Dr-169

ANL-76-45

ANL-76-45

Rev.

Rev.

109/76
7-9-76

**DEVELOPMENT OF LITHIUM/METAL SULFIDE BATTERIES
AT ARGONNE NATIONAL LABORATORY:**

SUMMARY REPORT FOR 1975

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

SPONSORED BY THE U.S. ENERGY RESEARCH

AND DEVELOPMENT ADMINISTRATION

Under Contract W-31-109-ENG-38

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (N-31-117-Rev 38) between the U. S. Energy Research and Development Administration, Argonne University Association and The University of Chicago, the University operates the said and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by its Association.

MEMBERS OF ARGONNE UNIVERSITY ASSOCIATION

The University of Arizona
 California Institute of Technology
 Case Western Reserve University
 The University of Chicago
 Harvard University
 Johns Hopkins University
 Massachusetts Institute of Technology
 The University of Michigan
 The University of Minnesota
 The University of Wisconsin

University of California
 The University of Illinois
 The University of Iowa
 The University of Maryland
 The University of Missouri
 The University of Nebraska
 The University of New Hampshire
 The University of New York
 The University of North Carolina
 The University of North Dakota

The Ohio State University
 The University of Oregon
 The Pennsylvania State University
 Princeton University
 Rice University
 Stanford University
 The University of South Carolina
 The University of Texas at Austin
 The University of Texas at Dallas
 The University of Wisconsin

ANL-76-45
Rev.

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

DEVELOPMENT OF LITHIUM/METAL SULFIDE BATTERIES
AT ARGONNE NATIONAL LABORATORY:
SUMMARY REPORT FOR 1975

P. A. Nelson	Manager, Battery Program
R. O. Ivins	Assoc. Manager, Commercial Development
N. P. Yao	Assistant Manager
J. E. Battles	Group Leader, Materials Development
A. A. Chilenskas	Group Leader, Battery Design
E. C. Gay	Group Leader, Electrode Development
R. K. Steunenberg	Group Leader, Cell Chemistry
W. J. Walsh	Group Leader, Cell Development

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

May 1976

Previous reports in this series:

ANL-8064	April 1974
ANL-75-20	March 1975

FOREWORD

This report is a summary of the accomplishments during 1975 in Argonne National Laboratory's program on high-temperature secondary batteries. The work is carried out principally in Argonne's Chemical Engineering Division, and involves the efforts of many scientists and technicians. Some of the efforts of these individuals are reflected in the list of publications at the end of the report, and in other publications planned for the near future. Although acknowledgment of the contributions of individuals is beyond the scope of this brief report, their efforts are essential to the success of the program.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
I. OVERVIEW OF BATTERY PROGRAM.	2
II. CELL AND BATTERY DESIGN.	4
III. COMMERCIAL DEVELOPMENT	9
IV. CELL DEVELOPMENT	11
V. ELECTRODE DEVELOPMENT.	16
VI. MATERIALS STUDIES.	18
VII. CELL CHEMISTRY	21
REFERENCES	25
ADDENDUM: PUBLICATIONS DURING 1975.	26

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Conceptual Design for Electric-Vehicle Battery Cell	4
2.	Conceptual Module for Electric-Vehicle Battery.	5
3.	Conceptual Battery for Electric Vehicle	6
4.	Design of Cell for Load-Leveling Battery.	7
5.	Design of Submodule for Load-Leveling Battery	8
6.	Design of Module for Load-Leveling Battery.	8
7.	Design of BEST Facility Battery	8
8.	General Design of Prismatic Cells	9
9.	Schematic Diagram of Prismatic Cell R-1	12
10.	Prismatic Cell R-1.	13
11.	Voltage Patterns for Li-Al/FeS _x Cells	14
12.	Tentative Phase Diagram of Lithium Aluminum System.	20

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Performance Goals for Lithium/Metal Sulfide Batteries	2
2.	Performance of Li-Al/FeS ₂ Engineering Cells	14
3.	Performance of Li-Al/FeS Engineering Cells.	15

DEVELOPMENT OF LITHIUM/METAL SULFIDE BATTERIES
AT ARGONNE NATIONAL LABORATORY:
SUMMARY REPORT FOR 1975

ABSTRACT

This report presents highlights for 1975 of Argonne National Laboratory's program on the development of lithium/metal sulfide batteries. The intended applications for these high-performance batteries are energy storage on utilities and electric vehicle propulsion. The battery cells have negative electrodes of a lithium-aluminum alloy and positive electrodes of FeS_2 or FeS and operate at 400-450°C. During the past year, a new cell design has been adopted; the cells are prismatic and are operated with the electrodes in a vertical orientation.

Contracts have been made with three industrial firms to develop fabrication techniques and to fabricate electrodes and cells for testing at Argonne. Contracts have also been made with industrial firms for the development of improved feedthroughs and electrode separators. By this means, the transfer of technology to industry is being implemented so that manufacturing capabilities will be available when the batteries are fully developed.

Conceptual designs for two types of batteries have been completed: an electric-vehicle battery that could be installed under the hood of a Mustang II, and a load-leveling battery for testing in the Battery Energy Storage Test Facility being planned by the Energy Research and Development Administration and the Electric Power Research Institute.

Promising methods for fabricating electrodes, now being actively pursued, include loading of powders into porous current collector structures, incorporation of active materials into a carbon-bonded matrix, and hot-pressing of powders. Receiving major attention is a design in which cells are assembled in the uncharged state, i.e., the negative electrode is a porous aluminum plaque and the positive electrode is a hot-pressed mixture of lithium sulfide, iron powder, and electrolyte. Upon first charge, the lithium is transferred to the negative electrode, where the lithium-aluminum alloy is formed. Engineering-scale Li-Al/FeS cells of this type have achieved specific energies of 100 W-hr/kg and peak specific powers of 130 W/kg.

Cell chemistry studies and materials studies are conducted to provide support to the cell effort. A method was devised for preparing lithium sulfide in a physical form suitable for use in uncharged cells; studies of cell overcharge reactions led to the establishment of optimum cell cutoff voltages. Corrosion tests and postoperative examinations continue to provide information on materials of construction and on the behavior of the active materials in the cell environment.

1. OVERVIEW OF BATTERY PROGRAM

Lithium/metal sulfide batteries are being developed for use as (1) energy storage devices for load-leveling on electric utilities and (2) power sources for electric automobiles. Batteries that are currently available are too expensive for the first application and have insufficient energy storage and power per unit weight for the second application. The installation of batteries on electric utility networks would permit the utilities to store energy generated at night by coal-burning or nuclear baseload plants and discharge the battery to the network during the day when demand is highest. This would reduce the need for gas- or oil-burning turbine generators. Electric automobile batteries could be recharged at night using electricity produced from coal or nuclear energy. The successful development of batteries for either application would reduce our dependence on foreign sources of oil.

The development effort on the energy storage battery, which is funded by ERDA, includes cell chemistry studies, materials studies, electrode development, cell development, battery development, and systems studies. The development of the electric-vehicle battery, which is also funded by ERDA, consists of systems design studies and cell and battery development; most of the more basic studies performed under the energy storage battery program are also applicable to the vehicle-propulsion effort. Through June 1975, the ERDA program for the car battery was supplemented by a design and cell-evaluation study for the Department of Transportation (DOT).

The long-range performance goals that we have set for off-peak energy storage and electric automobile batteries are unchanged from those of last year; these goals are presented in Table 1.

Table 1. Performance Goals for Lithium/Metal Sulfide Batteries

Battery Goals	Electric Vehicle Propulsion	Off-Peak Energy Storage
Power		
Peak	60 kW ^a	40 MW
Normal	21 kW	10 MW
Voltage, V	140	1000
Specific Energy, W-hr/kg	120-160	120-150
Energy Output	42 kW-hr	100 MW-hr
Discharge Time, hr	2	10
Charge Time, hr	5	5-7
Watt-hour Efficiency, %	70	80
Cycle Life	1000 ^b	1500 ^b
Cost of Capacity, \$/KW-hr	20-30 ^b	15-20 ^b
Heat Loss Through Insulation	150 W	100 kW

^aBased upon power required to accelerate a 1570-kg car from 0 to 60 mph in 23 sec.

^bTentative; to be specified by systems and cost studies.

Most of the present effort in the program is directed toward the development of cells having negative electrodes of a solid lithium-aluminum alloy, positive electrodes of either FeS_2 or FeS , and an electrolyte of LiCl-KCl eutectic (mp, 352°C) that fills the pores in the electrodes and the separator. The use of this electrolyte requires operation of the cell at about 400 to 450°C . Boron nitride fabric has proved to be a satisfactory electrode separator material in these cells, and the addition of metal sulfides to the positive electrodes, namely, Cu_2S to FeS and CoS_x to FeS_2 , has resulted in significant improvements in cell lifetime and performance. The experimental work on electrode and cell development in the past year was directed primarily toward vertically oriented cells having a prismatic shape. This type of cell was selected because it is more amenable than the previous cylindrical, horizontal cells to incorporation into a compact battery. The electrode and cell designs for the two applications differ; the major difference is that the power requirements for electric vehicle propulsion necessitate the use of thinner electrodes.

To increase the effort on the development of cell fabrication techniques and to begin the transfer of technology to industry, development contracts were made with industrial firms to fabricate electrodes and cells. As a result of these contractual efforts, we expect to achieve our near-term goals, which are less stringent than the long-range goals given in Table 1. The first contract was made in April 1975 with Gould Inc., and since that date contracts have also been made with Eagle-Picher Industries, Inc. (May 1975) and Catalyst Research Corporation (October 1975). The first cells fabricated under the Gould contract were received at Argonne in mid-November 1975. ANL is also subcontracting cell development work of a more basic nature to Atomics International, and contracts have been made with several industrial firms to develop improved electrode separators and electrical feedthroughs.

Battery design work is concerned principally with cell and battery design, component development, battery testing, and systems and cost analysis. Two major efforts during the past year were the design of an electric-vehicle battery that could be installed under the hood of a 1975 Mustang II and the design of a load-leveling battery for testing in the Battery Energy Storage Test (BEST) Facility. Work on the design and cost of this facility, which is being planned by ERDA and the Electric Power Research Institute (EPRI), was also performed by CEN battery program personnel.

The efforts in electrode and cell development have resulted in the identification of designs for electrodes and cells and new procedures for cell assembly and start up. Several promising types of positive electrodes have been designed for prismatic cells; these include (1) electrodes having porous current collector structures into which the active material is vibratorily loaded, (2) electrodes in which a mixture of the active material and electrolyte is hot-pressed onto a metal current collector, and (3) electrodes formed from a mixture of active material and carbon cement to give a carbon-bonded, porous structure that is easily penetrated by electrolyte. A major improvement has been achieved recently in the design of cells with hot-pressed FeS positive electrodes. The cells are assembled in the uncharged state, i.e., the positive electrode is a mixture of Li_2S , electrolyte, and iron powders, and the

negative electrode is a pressed aluminum-wire plaque. During the first charge, lithium is transferred to the negative electrode, and FeS is formed in the positive electrode. This method of assembly, along with the addition of copper to the positive electrode, has produced greatly improved performance in Li-Al/FeS cells and has significantly reduced the swelling previously encountered in FeS electrodes. A continuing effort is being made to incorporate these advances in technology into new battery designs and to transfer the technology as rapidly as possible to the industrial firms having development contracts with ANL.

II. CELL AND BATTERY DESIGN

A. Battery for Electric-Vehicle Propulsion

A conceptual design study was undertaken, in cooperation with Linear Alpha, Inc., to modify a compact American car for electric propulsion with a Li-Al/iron sulfide battery. Linear Alpha, Inc., under contract with ANL, performed the vehicle-design studies, including the selection and redesign of the car for electric propulsion, the selection of electrical components, and the calculation of the performance characteristics of the car and its total weight. ANL used these data to design a battery that would meet the performance characteristics set for the vehicle. The specifications for the battery, which was designed for either FeS₂ or FeS electrodes, were similar to those of the long-range goals given in Table 1.

The type of cell selected was of a cylindrical, multiplate configuration (Fig. 1), and the design assumed certain improvements in cell components and

Fig. 1. Conceptual Design for Electric-Vehicle Battery Cell

electrode performance which are considered attainable in the near future. The cell components for which improvements are required are the electrical feedthrough and the electrode separator; intensive efforts to develop both of these are under way.

The battery design comprises either 130 FeS-type cells or 110 FeS₂-type cells, separated into modules containing 13 FeS cells or 11 FeS₂ cells (see Fig. 2). The cell housings are insulated from each other and from the

Fig. 2. Conceptual Module for Electric-Vehicle Battery

module jacket, which is a hermetically sealed container that provides additional protection to the cells from the atmosphere. The cells are stacked in series by connecting the positive terminal of each cell to the housing (at negative potential) of the cell above. A voltage lead from each individual cell is connected to a multiple conductor feedthrough in the wall of the module jacket. The voltage of each individual cell can be monitored, and the charge of the individual cells can be adjusted by means of solid-state circuitry.

The design of the vehicle battery that would be required to meet the automobile performance requirements selected for the study is shown in Fig. 3. The dimensions of this battery are approximately the same as those of the space made available under the hood of a Mustang II by removing the gasoline engine, although some repackaging of cells and/or relocation of automobile components might be necessary for the battery to fit.

This design study demonstrated the feasibility of equipping a gasoline-powered automobile with a lithium/metal sulfide battery; however, it also revealed that fitting a battery into a standard gasoline-powered automobile was not the most practical approach to battery demonstration, because of problems related to vehicle design (*e.g.*, weight distribution). Moreover, as a result of cell and electrode development work (discussed later), emphasis

Fig. 3. Conceptual Battery for Electric Vehicle

in the program was shifted to cells of a vertically oriented, prismatic design, rather than the cylindrical design used in this study.

Some advantages foreseen for the prismatic design, as compared with a cylindrical design, are as follows:

(1) With presently available feedthroughs, prismatic cells can be stacked more compactly; thus, the volumetric energy density of the battery is improved and less battery space is required. Also, this design lends itself more readily to multiplate stacking within a cell; as a result, the number of feedthroughs and the amount of cell casing material per unit of capacity are decreased.

(2) The feedthrough is not in direct contact with the molten salt electrolyte (although some electrolyte may creep up the cell wall); this lack of direct contact is expected to result in less stringent requirements of leak-tightness and corrosion resistance for the feedthrough.

(3) Degassing of the cell during the salt filling operation may be facilitated because of the vertical orientation. Also, a space is provided for gas accumulation if off-gassing takes place after the cell is sealed.

Accordingly, a decision has been made to design and construct an electric-car battery having vertical, prismatic cells and to install the battery in a vehicle that is specifically designed for electric propulsion. With an accelerated program, which would require additional funding, we believe that a lithium/metal sulfide battery could be installed in a test vehicle within two years.

B. Battery for Utility Load-Leveling

A battery of Li-Al/FeS cells has been designed for testing in the Battery Energy Storage Test (BEST) Facility. This facility is being planned by ERDA, ANL, EPRI, and several utilities for testing advanced batteries on a utility network. The Li-Al/FeS battery design provides storage of 10 MW-hr with a 7-hr charge and 10-hr discharge, as specified for the BEST Facility.

The cells for this battery are vertically oriented, prismatic cells having a central positive plate of FeS with two facing negative plates of Li-Al alloy; they are hermetically sealed and can be fabricated individually. The conceptual cell design is shown in Fig. 4.

Fig. 4. Design of Cell for Load-Leveling Battery
ANL Neg. No. 308-4056

The cells are modularly combined to form a battery. Six cells are connected in parallel within a secondary stainless steel container housing to form a submodule having the configuration and specifications shown in Fig. 5. Five of these submodules, electrically insulated from each other, are stacked in a series arrangement to form a module that has the dimensions and specifications shown in Fig. 6. The module is the basic building block of the battery string and is the smallest replaceable unit.

The battery string, composed of 174 modules, is shown in Fig. 7. Two of these strings in parallel comprise the battery for the BEST Facility. As illustrated, consideration is being given to overhead loading with a crane and to utilizing an insulated shroud to permit modules to be removed and replaced while the battery is at operating temperature, which is above 400°C.

SUB-MODULE SPECIFICATIONS

Nominal Voltage	1.15
Theoretical Capacity	6000 A-hr
Nominal Capacity	4800 A-hr
Energy Output	5.5 kW-hr
Approx. Weight	42 kg
Specific Energy	130 kW-hr/kg

Fig. 5. Design of Submodule for Load-Leveling Battery

MODULE SPECIFICATIONS

Nominal Voltage	5.75
Energy Output	27.6 kW-hr
Approx. Weight	231 kg

Fig. 6. Design of Module for Load-Leveling Battery

BATTERY STRING SPECIFICATIONS

4.8 MW-hr AT 1000 V (Nominal)
 870 SUB-MODULES
 174 MODULES
 6 x 29 ARRAY

Fig. 7. Design of BEST Facility Battery

III. COMMERCIAL DEVELOPMENT

A. Cell Fabrication by Industrial Firms

An integral part of the ANL battery program is the transfer of Li-Al/iron sulfide battery technology to industrial firms as rapidly as possible. In this way, the industrial capability for the production of cells and components will be available when battery fabrication is needed. The participation of chemists and engineers from five industrial firms in our program, discussed in last year's report, is continuing, and plans to involve industrial firms in contracts to develop manufacturing techniques and to manufacture electrodes and cells were accelerated during the past year. Bids for contracts were requested from the five firms in the ANL industrial participation program in late January 1975, and proposals were received from all five by the end of February 1975. A contractor review and selection board was established to review the proposals, and three firms--Gould Inc., Eagle-Picher Industries, Inc., and Catalyst Research Corp.--were selected for contracts. Before the contracts were awarded, meetings were held with personnel from the three firms to discuss the work covered by the contracts. A steering committee was formed at ANL to provide technical direction to the contractual efforts.

The general design of the prismatic cells to be manufactured by the industrial firms is shown in Fig. 8; two thicknesses are specified for electrodes and cells. The thin types are suitable for electric-vehicle batteries,

Fig. 8. General Design of Prismatic Cells
(dimensions in inches)

and the thick types for off-peak energy storage batteries. The various contracts specified the thicknesses of electrodes and cells, the electrode fabrication techniques, the types of positive electrodes (FeS or FeS_2), and the number of electrodes and cells to be produced. Considerable latitude was permitted in the electrode design and fabrication techniques.

The first contract, which was made with Gould Inc. on April 1, 1975, has been completed. Under this contract, Gould developed techniques for fabricating electrodes by loading powdered materials into porous current collector structures. Gould also fabricated 24 aluminum plaques for negative electrodes, nine powder-loaded Li-Al electrodes, nine electrochemically formed Li-Al electrodes, six $\text{FeS} + \text{Cu}_2\text{S}$ electrodes, six $\text{FeS}_2 + \text{CoS}_2$ electrodes, six Li-Al/ FeS cells, and six Li-Al/ FeS_2 cells. The electrodes and cells were delivered to ANL in mid-November 1975, and evaluation and testing are under way.

The contract was initiated with Eagle-Picher Industries, Inc. on May 1, 1975. Under this contract Eagle-Picher is developing techniques for cold-pressing powders into electrode structures and will produce eighteen Li-Al electrodes, twelve $\text{FeS} + \text{Cu}_2\text{S}$ electrodes, twelve $\text{FeS}_2 + \text{CoS}_2$ electrodes, twelve Li-Al/ FeS_2 cells, and twelve Li-Al/ FeS cells. Pressing and glove-box facilities have been set up at Eagle-Picher and development efforts on pressing are now under way. In this connection, preliminary electrodes prepared in a dry-room atmosphere, rather than in a glove box, have been sent to ANL and are being tested in Cell BB-1 (Section IV). Delivery of the final versions of electrodes and cells is scheduled for the end of January 1976.

The contract with Catalyst Research Corp. was initiated on October 1, 1975. Under this contract, Catalyst Research is developing techniques for fabricating Li-Al electrodes by casting molten Li-Al within a porous structure.¹ The positive electrodes will be the same type as those fabricated by Gould. Techniques for fabrication and assembly of electrodes and cells in a "super" dry-room atmosphere (<1% relative humidity) are also being developed. Catalyst Research will test some cells and conduct post-test examinations on failed cells. In addition, eight Li-Al electrodes, four $\text{FeS}_2 + \text{CoS}_2$ electrodes, and two Li-Al/ FeS_2 cells will be delivered to ANL for testing.

These contracts represent the first in a series of contracts to develop alternative manufacturing methods; these methods will be evaluated in terms of the performance of the product cells and the economics of the processes involved. Future contracts are expected to involve the development and fabrication of carbon-bonded electrodes and pressed electrodes for cells assembled in the uncharged state.

B. Component Development

Boron nitride fabric (a product of the Carborundum Co.) has shown adequate performance as an electrode separator in full-scale engineering cells for more than 6400 hr; however, a lower-cost, thinner separator of improved performance is needed for commercial batteries. Contracts have therefore been issued to the Carborundum Co. and to the University of Florida* for the

---

* The contract with the University of Florida is funded directly by ERDA.

development of improved electrode separators. These separators must be corrosion-resistant in the cell environment, capable of maintaining electrical separation, and thin enough to permit close electrode spacing. The contract with the Carborundum Co. calls for the development of a porous paper separator from BN fibers. Initial development efforts were centered on producing thin (<0.35 mm), highly porous ($\sim 95\%$) papers using both organic binders (Resole, H-Resin, PVA, Latex, etc.) and inorganic (SiO_2 , Al_2O_3) binders. In-cell evaluations at ANL indicated that the initial samples were unsatisfactory owing to breakdown of the binders and separation of the fibers. More promising results were obtained with BN paper having a BN binder formed *in situ* by nitriding B_2O_3 binder. This fabrication process is being refined; also, thicker papers (0.7 to 1.5 mm) having porosities of about 85% are now being prepared for evaluation.

The work at the University of Florida emphasizes the fabrication of composite-type separators consisting of various combinations of fibers and ceramic-powder fillers. The fillers are expected to improve electrical separation and integrity and to reduce the amount of fiber needed. Preparations using BN fibers and ceramic powders (BN, MgO , LiAlO_2) with a small ($<4\%$) addition of asbestos fiber as a binder are presently being evaluated and show reasonably good mechanical properties. Separators with other combinations of fibers (Y_2O_3 , BN) and ceramic powders (Y_2O_3 , AlN) are also being prepared.

Yttria fibers have been obtained from Zircar, Inc. and further discussions are under way regarding the development of yttria fabrics and papers by Zircar's precursory process.* Discussions are also being held with a number of companies (W. R. Grace, Eagle-Picher, Herty Foundation, and Kimberly Clark) that may be interested in manufacturing separators on a commercial basis, using an already developed process.

Contracts have been made with several manufacturers of ceramics for the development of electrical feedthroughs. The 3-M Corp., Chattanooga, Tennessee, has applied nickel and gold platings to the braze zone of beryllia feedthroughs that were metallized by standard methods. ILC Technology, Sunnydale, California, is developing niobium-base brazes for beryllia and is producing prototype feedthroughs for in-cell testing. Coors Porcelain Co., Golden, Colorado, is producing yttria bodies and will metallize them with an oxide-base braze to form feedthroughs. Ceramaseal Inc., New Lebanon Center, N. Y., has developed a mechanical-type feedthrough, in which the seal is formed by forcing a beryllia body into a high-strength steel tube. Samples of the various feedthroughs are being procured for evaluation.

IV. CELL DEVELOPMENT

The effort in this part of the program is directed primarily toward the development of engineering-scale, sealed cells capable of meeting the

---

* In this type of process, a conventional type of fabric or paper is impregnated with, for example, a solution of yttrium chloride, dried, and treated in such a way that the fabric or paper burns, leaving a replica of yttria.

requirements for batteries for both of our applications. In previous work,² compact, lightweight cells were developed, and impressive specific energies (up to 150 W-hr/kg) were achieved. Recent work has been concentrated on improving the specific power and lifetime of the cells, and on establishing improved fabrication techniques.

The engineering-scale cells (~ 150 A-hr capacity) employ a design³ having a central positive electrode of iron sulfide (FeS_2 or FeS) and two facing negative electrodes of a solid Li-Al alloy. The first generation of engineering cells were cylindrical (13 cm in diameter, 3 to 5 cm high) and were operated in the horizontal position. Recent work has been concentrated on the development of prismatic cells (13 by 13 cm, 2 to 4 cm thick) of the type resulting from the design studies. Figure 9 is a schematic diagram of Cell R-1, the

Fig. 9. Schematic Diagram of Prismatic Cell R-1.

first engineering-scale, sealed, prismatic cell; Figure 10 is a photograph of Cell R-1. To date, in the cell development effort, 21 engineering cells have been tested, 12 with FeS_2 positive electrodes and 9 with FeS electrodes.

An effort is being made to develop improved fabrication procedures to reduce the cost and complexity of the cells. The relative ease and simplicity of the cell assembly that is possible with hot-pressed electrodes has been demonstrated with recent FeS cells. These cells have also been assembled in the uncharged state,³ a method of assembly that has several advantages, including reduced outgassing during startup, and reduced electrode expansion and shape change.

Fig. 10. Prismatic Cell R-1
ANL Neg. No. 308-4090

A. Li-Al/FeS₂ Cells

In the past year, eight engineering cells with FeS₂ electrodes have been tested; five of these cells were cylindrical (Cells W-9, -10, -11, -12 and -14) and three were prismatic Cells R-1, -2, and -3). The early W-series cells employed Li-Al electrodes prepared by a single-step electrochemical formation procedure; however, Cells W-12 and W-14 had negative electrodes consisting of powdered Li-Al loaded into a porous metal structure and the R-series cells had uncharged negative electrodes (plaques of compressed aluminum wires). The positive electrodes in early FeS₂ cells were enclosed by a molybdenum mesh basket and contained several molybdenum mesh current collectors. In later cells, an improved design resulted in the elimination of the basket. Cobalt sulfide has been added to the FeS₂ electrodes of recent cells to provide additional electrical conductivity^{6,7} and reduce the current collector requirement to a single sheet of molybdenum.

All of the cells tested had matched capacities of lithium and sulfur except Cells W-9, W-12, and W-14, which were operated only on the upper voltage plateau (FeS₂ → FeS) and thus had smaller lithium capacities. Figure 11 shows typical voltage patterns obtained for the three types of cells under

Fig. 11. Voltage Patterns for Li-Al/FeS_x Cells
[theoretical capacities (A-hr): W-9, 112; W-11, 150; R-7, 121]

development: a two-plateau FeS₂ cell, an upper-plateau FeS₂ cell, and an FeS cell. The two-plateau FeS₂ cells have achieved the highest specific energies (up to 150 W-hr/kg), whereas the upper-plateau cells have exhibited a high power capability that can be sustained throughout a deep discharge. The electrical performance results for these cells are summarized in Table 2.

Table 2. Performance of Li-Al/FeS₂ Engineering Cells

Cell No. ^a	Lifetime		Specific Energy, W-hr/kg		Energy Eff., %	Remarks
	Cycles	Hours	Max.	Typical		
W-9	76	1511	98	80-90	81	Thick, upper electrode cell; excellent power characteristics.
W-10	113	2688	128	110-120	78	Illustrated beneficial effect of CoS additive.
W-11	43	1128	122	100-110	82	CoS additive; good utilization and power with small amount of Ni current collector in FeS ₂ electrode.
W-12	20	150	50	30-40	74	CoS additive; thin, upper-plateau cell; high utilization and power.
W-14	107	1300	85	75-85	78	CoS ₂ additive; thin, upper-plateau cell; good sustained power capability.
R-1	53	1010	105	80-100	78	First prismatic cell; CoS ₂ additive; highly compact, thin electrodes.
R-2	143	1400	110	80-100	80	CoS ₂ additive; high peak power (165 W/kg).
R-3	13	300	90	50-60	75	CoS ₂ additive; Ni current lead fractured during startup.

^aW-series cells: cylindrical, horizontally oriented; R-series cells: prismatic, vertically oriented, assembled in the uncharged state.

The early prismatic cells exhibited somewhat erratic performance owing to broken current collectors and current leads; the breaks occurred because of the stresses within the cells. An improved current collector design incorporating a flexible current lead has been developed and is expected to eliminate this problem.

The specific energies of the first prismatic FeS_2 cells were considerably lower than those achieved in the cylindrical cells, primarily because the electrodes were thinner and the cells contained larger amounts of electrolyte. When fully developed, the prismatic FeS_2 cells are expected to attain specific energies equivalent to those of the cylindrical cells (about 130 to 150 W-hr/kg). The principal advantage of the prismatic cells is that they can be directly stacked in compact battery arrays, without the development of a compact, interlocking feedthrough. Present work is being concentrated on increasing the lifetime capability of these cells and on developing fabrication techniques that are amenable to low-cost mass production.

B. Li-Al/FeS Cells

Work is also in progress on a low-cost positive electrode that utilizes FeS as the active material and iron as the current collector. As demonstrated by the performance of Cell R-7, the recent advances in cell design have produced a compact FeS cell with greatly improved specific energy (about 100 W-hr/kg) and specific power (up to 130 W/kg). The two factors mainly responsible for improved performance are assembly of the cell in the uncharged state and the use of Cu_2S additive to the FeS electrode. Eight engineering cells having FeS electrodes have been tested during the past year; the electrical performance results are summarized in Table 3. The early FeS cells exhibited

Table 3. Performance of Li-Al/FeS Engineering Cells

Cell No. ^a	Lifetime ^b		Specific Energy, W-hr/kg		Energy Eff., %	Remarks ^c
	Cycles	Hours	Max.	Typical		
W-8	121	1700	82	40-60	77	Stable performance, long lifetime; low utilization.
W-13	9	168	59	40-50	68	Hot-pressed electrodes. Early short circuit.
R-4	46	688	65	50-60	80	LiF-LiCl-LiBr electrolyte used to eliminate potassium ion.
R-5	140	2400	66	40-50	85	Stable performance.
R-6	125	2000	60	40-50	86	Stable performance.
R-7	70	1700	110	100-105		Excellent performance. High specific power (130 W/kg).
R-9	7	185	110	100-105	86	Good performance, but early failure (short circuit).
BB-1	35	490	60	40-50	55	Electrodes and other cell components fabricated by Eagle-Picher.

^aAll R-series cells assembled in the uncharged state.

^bCells R-5, -6, and -7 and BB-1 were in operation as of the end of December 1975.

^cIn all cells except R-4 and -5, Cu_2S was added to the FeS electrode.

poor electrical performance and extreme expansions of the positive electrodes, the latter of which caused swelling of the cells or short-circuiting between the electrodes. The addition of Cu_2S to the FeS appears to have eliminated the formation of the J-phase,* which had produced high voltage polarization and poor electrical performance. Assembly of cells in the uncharged state appears to have greatly reduced the electrode expansion problem. (An improved procedure for producing the starting material for the uncharged FeS electrodes, described in Section VII., has contributed to the success of this method of assembly.) The good performance of Cell R-7 strongly indicates that a low-cost FeS cell can be developed for the off-peak energy storage application.

Cell BB-1, which was recently put into operation, has electrodes prepared by Eagle-Picher. These electrodes were made as part of their contractual effort on developing cold-pressing techniques. They were fabricated in a dry-room atmosphere rather than a glove-box atmosphere, and are considered preliminary versions of the electrodes to be produced in fulfillment of their contract.

V. ELECTRODE DEVELOPMENT

Electrode studies during the past year have been directed toward the development of both positive and negative electrodes that meet certain costs, performance, and cycle life requirements for prismatic cells. Emphasis has been placed on the development of electrodes that appear to be amenable to mass production. Investigations of both negative and positive electrodes have addressed the effects on electrode performance of electrode thickness, volume fraction of electrolyte in the electrode, purity of the electrolyte, type of current collector, method of electrode fabrication, and starting materials (*i.e.*, whether the electrode was assembled in the charged or uncharged state). Supporting work included the evaluation of (1) lithium alloys other than lithium-aluminum (*e.g.*, Li-Si), (2) metal sulfide additives to FeS_2 electrodes, and (3) various metal nitride and metal boride coatings for iron and stainless steel current collectors for use in FeS_2 electrodes.

A. Negative Electrodes

Studies of Li-Al/Li and Li-Al/Al cells have yielded information on some of the factors that influence lithium utilization in Li-Al electrodes. No effect on lithium utilization was noted when the volume fraction of electrolyte in the fully charged Li-Al electrode was varied from 0.2 to 0.4 or when electrolyte from two different sources was used. A marked decrease in lithium utilization occurred when the thickness of electrochemically formed electrodes was increased from 0.32 cm to 0.64 cm; however, good utilization was achieved in thicker electrodes (0.64 cm) fabricated by vibratorily loading Li-Al powder into porous metal current collector structures.

A continuing effort is being directed toward the development of improved Li-Al electrodes. Techniques are being sought for increasing the capacity

---

* Approximate composition, $\text{K}_{2.8}\text{Li}_{0.4}\text{Fe}_{12}\text{S}_{13}$.

per unit volume of the thin electrodes for electric-vehicle battery cells. Also, with the recent interest in assembling cells in the discharged state, pressed aluminum foil and porous aluminum structures are being tested for use as starting materials in uncharged negative electrodes.

Lithium-metal alloys other than Li-Al are being evaluated as possible alternative electrode materials for Li/metal sulfide cells. In the past year, alloys of Li-Si, Li-Al-Si, Li-Al-B, Li-Al-Zn, and Li-Si-B have been tested in Li/Li-M cells. The ternary Li-Al-M alloys were electrochemically reversible, but none of them exhibited electrochemical performance that equaled that of Li-Al. Lithium-silicon alloys show good performance at low current densities ($<0.064 \text{ A/cm}^2$), but the lithium utilization decreases markedly at higher current densities. If the performance of Li-Si electrodes can be improved at the higher current densities of interest, this system would provide an alternative negative electrode material.

B. Positive Electrodes

The change in cell design from a cylindrical, horizontally oriented configuration to a prismatic, vertically oriented one has necessitated significant changes in the design of the positive electrode. Initially, the principal area of concern was the possible slumping of the iron sulfide powders within the electrode structure, and this was taken into consideration in the new electrode designs.

In one of the first prismatic designs, which was discussed in last year's report, the active material (in the form of a powder) was vibratorily loaded into a porous metal or vitreous carbon foam current collector structure. Since that time, several modifications of this design have improved the performance of the vitreous carbon foam electrode: (1) the electrode structure was separated into two vertical compartments by a layer of carbon fabric or metal current collector to prevent excessive lithium deposition in one of the Li-Al electrodes in the event that one negative electrode has a lower resistance than the other, and (2) the electrode structure was further divided into horizontal compartments to prevent slumping of the active material.

Recently, a new type of positive electrode has been designed. This electrode is formed from a paste-like mixture of active material (FeS_2 or FeS), a noncontaminating volatile material (ammonium carbonate), and a binder (graphite cement). The resulting current collector is similar to the porous metal and carbon foam structures of vibratorily loaded electrodes, except that the active material is in more intimate electrical contact with the current collector structure. The carbon-bonding technique may permit the use of lower cost current collectors and easier control of the electrolyte loading.

Some of the cells that were operated to evaluate these electrode designs are discussed below.

C. Electrode Performance Testing

Cell S-77, a Li-Al/ FeS_2 - CoS_2 cell of cylindrical, horizontal configuration, was operated to test a positive electrode structure of vitreous carbon foam

and a negative electrode structure of porous iron. Both electrodes demonstrated high performance, and Cell S-77 achieved the longest lifetime of any ANL cell: it was operated for more than 6400 hr and 300 cycles with little decline in capacity before operation was voluntarily terminated for examination. This examination showed that corrosion probably would soon have caused cell failure.

Cell S-82, a Li-Al/FeS₂-CoS₂ cell of prismatic, vertical configuration, was operated primarily to evaluate a positive electrode in which FeS₂-CoS₂ was vibratorily loaded into a vitreous carbon foam structure having both vertical and horizontal compartments. The negative electrodes were prepared by vibratorily loading Li-Al powder into porous nickel current collector structures. Cell operating procedures, which were adopted on the basis of data from other cells, included the use of a discharge cutoff voltage of 0.9 V or greater and periodic operation on open circuit after long periods of cycling. The latter mode of operation allows the redistribution of lithium in the negative electrodes. Cell S-82 has now been operated for more than 4825 hr and 175 cycles with less than 10% variation in energy (generally about 150 W-hr). Operation of this cell in a lifetime test is continuing.

Cell KK-2 (Li-Al/FeS₂) was operated to test the carbon-bonded FeS₂ electrode in a compact welded cell designed for electric-vehicle application. The cell exhibited stable performance for 1825 hr and 90 cycles, when operation was voluntarily terminated.

VI. MATERIALS STUDIES

A. Electrical Feedthroughs

The design of the prismatic cell requires an electrical feedthrough to isolate the positive terminal from the cell housing, which is at negative potential. To minimize current leakage, the feedthrough insulators must be fabricated from high resistance materials. Moreover, the feedthrough must be leak-tight, compatible with the cell environment, and--for commercial application--small, light in weight, and inexpensive.

Two types of feedthroughs are being considered: their principal difference is in the method by which the seal is formed. In one the seal is formed mechanically, whereas in the other the seal is formed metallurgically by brazing. The mechanical feedthrough is lower in cost and the components are more compatible with the cell environment; on the other hand, the brazed type is more leak-tight and compact. (Work on feedthrough development by industrial firms is discussed in Section III.B.)

Significant progress has been made toward the development of both types of feedthroughs. The mechanical feedthrough that has been used successfully in our test cells incorporates a modified Conax thermocouple seal. The feedthrough housing was redesigned and the weak boron nitride bottom insulator was replaced with higher strength beryllia. Estimates on the cost of components for the entire feedthrough, in lots of 100,000 (representing small-scale mass production), indicated a unit cost (in 1975 dollars) of about \$2. Another mechanical-type feedthrough, wherein a beryllia plug is forced into

a high-strength metal sleeve, demonstrated good leak-tightness (helium leak rates of less than 1×10^{-9} cm³/sec). Brazed-type feedthroughs were developed in which niobium-base alloys were used as braze materials with great success. Also, brazed-type feedthroughs have been produced in which conventional brazes are protectively coated. Work is also under way to fabricate yttria bodies and to coat them with a mixed-metal-oxide braze; the yttria components are being considered as possible alternatives to beryllia components. Screening tests to determine compatibilities of the various feedthroughs are being performed to determine the most suitable feedthrough for prototype commercial cells.

B. Electrode Separator Studies

For a compact, lightweight cell, a porous electrode separator is required that is resistant to the cell environment, maintains electrical separation, and permits close electrode spacing. Boron nitride fabric has been used successfully as a separator in ANL cells, but its present cost (\$515/ft²) and projected cost for mass production (\$6-10/ft²) preclude its use in commercial cells. The use of a paper separator that contains less fiber per square foot would reduce the separator cost considerably; moreover, the relatively expensive weaving process would be eliminated. Therefore, efforts are being concentrated on the development of suitable papers prepared from BN or other stable, lower-cost ceramic fibers. Some of the work being done in this area by the Carborundum Corp. and the University of Florida has been discussed earlier.

A major effort will be continued on the development of paper separators and evaluation of new fibers. At ANL, particular emphasis will be placed on evaluating binding agents and fiber-resistant schemes; equipment will also be procured for fabricating test ceramic papers in order to evaluate new materials and fabrication techniques as quickly as possible. In addition, efforts by the two outside agencies will continue.

C. Lithium-Aluminum Phase Diagram

A study was undertaken of the phase relationships in the Li-Al system because its published phase diagram⁶ appeared to be in error. Alloys were prepared by melting weighed amounts of lithium and aluminum in a tantalum crucible, stirring, casting, homogenizing, and then quenching. Phases were identified by metallographic examination and X-ray diffraction; phase-transformation temperatures were established by differential thermal analysis.

The results of our investigation to date are summarized in the phase diagram shown in Fig. 12. The liquidus and solidus temperatures over the entire diagram, except those near the 335°C isotherm, are in agreement with previous work. The aluminum-rich boundary of the intermediate solid-solution β -phase (LiAl) is at 47 at. % Li; the lithium-rich boundary, although not yet completely established, lies somewhere between 57 and 60 at. % Li. The isotherms at 520°C and 335°C result from the peritectic formations of Li₃Al₂ and Li₉Al₄, respectively. The isotherm at 275°C results from a polymorphic transition in Li₉Al₄, the low-temperature form of which is monoclinic. The lithium-rich eutectic transformation occurs at 180°C.

Fig. 12. Tentative Phase Diagram of Lithium-Aluminum System (α = Al, β = LiAl, γ = Li_3Al_2 , δ = Li_9Al_4 below 275°C , δ' = Li_9Al_4 above 275°C)

Future efforts will be directed toward determining the structure of the high-temperature form of Li_9Al_4 and the lithium-rich limit of composition of the LiAl phase, and toward confirming the limit of solid solubility of lithium in aluminum.

D. Evaluation of Materials

Because corrosive conditions differ in the Li-Al, FeS_2 , and FeS electrode environments, static corrosion tests are used extensively to screen candidate materials of construction for their compatibility with each environment. These tests also aid in identifying the mechanisms by which various electrochemical reactions occur.

Long-term (1000-hr) corrosion tests of metals and alloys have been conducted at 500°C in $\text{FeS} + \text{LiCl-KCl}$ and $\text{FeS}_2 + \text{LiCl-KCl}$. The materials included six Fe-Mo-Ni alloys prepared at ANL and commercially available Armco iron, nickel, niobium, molybdenum, Hastelloy B, and Hastelloy C. The tests in $\text{FeS} + \text{LiCl-KCl}$ indicated that the following materials have acceptable corrosion resistance: molybdenum, Hastelloy B and C, niobium, nickel, 10Mo-20Ni-Fe, 15Mo-20Ni-Fe, and 15Mo-30Ni-Fe. In the $\text{FeS}_2 + \text{LiCl-KCl}$ environment, only molybdenum showed sufficient corrosion resistance at 500°C ; however, at 400°C , Hastelloy B showed marginally acceptable corrosion resistance.

In the postoperative, microscopic examinations of cells operated at temperatures higher than 450°C , the formation of a brittle, aluminum-rich

Fe-Al reaction layer has been observed on cell housings and negative-electrode current collectors. Electron microprobe analysis established the composition of the reaction product as FeAl_2 . A series of tests employing dissimilar metal couples has established that this reaction occurs near the end of a discharge cycle when a galvanic couple is established between the Li-depleted Li-Al and the electrode housing. The dissimilar metal couple tests, which employed various housing materials for the cathodic members, showed several common characteristics. At 400°C , the galvanic reaction occurred at an acceptably low rate. For 500°C tests using very pure LiCl-KCl (Anderson Physics Laboratory), the reaction rates were one to two orders of magnitude higher and resulted in the formation of a significant amount of the Fe-Al intermetallic; however, in tests at 500°C in Lithcoa LiCl-KCl, which contains several anionic impurities such as carbonate and hydroxide, the reaction rates were near those at 400°C . It is believed that the decrease in reaction in Lithcoa electrolyte was the result of a passivation effect.

E. Postoperative Cell Examination

Postoperative examinations are conducted on cells to determine materials behavior and to obtain information on electrode performance. These examinations include microscopic, X-ray diffraction, chemical, and electron-microprobe analysis. Recent examinations have been principally of vertically oriented, prismatic cells.

Macro examination of vertical cross sections of several of these cells has showed no evidence of electrode slumping, which had been a major concern in the design of vertically oriented cells. This observation was supported by the sulfur analyses that were performed on sections taken from top to bottom of the positive electrodes of three prismatic cells (PR-1, R-1, and R-2). None of the cells showed a higher concentration of sulfur at the bottom; in fact, two cells showed slightly higher concentrations of sulfur in the upper portions. Low concentrations of sulfur (typically, ~ 0.1 wt %) have been detected in the negative electrodes.

Metallographic examination of the negative electrodes from Cells PR-1, R-1, and R-2 showed considerable nonuniformity both in the Li-Al alloy structure and in the lithium distribution within the electrodes. The lithium concentration was highest at or near the negative electrode/positive electrode interfaces. Also, the finer Li-Al particle structures in the areas nearest the positive electrode indicate that most of the electrochemical cycling reaction occurred there.

VII. CELL CHEMISTRY

The cell chemistry studies have been directed toward various problems arising in the development work, innovations and improvements in the cell chemistry, and a better understanding of the processes that occur within the cells. Some highlights of this work are as follows:

Laboratory studies have indicated the feasibility of starting Li-Al/FeS cells from an uncharged state, using mixtures of iron and Li_2S powders in the positive electrode. The success of this procedure was found to depend upon

the use of sintered, well-crystallized Li_2S , rather than the amorphous, moisture-sensitive, as-received powder. The use of initially uncharged electrodes has now been demonstrated in engineering-scale cells (Section IV). As an adjunct to this study, the preparation of Li_2S by the direct reduction of Li_2SO_4 with carbon was explored in small-scale tests. The reaction proceeded satisfactorily at 1000–1100°C under a helium atmosphere or at about 850°C under vacuum.

Further investigations of the chemistry of FeS electrodes indicated that when a Li-Al/LiCl-KCl/FeS cell is charged, the first material to be formed in the FeS electrode is the J-phase (approximate composition, $\text{K}_{2.8}\text{Li}_{0.4}\text{Fe}_{12}\text{S}_{13}$). This reaction is followed by the formation of FeS, but only at an IR-free charge cutoff voltage greater than 1.7 V at 400°C; at higher temperatures, this voltage is slightly lower.

Experiments were conducted to determine suitable charge cutoff voltages for cells having FeS_2 positive electrodes. Five Li/FeS₂ cells were charged to successively higher cutoff voltages and the reaction products in the FeS₂ electrode were examined. The results indicated that charging above 2.64 V vs. Li increased the porosity of the FeS₂ electrode and decreased the current efficiency. The overcharge reaction products were identified as free sulfur and FeCl_2 (complexed as KFeCl_3 or K_2FeCl_4). Complementary cyclic voltammetry studies showed that the overcharge reaction is irreversible and diffusion-limited. The results of the cell tests and cyclic voltammetry measurements were in excellent agreement, and showed that the charge cutoff voltage for Li-Al/FeS₂ cells should not be allowed to exceed 2.35 V.

Recommended limitations on the discharge cutoff voltage for Li-Al/FeS₂ cells were also determined. A cell of the type Al/LiCl-KCl/Li₂S·FeS was operated to simulate the conditions that exist in a cell if the capacity of the Li-Al electrode is less than that of the FeS₂ electrode. Two types of aluminum that have been used in the engineering-scale cells were tested. One was relatively high-purity (99%) aluminum; the other, in the form of demister wire, contained ~5 wt % magnesium. The results indicated that discharge cutoff voltages for Li-Al/FeS₂ cells should not be lower than 0.7 V for the high-purity aluminum electrodes and 0.9 V for the demister-wire electrodes. Otherwise, the negative electrode may be anodically oxidized to form soluble aluminum or magnesium species in the electrolyte.

In the operation of a cell it is important that the porous separator fabric between the electrodes be well wet by the electrolyte to permit easy passage of the lithium ions. Therefore, tests were conducted to determine whether molten LiCl-KCl would penetrate BN fabric, which is being used in electrode separators. Also of interest was the penetrability of carbon and ZrO_2 fabrics, which are used to contain particulates in the electrodes. The ZrO_2 fabric was penetrated easily by the molten salt. However, wetting and penetration of the BN and carbon fabrics occurred only when both sides were covered by the molten salt, and the furnace-well atmosphere was evacuated and then repressurized with helium. The BN and carbon fabrics thus behaved as nonwetable surfaces on first contact with the salt, but once they were penetrated by the salt they behaved as wettable surfaces. This behavior is consistent with earlier measurements of the contact angles of electrolyte drops on solid surfaces of the three materials. A large hysteresis effect was

observed with nonwetting advancing angles and wetting receding angles. In the earlier experiments, ZrO_2 proved to be the most wettable of the three materials.

Although purity requirements for the LiCl-KCl electrolyte have not yet been established, analytical methods for determining impurities were investigated to provide a means for correlating impurity levels with cell performance. Linear-sweep voltammetry proved to be a useful method for determining water and its reaction products (OH^- , O^{2-}) in molten LiCl-KCl ; these species undergo reversible oxidation at a platinum electrode and give rise to diffusion-limited current peaks proportional to their concentrations. Their apparent diffusion coefficients were also determined. Other techniques were used to determine metallic impurities, pH, and CO_3^{2-} content. Preliminary results suggest that lithium utilization in Li-Al electrodes may be decreased by the presence of OH^- .

Basic studies were started on the mechanisms and rate of electrochemical reactions occurring at iron sulfide and Li-Al electrodes. Cyclic voltammetry measurements of FeS solutions showed that the charge-discharge reaction of FeS electrodes involves only one of a number of oxidation-reduction waves in the potential range from 1.1 to 2.8 V vs. Li. Potentiometric measurements yielded the solubility and solubility product constant of FeS in LiCl-KCl at 450°C . Other basic electrochemical studies on the charging of lithium into aluminum and Li-Al alloy showed that solid-state diffusion is a slow process. A marked overpolarization that was observed at high current densities may have resulted from impurities on the electrode surface or a slow incorporation of lithium atoms into the Li-Al lattice.

A statistical model for the resistance of a randomly packed, porous bed of electroactive material was developed to treat the polarization characteristics of electrodes used in the cells. The model combines the effect of random packing with a steep reaction gradient. Under the fairly general model assumptions, the bed resistance was expected to be a cumulative log-normal function of electrode utilization. The model provided excellent fits to experimental polarization data for 0.32- to 0.75-cm-thick Li-Al electrodes at discharge current densities up to 300 mA/cm^2 . The experimental data were from Li/LiCl-KCl/Li-Al cells, in which the lithium served both as a reference and counter electrode. Current-interruption data were used in subtracting the nearly constant ohmic potential drop in the electrolyte outside the porous bed. Alternating-current impedance measurements showed that solid-state diffusion is significantly limited only when the lithium in a Li-Al electrode is nearly depleted and the electrode has relatively large particles ($\sim 10^{-2} \text{ cm}$). The modeling studies have shown that Li-Al polarization characteristics can be represented satisfactorily by simply considering the resistances in the randomly packed bed. The statistical model is to be tested next on $\text{Li-Al/LiCl-KCl/FeS}$ cells to determine whether the concept has more general applicability.

Research studies were started on alternatives to lithium/iron sulfide cells that may be able to use low-cost, more abundant materials while maintaining the performance levels required for electric vehicles or load leveling. The initial work has been focused primarily on calcium cells with molten-salt electrolytes. Calcium, like lithium, forms a series of compounds

with aluminum and silicon. The reduced activity of calcium in these compounds permits the use of molten-salt electrolytes that are not stable toward calcium itself. For example, CaAl_4 and CaSi are rechargeable in molten NaCl-CaCl_2 electrolyte, which is used for the electrolytic production of sodium. Cell cycling tests were conducted with various $\text{Ca}_x(\text{Al},\text{Si})$ negative electrodes and FeS positive electrodes, using the following electrolytes: NaCl-CaCl_2 (mp, 506°C), NaBr-KF-CaCl_2 (mp, 457°C), and LiCl-KCl-CaCl_2 (mp, 346°C). These cells produced a higher voltage than the corresponding lithium cells, and exhibited good cycling characteristics. Engineering work on sealed cells using calcium silicide and iron sulfide with the LiCl-KCl-CaCl_2 electrolyte has started, and laboratory studies of the other systems are continuing.

REFERENCES

1. Z. Tomczuk, T. W. Olszanski, and J. E. Battles, patent applied for.
2. W. J. Walsh *et al.*, "Development of Prototype Lithium/Sulfur Cells for Application to Load-Leveling Devices in Utility Networks," *Proc. 9th IECEC, San Francisco, August 26-30, 1974*, pp. 911-915 (1974).
3. W. J. Walsh, A. A. Chilenskas, E. J. Cairns, and P. A. Nelson, "Modular Electrochemical Cell," U. S. Patent No. 3,887,396 (June 3, 1975).
4. N. P. Yao and W. J. Walsh, "Discharged Electrochemical Cell", patent applied for.
5. W. J. Walsh, C. C. McPheeters, N. P. Yao, and N. Koura, "Metallic Sulfide Additives for Positive Electrode Material Within a Secondary Electrochemical Cell," patent applied for.
6. C. C. McPheeters, W. W. Schertz, and N. P. Yao, Performance and Cost Improvement in Li-Al/FeS₂ Cells Through the Use of Cobalt Sulfide Additives," Electrochemical Society Meeting, Dallas, Texas, October 5-10, 1975. Extended Abstracts of Battery Division, Vol. 75-2, pp. 70-71 (1975)
7. M. Hansen, and K. Anderko, Constitution of Binary Alloys, p. 104, McGraw Hill Book Co., New York (1958).

ADDENDUM: PUBLICATIONS--1975

A. Open Literature Publications

- J. E. Battles, F. C. Mrazek, J. A. Smaga, and W. D. Touhig
Corrosion Studies of Materials for A High-Temperature Lithium/Sulfur Cell
Extended Abstracts of Battery-Electronics Division, Electrochemical Society Meeting, Toronto, Canada, May 11-16, 1975, Vol. 75-2, pp. 80-81 (1975)
- J. R. Birk and R. K. Steunenbergh
Chemical Investigations of Lithium/Sulfur Cells
Adv. Chem. Ser. 140, 189-202 (1975)
- R. C. Elliott and T. O. Cooper
Volumetric Changes of Electrodes in LiAl/FeS_x Cells
Extended Abstracts of Battery-Electronics Division, Electrochemical Society Meeting, Toronto, Canada, May 11-16, 1975, Vol. 75-1, pp. 85-86 (1975)
- E. C. Gay, F. J. Martino, and Z. Tomczuk
Development of High-Performance Iron Sulfide Electrodes with Porous Current Collector Structures
Proc. 10th IECEC, Newark, Delaware, August 17-22, 1975, pp. 627-633 (1975)
- N. Koura, J. F. Kinsinas, and N. P. Yao
Coated Metal Current Collectors for Iron Sulfide Electrodes in High Temperature Cells
Extended Abstracts of Battery Division, Electrochemical Society, Meeting, Dallas, Texas, October 5-10, 1975, Vol. 75-2, pp. 81-83 (1975)
- C. C. McPheeters, W. W. Schertz, and N. P. Yao
Performance and Cost Improvement in Li-Al/FeS₂ Cells Through the Use of Cobalt Sulfide Additives
Extended Abstracts of Battery Division, Electrochemical Society Meeting, Dallas, Texas, October 5-10, 1975, Vol. 75-2, pp. 70-71 (1975)
- K. M. Myles, J. L. Settle, T. W. Olszanski, and C. W. Handrick
Development of Pyrometallurgical Lithium-Aluminum Electrodes for High Performance Secondary Batteries
Extended Abstracts of Battery-Electronics Divisions, Electrochemical Society Meeting, Toronto, Canada, May 11-16, 1975, Vol. 75-1, pp. 73-74 (1975)
- P. A. Nelson, E. C. Gay, and W. J. Walsh
Performance of Lithium/Iron Sulfide Cells
Proc. 26th Annual Power Sources Conf., Atlantic City, New Jersey, April 29-30, 1974, pp. 1-4 (May 1975)

- M. F. Roche, W. W. Schertz, J. W. Allen, S. J. Preto, and J. R. Selman
Current-Interrupter Measurements on Li(Al)/LiCl-KCl/ Iron Sulfide Cells
Extended Abstracts of Battery-Electronics Division, Electrochemical
Society Meeting, Toronto, Canada, May 11-16, 1975 Vol. 75-1, pp.
885-886 (1975)
- W. W. Schertz, A. A. Chilenskas, and V. M. Kolba
Battery Design and Cell Testing for Electric-Vehicle Propulsion
Proc. 10th IECEC, Newark, Delaware, August 17-22, 1975, pp. 634-
641 (1975)
- W. W. Schertz, M. F. Roche, J. Allen, S. Preto, and J. R. Selman
Current-Interrupter Measurements on Lithium-Aluminum Electrodes in
Molten LiCl-KCl Electrolyte
Extended Abstracts of Battery Division, Electrochemical Society
Meeting, Toronto, Canada, May 11-16, 1975, Vol. 75-1, pp. 884-885
(1975)
- J. R. Selman, K. K. DeNuccio, C. J. Cajigas, and R. K. Steunenber
EMF Studies of Lithium-Aluminum Alloys for High-Performance Secondary
Batteries
Extended Abstracts of Battery-Electronics Divisions, Electrochemical
Society Meeting, Toronto, Canada, May 11-16, 1975, Vol. 75-1, pp.
75-77 (1975)
- D. R. Vissers, M. F. Roche, and K. E. Anderson
Parametric Characterization Studies of Electrochemically Prepared Li-Al
Electrodes in Li/LiCl-KCl/Li-Al Cells
Extended Abstracts of Battery Division, Electrochemical Society
Meeting, Dallas, Texas, October 5-10, 1975, Vol. 75-2, pp. 56-57
(1975)
- N. P. Yao and J. R. Birk
Battery Energy Storage for Utility Load Leveling and Electric Vehicles:
A Review of Advanced Secondary Batteries
Proc. 10th IECEC, University of Delaware, Newark, Delaware, August
17-22, 1975, pp. 1107-1119 (1975)
- N. P. Yao, W. G. Howard, T. D. Kaun, and W. A. Kremsner
Development of Positive Electrodes for Prismatic Lithium-Aluminum/
Iron Sulfide Cells
Extended Abstracts of Battery Division, Electrochemical Society
Meeting, Dallas, Texas, October 5-10, 1975, Vol. 75-2, pp. 72-73
(1975)
- B. ANL Reports**
- P. A. Nelson, J. E. Battles, A. A. Chilenskas, E. C. Gay, R. O. Ivins,
R. K. Steunenber, and W. J. Walsh
High-Performance Batteries for Off-Peak Energy Storage and Electric-
Vehicle Propulsion. Progress Report for the Period January - June 1974
ANL-8109

- P. A. Nelson, A. A. Chilenskas, and R. K. Steunenberg
The Need for Development of High-Energy Batteries for Electric
Automobiles
ANL-8075
- P. A. Nelson, R. O. Ivins, J. E. Battles, A. A. Chilenskas, E. C. Gay,
R. K. Steunenberg, and W. J. Walsh
Development of Lithium/Metal Sulfide Batteries at ANL: Summary Report
for 1974
ANL-75-20
- P. A. Nelson, R. O. Ivins, J. E. Battles, A. A. Chilenskas, E. C. Gay,
R. K. Steunenberg and W. J. Walsh
High-Performance Batteries for Off-Peak Energy Storage and Electric-
Vehicle Propulsion. Progress Report for the Period July-December 1974
ANL-75-1

C. Papers Presented at Scientific Meetings

- J. E. Battles
Materials Opportunities in the Transportation Industry
Presented at the 4th Material Conference, University of Michigan,
Ann Arbor, Michigan, September 9-12, 1975
- R. C. Elliott and T. O. Cooper
Volumetric Changes of Electrodes in LiAl/FeS_x Cells
Presented at the Meeting of the Electrochemical Society, Toronto,
Canada, May 11-16, 1975
- E. C. Gay
Development of High Performance Rechargeable Batteries for Off-Peak
Energy Storage and Electric Vehicle Propulsion
Presented at the National Black Chemists and Chemical Engineers
Conference, Howard University, Washington, D.C., April 10-13, 1975
- R. O. Ivins, A. A. Chilenskas, V. M. Kolba, W. L. Towle, and P. A. Nelson
Design of a Lithium/Sulfur Battery for Load Leveling on Utility Net-
works
Presented at the IEEE Symposium, Charlotte, North Carolina, April
5-11, 1975
- P. A. Nelson
Evaluation of Lithium/Sulfur Batteries for Automobiles
Presented at the Automotive Energy Efficiency Program Contactors
Coordination Meeting, Department of Transportation, Boston
Massachusetts, January 14-15, 1975
- P. A. Nelson
Lithium/Metal Sulfide Secondary Batteries
Presented at the International Society of Electrochemistry Biennial
Meeting, Laboratoires de Marcoussis, France, May 26-27, 1975

- J. A. Smaga and J. E. Battles
Corrosion Studies of Materials for Lithium-Alloy/Metal Sulfide Batteries
Presented at the Regional N.A.C.E. Conference, Milwaukee, Wisconsin,
October 21-23, 1975
- R. K. Steunenberg
Chemical Studies of Lithium/Metal Sulfide Batteries
Seminar presented to the Chemistry Department, University of
Illinois, Circle Campus, Chicago, Illinois, January 28, 1975
- W. J. Walsh
ANL Battery Program
Seminar presented at the Ford Motor Company, Detroit, Michigan,
April 29-30, 1975
- N. P. Yao
Advanced Battery Development Programs in U.S.A.
Presented at the 42nd Meeting of the Electrochemical Society,
Yamanashi University, Japan, April 5-8, 1975