get gasoline equivalent.

Fig. 1. Five-passenger vehicle acceleration times.

theory that adsorption of phosphoric acid species on the cathode is responsible for performance losses. Research is required on electrocatalysts and electrolytes to either modify the adsorption process or alter the cathode reaction so this adsorption does not interfere so strongly. In the SPE system, cost and performance are predicted on lower catalyst loadings and less expensive membranes. Both require extensive research.

CHARACTERISTICS OF AN NH_3 -AIR ALKALINE FUEL CELL IN A VEHICLE APPLICATION¹

The use of hydrogen-air alkaline fuel cells in a consumer vehicle application was examined by LBL. Liquid anhydrous ammonia was found to be an excellent storage medium for hydrogen, even though the endothermicity of the NH_3 cracking reaction results in some efficiency penalty. The advantages of the alkaline fuel cell relative to any acid fuel cell are higher power density (factor of 2-3) and lower cost (factor of 2) resulting in significantly lower total cost (factor of 4-6).

Single cell testing indicated system thermal efficiencies of 34-44% can be achieved at power densities of $2600\text{--}1000 \text{ W/m}^2$, using currently known electrode technology that does not require the use of precious metal (e.g., Pt) catalyst. Computer simulations of vehicle characteristics showed that the ammonia fuel cell vehicle is more than twice as efficient as a comparable methanol ICE vehicle. The result is a primary energy consumption one-half that of the ICE vehicle.

LOS ALAMOS RESEARCH AND DEVELOPMENT

Electrochemical Research

Adsorption characteristics of trifluoromethanesulfonate anions on electrodes. Because of encouraging results in power density and efficiency that have been obtained in fuel cells with TFMSA or Nafion as the electrolyte, interest in using such fluorinated sulfonic acids in advanced transportation fuel cells is high. To elucidate the adsorption characteristics of the CF_3SO_3^- anion, it was decided to investigate the interface of mercury with aqueous solutions of $\text{CF}_3\text{SO}_3\text{K} + \text{KF}$ at constant ionic strengths using differential capacity measurements. Mercury was chosen as the electrode material because of its well-known advantages for interfacial studies. Further, most studies have shown that the characteristics of adsorption of ions on mercury can be extended to solid metals. Constant ionic strength solutions [$x\text{M } \text{CF}_3\text{SO}_3\text{K} + (1-x)\text{M } \text{KF}$] were chosen to minimize the effect of the diffuse double layer.

Figure 2 shows the differential capacity-potential curves at the mercury/electrolyte interface at 25°C for 1M KF, 1M $\text{CF}_3\text{SO}_3\text{K}$, and the mixed solution for $x = 0.1$. It is evident that, from the capacity point of view, the behavior of $\text{CF}_3\text{SO}_3\text{K}$ is very different from KF; this difference can only be accounted for by specific adsorption of the CF_3SO_3^- anion. This is confirmed by the shift of the potential of zero charge (E_z) toward negative potentials as the concentration of CF_3SO_3^- increases. At highly negative potentials, CF_3SO_3^- is electrostatically repelled from the surface and all of the curves coincide. No difference was observed between the capacity curves for $x = 0.005$ and for pure KF; this indicates that the CF_3SO_3^- anion is less strongly adsorbed than are the halides in this concentration range. A pronounced hump develops in the capacity curve as the concentration of CF_3SO_3^- increases, mainly due to increasing specific adsorption, and hence decreasing the inner layer capacity on the anodic side of E_z .

A thermodynamic analysis of these results indicates that the extent of specific adsorption of TFMSA anions is small, and the anions even desorb from the surface at sufficiently positive electrode charges. The structure of the inner layer was elucidated, and, based on electrostatic models of the double layer, an isotherm for the adsorption of CF_3SO_3^- ion was derived. The results indicate that, at the potentials for the electroreduction of oxygen, CF_3SO_3^- anions will not interfere with the adsorption of the reactant and of intermediates, thus allowing faster rates of oxygen reduction to be achieved.

Structure of the double layer at the mercury/phosphoric acid interface from studies of adsorption of thiourea and its implications on oxygen reduction kinetics. Because the efficiency loss of PAFCs is determined mainly by the slow kinetics of the oxygen reduction reaction, there is a need for understanding why this reaction is slower in concentrated phosphoric acid than in aqueous solutions of strong acids. In this work, the structure of the double layer at the mercury/concentrated phosphoric acid interface was examined at room temperature by using thiourea as a probe species. For this purpose, the differential capacity of the interface was measured as a function of the electrode potential in 95% phosphoric acid and in the same electrolyte with nine concentrations of added thiourea. Analysis of the results indicates that thiourea adsorbs with the positive end of the dipole towards the metal; the amount adsorbed is sufficiently small and can be described by a Henry's law

Fig. 2. Differential capacity-potential plots with (1) 1M KF, (2) 0.1M $\text{CF}_3\text{SO}_3\text{K}$ + 0.9M $\text{CF}_3\text{SO}_3\text{K}$, and (3) 1M $\text{CF}_3\text{SO}_3\text{K}$ at 25°C. Arrows indicate the potential of zero charge on mercury for each electrolyte.

type of isotherm. Analysis of the inner-layer parameters shows that in this region the permittivity has values similar to those found in water, but the distance from the metal to the outer Helmholtz plane is much larger. Thus, slower oxygen reduction kinetics can be explained in terms of a wider barrier for the rate-determining electron transfer step.

Design and fabrication of single cells for evaluation of electrode and fuel cell performance under simulated vehicle operating conditions. Preliminary experiments were carried out with hydrogen and oxygen as the reactants to test two types of cells constructed. Fuel cell electrodes from ERC (Pt loading 0.5 mg cm^{-2}) or prepared at Los Alamos (Pt loading 1 mg cm^{-2}) were used. Typical single- and half-cell potential-current density measurements on ERC electrodes in two cells are shown in Figs. 3 and 4.

Vehicle Simulation Program

The fuel cell/battery vehicle simulation program has provided better understanding of the fuel cell characteristics required for a vehicular power plant, enabled design and evaluation of fuel-cell-powered vehicles, and yielded insights into the design tradeoffs available with a fuel cell power plant. For example, changing the operating point of the fuel cell has a pronounced effect on the vehicle. The same nominal power can be obtained from a smaller fuel cell operating at a higher power density; this reduces fuel cell weight, volume, and cost, but increases fuel consumption and degrades performance. Also, large peak currents have been calculated during full throttle accelerations. Their magnitude and duration have a strong influence on the fuel control system, the cooling system, and the size of the fuel processor.

In 1981, three manufacturers assessed three different fuel cell technologies for vehicular applications. Data from these assessments were used to evaluate the performance of a consumer vehicle with a near-term PAFC system, an advanced PAFC system, and an SPE fuel cell system (Table 1).

Both the advanced PAFC and the SPE systems showed substantial improvement over the target system. To evaluate the characteristics of a high-performance fuel cell system in an advanced vehicle, the GE-Chrysler Electric Test Vehicle-1 (ETV-1) was analyzed with the SPE system (see Table 2).

Because of its reduced rolling friction and improved aerodynamics, the cruising speed of an ETV-1 with the 20-kW SPE fuel cell is 71 mph (rather than 60 mph for the X-car), and the top speed is 80 mph.

Fig. 3. Potential vs current density for hydrogen-oxygen fuel cell with phosphoric acid electrolyte at 170°C in single cell with no reference electrode using ERC electrodes (Pt loading 0.5 mg cm⁻²).

Fig. 4. Potential vs current density for hydrogen-oxygen fuel cell with phosphoric acid electrolyte at 170°C in single cell with reference electrode using ERC electrodes.

Table 2. ETV-1 performance with GE SPE fuel cell system.

Curb weight + 300 (lb)	2966
0-50 mph time (s).	10.2
mpg of methanol	
UDS	32.8
HDS	43.8
UDS energy efficiency	
improvement (%)	198

Simulation and Interface Verification Test Bed Vehicle

A fuel-cell-powered golf cart was initially completed in October 1979 and employed an ERC PAFC was rated at a nominal 1.5 kW at 40 A. Total operating time on the stack was 41.7 hours with approximately 125 cold starts. A second PAFC stack was received from ERC in January 1981. This newer stack had a nominal 2-kW rating at 40 A and a peak power of 5 kW, a 67% improvement over the first stack in approximately 70% of the volume. Installation of this stack was completed in March 1981.

Hydrogen fuel for the stack has been supplied by carrying pressurized hydrogen in cylinders mounted on the fenders. This approach has proved quite acceptable in a laboratory environment because of the ready availability of hydrogen. Also, principal interest initially was to establish the interactions between the fuel cell and the vehicle under varying load and conditions. This knowledge has allowed better understanding of the needs of the fuel-cell and fuel-control system by minimizing the number of fuel-control variables. However, the weight penalty for carrying hydrogen in the gaseous, liquid, or hydride form is fairly severe for a viable transportation vehicle.

Preliminary work on evaluating a reformer furnished by the U.S. Army Mobility Equipment Research and Development Command (MERADCOM) began in May 1981. This 6-year-old reformer was designed by ERC for the Army to supply 120% of the hydrogen requirements of a 1.5-kW stack. A properly designed reformer will convert a mixture of 1M methanol and 1.3M water to hydrogen and

carbon dioxide with less than 0.3% carbon monoxide. Because the overall reaction is endothermic, a burner is usually supplied as part of the reformer unit. The RC reformer was designed to burn the methanol/water mix until an operating temperature near 200°C was reached. Excess hydrogen from the stack was burned after the operating temperature was reached. Early experiments with this rather old reformer soon demonstrated the difficulty of predictably and reliably establishing a controlled burn.

A new reformer was purchased from ERC and was received in October 1981, but it too would not generate a smooth and reliable burn. A complete redesign of the burner subsystem was begun in December 1981. A design of the fuel control system is being developed in parallel with the reformer experiments as the variables become better understood.

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