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

SUMMARY REPORT FOR 1978

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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

SUMMARY REPORT FOR 1978

P. A. Nelson	Director, Chemical and Electrical Systems
D. L. Barney	Director, Advanced Battery Projects
R. K. Steunenberg	Manager, Lithium/Metal Sulfide Battery Program
A. A. Chilenskas	Manager, Advanced Battery Technology Development
E. C. Gay	Section Manager, Battery Engineering
J. E. Battles	Group Leader, Materials Development
F. Hornstra	Group Leader, Battery Charging Systems
W. E. Miller	Group Leader, Industrial Cell and Battery Testing
D. R. Vissers	Group Leader, Cell Chemistry
M. F. Roche	Group Leader, Calcium/Metal Sulfide Battery Development
H. Shimotake	Group Leader, Cell Development and Engineering
R. Hudson	Program Manager, Eagle-Picher Industries, Inc.
R. J. Rubischko	Program Manager, Gould Inc.
S. Sudar	Program Manager, Rockwell International

July 1979

Previous reports in this series

ANL-75-20	March 1975
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ANL-77-18	March 1977
ANL-78-20	March 1978

PREFACE

This program on high-temperature secondary batteries consists of an in-house research and development effort at Argonne National Laboratory and subcontracted work by industrial laboratories. The work at Argonne is carried out primarily in the Chemical Engineering Division, with assistance on specific problems being given by the Materials Science Division and, from time to time, by other Argonne divisions. The individual efforts of many engineers, scientists, and technicians are essential to the success of the program; recognition of these efforts is given by the individual authors that are cited throughout the report.

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ABSTRACT

This report consists of highlights for 1978 of Argonne National Laboratory's program on the development of lithium/metal sulfide batteries. These batteries are being developed for electric-vehicle propulsion and for stationary energy-storage applications. The present cells, which operate at 400-450°C, are of a vertically oriented, prismatic design with one or more inner positive electrodes of FeS or FeS_2, facing electrodes of lithium-aluminum alloy, and molten LiCl-KCl electrolyte.

During 1978, cell and battery development work has continued at ANL, Eagle-Picher Industries, Inc., Gould Inc., and the Energy Systems Group of Rockwell International. Fabrication of a 40 kW-hr battery by Eagle-Picher for testing in an electric van is nearing completion. Cost and design studies for a Mark II electric-vehicle battery, which will have somewhat higher performance and use potentially low-cost materials and fabrication methods, have been conducted by all three subcontractors, and contracts are being negotiated for development of Mark II batteries. Conceptual design studies have continued at Rockwell International on a 100 MW-hr stationary energy-storage module. The present plan is to construct a module based on these designs for testing at the BEST (Battery Energy Storage Test) Facility. Work has also been in progress at the Carborundum Co., General Motors Research Laboratories, and various other organizations on developing materials and components for cells.

I. OVERVIEW OF BATTERY PROGRAM

The lithium/metal sulfide battery program at ANL is concerned with the development of high-performance, electrically rechargeable batteries for electric-vehicle propulsion and for stationary energy-storage devices. The widespread use of electric vehicles would conserve petroleum fuels, since the energy for charging the batteries could be provided by coal, nuclear, hydroelectric, or other energy sources; a side-benefit would also be realized in decreased air pollution in congested urban areas. The use of stationary energy-storage batteries for load leveling on electric-utility systems could save petroleum by reducing the need for gas turbines to meet peak power demands. The stationary storage batteries may also find application in systems involving solar, wind, or other cyclic or intermittent energy sources.

The battery cells that are currently under development consist of a lithium-aluminum or lithium-silicon negative electrode, an FeS or FeS_2 positive electrode, a separator to provide electrical isolation of the electrodes, and molten LiCl-KCl electrolyte. The melting point of the electrolyte (352°C at the eutectic composition of 58.2 mol % LiCl) requires a battery operating temperature in the range of about 400-500°C. The overall electrochemical reaction for the Li-Al/FeS cell can be written as follows:

$$2LiAl + FeS \overset{2e^-}{\rightleftarrows} Li_2S + Fe + 2Al \qquad (1)$$

The theoretical specific energy for reaction 1 is about 460 W·h/kg, and the voltage vs. capacity curve has a single voltage plateau at about 1.3 V. The reaction is actually much more complex than shown; for example, an intermediate compound, $LiK_6Fe_{24}S_{26}Cl$ (J phase), is formed through a reaction with the KCl in the electrolyte (see Section VII). The overall reaction for the Li-Al/FeS_2 cell can be written in two steps:

$$2LiAl + FeS_2 \overset{2e^-}{\rightleftarrows} Li_2S + FeS + 2Al \qquad (2)$$

$$2LiAl + FeS \overset{2e^-}{\rightleftarrows} Li_2S + Fe + 2Al \qquad (3)$$

The total theoretical specific energy for reactions 2 and 3 is approximately 650 W·h/kg. The voltage vs. capacity curve has two voltage plateaus, one at about 1.7 V (reaction 2) and the other at 1.3 V (reaction 3). The Li-Al/FeS_2 cells are often designed to operate only on the upper voltage plateau; these are referred to as "upper plateau" cells. Reactions 2 and 3 also involve several complex intermediate phases (generally compounds of lithium, iron, and sulfur).

Most of the cells that have been fabricated until recently have been of a prismatic, bicell design with a central positive electrode and two facing negative electrodes. Recently, multiplate cells (see Fig. 1), which have two or more positive electrodes and facing negative electrodes, have been developed. Testing of multiplate cells has shown that they can achieve higher specific energy and specific power than the bicells.

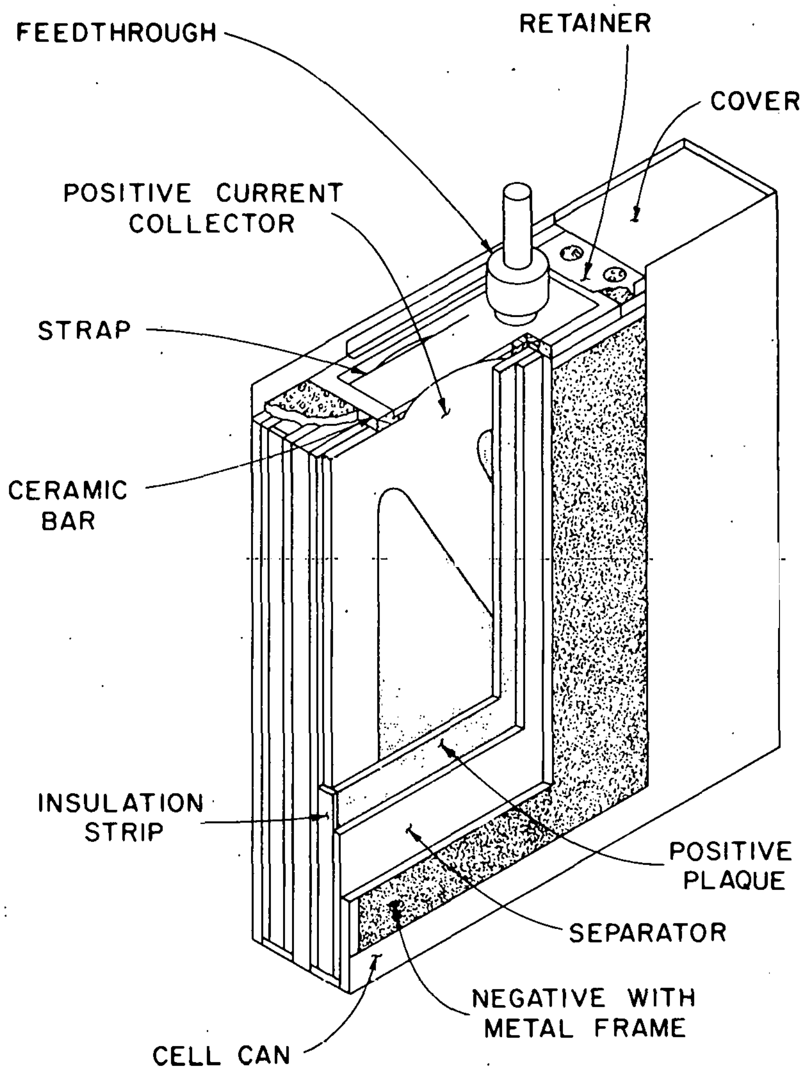

Fig. 1. Multiplate Cell Design

In the lithium/metal sulfide cell, porous separator sheets between the electrodes serve as electronic insulators, while at the same time providing a path for the migration of lithium ions through the electrolyte absorbed in the separator material. Since both the negative and positive electrodes consist of particle beds or porous structures of the active material filled with electrolyte, screens or cloths are often used on the electrode faces to prevent the escape of particulate material from the electrodes into the separator. To enhance the electronic conductivity of the electrodes, metallic current collectors are used to provide a low-resistance current path from all areas of the electrode to the terminal. In nearly all of the present cell designs, the negative electrodes are grounded to a steel can or housing, and the terminal of the positive electrode extends through the top of the cell can *via* an electrically insulating feedthrough. The top of the cell can is also provided with a tube, which is closed off later by a weld, to permit the addition of electrolyte to the cell after assembly. In many of the cells, "picture-frame" structures around the perimeter of the electrodes are used to hold the electrode components together as a unit.

The lithium/metal sulfide cell can be assembled in a charged, uncharged, or partially charged state. To assemble a Li-Al/FeS or Li-Al/FeS_2 cell in the charged state, the negative electrodes are normally cold- or hot-pressed from Li-Al powder (usually 46-50 at. % lithium), which may or may not be mixed with some of the LiCl-KCl electrolyte powder. The positive electrodes are formed similarly by cold- or hot-pressing FeS or FeS_2 powder with or without added electrolyte powder. In the case of the uncharged cells, the electrode plaque is pressed from a mixture of Li_2S and iron powder in the appropriate proportions; the negative electrode in this case is an aluminum structure (e.g., pressed wire, porous metal, solid plate) which is converted to the Li-Al alloy electrochemically when the cell is charged. Partially charged cells can be fabricated from mixtures of the above materials in intermediate ratios.

In general, the electric-vehicle battery must have a high specific energy to permit an adequate driving range, and a high specific power to maintain normal highway speeds and to provide sufficient power for passing and hill climbing. The volumetric energy and power densities must also be high because of the limited space available in most vehicles for installation of the battery. For large-scale application in electric vehicles, the battery will probably have to have a maximum cost of \$40-50/kW·h and a minimum lifetime of 1000 equivalent deep-discharge cycles. The performance and lifetime goals for the electric-vehicle battery are presented in Table 1. The progression of performance goals shown in the table is based on specific improvements that are anticipated in the cell and battery designs as the technology is developed.

The most significant event in the development of the electric-vehicle battery during the past year has been the initiation of a contract with Eagle-Picher Industries, Inc. for the development, design, and fabrication of a 40-kW·h battery, designated Mark IA, which is scheduled for an in-vehicle test in early to mid-1979. The Mark IA battery will consist of multiplate Li-Al/FeS cells, and will be tested primarily to evaluate the technical feasibility of the lithium/metal sulfide system for use in electric vehicles. In the original plan for the electric-vehicle battery, the Mark IA battery was to be followed by Mark IB and IC versions, which would fully meet the Mark I goals (presented in ANL-78-20, p. 3). However, the advances in the technology, particularly in the development of separators, have been such that a decision was made to proceed directly from the Mark IA to the Mark II battery. The Mark II battery will also consist of multiplate Li-Al/FeS cells, but will have somewhat higher performance than Mark IA. The primary purpose of the Mark II battery is to develop materials and fabrication methods that have a low cost in mass production. Cost and design studies on the Mark II battery were completed by Eagle-Picher Industries, Inc., Gould Inc., and Rockwell International in November 1978. In addition, a request for proposals for development work and fabrication of a 50-kW·h Mark II battery was issued in October 1978. The Mark III program, which is aimed at a high-performance battery for passenger automobiles, is expected to begin in 1981. The type of cells for the Mark III battery has not yet been determined, but they will probably be multiplate Li-Al/FeS_2 cells.

Table 1. Program Goals for Lithium/Metal Sulfide Electric-Vehicle Batteries

	Mark IA	Mark II	Mark III	Long Range
Specific Energy,[a] W·h/kg				
Cell (average)	80	125	160	200
Battery	60	100	130	155
Energy Density,[a] W·h/L				
Cell (average)	240	400	525	650
Battery	100	200	300	375
Peak Power, W/kg				
Cell (average)	80	125	200	250
Battery	60	100	160	200
Heat Loss through Jacket, W	400	150	125	75-125
Lifetime				
Deep Discharges[b]	200	500	1000	1000
Equivalent Distance, km	30,000	100,000	200,000	300,000
Target Dates				
Battery Test	1979	1981	1983	-
Pilot Manufacture	-	1983	1985	1990

[a] Calculated at the 4-h discharge rate.

[b] Utilization of more than 50% of the theoretical capacity every 10 cycles.

The goals for the stationary energy-storage battery are listed in Table 2. The specific-energy and specific-power requirements for this application are less demanding than those for the electric-vehicle battery, but low cost (about \$40-50/kW·h) and long lifetime are essential. Most of the effort during the past year on the stationary energy-storage battery has involved conceptual design studies of a 100-MW·h energy-storage plant. These studies, which were conducted as a cooperative effort between the Energy Systems Group of Rockwell International and ANL, have provided a general basis for a design of a multiplate LiSi/FeS cell with a capacity of 2.5 kW·h.

A major objective of the program at ANL is to transfer the technology to interested commercial organizations as it is developed, with the ultimate goal of a competitive, self-sustaining industry for the production of lithium/metal sulfide batteries. Technology transfer is implemented by various means, including the assignment of engineers or scientists from industrial companies to ANL on a cost-sharing basis, and the subcontracting of development work on cells, batteries, and auxiliary items to industrial firms. Cost, design, and marketing studies are also conducted with the assistance of subcontractors and consultants. Various academic institutions are also involved in the program through temporary student and faculty assignments, subcontracts, and

Table 2. Program Goals for Lithium/Metal Sulfide Stationary Energy-Storage Batteries

Goal	BEST[a] 1983	Demonstration 1987
Battery Performance		
Energy Output, kW·h	5,000	100,000
Peak Power, kW	1,500	25,000
Sustained Power, kW	1,000	10,000
Cycle Life	500-1,000	3,000
Discharge Time, h	5	5-10
Charge Time, h	10	10
Cell Performance		
Specific Energy, W·h/kg	60-80	60-150
Specific Power, W/kg	12-20	12-20
Cell Cost, $/kW·h	30-35[b]	25-30[b]

[a] Battery Energy Storage Test Facility. This facility, which is being constructed under joint sponsorship by the U.S. Department of Energy, the Electric Power Research Institute, and the Public Service Co. of New Jersey, will be used to test various types of batteries as load-leveling devices on an electric utility system.

[b] Projected cost for a production rate of 2000 MW·h/y in 1979 dollars.

consultants, mainly in the area of electrode modeling. At the present time, approximately one-half of the funding for this program is used for subcontracted work.

The research and development work at ANL includes cell and battery testing, post-test examinations of cells, cell and battery engineering development, materials development and testing, cell chemistry studies, and commercialization studies. As improvements are made in the ANL cell materials and designs, they are incorporated into the cells fabricated by the subcontractors.

In addition to the research and development program on lithium/metal sulfide batteries, a small effort on alternative cell systems has been maintained under a separate budget activity. The objective of this work is to develop a new battery system that uses abundant, low-cost materials while maintaining the performance levels required for electric vehicles or stationary energy storage. During the past year, this program has been focused on the use of calcium alloys as the negative electrode material.

II. COMMERCIALIZATION STUDIES

The objective of the commercialization studies at ANL is to provide data on the manufacturing cost and market requirements for the lithium/metal sulfide battery. The commercialization studies are conducted at ANL with assistance from industrial subcontractors and consultants. These studies involve the identification of potential markets, manufacturing cost analyses, financial plans, and evaluations of competing technologies.

The first commercial production of lithium/metal sulfide batteries will probably be for limited (low volume and high cost) markets such as postal vans, buses, mining vehicles, and submarines. In these near-term (1982-1990) markets, the relatively high price of the batteries should be offset by their favorable performance characteristics.

The bus market is of special interest to potential electric-vehicle manufacturers, both in the U.S. and throughout the world, because the cost of purchasing buses is very often subsidized by national or local governments. In the U.S., the Urban Mass Transportation Authority provides an 80% federal subsidy for bus purchases. An analysis has shown that a significant bus market of about 40 MW·h/y could be achieved by 1982; this market could then rapidly expand to about 580 MW·h/y in 1987 and to about 934 MW·h/y in 1990, which is enough to support the output from one automated battery plant.

The van market after 1987 could become very large. An estimate has been made that this market could support 300,000 battery-powered vans per year, which would require 18,900 MW·h/y of plant capacity. This market alone would require the output from about 17 automated battery plants rated at 1,100 MW·h/y.

Another potential near-term market for the Li/MS_x battery is fork-lift trucks for the U.S. Army. Eagle-Picher Industries, Inc. has been contracted to deliver several cells and a 6-V battery module to Fort Belvoir for test evaluation.

Institutional agencies with responsibilities in resource surveillance and management are interested in the effect of mass production of lithium/metal sulfide batteries on world lithium resources. Consequently, we determined the projected lithium requirements for use in lithium/metal sulfide batteries for electric-vehicle and stationary energy-storage applications by the year 2000. The results showed that a significant production of utility and electric-vehicle batteries, about 110 GW·h by the year 2000, would require about 15% of the U.S. reserves or about 5% of the world reserves.

III. TESTING OF INDUSTRIAL CELLS AND BATTERIES

Three major subcontractors--Eagle-Picher Industries, Inc., Gould Inc., and Rockwell International's Energy Systems Group--are developing manufacturing procedures as well as fabricating and testing cells. In addition, some of the industrially fabricated cells are being tested at CEN's testing facilities.

Eagle-Picher and Gould fabricated Li-Al/FeS and Li-Al/FeS_2 cells. These cells were assembled in the charged and uncharged states, with pressed negative and positive electrodes of approximately equal capacity (A·h) or with some excess capacity (10-50%) in the negative electrodes.

For the past several years, Cu_2S has been added to the positive electrode of Li-Al/FeS cells to eliminate the formation of J phase, which produces diffusional overvoltage and poor electrical performance. Post-test examinations of cells of this type at ANL (see Table 9) have indicated, however, that cell failure is sometimes caused by deposition of copper in the separator.* Recent cell-chemistry studies (see Section VII) indicated that the formation of J phase can be inhibited by either increasing the LiCl content above that of the eutectic electrolyte, or operating the cell at high temperatures (about 500°C).† Both of these approaches have been tested in recent industrial cells.‡ In the case of Li-Al/FeS_2 cells, cobalt sulfides of various sulfur-to-metal ratios have been added to the FeS_2 electrode to increase its electronic conductivity; however, the effectiveness of the cobalt sulfide additive in improving cell performance has not yet been clearly demonstrated.

Boron nitride fabric has been used as the separator material in most of the Eagle-Picher and Gould cells fabricated thus far. Recently, improvements have been made in boron nitride felts, and this material is now being used successfully in cells. The felts offer significant advantages over the fabric both in improved cell performance and lower cost. Various materials, including metal screens, Y_2O_3 cloth, and ZrO_2 cloth have been used as particle retainers at the electrode faces. In most current cells, particle retainers of stainless steel screen are used; however, there appears to be a good chance that the particle retainers can be eliminated completely in future cell designs. A wide variety of current collector designs has been used in these industrial cells, including flat sheets and honeycombs. Iron is a satisfactory current collector material in Li-Al electrodes, and can be used for a limited period (<1 y) in FeS electrodes; nickel, iron-based alloys, and several other materials show promise for longer-term use in FeS electrodes. The only current-collector material that has been used successfully in FeS_2 electrodes to date is molybdenum, which is expensive and difficult to fabricate; alternatives such as protective coatings for inexpensive metals are under investigation at ANL (see Section VI.C).

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[*] Significant copper deposition does not occur until after the cell has operated for a long period of time; consequently, copper deposition is not expected to be a problem in batteries for which the required cell lifetime is relatively short, such as the Mark IA.

[†] Industrial cells have normally been operated at 400-450°C.

[‡] Before testing LiCl-rich electrolyte in industrial cells, it was first tested in small-scale ANL cells (see Section IV.A).

During the past year, Rockwell International fabricated Li-Si/FeS cells. These cells were assembled in the uncharged state, and usually had a eutectic LiCl-KCl electrolyte. Most of these cells had the following cell components: separator, AlN powder; positive current collector, nickel honeycomb; negative current collector, steel honeycomb; and particle retainer, porous nickel sheet or nickel screen. Other types of cell components were also tested in these cells.

The results of the industrial cell testing are briefly summarized below.

A. Eagle-Picher Industries, Inc.

Over the past two years, Eagle-Picher has fabricated about sixty Li-Al/FeS-Cu_2S and Li-Al/FeS_2-CoS_2 bicells with many variations in design (e.g., electrode thickness, electrode capacity loading, and current collector designs). These electric-vehicle cells were tested at ANL and evaluated using a standardized procedure that permits a comparison of the performance of cells with different designs. During the past year, five Li-Al/FeS-Cu_2S bicells were cycled, and all but one operated for between 500 and 1200 cycles. However, the specific energy and specific power of these cells were significantly below the goals set for the Mark IA battery (see Table 1). Operation of a few of these FeS cells at high temperatures (450-500°C) produced a significant improvement in performance; but operation at these high temperatures for long periods is expected to increase the corrosion rates of the FeS cell components, thereby shortening the cell lifetime.

In this same period, eighteen Li-Al/FeS_2-CoS_2 bicells were tested at ANL, and most of these cells attained very high specific energy and specific power, but operated for less than 250 cycles. Table 3 gives the design characteristics and performance data of two recently tested FeS_2 cells (I8H and I8L) and two baseline cells. As can be seen in this table, an increase in electrode loading resulted in a significant increase in specific energy. In addition, Cells I8H and I8L had an improved honeycomb design for the positive current collector, which reduced cell resistance and consequently increased power.

Eagle-Picher was awarded a contract in February 1978 for the development, design, and fabrication of the 40-kW·h Mark IA battery. The technical goals for the Mark IA battery are given in Table 4. On the basis of previous test results from Li-Al/FeS and Li-Al/FeS_2 bicells, Eagle-Picher selected a Li-Al/FeS multiplate cell design (three positive and four negative electrodes) for this battery. As of the end of 1978, about 130 multiplate cells had been fabricated; and most of these cells have been or are being tested by either Eagle-Picher or ANL to determine the effect on performance of the following design variables: method of particle retention, current collector design, additives to the positive electrode, and LiCl content of the electrolyte. Some of the cells have achieved very high specific energies--greater than 100 W·h/kg at the 4-h rate; however, several problems were encountered during the development phase of this program, including high cell resistance, loss of capacity during cycling, and poor wetting of the separator by the electrolyte. These problems appear to have been resolved through intensive efforts both at ANL and at Eagle-Picher. The test results from individual cells indicate that the Mark IA cells, which will be fabricated in early 1979, will meet the performance and lifetime goals listed in Table 1.

Table 3. Test Results from Eagle-Picher Li-Al/FeS_2-CoS_2 Cells

	2A5[a]	2B4[a]	I8H	I8L
Electrode Thickness, mm				
Positive[b]	3.4	6.3	2.8	5.1
Negative	3.3	6.8	4.2	7.6
Cell Capacity, A·h				
Positive Electrode	70	155	117	220
Negative Electrode	70	155	148	290
Electrode Loading, A·h/cm^3				
Positive	0.67	0.79	1.35	1.39
Negative	0.67	0.73	1.10	1.21
Specific Energy,[c] W·h/kg	44.0	54.5	83.8	99.1
Peak Power, W	84.5	97.5	136	106
Peak Power Flux,[d] W/cm^2	0.22	0.21	0.25	0.19
Cell Resistance, mΩ	8.5	7.5	5.3	6.6

[a] Baseline cells.

[b] Because the cells have two negative electrodes and one positive electrode, the positive electrode is considered to consist of two halves, each having the thickness given here.

[c] Calculated at a current density of 80 mA/cm^2.

[d] Calculated at 50% discharge.

Table 4. Technical Goals for the Mark IA Battery

Battery Characteristics	Goals
Energy Output,[a] kW·h	40
Power Output,[b] kW	30
Maximum Weight, kg	667
Maximum Volume, L	400
Specific Energy,[a] W·h/kg	60
Energy Density,[a] W·h/L	100
Operating Temperature, °C	400-500
Maximum Heat Loss, W	400
Battery Voltage, V	144
Cycle Life[c]	200

[a] Discharge to 1.0 V/cell at the 4-h rate.

[b] 15-s pulse at 50% discharge.

[c] To 20% loss of the design capacity.

The Mark IA battery will consist of two 20-kW·h modules, each module having 60 multiplate cells connected in series and housed in a thermally insulated case (see Fig. 2). After the Mark IA has been fabricated, it will undergo laboratory and in-vehicle testing at ANL (scheduled for early to mid-1979). Prior to these tests, however, a small (1.8 kW·h) Li-Al/FeS battery, also fabricated by Eagle-Picher, will be tested at ANL in a Volkswagen van presently powered by twelve 1.8-kW·h lead-acid batteries; testing of this battery will aid in developing the final design for the Mark IA.

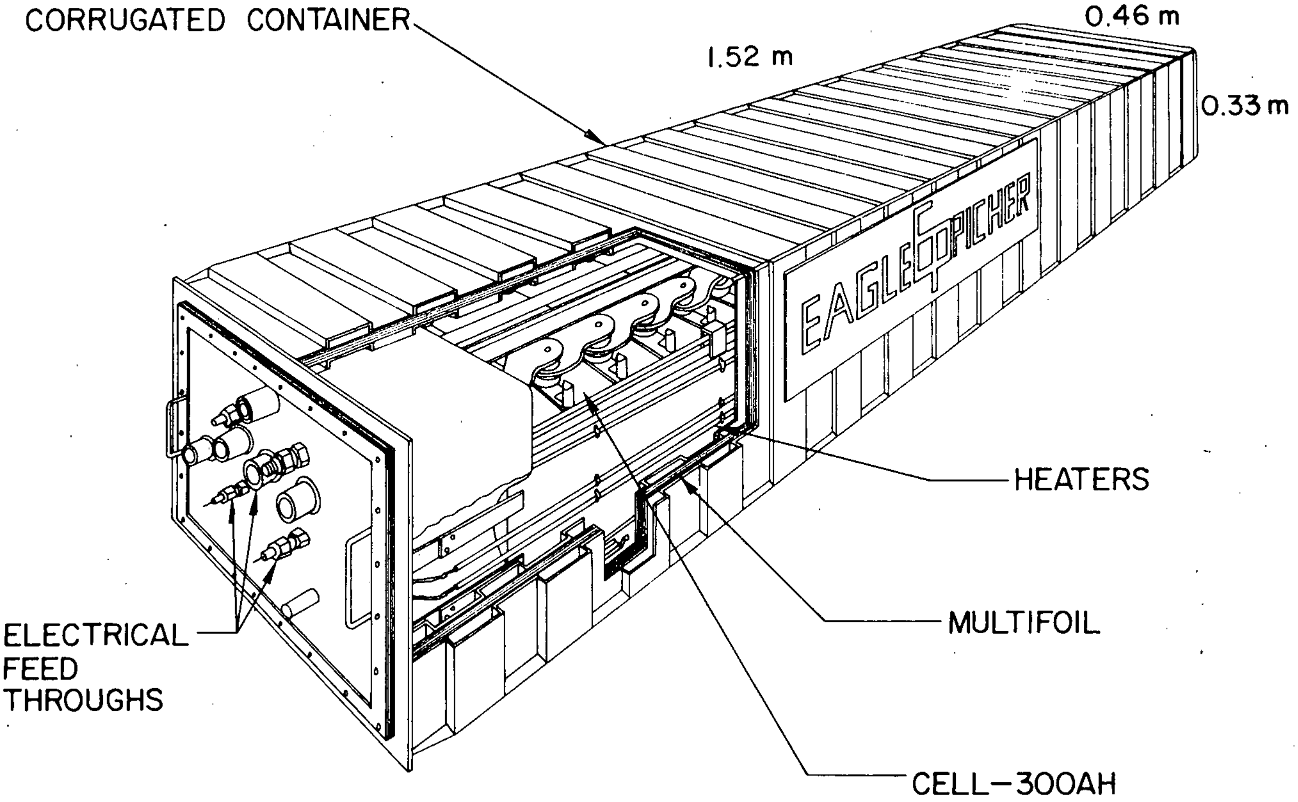

Fig. 2. Battery Case for a 20-kW·h Battery Module

B. Gould Inc.

During the past year, Gould fabricated and tested about 40 electric-vehicle bicells with FeS electrodes. The testing of these cells indicated that the cell resistance could be reduced by two design modifications: the substitution of BN felt for the previously used BN cloth separator, and the substitution of a thin nickel sheet for the iron sheet previously used as the current collector. In addition, a Li-Al/FeS cell having carbon, cobalt, and excess iron added to the positive electrode and a LiCl-KCl electrolyte with a high LiCl content (62.8 mol % LiCl) showed a 35% higher positive-electrode utilization than that of a baseline Li-Al/FeS-Cu_2S cell. The test results to date indicate that the near-term (1978-1981) performance goals for the electric-vehicle battery can probably be met or exceeded with the Li-Al/FeS system.

During 1977-1978, Gould Inc. fabricated 55 upper-plateau electric-vehicle bicells with FeS_2 electrodes. These cells are being tested at ANL to determine the effect on performance of the following design features: method of particle retention, thickness and electrolyte content of the positive electrode, lithium content in the negative electrode, and design of the current collector. The following conclusions were reached from the testing of these cells. First, the use of more than 30 vol % electrolyte in the FeS_2 electrode does not appear to offer any benefit in cell performance. Second, for FeS_2 electrodes that are more than 5.6-mm thick, an increase in the electrode thickness results in a decrease in the utilization of the active material. Third, to attain optimum capacity, the cell should be designed to have 50 at. % lithium and to utilize 70% of the lithium in the negative electrode. In cells designed for negative-electrode utilization higher than 70%, the capacity becomes limited by the negative electrode. In cells designed for negative-electrode utilizations less than 70%, greater than 85% utilization of the positive electrode was achieved at high current densities (100 mA/cm^2). Even though not designed for minimum weight, cells built in this manner have attained specific energies of 75 W·h/kg at the 4-h rate. Testing of the Gould cells will continue in 1979.

C. Rockwell International

The Energy Systems Group at Rockwell International (RI) is developing Li-Si/FeS cells for electric-vehicle and stationary energy-storage applications.

During 1978, a Li-Si/FeS multiplate cell (capacity, 2.5 kW·h) for stationary energy-storage applications was fabricated and tested at RI. This cell, which was operated at about 460°C, had nine negative and eight positive electrodes (23 x 23 cm) and LiCl-KCl eutectic electrolyte; this is believed to be the largest lithium/metal sulfide cell ever operated (see Fig. 3). The cell operated for a short time (<35 cycles), and post-test examinations revealed that the particle retainer for the positive electrode (porous nickel sheet) had ruptured in many places, the particle retainer for the negative electrode (nickel screen) had allowed material to escape, and the separator (AlN powder) had not been sufficiently wet by the electrolyte. Another 2.5-kW·h cell is presently under development.

Testing of sixteen Li-Si/FeS bicells for electric-vehicle applications was also completed at RI. These cells showed significant improvements in performance, similar to those of the Li-Al/FeS bicells, when operated at high temperatures (between 450 and 500°C) or when the LiCl-KCl electrolyte had a high LiCl content. Although substantial progress has been made at RI in the development of an electric-vehicle Li-Si/FeS cell, further work is needed to attain the required cost and performance goals.

D. Industrial Cell and Battery Testing Facilities

A major effort at ANL is directed toward performance and lifetime testing of cells fabricated by industrial contractors. Additional facilities are being installed at ANL both for cell lifetime tests and for laboratory tests of electric-vehicle batteries.

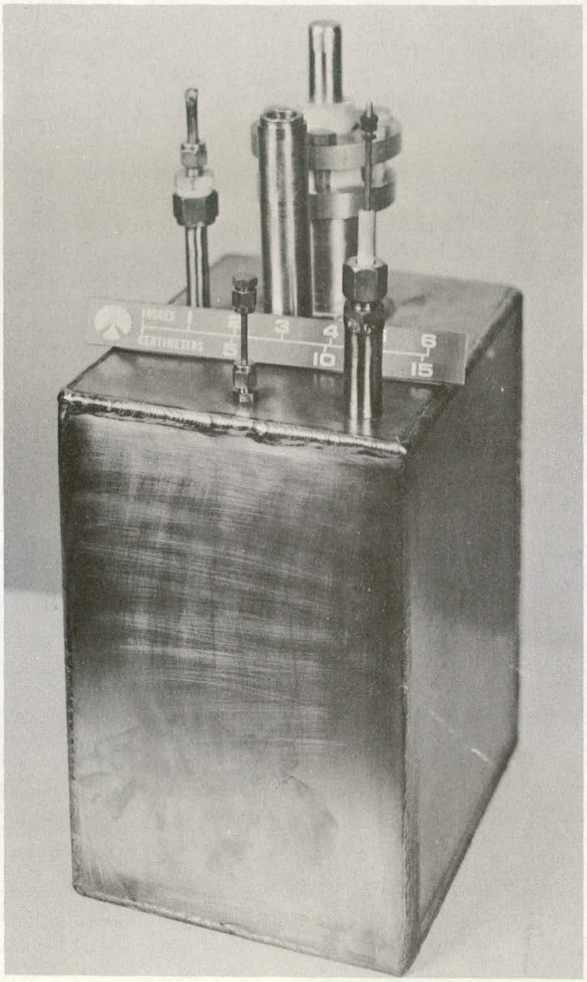

Fig. 3. Load-Leveling Cell (2.5 kW·h)

1. Fifty-Cell Lifetime Test Facility

Construction of a facility for simultaneous lifetime testing of up to 50 cells for the electric-vehicle program is nearing completion. Part of the facility is now in operation; its completion and full-scale operation are scheduled for early 1979. Emphasis will be placed on the testing of cells fabricated by industrial contractors to acquire statistical data on cell performance and lifetime.

Each cell test-station is a module consisting of an open relay rack which contains a furnace, a furnace temperature-control panel, a cell cycler, and a power supply. Figure 4 is a view of a completed module. The furnaces are 114-L (30-gal) steel drums containing a rigid insulating material and heating elements. The cell under test is suspended from the lid of the drum along with heat shields and insulating materials. All of the furnaces are connected to a low-pressure manifold that provides an argon blanket at positive

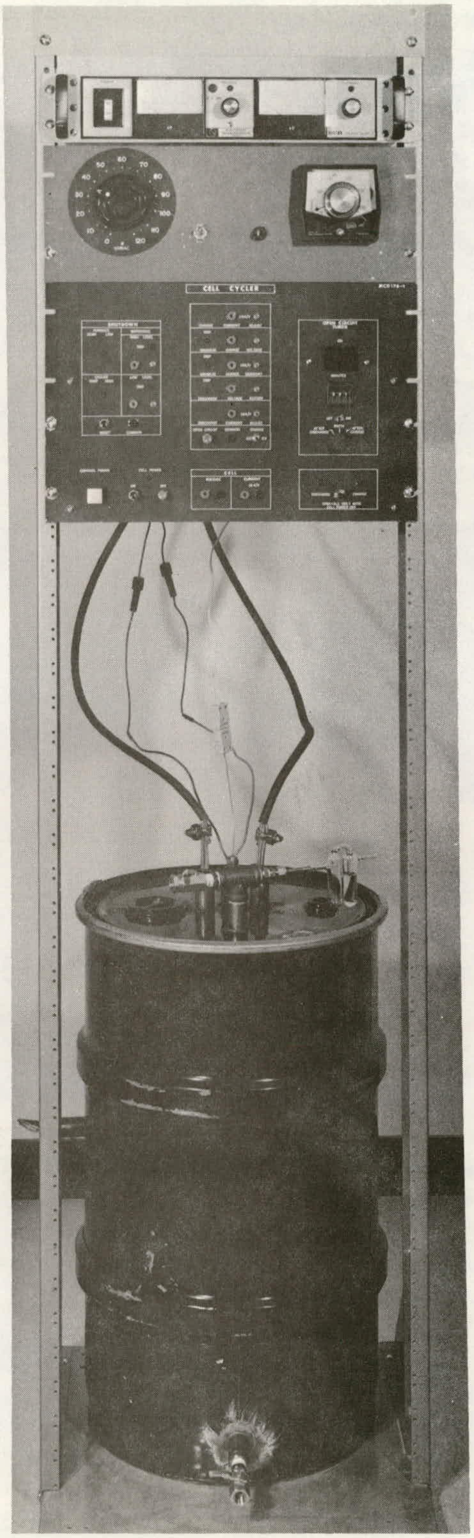

Fig. 4.

Individual Cell Testing Module.
ANL Neg. No. 308-78-178.

pressure to minimize atmospheric corrosion. After a prototype cell cycler for this facility had been designed and built by the ANL Electronics Division, the required number of cyclers were ordered from a commercial vendor.*

All data from the 50-cell test facility will be fed to a data-acquisition computer system that will store and compute the desired information on cell performance. The data will be sent to a PDP 11/34 computer, which will process the information into the required form. The following data on cell performance will be available: capacity (A·h), energy (W·h), elapsed time (h), voltage (V), current (A), and temperature (°C).

2. Electric-Vehicle Battery Test Facility

A laboratory is being prepared and equipped for testing of two full-scale (up to 60 kW·h) electric-vehicle batteries. Provisions are being made to test the batteries under a variety of modes, e.g., discharges and charges at constant current or constant power; discharges that follow a driving schedule such as a SAE J-227 profile;[1] and charges at constant voltage followed by cell equalization after bulk charging.

The electric-vehicle battery test facility employs computer-controlled power supplies. A block diagram of the system is shown in Fig. 5. Robicon programmable power supplies† (shown as "cycler" in Fig. 5) provide the means for charging and discharging the battery. These units are capable of charge currents up to 300 A and discharge currents up to 1200 A; the maximum voltage is 250 V. The current is controlled by a micro-computer (Plessey Micro-1), which permits operation in various modes. The computer also provides safety monitoring of the battery under test and switching of modes of operation. Battery and cell voltages, battery current, and battery temperatures are monitored on a periodic basis, using multiplexers and analog-to-digital (A/D) converters coupled to a CAMAC system.‡ Data from this system enter the computer for comparison, integration, and processing. A 20-K core memory and 5-megabyte disc memory provide storage for the programs, data acquisition, and data reduction. A visual display is provided by a Decscope** and hard copy by a Decwriter.**

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*Paraplegic Manufacturing Co., Inc., Bensenville, Illinois.

†Manufactured by the Robicon Corp., Pittsburgh, PA.

‡The CAMAC system is an international, modular data-acquisition and control standard which, when interfaced to a computer, allows the use of remote stations to gather data and control various types of equipment used in industrial and specialized research applications.

**Manufactured by Digital Equipment Corp., Maynard, MA.

[1] U.S. Energy and Development Administration (ERDA), Office of Electric and Hybrid Vehicles, Test and Evaluation Procedures for Electric Vehicles (1976).

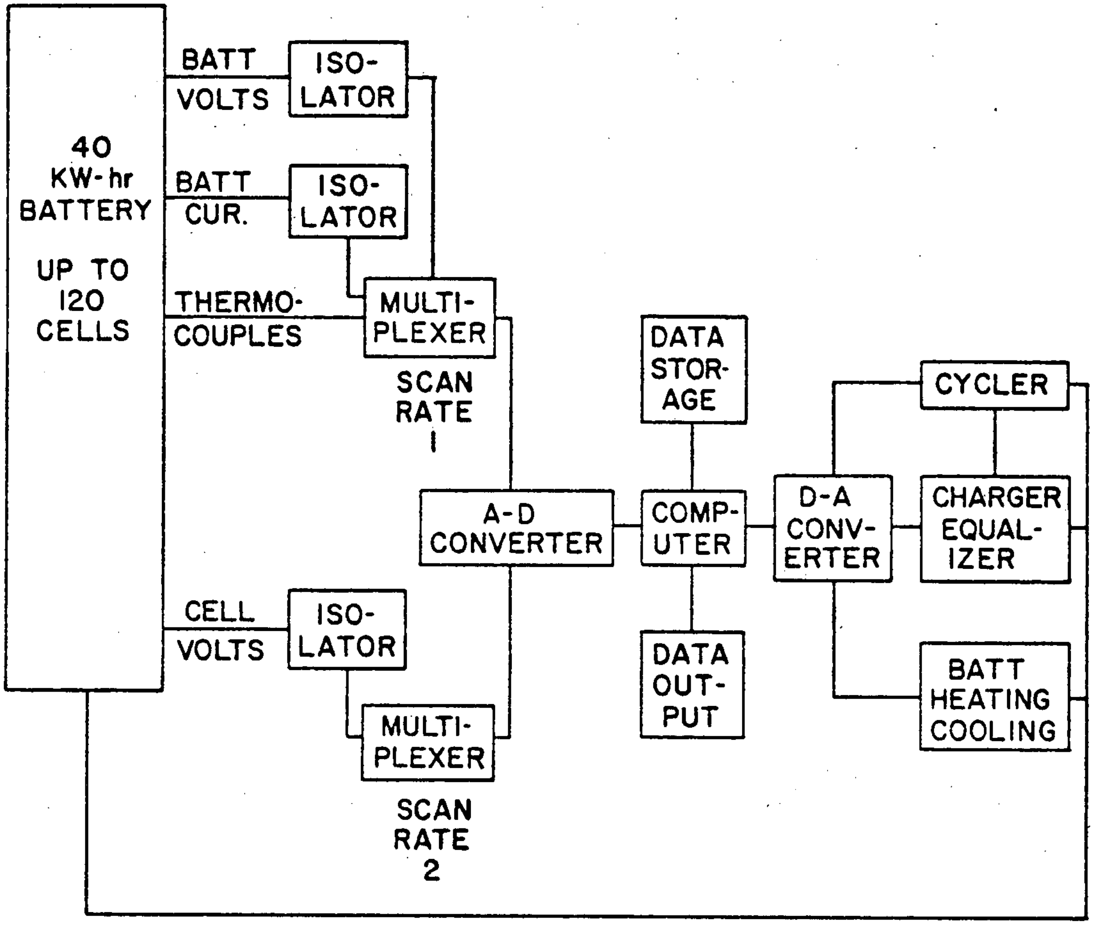

Fig. 5. Computer Control and Data-Acquisition System for Testing of Electric-Vehicle Batteries

For the first full-scale, electric-vehicle battery (Mark IA), it is anticipated that cell equalization will be required after about ten cycles to bring all cells to the same state of charge. An individual power supply for each cell is provided for this purpose. These power supplies have a current limit of 10 A at a constant voltage (adjustable) of about 1.62 V, and each has its own voltage-sensing leads. The power supplies have been assembled in two modules, each containing 60 power supplies. The modules can be controlled independently, or together as a complete system.

This test facility will be used for laboratory tests of the Mark IA battery. It will also be used to charge the battery for in-vehicle tests.

IV. TESTING OF ANL CELLS

Over the past year, ANL has fabricated and tested nearly 40 lithium/metal sulfide engineering-scale bicells. These cells were assembled in the charged, uncharged, or partially charged state. For most of the ANL cells, the electrodes are pressed mixtures of active materials and electrolyte, the separators are a felt material (BN or Y_2O_3), and the electrolyte is LiCl-KCl eutectic. The ANL cells have designs that are expected to reduce cost, or improve lifetime and specific energy at high discharge current densities (>75 mA/cm^2). Whenever advances in cell technology are demonstrated, these advances are incorporated as quickly as possible into the industrial contractors' cells.

A. Small-Scale Cells

Cell-chemistry studies have indicated that the formation of J phase ($LiK_6Fe_{24}S_{26}Cl$) in FeS electrodes has an adverse effect on the electrode kinetics, and that J-phase formation can be decreased by increasing the LiCl content of the LiCl-KCl eutectic (Section VII). Accordingly, tests were performed on two small-scale FeS cells (15-cm^2 electrode area) to determine the effect of electrolyte composition on positive-electrode utilization. The following electrolyte compositions were tested: 53, 58, 61, 65, and 67 mol % LiCl (liquidus temperatures, 415, 350, 375, 400, and 425°C, respectively). The results indicated that positive-electrode utilization increases significantly with increased LiCl content in the electrolyte of FeS cells. The positive electrode in the cell with the 53 mol % LiCl had the lowest utilization--25%. When an electrolyte of 67 mol % LiCl was used, a positive-electrode utilization of 80% was achieved. In another series of tests, the peak power density (W/cm^2) in small-scale FeS cells was found to be significantly increased by the use of a 67 mol% LiCl-33 mol % KCl electrolyte.

B. Cells with Pressed Electrodes

Over the past year, about ten engineering-scale Li-Al/FeS cells with pressed electrodes were tested in a continuing effort to determine the effect on performance of the Cu_2S positive-electrode additive and the LiCl-rich electrolyte. Performance data for five of the cells are given in Table 5. These five "M-series" cells* were also tested to determine the effect of a high positive-electrode loading (1.6 A·h/cm^3) on cell performance. As can be seen in the table, both the Cu_2S additive and the LiCl-rich electrolyte improved the performance of the Li-Al/FeS cell. In addition, the use of a high positive-electrode loading appeared to result in somewhat better cell performance.

In the past, although FeS_2 cells have achieved high specific energy and specific power, they have generally had limited lifetimes (<200 cycles). Studies by the cell-chemistry group have shown that gradual loss of capacity in Li-Al/FeS_2 cells may result from irreversibility of the FeS_2 electrode. As a potential solution to this problem, a lower sulfur-to-metal ratio, 1.44, was tested in the positive electrode of two engineering-scale cells--M-4 and M-7. These two cells differed in capacity loading of both electrodes and in lithium

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*The basic design for this type of cell was presented in ANL-78-20, pp. 14-15.

Table 5. Cell Characteristics and Performance Data for Five M-Series FeS Cells

	M-6	M-8	M-9	M-10	M-11
Cu_2S Addition to FeS, mol %	16	0	16	0	0
LiCl Content of Electrolyte, mol %	58[a]	67	58[a]	58[a]	67
Pos. Electrode Loading, A·h/cm^3	0.7	1.4	1.6	1.4	1.6
Specific Energy,[b] W·h/kg	54	59	65	42	53
Specific Power,[c] W/kg	51	62	76	66	75
Cycle Life	64	347	244	300	365

[a] Eutectic composition.

[b] Measured at a current density of 75 mA/cm^2.

[c] Peak power sustainable for 15 s at 50% discharge.

content of the negative electrode. The capacity that Cell M-4 could achieve was limited by the capacity of the negative electrode (165 A·h vs. 267 A·h for the positive), whereas the capacity of Cell M-7 was limited by the capacity of the positive electrode (233 A·h vs. 194 A·h). The lithium content of the negative electrode was 48 at. % in Cell M-4 and 55 at. % in Cell M-7.

As shown in Table 6, the specific energy and specific power in both of these cells were high. After 255 cycles of operation, the capacity of Cell M-4 had declined by only 11%, from 107 to 95 A·h. The stable performance of this cell is very encouraging. Because of the limiting capacity of the negative electrode, the positive-electrode utilization was typically about 38%. The reserve of active material in the positive electrode may have been partly responsible for its extended operation. Cell M-7 demonstrated similar performance stability for about 135 cycles, and achieved a positive-electrode utilization of about 42% (85 A·h); operation of the cell was terminated, however, because

Table 6. Performance Data for Two M-Series FeS_2 Cells

	Cell M-4[a]	Cell M-7[b]
Specific Energy,[c] W·h/kg	87	97
Specific Power,[d] W/kg	90	125
Cycle Life	300	138

[a] Capacity loading: 165 A·h (neg.)/267 A·h.(pos.).

[b] Capacity loading: 233 A·h (neg.)/194 A·h.(pos.).

[c] Calculated at a current density of 93 mA/cm^2.

[d] Peak power sustainable for 15 s at 50% discharge.

of a sharp decrease in its coulombic efficiency. These results suggest that the use of sulfur-to-metal ratios that are somewhat less than 2.0 in Li-Al/MS_x cells probably stabilizes cell capacity for at least a few hundred cycles.

During 1977, in a number of Li-Al/MS_x cells, NiS_2 was substituted for iron sulfide as the active material in the positive electrode or was used as an additive to improve cell lifetime. Testing of these cells indicated that the relatively small benefit in lifetime resulting from the use of nickel sulfide is not offset by the high cost of nickel. Therefore, testing of this type of cell has been discontinued.

C. Cells with Carbon-Bonded Electrodes

Carbon-bonded positive electrodes are being developed as an alternative to those made by pressing techniques. In the carbon-bonded electrode, the particulate active material is supported in a pyrolyzed-carbon matrix having a void volume of 95%. This structure is formed by the pyrolysis (at 450-550°C) of a paste-like mixture consisting of active material (*e.g.*, FeS or FeS_2), a volatile pore-forming agent (ammonium carbonate), a binder (furan resin), and a carbonaceous filler. In an investigation of potential manufacturing methods for carbon-bonded electrodes, the use of a heat-activated catalyst (1 wt % maleic anhydride) to polymerize the furan resin was found to reduce the curing time. A successful attempt to extrude the paste indicated that extrusion is a potential fabrication method.

Tests have been conducted on three engineering-scale cells having carbon-bonded positive electrodes (one of FeS and the other two of FeS_2) and a design similar to that of the M-series cells. These tests have shown that carbon-bonding is a promising alternative to cold- or hot-pressing techniques for the fabrication of electrodes and that the electrodes have good electrical performance characteristics. A choice between carbon bonding and pressing probably will depend primarily on relative costs and adaptability to mass production.

D. Cells with Powder Separators

Earlier work had indicated that nonconductive ceramic powders are possible low-cost alternatives to the BN fabric and felt that are currently being used as electrode separators in lithium/metal sulfide cells. The use of MgO-powder separators has now been evaluated in eight engineering-scale Li-Al/FeS cells. Two techniques, vibratory compaction and hot pressing, were used to form the powder separators. The vibratory-compaction procedure consists of vibrating the MgO into the space between the electrodes, which are separated by temporary spacers. The hot-pressed separator is formed by premixing the insulating powder with electrolyte and hot-pressing the mixture onto a previously fabricated positive electrode.

In general, the cells with powder separators have a high coulombic efficiency (>99%) and stable capacity after break-in cycling; and the method of formation of the powder separators has little, if any, effect on the performance characteristics of the cells. The results of these cell tests indicate that powder separators may be an alternative to BN felt or fabric. They offer several potential advantages--ease of fabricating various shapes, the possibility of using a variety of different ceramic powders, and low cost. It is also possible that a thinner powder separator can be developed, with a resulting decrease in the weight of the cell and an improvement in power characteristics. Further work is needed to demonstrate the long-term stability of powder separators, particularly when the cell is being rapidly vibrated, and to develop multiplate cell designs that can accommodate powder separators.

V. SYSTEMS DESIGN AND DEVELOPMENT

The approaches taken in the design of the battery components other than cells differ significantly for the electric-vehicle and stationary-storage applications. The work done on the design and development of this equipment is discussed below; also discussed is a model developed for optimization of the electric-vehicle cell design.

A. Electric-Vehicle Propulsion

Eagle-Picher Industries, Inc. has designed a thermally insulated case for the Mark IA battery based upon a conceptual design devised at ANL. This case will consist of double-walled metal (Inconel 718) with multilayered foil in the evacuated space (see Fig. 2), and will enclose 60 cells with a total capacity of 20 kW·h. Eagle-Picher has contracted two firms--Thermo Electron Corp. and Budd Co.--to construct the case, and this task is nearly complete. Other Mark IA hardware is also being designed and fabricated by Eagle-Picher. This hardware includes a cell tray, temperature-control and fail-safe equipment, and electrical/electronic components. Great care has been taken to minimize hardware weight without adversely affecting battery performance.

During the past year, ANL constructed a charging system for electric-vehicle batteries that also provides individual cell-capacity equalization with very close control of individual cell voltages. (Close voltage control is important in ensuring long cell life.) The ANL charger/equalizer, shown in Fig. 6, is based on a design which TRW Systems developed under a contract with ANL; the unit can be preset to charge battery systems containing from one to six cells. The test unit has performed accurately and reliably over a variety of operating conditions.

Two studies on the thermal management of Li/MS_x batteries have been initiated at ANL. In one of these studies, an assessment was made of the optimal shape for a 50-kW·h battery case, rectangular or cylindrical. The results, although still preliminary, indicate that the cylindrical shape has advantages over the rectangular one with respect to weight and volume, heat loss, and manufacturing cost. In the second study, an experimental method was devised for calculating the reversible heating ($T\Delta S$) of Li-Al/FeS cells. The information obtained from these calculations will be used in the design of future electric-vehicle battery cases.

Engineering modeling studies are being conducted at ANL with the objective of developing empirical equations that relate cell performance to the physical and chemical characteristics of the cell and the mode of cell operation. Very general equations have been developed to fit FeS and FeS_2 bicells and multiplate cells; the coefficients in the equations are determined by multiple regression analysis. Operating and performance data of 26 cells[*] were used to develop the model, and data from a second group of 16 cells[*] were

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[*] Fabricated by Eagle-Picher, Gould, and ANL.

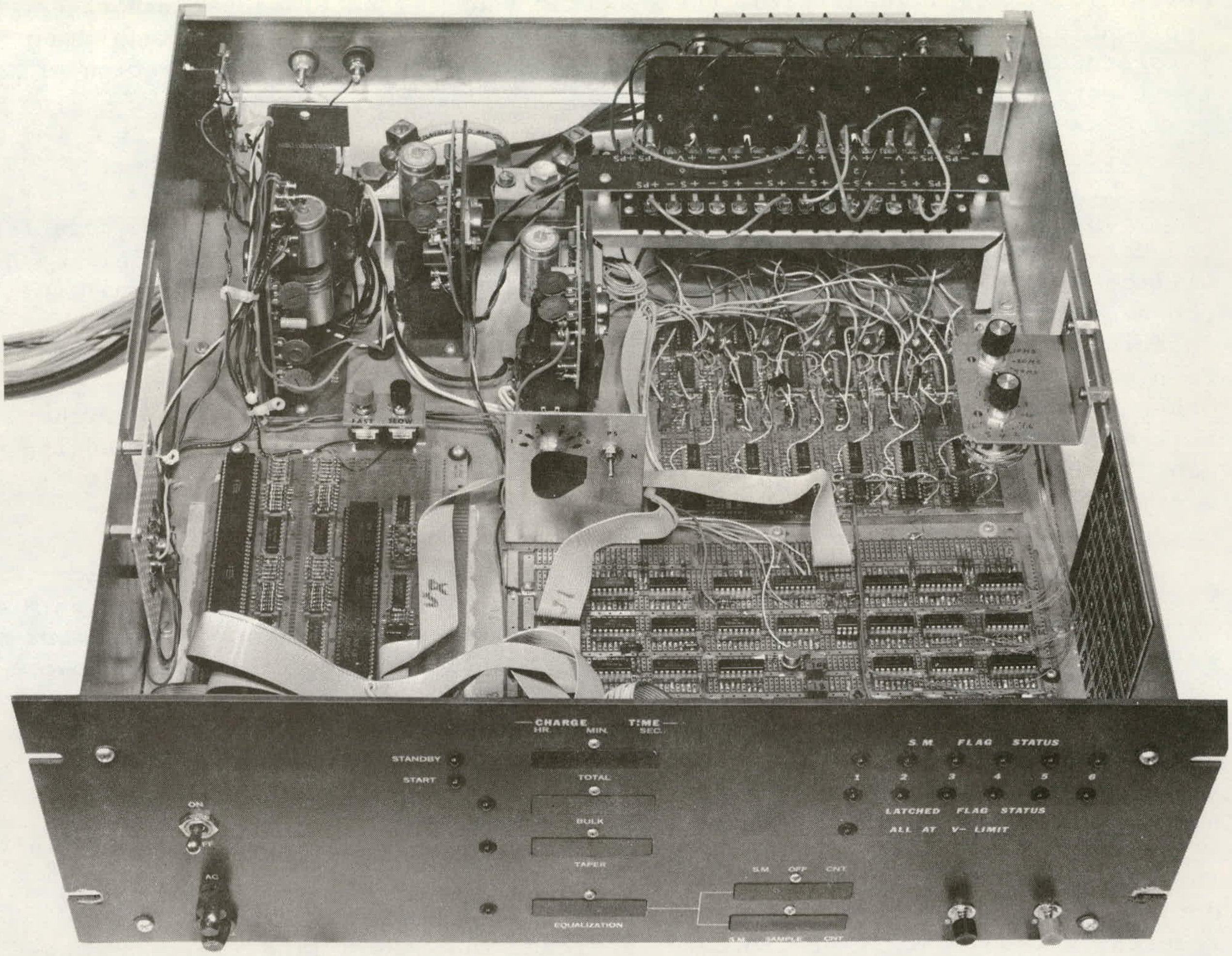

Fig. 6. ANL Charger/Equalizer

used as a subsequent check of the model. Good agreement has been obtained between predicted and actual cell performance. The model will be very useful in the optimization of the electric-vehicle cell design.

B. Stationary Energy Storage

Rockwell International (RI) has been performing conceptual design studies of a 100-MW·h energy-storage plant; recently, this design was combined with a conceptual design conceived at ANL. The cell chosen for this plant is the 2.5-kW·h multiplate cell (see Section III.C). In the RI/ANL design, four of these cells will be electrically connected (in parallel) to

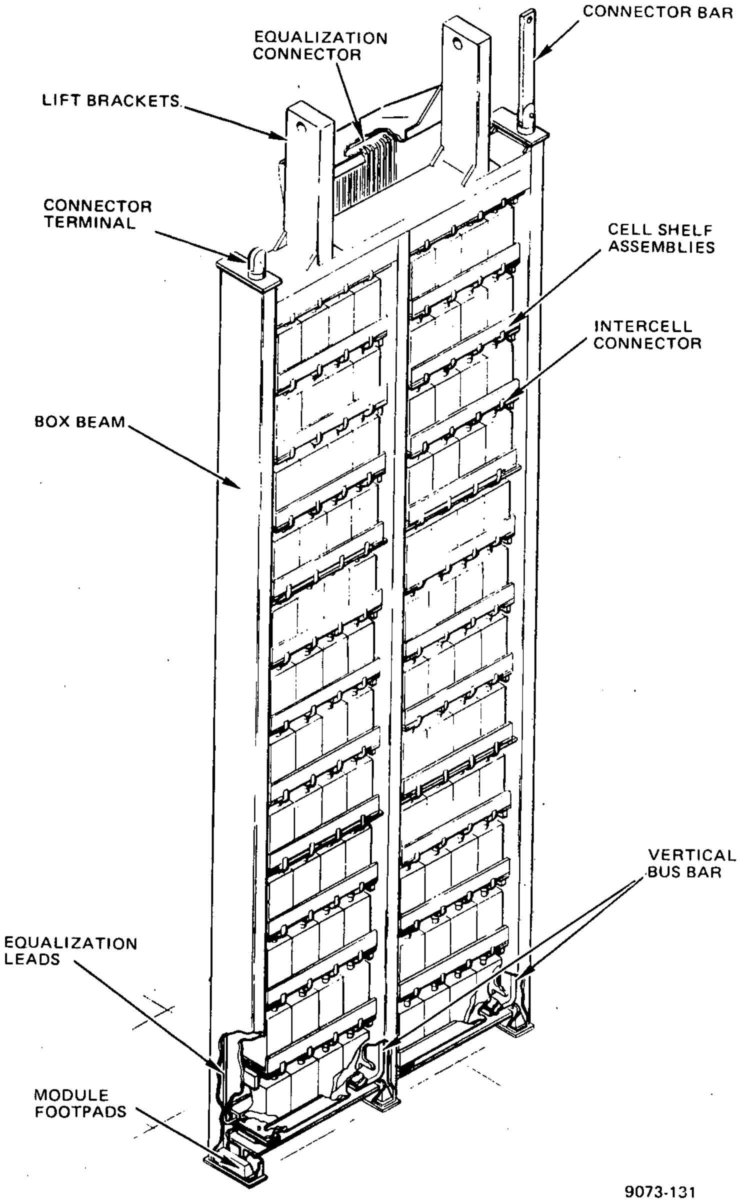

Fig. 7. Submodule for the Stationary Energy-Storage Plant

form a 10-kW·h assembly, which will be the basic replaceable unit of the plant. Twenty-four such assemblies will be stacked in two sets of twelve to form a submodule (see Fig. 7). A module will consist of six rows of six submodules each (a total of 864 cell assemblies) connected in series. Nominal dimensions for an uninsulated, assembled module are 12 x 2.8 x 6 m. Fiberglass insulation panels, 43 cm thick, will be attached to the sides of the module to reduce heat losses.

The 100-MW·h facility design (Fig. 8) contains two groups of six modules (designated a "battery bank") arranged on either side of an electrical-power processing center. This central area contains ac-dc converters, circuit

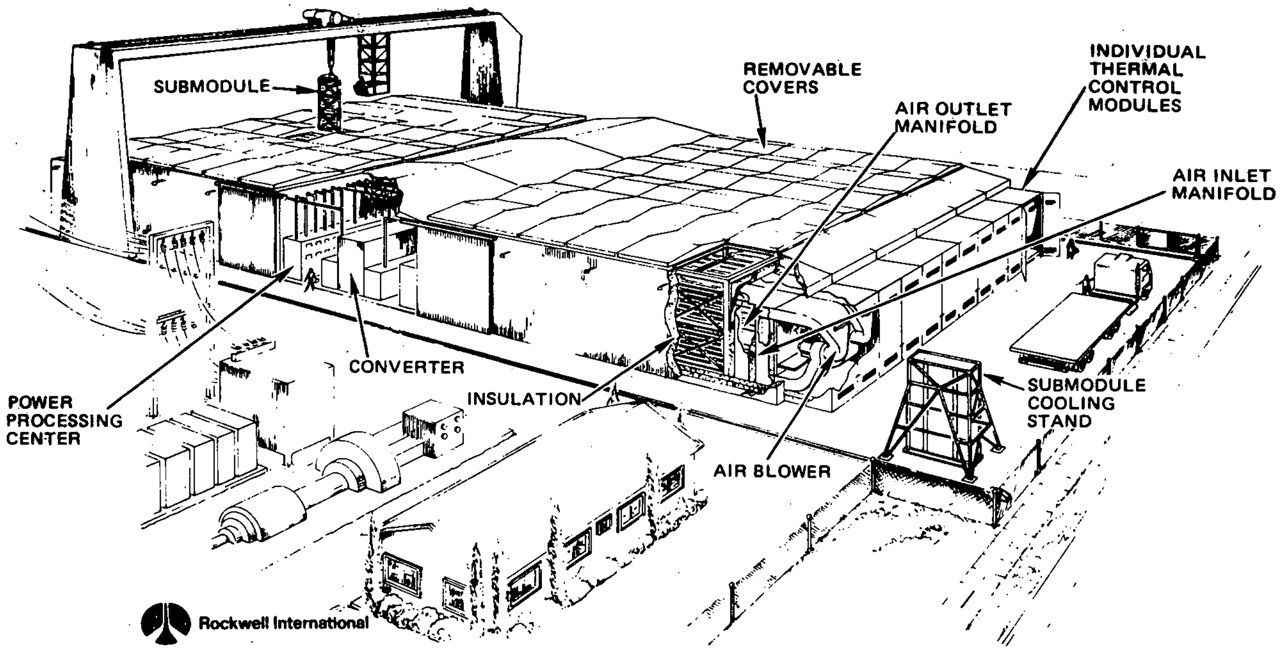

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Fig. 8. 100-MW·h Stationary Energy-Storage Plant

breakers, and transformers interfacing with the utility distribution or transmission system. Each module group has a 10-MW converter; interties permit reassignment of the converters to alternate battery banks. Also in the central area are ancillary buildings (sheet-metal sheds) which house switchgear, equalizer electronics, and other instrumentation. Centrifugal blowers for the thermal management system are housed in sheet-metal structures on the outside of each bank. A gantry spans the 23-m width of the plant for loading or replacing the submodules. The submodules can be trucked to the plant site and brought up to operating temperature in an external furnace on site.

Cost estimates for the plant are being prepared by ANL and RI. Preliminary cost estimates by ANL suggest that the cost of the battery plant as presently described (including cells but excluding ac/dc converters) is well over the battery cost goal of \$50/kW·h.* During the next fiscal year, ANL and RI will try to find a way to reduce this cost.

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*A cell cost of \$30/kW·h was assumed for this estimate.

VI. MATERIALS DEVELOPMENT

Efforts in the materials program are directed toward the development of various cell components (electrode separators, current collectors, and cell hardware), testing and evaluation of potential cell materials (for corrosion and wettability), and post-test examinations of cells to evaluate the behavior of the electrodes and construction materials. The results of these studies form the basis for recommending materials, components, and cell designs.

A. Testing of Electrode Separators

The separator is a key component of the cell, and it must meet several requirements, including compatibility with the electrode materials and electrolyte, good wettability by the electrolyte, adequate mechanical strength, acceptable cost, suitable porosity and thickness, and lack of electronic conductivity.

In the past, BN fabric has been used successfully in engineering cells; however, the projected cost for mass production precludes its use in commercial cells. Consequently, three types of potentially low-cost separators have been under study: felts, ceramic powders, and sintered porous ceramics. The ceramic-powder and sintered-ceramic separators have the advantages of utilizing materials that are not available in fibrous form (e.g., AlN, MgO, and β-Si_3N_4) and are amenable to low-cost mass production. The primary disadvantage of the ceramic separators is their low porosity (ceramic powder, 40-50% porosity; sintered ceramic, 50-70% porosity; felt, 90-93% porosity), which restricts ionic transport at high current densities (>75 mA/cm^2).

Testing of experimental cells has demonstrated the technical feasibility of each type of separator. The separators being tested had thicknesses between 0.9 and 1.6 mm. At low current densities (<40 mA/cm^2), the thickness and porosity of the separator had little effect on the utilization of the active material. However, at high current densities, the utilization of cells with powder or sintered separators (i.e., low porosity) was significantly lower than that of cells with felt separators. In addition, at high current densities, utilization was lower in cells with thicker separators. Efforts are continuing on the optimization of the design of ceramic-powder and sintered-ceramic separators; felt separators are being tested in contractor-fabricated cells.

B. Electrolyte Wetting Studies

In the operation of a cell, the separator and active materials must be well wet by the electrolyte; the internal resistance is determined, in part, by the extent to which these components are filled with electrolyte. Therefore, over the past few years studies have been conducted to determine the wettability by molten LiCl-KCl of candidate separator materials and active materials. For these studies, the advancing and receding contact angles of molten LiCl-KCl electrolyte were measured on the following cell materials: LiAl, Al, FeS_2, FeS, Li_2S (active materials), Type 304 stainless steel, Y_2O_3, MgO, BN, Al_2O_3, C, and ZrO_2 (candidate materials for separators and particle retainers). Only the LiAl, Al, Type 304 SS, and Y_2O_3 were easily wet by the electrolyte.

Owing to the difficulty of wetting most of the above materials, studies are being conducted to identify pretreatment processes to improve wettability. This effort has identified $LiAlCl_4$ as an effective wetting agent for separator materials. At room temperature, a low concentration of $LiAlCl_4$ is added to the separator material in the form of a powder; at temperatures above 150°C, this powder melts and spreads over the separator material, thereby producing a material that can be easily penetrated by molten LiCl-KCl. This wetting agent has been successfully tested in engineering-scale cells.

C. Corrosion Studies

Corrosion testing is an integral part of the selection of suitable materials of construction for lithium/metal sulfide cells. Initial evaluations are made on the basis of static corrosion tests, and the more promising materials are tested further in experimental cells.

The search for construction materials for FeS and FeS_2 electrodes is being continued. Results of static corrosion tests have indicated that a number of nickel-base alloys (Hastelloys B and C and some of the Inconel alloys) should have low corrosion rates (<5 μm/y) in the FeS electrode. Iron-base alloys developed at ANL have also looked promising in static tests. However, all these alloys have higher resistivities than those of nickel and iron, and are thus less desirable. For the FeS_2 electrode, corrosion tests have shown that only molybdenum and graphite are sufficiently resistant to sulfide attack. However, graphite has a high resistivity, molybdenum is very expensive, and both materials are difficult to fabricate into suitable current collector shapes. Major efforts are presently being directed toward the development of inexpensive conductive ceramics for use as a coating material for inexpensive metallic current collectors in FeS_2 electrodes. So far, coatings of TiN and TiB_2 look very promising. This effort is being expanded to include studies of other coating materials, both metal and conductive ceramics (or glasses). During the next year, in-cell testing of the promising coating materials is planned.

D. Post-Test Cell Examinations

Post-test examinations are conducted to determine electrode morphology (*e.g.*, microstructure, active material utilization and distribution, reaction uniformity, impurity effects, and cross-contamination); in-cell corrosion reactions and kinetics; and causes of cell failure. These results are evaluated, and appropriate recommendations for improving cell performance are made to engineering personnel.

During the year, 52 engineering cells were subjected to post-test examinations. All of these cells had bicell designs except four, which had multiplate designs. Of the 52 cells, 43 were fabricated by industrial contractors and the rest by ANL. A summary of the causes of cell failure in 46 cells is presented in Table 7. Six cells completed the scheduled test period and have been included in the table only to complete the record of post-test examinations.

Table 7. Summary of Cell Failure Modes

Cause of Failure	No. of Cells
Extrusion of active materials (inadequate confinement)	5
Metallic copper deposits in separator[a]	3
Metallic[b] and/or sulfide deposits across separator	4
Separator cut by honeycomb current collector	11
Equipment malfunction[c]	2
Short circuit in feedthrough	4
Cell assembly difficulties	10
Unidentified	
Declining coulombic efficiency	1
Short circuits	3
Loss of capacity/poor utilization	3
End of test	6

[a] FeS cells with Cu_2S additive.

[b] Other than copper.

[c] Resulting in overcharge, temperature excursion, or accidental polarity reversal.

Cell operation has been terminated principally because of electrical short circuits, although in a few cases loss of capacity and declining coulombic efficiency were the causes. For the past year, the major causes of short circuits have been cutting of separators by the current collector (11 cases) and problems with cell assembly (10 cases). The cells with cut separators were fabricated before the recommendation had been made to add protective screens; the screens have proved effective in preventing this problem. Cell assembly difficulties included misaligned (or broken) electrodes, misplaced (or skewed) separators, and contact of ZrO_2 cloth (conductive after reaction with lithium) with both electrodes. Extrusion of active material, a major problem in past years, appears to have been solved in the cells with newer designs. The causes of the short circuits are mechanical and can be avoided by modification of cell designs and by better quality control.

In the four multiplate cells, metallographic examinations showed a significant deficiency of electrolyte in the negative electrodes and separators; the electrolyte deficiency was caused by incomplete filling and/or expansion of the electrodes. These examinations also showed that agglomeration (densification) had occurred to a considerable extent in the center portion of the negative electrode. At this time, Li-Al agglomeration and electrolyte deficiency are believed to be major factors in the high rate of capacity decline presently observed in multiplate cells.

E. Materials Development by Contractors

In the area of materials and components, the Carborundum Co. is developing BN-felt electrode separators, the Illinois Institute of Technology is investigating the electrochemical deposition of molybdenum for joining and plating current-collector structures, and ILC Technology is developing insulated electrical feedthroughs.

VII. CELL CHEMISTRY

The cell-chemistry studies are directed toward (1) solving the chemical and electrochemical problems that arise in the cell and battery development work, (2) identifying new cell designs that may improve performance and lifetime, and (3) acquiring an understanding of the processes that occur within the cells. Most of the cell-chemistry studies at ANL this year were concerned with the properties of metal sulfide electrodes. In addition, General Motors Corp. has been contracted to conduct an experimental investigation of the characteristics of the FeS_2 electrode.

Studies are being conducted on the Li_2S-FeS_2-Fe field of the Li-Fe-S phase diagram. The findings of these studies have been incorporated into the phase diagram shown in Fig. 9.

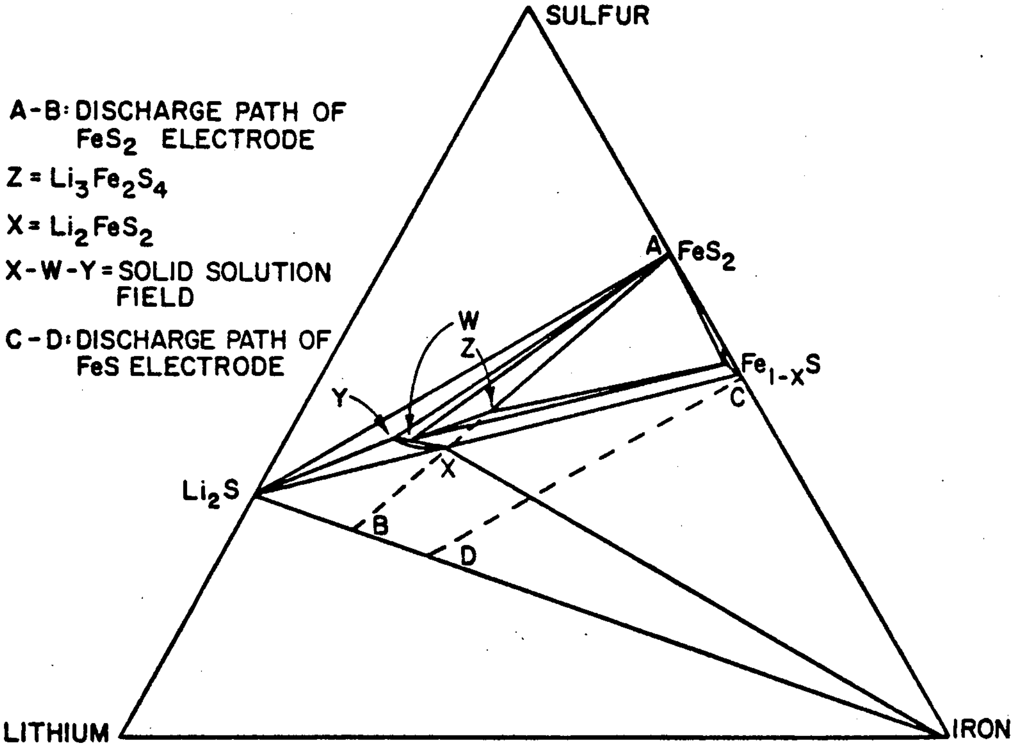

Fig. 9. Isothermal Section of Li-Fe-S Phase Diagram

The path representing the change in average composition of an FeS_2 electrode as it is charged and discharged at 450°C is indicated by the line A-B. The fully charged electrode contains FeS_2 (point A) and the fully discharged electrode contains Li_2S and iron (point B). Between these extremes, two well-defined compounds are found on the line A-B, namely, Z phase ($Li_3Fe_2S_4$) and X phase (Li_2FeS_2). In addition, more complex phases are found in the region between the Z and X phases, e.g., mixtures of $Fe_{1-x}S$, W (approximate composition, $Li_{12}Fe_4S_{11}$), and Z.

The discharge behavior of FeS_2 electrodes can be described with the aid of Fig. 9. During discharge, FeS_2 is converted to Z phase. Next, Z phase is converted to a mixture of the compounds $Fe_{1-x}S$ and W. The latter compound lies on the boundary of a solid-solution field labeled X-Y.* The extent of this solid-solution field and the approximate location of the W compound on the field boundary are indicated in the figure. Further discharge of the compounds $Fe_{1-x}S$ and W leads to formation of the single-phase compound, X phase. Finally, X phase is discharged to a mixture of Li_2S and iron. The phases formed during charge are much more complex than those formed during discharge, and are still under investigation.

Cyclic voltammetry studies have been used to elucidate the charge and discharge reactions of the FeS_2 electrode vs. Li-Al in LiCl-KCl electrolyte. The FeS_2 electrode was initially cycled over a broad voltage range (1.0-2.0 V) with a very low voltage scan rate (0.015-0.020 mV/s). In the high-voltage region of the voltammogram (1.5-2.0 V), a large voltage separation, 0.12 V, was found between the charge and discharge reactions, thereby indicating kinetic hindrance of the electrode reaction. In subsequent experiments, voltammograms of the FeS_2 electrode were taken at four discharge cutoff voltages--1.43, 1.56, 1.61, and 1.65 V; and, as the cutoff voltage was increased, the voltage separation was found to decrease due to a shift in the charge peak to a higher voltage (the discharge peak remained fixed). At the 1.65-V discharge cutoff, the voltage separation between the charge and discharge reactions was less than 0.02 V. This result indicates that when the FeS_2 electrode is discharged beyond the Z phase (i.e., the upper voltage plateau) the charge reaction becomes kinetically hindered. Thus, one may conclude that the reactions in FeS_2 electrodes depend strongly on the depth of discharge.

Further investigations of the chemistry of the FeS electrode indicated that, when a Li-Al/LiCl-KCl/FeS cell is charged, the first material to form in the FeS electrode is X phase (Li_2FeS_2). This reaction is followed by the formation of J phase (approximate composition, $LiK_6Fe_{24}S_{26}Cl$), and then by the formation of FeS. The J phase is formed through a reaction with the KCl in the electrolyte, and has been found to adversely affect electrode kinetics. In the absence of J phase, the FeS electrode material traverses two composition triangles during charge and discharge (see line C-D in Fig. 9). The phases present in the electrode during the first half of the charge (or conversely during the second half of discharge) consist of Li_2FeS_2, Li_2S, and Fe (mixture 1). During the second half of charge (or conversely during the first half of discharge) the phases consist of FeS, Li_2FeS_2, and Fe (mixture 2). The two mixtures probably react with electrolyte to form J phase according to the following reactions:

$$6KCl + Fe + 23Li_2FeS_2 \rightleftarrows J + 5LiCl + 20Li_2S \tag{4}$$

$$6KCl + Fe + 20FeS + 3Li_2FeS_2 \rightleftarrows J + 5LiCl \tag{5}$$

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*Approximate composition of Y phase, $Li_7Fe_2S_6$.

Preliminary tests by CEN's Basic Energy Sciences program indicated that these reactions are strongly dependent on temperature and on the composition of the electrolyte. Therefore, investigations were carried out to determine the maximum temperature for formation of J phase, T_J, when mixtures (1) and (2) are blended with electrolyte of various compositions. The results showed that the addition of LiCl to LiCl-KCl eutectic significantly decreased T_J. With mixture 2, for example, T_J was 623°C with LiCl-KCl eutectic (58 mol % LiCl), but only 481°C with electrolyte containing about 76 mol % LiCl. Thus, the use of a LiCl-rich electrolyte in Li-Al/FeS cells should result in substantial improvements in performance.

Tests were conducted with Li-Al(10 A·h)/FeS (6.5 A·h) cells having LiCl-KCl electrolytes containing 53, 58 (eutectic), 63, and 67 mol % LiCl to evaluate the effect of electrolyte composition on the utilization of the FeS electrode at 450 and 500°C. (The cells were cycled at current densities of 50 and 100 mA/cm^2.) In the cells with the 53 and 58 mol % LiCl electrolyte, the higher temperature resulted in a significantly increased utilization; this effect was not observed in the cells with the other two electrolyte compositions. In general, the utilization of the positive electrode increased with increasing LiCl content. Thus, the highest utilization (85-90%) was achieved in the cell with an electrolyte containing 67 mol % LiCl.

VIII. ADVANCED BATTERY RESEARCH

The objective of this program is to develop high-performance cells that use inexpensive, abundant materials while maintaining the performance levels required for electric vehicles or load leveling. These cells are expected to follow the lithium/metal sulfide cells into commercial production. The present goals for the cells are a specific energy of 160 W·h/kg and a maximum materials cost of $10-15/kW·h in mass production. During the past year, studies were conducted with cells having negative electrodes of either calcium or magnesium alloy, positive electrodes of metal sulfide or metal oxide, and a molten-salt electrolyte. The operating temperature for these cells was between 400 and 450°C.

In testing of magnesium cells, two major problems have been discovered: unacceptably low utilization of the positive electrode, and the formation on the negative electrodes of dendrites which cause short circuits. Therefore, we have decided to concentrate further efforts on development of the more promising calcium cell.

During the past year, a prismatic $Ca(Mg_2Si)/LiCl-KCl-CaCl_2/NiS_2$ cell with a theoretical capacity of 70 A·h was tested to evaluate the behavior of calcium electrodes in an engineering-scale cell. The cell, although not of optimum weight, achieved a specific energy of 42 W·h/kg at the 6-h rate. Operation was terminated after 120 cycles because of declining coulombic efficiency. The results of this test were very encouraging.

The electrolyte used in the cell was relatively expensive because of its high lithium content (54 mol % LiCl); therefore, a search was made for less expensive electrolytes. The most promising salt identified is 29 mol % LiCl-20 mol % NaCl-35 mol % $CaCl_2$-16 mol % $BaCl_2$ (m.p., 390°C).

Small-scale cell (1.5 A·h) tests were conducted to identify promising negative electrodes other than the Ca-Mg-Si system; negative electrodes evaluated included Ca-Si, Ca-Al-Zn, and Ca-Pb. The Ca-Si electrode was the only system that had acceptable utilization. The Ca-Si and Ca-Mg-Si electrodes will be compared in tests of engineering-scale cells during the next year.

In cyclic voltammetry measurements on MS_2 electrodes (FeS_2 and NiS_2) vs. $CaAl_4$, conducted in $LiCl-KCl-CaCl_2$ and $LiCl-NaCl-CaCl_2-BaCl_2$ electrolyte, the high-voltage reactions (>1.6 V) of FeS_2 and NiS_2 exhibited poorer electrochemical reversibility than the lower voltage reactions. The cause of the poor reversibility and methods of correcting it will be sought in future experiments. The utilization of both the FeS_2 and NiS_2 electrodes was much higher in the $LiCl-NaCl-CaCl_2-BaCl_2$ electrolyte than in the $LiCl-KCl-CaCl_2$ electrolyte; thus the $BaCl_2$-containing electrolyte appears more suitable for use in calcium cells.

The results described above are promising. We believe that the cell performance goal (160 W·h/kg) can eventually be achieved in calcium alloy/$LiCl-NaCl-CaCl_2-BaCl_2/FeS_2$ (or NiS_2) cells having multiplate designs. Our goal during the coming year is to design and operate prismatic bicells having specific energies greater than 100 W·h/kg.

ADDENDUM: PUBLICATIONS--1978

A. Open-Literature Publications

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