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9700 South Cass Avenue
Argonne, Illinois 60439

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Li-ALLOY/FeS CELL DESIGN AND ANALYSIS REPORT

by

E. C. Gay, R. K. Steunenberg, W. E. Miller, J. E. Battles,
T. D. Kaun, F. J. Martino, J. A. Smaga, and A. A. Chilenskas

E. C. Gay (compiler)

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MASTER

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ABSTRACT

This report contains historical information on the Li-alloy/FeS system that will be useful in its future applications. The results will also be of interest to advanced battery developers and will provide a basis for comparison of the performance characteristics of Li-alloy/FeS batteries to those of other battery systems. Although most of this information has been published in progress reports, proceedings papers, and journal articles, it has not been collected and organized in a single document that portrays the state of the art for the system.

This document includes the following: (1) the chemical and electrochemical reactions for the Li-alloy/FeS system, accomplishments in past cell development efforts, and performance attained by state-of-the-art cells vs. performance goals; (2) detailed drawings of state-of-the-art cell designs, documentation of cell fabrication techniques, and comparisons of alternative types of cell components (such as BN felt vs. MgO powder separators, stainless vs. low-carbon steel cell housings) and fabrication techniques (such as charged vs. uncharged electrodes); (3) results of post-test cell analyses, including cell failure mechanisms, electrode morphology and active material distribution, and in-cell corrosion rates; (4) data from trade-off studies between specific power and energy; (5) discussion of battery design considerations (e.g., volumetric energy density, battery charger, and high-efficiency thermal insulation); (6) results of cost studies, which include materials and manufacturing costs of cells and batteries and heating costs involved in battery operation; and (7) projections of cell designs having the greatest potential for meeting electric-vehicle performance requirements.

1.0 INTRODUCTION (R. K. Steunenbergh)

1.1 Purpose

During approximately the past decade, research and development work has been under way at Argonne National Laboratory (ANL) and at subcontractors' laboratories on the development of high-performance batteries for electric-vehicle propulsion and for stationary energy-storage applications such as load leveling on electric utility systems or storage of electrical energy produced by wind, solar, or other sources. The widespread use of electric vehicles would conserve petroleum fuels, and a side benefit would be realized in decreased air pollution in densely populated areas. The use of storage batteries for load leveling could save petroleum by reducing the need for gas turbines or other devices to meet peak power demands. During the past few years, the primary emphasis of the program has been on the electric-vehicle application.

For a first-generation electric-vehicle battery, the performance goals* established for the individual cells are as follows: specific energy, 125 Wh/kg at a 3-h discharge rate; peak specific power, 185 W/kg at 50% state of charge; mean time to failure, 500 deep (80%) discharge cycles. The cells currently under development have capacities in the range of 150-300 Ah. Although these goals have been approached or met by individual cells, further design optimization work will be needed before they can be met routinely. An effort on design optimization will require an analysis of all the available data to arrive at the design improvements having the greatest likelihood of resulting in cells and batteries capable of meeting the performance and lifetime goals.

During the course of this program, a large body of information has been accumulated on the results of research and development on the Li-Al/FeS battery for electric vehicles. Although most of this information had appeared in various progress reports and other technical publications, it had not been collected and organized into a single document that represents the state of the art for the system. This information has been generated mainly from (1) the ANL research and development program, which has included supporting chemical and electrochemical research, materials testing and evaluation, cell resistance mapping and polarization measurements, cell modeling and power vs. energy trade-off studies, and cell design and fabrication; (2) cell development, design, and fabrication efforts at Gould Inc. and Eagle-Picher Industries, Inc; (3) performance and lifetime testing of Gould, Eagle-Picher, and ANL cells; and (4) post-test examinations of these cells. In addition, several small batteries of LiAl/FeS cells were built and operated during the course of the program.

The purpose of this document is to provide (1) a concise collection of these results and (2) an analysis of the data that should result in a consensus on the most suitable cell and battery designs for electric-vehicle propulsion. An attempt has been made to provide sufficiently detailed information so that little, if any, additional technology transfer would be needed

*These performance goals are suitable for an electric van. Higher peak power will probably be required for an electric automobile.

by an organization to continue the development of this system to the advanced engineering and manufacturing stages. This document is also expected to be useful to advanced battery developers who are interested in applications other than electric-vehicle propulsion, and it should provide a basis for comparing the performance of Li-Al/FeS batteries with that of other battery systems.

1.2 Background

Investigations of electrochemical cells having alkali-metal electrodes and molten-salt electrolytes began at ANL in 1961 as an effort to develop thermally regenerative galvanic cells for the direct conversion of heat to electricity. This work led to the invention of the lithium/sulfur cell in 1968, in which elemental lithium and sulfur were used as the active materials in the electrodes with molten LiCl-KCl electrolyte. The melting point of the LiCl-KCl eutectic is 352°C, which requires that the cell operating temperature be maintained above 400°C. Lithium and sulfur are attractive materials for a high-performance battery because they have low equivalent weights, develop a high voltage (about 2.3 V), and are capable of high current densities ($>1 \text{ A/cm}^2$). Attempts to develop the lithium/sulfur cell, however, led to several problems related mainly to the solubility of sulfur in the electrolyte and difficulty in retaining the liquid lithium in the negative electrode. In 1973, these problems were overcome by substituting lithium-aluminum alloy for lithium in the negative electrode and iron sulfide (FeS or FeS₂) for sulfur in the positive electrode. The lithium-aluminum alloy and the iron sulfides are both solid materials that form porous structures which can be filled with the molten-salt electrolyte. Other lithium alloys, such as lithium-silicon, and different metal sulfides have been investigated as alternative active materials in the negative and positive electrodes, and they are considered to show promise for future development. At the present time, however, the Li-Al/FeS cell is the most technically advanced system of this type in terms of engineering development.

Throughout the course of this program, a major objective was to involve industrial organizations in the effort in order to provide a means of transferring the technology to them as it is developed. The industrial effort also provided feedback to the more basic research work. This effort began in 1973 with a solicitation of battery firms for the assignment of one or more of their scientists or engineers to assist in the development of the battery and to assess its likelihood of future commercial feasibility. To date, approximately 20 industrial participants have worked on the program at ANL for periods of a few weeks to a year, with the cost shared by ANL and the industrial organization.

In 1975, cell development and fabrication programs were initiated at three of the battery firms that had industrial participants at ANL (Gould Inc., Eagle-Picher Industries, Inc., and Catalyst Research Corp.). At about the same time, management of a program at the Atomic International Division of Rockwell International on the development of lithium/metal sulfide batteries was transferred to ANL. Gould and Eagle-Picher continued to develop and fabricate electric-vehicle battery cells and a few small batteries up to the end of 1982.

The original research leading to the development of the lithium/iron sulfide battery was funded by the Atomic Energy Commission (AEC), Division of Research. Several other federal agencies that supported the research and development work in the early stages of the program included the U.S. Army MERDC; the Environmental Protection Agency, Office of Air Programs; the National Heart and Lung Institute of the Department of Health, Education and Welfare; the National Science Foundation (RANN Program); and the AEC Division of Applied Technology. The major support, however, has been provided by the Energy Research and Development Administration and, more recently, by the Department of Energy (Division of Energy Storage Technology). In 1981, overall management responsibilities for this program were transferred from ANL to two lead laboratories, Sandia National Laboratories and Lawrence Berkeley Laboratory. A decision was also made in 1981 to phase out the work on the Li-Al/FeS battery.

1.3 Description of Li-Al/FeS Cell

The Li-Al/FeS cells consist of Li-Al negative electrodes, FeS positive electrodes, and molten LiCl-KCl electrolyte. The normal operating temperature is in the range of 430-500°C. This cell discharges with a single voltage plateau at a reversible potential of 1.33 V, and under load at an average voltage of 1.18 V at the 3-h rate. The normal charge and discharge cutoff voltages are 1.55 and 1.00 V, respectively. The overall discharge reaction may be written as

The theoretical specific energy for this reaction is approximately 460 Wh/kg.

1.3.1 Negative Electrode

The phase diagram of the Li-Al system,¹ which has been redetermined recently, is shown in Fig. 1.1. At a cell operating temperature of 450°C, the solubility limit of lithium in aluminum is 10 at. %, which is the boundary of the α -Al phase field. The β -LiAl field has a composition width of 9 at. % (between 47 and 56 at. % lithium). The Li-Al electrode is usually cycled across the two-phase region between 10 and 47 at. % lithium, within which the emf of the electrode remains constant at 292 mV relative to elemental lithium.² If the lithium content is increased above 47 at. % into the β -LiAl phase, the potential decreases very rapidly and approaches that of lithium.³ The theoretical capacity of Li-Al containing 47 at. % lithium, which has a density of 1.75 g/cm³, is approximately 0.74 Ah/g or 1.3 Ah/cm³ when the material is discharged to 10 at. % lithium.⁴

Metallographic and scanning electron microscopic examinations show that the Li-Al alloy, when cycled electrochemically, forms a porous, interconnected (skeletal) microstructure.⁵ This type of microstructure is formed regardless of whether the starting material is Li-Al particles, Li-Al cast plates, or aluminum wire charged electrochemically with lithium. This porous microstructure appears ideal for high-rate, efficient electrodes. Under certain conditions (e.g., unfavorable electrode loadings), agglomeration of the active material can occur, with a resulting loss of cell capacity. This phenomenon is not observed, however, in well-designed Li-Al electrodes.

Fig. 1.1.

Lithium-Aluminum Alloy Phase Diagram

Examinations of cells that have undergone both short and long periods of charge-discharge cycling (<25 cycles, >1000 cycles) indicate that the microstructure is formed during early cycling and does not change appreciably throughout the life of the cell.

1.3.2 Positive Electrode

The chemistry and electrochemistry of the FeS electrode have been investigated in detail, and the results indicate that the reactions are much more complex than shown earlier for the overall cell reaction.^{6,7} The cell reactions that can be deduced from the Li-Fe-S phase diagram (Fig. 1.2) are as follows:

These two reactions appear as one on the discharge voltage plateau, since the Gibbs energy of formation of Li_2FeS_2 is less than 1 kcal/mol.⁸ However, microscopic examinations of the phases present in the electrode after cycling indicated that the major voltage plateau corresponds to the formation of $\text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl}$.^{9,10} (In the literature, Li_2FeS_2 is sometimes referred to as "X-phase" and $\text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl}$ as "J-phase".) In addition to the above two reactions, three other electrochemical and four chemical reactions have been identified:

Fig. 1.2.

Phases in the Li-Fe-S System at
450°C

Electrochemical Reactions

Chemical Reactions

Emf data and thermodynamic information on these reactions are available in detail in the literature.¹¹

During the development of the FeS cell, it became evident that the formation of $\text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl}$ ("J-phase"), which occurs through reactions with the KCl in the LiCl-KCl electrolyte, hinders the kinetics of the FeS electrode. At one time CuS was added to the positive electrode to inhibit the formation of this phase, but subsequent post-test examinations of the cells indicated that this tended to cause early cell failures due to the precipitation of metallic copper in the electrode separators, which resulted in short circuits.^{12,13} Small-scale cell tests⁷ and thermodynamic studies¹⁴ indicated that the stability of this phase can be decreased either by increasing the LiCl content of the electrolyte or by raising the operating temperature of

the cell. The formation of $\text{LiK}_6\text{Fe}_{24}\text{S}_{26}\text{Cl}$ can be entirely avoided by the use of an electrolyte that contains only lithium cations, e.g., LiF-LiCl-LiBr . Although cell performance can be improved considerably by increasing the lithium ion content of the electrolyte (either by increasing the LiCl concentration or by the use of an all-lithium-cation electrolyte), this increased lithium content results in a higher liquidus temperature or melting point for the electrolyte. Consequently, the cell operating temperature must be raised above 450°C . The present Eagle-Picher and ANL cells use the LiCl -rich LiCl-KCl electrolyte (68 mol % LiCl -32 mol % KCl), whereas the Gould cells use the all-lithium cation electrolyte (22 mol % LiF -32 mol % LiCl -46 mol % LiBr).

Various other sulfides, such as those of the transition metals (iron, cobalt, nickel), copper, and titanium, have been used in experimental cells with lithium-alloy negative electrodes and molten-salt electrolytes. This report, however, deals only with the Li-Al/FeS system.

1.3.3 Separator

The choice of electrode separator materials is severely limited in the case of Li-Al/FeS cells by the high lithium activity of the lithium-aluminum alloy in the negative electrode, the sulfur activity in the positive electrode, and the corrosiveness of the molten-salt electrolyte. Boron nitride (BN) and magnesium oxide (MgO) have both exhibited sufficient corrosion resistance under these conditions to serve as separator materials.¹⁵⁻¹⁸ The BN is made by the reaction of boric oxide (B_2O_3) with ammonia, followed by a heat treatment with nitrogen at 1700°C . Since the B_2O_3 can be drawn or spun into fibers prior to its conversion into BN , the BN product is available in a fibrous form. Magnesium oxide has not proved to be a satisfactory material in the form of solid bodies because impurities in the grain boundaries are attacked by the lithium.^{18,19} It can, however, be used in the form of a powder.

In the early work on Li-Al/FeS and Li-Al/FeS_2 cells, woven BN cloth separators were used satisfactorily, but the projected cost of this material in mass production was considered too high for commercial applications. The material also presented a problem in that the interstices of the fabric were too large to serve as a particle barrier; this necessitated the use of yttria (Y_2O_3) and zirconia (ZrO_2) felts at the electrode faces for particle retention. This problem was solved by the development of BN felt by the Carborundum Company²⁰ under a subcontract from ANL. This material is currently being used in the Eagle-Picher and ANL cells as electrode separators. Cost projections for the felt have indicated that the material can be manufactured in large quantities at an acceptable price.

Magnesium oxide separators are made by pressing high-purity powder into a solid plaque.^{16,21} Powder separators of this type are used in the present Gould cells. Although cells having powder separators have not yet achieved the average lifetimes of those with BN felt separators, they show promise of being fully satisfactory with some further development work. Cells with MgO powder separators show the potential for much lower cost in the near term.

Cells having the BN woven fabric separators have been subjected to extended vibration tests with no observable deleterious effects. Neither the BN felt nor the MgO powder separators have been subjected to vibration testing at the present time.

1.3.4 Other Cell Components

In the present Li-Al/FeS cell designs, the Li-Al electrodes are in direct contact with the cell housing, which must therefore be compatible with both the electrolyte and Li-Al alloys of varying composition. Corrosion studies have indicated that both low-carbon and stainless steels are suitable materials for cell housings.^{18,19} In most of the recent cells, the housings have been AISI-1008 or -1010 steel. Although these steels undergo a slow reaction with the aluminum in the electrode to form aluminum-iron intermetallic compounds, this reaction is not significant at cell operating temperatures below about 500°C.¹⁹

A wide variety of current-collector designs, including flat sheets, perforated facial sheets, honeycombs, foamed structures, and pressed or woven configurations, have been used in Li-Al/FeS cells. Low-carbon steels, stainless steels, and nickel are all potential current-collector materials for the negative electrode, with the low-carbon steels being favored because of their low cost, high electrical conductivity, and ease of fabrication.

In the positive electrode, the conditions are somewhat more severe due to the high sulfur activity of the FeS and the high electrical potential, particularly under overcharge conditions. Again, low-carbon steels are the preferred material for current collectors in the positive electrode. In-cell test data for low-carbon steel in the FeS electrode show an initial period of rapid corrosion, after which the rate drops markedly.⁵ This behavior is attributed to the generation of iron particles in the electrode matrix by intergranular corrosion, which tends to protect the current-collector structure from further attack. On this basis, tests were conducted in which iron powder was added to the electrode initially; this resulted in a significant reduction in the corrosion rate.²² These results indicate that the useful life of low-carbon steel can be extended from about one year to approximately five years under normal conditions of cell operation.²³ Preliminary tests with nickel and nickel-based alloys indicate that these materials may have the potential for a service life of as much as ten years.²⁴

The electrical feedthroughs currently being used in Li-Al/FeS cells (Fig. 1.3) are of a mechanical compression design, with a lower solid insulator of beryllia (BeO) and an upper one of alumina (Al₂O₃).²⁵ The actual seal, which is formed by a compressed bed of BN powder, is effective in preventing the escape of electrolyte from the cell, but it is not fully hermetic. A hermetic seal is possible with a brazed feedthrough. Different designs were tested unsuccessfully under conditions appropriate for FeS₂ cells, but success is more probable for FeS cells because of the reduced constraints on materials selection. The possibility of using a supplemental seal of solder glass or similar material in addition to the BN powder seal has been considered, but this concept has not been pursued fully.

REPRODUCED FROM
BEST AVAILABLE COPY

Fig. 1.3.

Feedthrough Design

ADVANTAGES

RUGGEDNESS
SIMPLICITY
FLEXIBILITY IN CELL ASSEMBLY
LIGHT-WEIGHT
LOW-COST POTENTIAL

DISADVANTAGES

INSUFFICIENT LEAK-TIGHTNESS
(ADD GLASS SEAL)

1.3.5 Cell Design

The first full-size cells to be built were of a cylindrical design, illustrated in Fig. 1.4.²⁶ These cells were 13 cm in diameter and 3-5 cm thick and had a central FeS electrode and two facing Li-Al electrodes (an arrangement often referred to as a "bicell"). They weighed from 1.0 to 1.7 kg and had theoretical capacities in the range of 112-150 Ah. Several Li-Al/FeS cells of this design were built and operated at ANL in the early 1970s.

The cylindrical bicells performed satisfactorily, and the design has been used subsequently at General Motors Research Laboratories for Li-Si/FeS₂ cells. However, the development efforts in recent years on Li-Al/FeS cells have been focused primarily on the development of rectangular, vertically oriented, prismatic cells (Fig. 1.5) because they can be stacked more compactly in a battery case, thereby improving the volumetric energy density. The prismatic design also simplifies the feedthrough somewhat. Prismatic bicells having theoretical capacities of 120-150 Ah have been fabricated by Eagle-Picher Industries,²⁷ Gould,²⁸ Rockwell International,²⁹ and ANL.³⁰

In 1978, ANL awarded a contract to Eagle-Picher for the development, design, and fabrication of a 40-kWh battery (designated Mark 1A).²⁷ Multiplate cells having three positive and four negative electrodes were developed for this battery. This multiplate cell was essentially the same as the electrodes of three bicells in a common housing, with appropriate changes in the bus bars and feedthroughs. All recent Li-Al/FeS cells have been of the prismatic, multiplate design.

Fig. 1.4. Cylindrical Bicell Design

Fig. 1.5.

Prismatic Bicell Design

1.3.6 Batteries

From time to time during the course of this program, small batteries consisting of up to ten cells were assembled and operated. In addition, the Mark IA battery, which consisted of two 20-kWh modules connected in series, was built and fabricated by Eagle-Picher. Each module consisted of 60 multiplate cells, in two rows of 30 cells each, connected in series and enclosed in a case of high-efficiency thermal insulation. During the initial test of this battery, one of the modules failed by short circuit resulting from leakage of electrolyte from some of the cells.³¹ The other module was unaffected by the event. As a result of this failure, the research and development effort in the program was redirected toward increasing the reliability and improving the performance of the cells (the Mark II program). Since that time, it is believed that significant improvements in both of these areas have been made.

1.4 Current Status and Outlook

The achieved performance of Li-Al/FeS cells might be summarized as: specific energy, about 100 Wh/kg at the 3-h rate; specific power, approximately 150 W/kg at 50% state of charge; and mean time to failure, about 350 deep-discharge cycles. However, higher values than these have been achieved by individual cells or small groups of cells. For example, five cells built recently by Eagle-Picher achieved a mean time to failure of 1023 cycles, with only a small capacity loss (0.022 %/cycle) and no observable change in coulombic efficiency.

With regard to electrical performance, a trade-off exists between specific energy and power. It seems reasonable to expect that a specific energy of 115 Wh/kg and a specific power of about 175 W/kg can be achieved for an optimized cell design. Design studies* carried out at ANL indicate that performance of 130 Wh/kg and 300 W/kg may be possible for Li-Al/FeS bipolar cells. A reduction in the projected manufacturing cost is also necessary. This may be achieved, at least in part, by the use of powder separators.

*H. Shimotake, unpublished, January, 1983.

2.0 STATE-OF-THE-ART CELL DESIGNS (W. E. Miller and J. E. Battles)

In the late 1970s, Eagle-Picher Industries and Gould Inc. were contracted to develop and fabricate electric-vehicle battery cells and a few small batteries. As part of this program, the contractors were required to fabricate groups of 12 or more cells of identical design (referred to as "status cells"), which were then tested at ANL. These cells were discharged at the 4-h rate and charged at the 8-h rate. The end of cell life was defined as a 20% loss of capacity or operation at less than 95% coulombic efficiency. Both contractors also fabricated groups of "development cells," which were tested at ANL to assess design improvements over status cells. To provide the contractors with recommendations on improving cell designs, ANL also conducted post-test examinations of their cells.

Described below are the state-of-the-art cell designs developed by Eagle-Picher and Gould as part of the Mark II program. Also given is the design of a cell developed by Eagle-Picher for fork-lift applications; this effort was funded by the U.S. Army Mobility Equipment and Research and Development Command (MERADCOM).

2.1 Eagle-Picher Cells

2.1.1 Electrode Composition

The compositions for the as-built electrodes in three groups of recent Eagle-Picher cells (Group IX, 12 status cells; Group X, 5 MERADCOM cells; and Group XI, 5 development cells) are shown below in Table 2.1. The values are for the materials which are pressed and do not include the current collector or the bulk electrolyte that is added to the cell after cell assembly.

2.1.2 Current Collector Design

The approximate weights and thicknesses of current collectors used in the three groups of Eagle-Picher cells are shown in Table 2.2.

There was essentially no difference between the current collector design for the Group IX status cells and the Group X MERADCOM cells. Figures 2.1 and 2.2 are representative engineering schematics of the collectors used in these cells. The positive current collector consisted of a solid perimeter frame with outside dimensions of 18.4 by 17.5 by 0.30 cm (7.25 by 6.9 by 0.12 in.). The frame was constructed of AISI 1010 bar stock. The internal structure consisted of one horizontal and two vertical cross members and six honeycomb sections. The cross members are fusion welded in position. The honeycomb sections are made from 5-mil ribbons of AISI 1010 steel. The honeycomb core size is greater than 0.3 cm (0.12 in.) and less than 0.94 cm (0.37 in.). The current collectors for the inner negative electrode are the same overall size as the positive collector. The perimeter frame in this case is made from a channel (opening outward) of 24-gauge AISI 1010 steel. The internal structure is a gridwork of eight vertical and three horizontal members. These members are fusion welded into place. Appropriate electrode tabs are welded to all perimeter frames so that, in cell assembly, the tabs mate with the internal negative and positive bars. The current collectors for the outer and inner negative electrodes are similar except for the weight and thickness.

Table 2.1. Electrode Compositions of Eagle-Picher Cells

	FeS, g	Fe, g	Li ₂ S, g	Electro- lyte, ^a g	Sulfur, Ah	Lithium, Ah
Positive Electrode ^b						
Group IX	198.7	11	9	33	131.6	10.5
Group X	182.0	20	16.5	30	130.2	19.3
Group XI	213	--	--	100	130.0	

Inner Negative Electrode^c

	LiAl, g	LiSi, g	Electro- lyte, g	Lithium, Ah	Neg. to Pos. Capacity Ratio
Group IX	230(46) ^d	--	32	159.8	1.29
Group X	210(46)	--	35	145.7	1.26
Group XI	144(46)	36	80	161.3	1.24

Outer Negative Electrode^c

	LiAl, g	LiSi, g	Electro- lyte, g	Lithium, Ah
Group IX	115(46)	--	16	80.0
Group X	105(46)	--	17	72.9
Group XI	72(46)	18(44)	40	80.7

^a53 wt % LiCl-47 wt % KCl. The electrodes are cold pressed from ground and screened powders. Particle sizes used in the electrodes were -40, +150 for LiAl, LiSi, and FeS; -40, +200 for Li₂S; -100, +300 for the electrolyte; and 100 mesh for iron.

^bThree such electrodes are used in each cell.

^cTwo such electrodes are used in each cell.

^dNumbers in parentheses are in units of at. %.

Table 2.2. Weights and Thicknesses of Eagle-Picher Current Collectors

	Positive		Inner Negative		Outer Negative	
	Wt, g	Thick., cm	Wt, g	Thick., cm	Wt, g	Thick., cm
Group IX	118	0.305	120	0.610	68	0.305
Group X	118	0.305	116	0.610	66	0.305
Group XI	129	0.330	184	0.635	96	0.318

Fig. 2.1. Eagle-Picher Current Collector for Positive Electrode
(dimensions in inches)

The current collectors for the Group XI cell are quite different from collectors for the earlier cell groups. The perimeter frame for the positive collector has the same overall dimensions as earlier cells except for the thickness (0.152 cm, 0.060 in.), which is one-half that of earlier cell collectors. A 5-mil-thick sheet of AISI 1010 steel is welded to one side of the perimeter frame. Two of these assemblies are then welded together, back to back so that the steel sheets are in a plane running through the center of the electrode current collector. The current collectors for the inner negative electrodes are essentially the same as those of the positive collector except for the overall thickness. The current collector frames for the outer negative electrodes are the same as the inner and have the steel sheet welded to one

NOTES:

1. CHANNEL FRAME THICKNESS 0.022"
2. RIBBON CROSS-SECTION
0.022" x 0.126" FOR PART NO. 1
0.022" x 0.250" FOR PART NO. 2
3. HORIZONTAL AND VERTICAL RIBBON
ENDS CAN BE BENT EITHER WAY

Fig. 2.2. Eagle-Picher Current Collector for Negative Electrode
(dimensions in inches)

side. However, in the outer collector this arrangement constitutes the entire collector, whereas in the inner negative collectors, these welded units are joined together to make up the total collector. Appropriate electrode tabs are welded to the frames as was the case with the Group X cells; these tabs are joined to the terminal connections for the negative and positive bus bars during assembly of the cell. The current collectors have no rib or honeycomb internal structure.

2.1.3 Particle Barrier Design

For the Group IX cells, the particle retainer for both the positive and negative electrodes consists of a 4-mil-thick photoetched screen of 304 stainless steel. This screen, which has 0.20 mm dia (0.008 in.) hole size and approximately 26% open area covering the faces of the electrode, is welded at the outer edges of the electrode to the perimeter frame of the current collector. An electrode band encloses the electrode perimeter; this is a channel-shaped section of low-carbon steel (5-mil thick) that encloses and covers the attachment weld of the particle retainer to the current-collector perimeter frame. The band is notched for the electrode tab.

For the Group X and Group XI cells, the particle retainer for both the positive and negative electrodes consists of two screens in series on each electrode face. The inner screen is a 300 series stainless steel of 200 mesh and has 0.074 mm openings; approximate thickness of the screen is 2 mil. This screen is welded to the current collector perimeter frame. The outer screen is 304 stainless steel sheet (5 mil thick) with photoetched holes, approximately 0.30 mm in diameter, on a square pattern with 0.56 mm spacing.

The photoetched sheet is welded at the edges to the current-collector perimeter frame. The edges of the electrode are enclosed in a perimeter band as in the Group IX cells. Figure 2.3 is a representative engineering schematic of the particle retention barrier for these cells.

Fig. 2.3. Eagle-Picher Particle Barrier (dimensions in inches)

2.1.4 Separator Investigations

Boron nitride felt is wet very poorly by the molten salt electrolyte if it is not treated with wetting agents. The wetting agent applied in the Eagle-Picher cell is magnesium oxide. The BN felt is formed and pre-treated in a wet process to obtain uniform distribution of the wetting agent in the finished separator. The pretreatment process is proprietary and is described here only in a very general way. To begin, one selects two BN felt sheets which have been inspected and found acceptable and which are slightly larger than the electrode size in length and width. The two sheets are placed together and steel spacer screens are placed on the outside, sandwich style. This sandwich is then clamped between restraint plates that have a fixed dimension between them, set by spacer sleeves on the clamping bolts. This arrangement provides porosity between the faces of the BN felt and the clamping plate. This assembly is then placed into a tank filled with magnesium nitrate aqueous solution. The tank is subjected to alternate vacuum and pressure in order to expel trapped gases from the felt and saturate it with the solution. After impregnation, the assembly containing the felts is allowed to drain and

is then placed in an oven at 450°C. The oven is slowly evacuated and held under vacuum for 3 h at 450°C. The assembly is removed from the oven and taken apart to retrieve the felts. The bare felt is changed by the above process from a soft, pliable material into essentially a stiff board. The bare felt boards are baked out further in a vacuum oven at 500°C to complete the conversion of the nitrate to oxide and to remove volatile materials. After this treatment, the felt boards are measured and weighed to determine the amount of MgO in the felt. Acceptable felts have an MgO content of greater than 5 mg/cm² of separator area and an overall thickness of 0.203 ± 0.025 cm (0.080 ± 0.010 in.) for the two-layered separator. Separators are trimmed to 18.57 by 18.80 cm (7.312 x 7.400 in.) for use in the cell.

2.1.5 Feedthrough Experimentation and Cell Assembly

The Group IX and Group X cells have essentially the same positive feedthrough. In the present cell designs, the positive feedthrough requires an electrical insulating seal; the negative feedthrough is part of the cell can, which is at the negative electrode potential. The positive electrode is, therefore, attached to the feedthrough, which must remain free of short circuits throughout the cell lifetime and must, at the same time, prevent electrolyte escape from the cell.

Testing of Group IX cells has been completed, with cell lifetimes ranging from 193 to 517 cycles. In no case was cell operation terminated because of feedthrough failure. In some earlier cell groups, cells having feedthroughs of an essentially identical design had logged over 1000 cycles without feedthrough failure. Testing of Group X cells has been completed, with cell lifetimes ranging from 849-1319 cycles. No feedthrough failures occurred in this five-cell group. The current reference feedthrough design is, therefore, judged to be adequate.

To achieve a lower cell resistance, a feedthrough that is larger in diameter than the reference design was developed by Eagle-Picher and installed on some Group XI cells. The new (1.3-cm dia) feedthrough had a (0.960-cm dia) copper core and required new closing equipment based on rolling the ends up the feedthrough housing instead of crimping the end of the housing, as was done for the smaller (0.8 cm dia) reference feedthrough (0.635-cm dia copper core). Development of this larger feedthrough is now essentially complete, but testing of cells with the new feedthrough of larger size is just beginning; thus, it is not known at this time if the transition to the larger size has been successful (long cycle life without leakage and no short circuiting). The description given below is for the smaller-diameter reference feedthrough, which is the proven reliable design at the time.

Figure 2.4 is a feedthrough assembly drawing. Figures 2.5 and 2.6 show how the positive and negative terminals relate to the cell bus bars and, hence, to the parallel-plate electrode tabs within the cell. On Fig. 2.4, it should be pointed out that part numbers 1, 2, and 3 are preassembled as a unit (more details of this are given on Fig. 2.5) and that part number 4 is welded to the cell can cover prior to assembly of the feedthrough, which occurs when the cell is closed. Cell assembly is accomplished by first aligning the stack of alternating layers of electrodes and separators in a fixture. The alignment fixture also positions the positive and negative terminals with attached bus bars correctly for welding these bus bars to

Fig. 2.4. Eagle-Picher Positive Terminal Feedthrough

Fig. 2.5. Relationship between Eagle-Picher Positive Terminal and Bus Bar (dimensions in inches)

Fig. 2.6. Relationship between Eagle-Picher Negative Terminal and Bus Bar (dimensions in inches)

the electrode tabs. Edge insulator strips (two layers of BN felt) and a strip of shim stock are wrapped around the bottom and two side edges of the electrode-separator stack, and the stack is then transferred from the alignment-terminal welding fixture into the cell can. A drawing of the stack assembly is shown on Fig. 2.7. A formed plastic block is placed on top of the stack assembly, and the stack is pushed to the can bottom in a mechanical press which forces down the plastic pusher block. The pusher block applies force on the current collector frames and prevents deformation of the separators as this force is applied. The positive bus bar insulator is lowered into place over the positive terminal. The cell cover (with positive feedthrough housing attached) is placed on the cell can. The lower insulator of the positive terminal is pushed into place, and the snap ring is set into the ring groove (see Fig. 2.4). The cell can cover is TIG-welded into place, and the seal weld is made between the can cover and the negative terminal. The cell is placed in the feedthrough closure press. In this press, the cell is supported on a shoulder in the feedthrough housing. This shoulder resists the pressing force which is applied to compress the BN powder and BN pellets and thus make the compression seal around the positive terminal rod. The snap ring prevents the pressing force from being transmitted by the positive terminal to the electrodes. After the last pressing force is applied to the compression ring, a second ram in the press crimps the top of the feedthrough housing to retain the compressive force when the press is released. Thus, the compression seal is achieved as part of the cell assembly procedure, without stressing the cell electrodes or can.

Fig. 2.7.

Stack Assembly of Eagle-Picher Cell

2.1.6 Cell Design and Electrolyte Loading Technique

Table 2.3 shows the weight breakdown of a typical Group IX cell. The cell is assembled "dry" and the bulk of the electrolyte is added as a liquid. The electrodes contain about 200 g of electrolyte, which is pressed as solid with the active materials; thus the total electrolyte in the cell is about 1250 g, which is 27% of the overall cell weight. Total active material weight (FeS, Fe, Li_2S , LiAl) is 1346 g, which is 29% of the total cell weight. Cell weight per unit of theoretical capacity is 11.73 g/Ah.

The cell is activated by filling the heated cell with molten electrolyte. The filling procedure begins by attaching a closed fill can, containing solid electrolyte, to the cell through a "Swagelock" coupling on the cell fill tube. The cell is bolted between restraint plates for the filling operation. This is done while the apparatus is at room temperature. The fill can is equipped with a heater coil and thermocouple. This cell-fill can assembly is placed in a heated well, and a vacuum-gas line is attached to the fill can. The assembly is evacuated to 0.1 atm (29 in. Hg) vacuum and the cell is brought up to a temperature of about 475°C. When the cell reaches this equilibration temperature, the fill can heater is turned on and its temperature is raised to greater than 500°C. When the fill-can equilibration temperature is reached, the vacuum source is shut off and argon is added to 1 atm. Three vacuum-pressurization cycles are applied to the cell-fill-can assembly over a period of about 1 1/2 h; this removes gases from the cell, which are replaced by molten electrolyte.

Table 2.3. Component Weights for Eagle-Picher Group IX Cell (theoretical capacity, 394 Ah)

	Component Weight, g
Positive Electrodes^a	
Current Collectors	354
Pressed Materials	755
Particle Retainers	132
Electrode Bands	<u>30</u>
Total	1271
Negatives Electrodes^b	
Current Collectors	360
Pressed Materials	786
Particle Retainers	188
Electrode Bands	<u>40</u>
Total	1374
Separators	140
Cell Liner Shim	20
Electrode Edge Insulators	12
Cell Container	410
Cell Cover (includes feedthrough housing)	140
Positive Terminal Assembly	105
Negative Terminal Assembly	80
BN Insulators, Positive Feedthrough	<u>20</u>
Total Dry Cell Weight	3572
Vacuum Loaded Electrolyte	1050
Total Cell Weight	4620

^aThese weights are for three-electrode assemblies.

^bThese weights are for two inner- and two outer-electrode assemblies.

During cycling, the active materials within the electrodes alternately expand and contract as the composition of the electrode material changes due to lithium transport. This alternating action not only causes electrolyte liquid to pump in and out of the electrodes, but also subjects the active material solids to forces that tend to disperse particles out of the electrode boundary. The tendency of the electrode particles to disperse is overcome by two approaches in this cell design.

One is the mechanical design of the particle retention system, which tends to keep the particles within the electrode by a filtering, trapping action. (The particle barrier design was discussed in Section 2.1.3.) The other means of overcoming particle transport is to adjust the active material loading density so that the particle-retention system is not unduly stressed by swelling forces in the electrode. This is expressed in terms of void fraction in the electrode space. The void fraction in this case is the ratio of space occupied by electrolyte to space occupied by electrolyte plus active electrode solids (current collector free). Values for void fractions typical of present Eagle-Picher cells are shown on Table 2.4.

Table 2.4. Void Fraction in Electrodes
of Group IX Cells

Cell Condition	Void Fraction ^a	
	Negative Electrodes	Positive Electrodes
As-Built	0.30	0.49
Fully Charged	0.28	0.53
Discharged ^b	0.47	0.12

^aCalculated assuming no electrode swelling. Void fraction in this case is that fraction of space in the active electrode which may be occupied by electrolyte at operating temperature. This includes the true volume of the hot electrolyte plus void volume.

^bDischarged to 86% sulfur utilization.

2.1.7 Cell Performance

One of the major problems in cell development has been the attainment of long cycle life. The approach has been to build a group of identical cells and then cycle them until failure. Results for the Group IX status cells are shown on Fig. 2.8. The mean time to failure (MTTF) at the 4-h discharge rate for the 12-cell group was 345 cycles, with a Weibull slope of 3.2. The longest life was 517 cycles and the shortest was 193 cycles. The average peak specific energy (peak specific energy for each cell is the average specific energy for cycles 6 through 10) for the 12 cells was 90 Wh/kg.

End of life defined by 20% loss of capacity or 5% loss of coulombic efficiency.
Numbers above bar show percent capacity loss.

Fig. 2.8. Cycle Life and Performance of Eagle-Picher Group IX Cells

Peak specific power, measured on one representative cell from the group, was 80 W/kg at 50% depth of discharge (DOD). For the 12-cell group, the standard deviation in discharge capacity (average 340 Ah) was $\pm 2.1\%$, indicating good uniformity in cell manufacture. The average capacity loss rate for this group was 0.024% per cycle.

The lifetime of 193–517 cycles was a significant improvement over the previous group of status cells, Group VI, which had the first cell failure at 100 cycles, the final cell failure at 201 cycles, and a MTTF of 138 cycles. As can be seen from Fig. 2.8, all of the cells failed due to loss of coulombic efficiency, which was normally indicative of formation of a short circuit; none failed due to capacity loss. The average capacity loss rate of 0.024% per cycle indicates an expected average life, based on 20% capacity loss, of over 800 cycles after cell shorting problems are solved.

As discussed in Section 2.1.8.2, the cause of failures for the Eagle-Picher Group IX cells was Li-Al electrode protrusions. For these cells, the number of protrusions had been greatly reduced over that of the Group VI cells by reducing the size of the openings in the negative electrode retainers from 0.33- to 0.23-mm dia. The modification increased the MTTF for the Group IX cells. For the Group X cells, the hole size was further reduced by placing a 200-mesh screen (opening size, 0.074 mm) between the photoetched retainer and the electrode face, as described in Section 2.1.3. This five-cell group attained a MTTF over 1000 cycles. This is a dramatic improvement in cycle life and is due to the improved particle barrier design. The rate of capacity decline for these cells is 0.02 %/cycle, which is the expected norm.

Lifetime testing of the Eagle-Picher Group XI cells was initiated recently, and test results are not yet available.

2.1.8 Post-Test Cell Examinations

Post-test examinations, which have been an important part of the Li-alloy/FeS battery development program, have provided valuable information for recommendations on design changes to achieve improved cell performance and reliability. The major objective of the post-test examinations has been the determination of cell failure mechanisms. Other objectives are the determination of the electrode microstructure; the distribution, uniformity, and utilization of active materials; and the in-cell corrosion of current collector materials. These post-test examinations include metallography, chemical analysis, X-ray diffraction, ion and electron microprobe analysis, and scanning electron microscopy.

2.1.8.1 Description of Examination Facility and Procedures

Because the cell materials (i.e., Li-Al alloys, LiCl-KCl electrolyte, and lithium-containing sulfides) react rapidly with the ambient atmosphere, the dissection of cells and the complete metallographic procedures (i.e., sampling, mounting, polishing, and examinations) are conducted in a helium-atmosphere glovebox facility constructed especially for this program. Samples for chemical, X-ray diffraction, and probe analyses are also prepared in this glovebox facility.

The metallographic glovebox facility is similar to one developed by the Chemical Technology Division of ANL several years ago for the physical handling of toxic materials. The helium atmosphere within the glovebox is recirculated through a purification train at the rate of 250 L/min. The pressure within the glovebox is maintained at 3 to 6 mm H₂O positive to atmospheric pressure. A sealed blower forces the helium to leave the glovebox and move through a room-temperature, activated-charcoal bed to remove organic contaminants. The helium then moves through a molecular sieve bed for moisture removal, and finally travels through an activated-charcoal bed at liquid-nitrogen temperature for oxygen and nitrogen removal. Regeneration of the activated charcoal and molecular-sieve bed is accomplished by heating these beds under a nitrogen purge. The cryogenic activated-charcoal bed is regenerated by heating the charcoal under a dynamic vacuum. Typical analysis of the helium in the glovebox showed 10 ppm O₂, 40 ppm N₂, and generally 2-10 ppm H₂O, depending on the relative humidity of the surrounding room air. Samples and supplies are transferred into and out of the glovebox through a vacuum port attached to one end of the glovebox.

The glovebox contains all of the equipment necessary for the preparation of samples for microscopic examination. A photograph of the complete facility is shown in Fig. 2.9. A small glovebox was fabricated to house the lower end of the microscope, which is used to examine the air-sensitive samples. This microscope is unique in that it was designed by the manufacturer* specifically for glovebox installation. To accomplish this, an optical repeater was positioned between the objective lens (inside the glovebox) and the ocular-photographic tube (outside the glovebox). The

*E. Leitz, Inc., Rockleigh, New Jersey.

Fig. 2.9. Photograph of ANL Glovebox Used for Post-Test Examinations of Molten-Salt Cells

incorporation of the optical repeater permits a gastight seal to be established between the lower end of the microscope (inside the glovebox) and the ocular-photographic portions of the microscope. The microscope enclosure is separated structurally from the main glovebox to eliminate vibrations generated by normal glovebox operations. Also the microscope is placed on a vibration-absorbing analytical balance stand to eliminate vibrations from the floor. This microscope enclosure is joined to the main glovebox with a 20-cm dia, leaktight, flexible coupling which connects the inert atmosphere between the two enclosures and allows sample movement to and from the microscope stage area. In addition to the normal photographic capabilities, the microscope is equipped with a closed-circuit color TV camera, a 30-cm display screen, and a video cassette recorder. This capability is a valuable aid because the display screen allows more than one person to observe the material microstructure simultaneously and because a recording of the microscopic examination is made.

When microscopic examination suggests further study, a sample can be removed from this facility and examined on such instruments as an electron microprobe analyzer, an ion microprobe mass analyzer, or a scanning electron microscope. Before a sample is removed from the glovebox for further analysis, its surface is coated with carbon or gold by the vacuum-deposition technique. This provides the necessary surface electrical conductivity for further analyses and retards the reaction with the atmosphere during the short period of transfer. This procedure is carried out entirely within the glovebox in a 30-cm dia bell jar containing evaporation fixtures and power-supply leads, along with an externally mounted vacuum system located beneath the glovebox.

The cells for post-test examination are received in various states of charge, ranging from fully discharged to fully charged. The resistance of each cell is measured to determine whether or not the positive electrode is electrically short circuited to the negative electrode. In cells with short circuits, the specific location of each short circuit is determined by placing a heat-sensitive liquid-crystal film on the surface of the cell and then applying a low voltage to produce a 5-10 A current between the cell terminals. In this manner, sufficient heat is generated in the short-circuited area to cause a color change in the film.* In severe cases, the short circuit area can be located by simply examining the cell for hot spots with the bare hand. After the general area of the short circuit is located, the top of the cell containing the electrical feedthrough is removed. The remainder of the cell is sectioned vertically for macroexamination, and the cross sections are photographed. A horizontal band saw located in a glovebox separate from the metallographic facility is used for dissecting the cells. After the cross sections are photographed, they are further dissected to obtain samples for metallography. These metallographic examinations give information on causes of cell failure, electrode morphology, and in-cell corrosion. Additional samples are selected for X-ray diffraction and chemical analysis. The samples for metallography are normally mounted in either a 3.2- or 7.6-cm dia mold, using an epoxy resin which cures at room temperature. The mounted specimens are ground on a revolving wheel with 20-cm dia SiC paper (80-600 grit). During the grinding process, the samples are either hand-held or loaded into an automatic multiple-sample grinding fixture. The final polishing, which depends on sample characteristics, is accomplished with either a 1- μ m diamond paste on a revolving wheel or with a 0.3- μ m Al_2O_3 powder slurry in a vibratory polishing apparatus in which the weighted sample moves freely across the vibrating, nonrotating surface. Two cutting fluids found to be compatible with the active materials of the Li/MS_x cell system are dimethyl silicone and dry kerosene. After final polishing and cleanup with toluene (rather than alcohol), the samples are transferred to the metallographic glovebox for examination. The results of these examinations are discussed in the following sections.

2.1.8.2 Cell Failure Analysis

Important functions of post-test examinations are to determine the causes of cell failure and to provide recommendations on cell design and assembly techniques that will eliminate these failure modes. Cell failure is generally indicated by a sharp decline in the coulombic efficiency, which is the manifestation of an electrical short circuit between the positive and negative electrodes. Combinations of macroscopic and microscopic examinations are utilized to identify the nature of the short circuits. Cell failure analysis was conducted on bicells (<100 Ah size) from the early cell development program and on multiplate cells (about 200 and 400 Ah capacity) from the Mark IA and Mark II programs. The results of the cell failure analysis for the bicells (~163 cells) and for the Mark IA multiplate cells were discussed in detail in the topical report ANL 80-130⁵ and are discussed here for purposes of comparison with Mark II cells.

*An alternative approach to locating a short circuit is to progressively section the cell until the short circuit is isolated in a small section. This section is then microscopically examined.

The principal causes of short circuit cell failures for the bicells from the early development program were (1) extrusion of active material from the edge of one electrode, because of inadequate mechanical restraint in the design or a mechanical defect, and subsequent contact of that material with the opposite electrode or the cell can, (2) cutting of electrode separator by the honeycomb current collector of the positive electrode,* (3) formation of metallic copper deposits across the separator from the Cu_2S added to the positive electrode for improved conductivity, and (4) difficulties in cell assembly such as misaligned electrodes. Failures caused by metallic copper deposits and cut separators were eliminated by removal of the Cu_2S additive to the positive electrode and by the addition of a retainer screen to both the positive and negative electrodes. Improvements in the quality assurance procedures decreased the cell failures caused by assembly difficulties.

For the Mark IA multiplate cells, the leading causes of short-circuit cell failures were (1) extrusion of active material from the positive electrode through a rupture in the retainer screen at the edge and the overlapping BN fabric cups (the separator) and subsequent contact of the active material with the cell can or the negative electrode and (2) the development of short circuits in the electrical feedthroughs because of a metallic bridge caused by corrosion initiated by electrolyte leakage through the BN powder seal.

In the Mark II program, progress in the fabrication and development of cells was determined by life tests at ANL for groups of 12 or more status cells. These cells contained BN-felt separators, whereas previous cells contained BN-fabric separators.

The failure analysis has been completed for the Eagle-Picher Group I, III, VI, and IX status cells, and the failure modes are summarized in Table 2.5. In all cases, failure occurred by an electrical short circuit between opposing electrodes, which is indicated by a decline in the coulombic efficiency.

Two major failure modes were identified for the Mark II status cells. The first is the formation of Li-Al protrusions that penetrate the BN-felt separator and contact the positive electrode. A typical example of a protrusion, with the porous microstructure typical of the Li-Al negative electrode, is shown in Fig. 2.10. This failure mode was most prevalent in the Group III, VI, and IX cells (23 of 36 cells failed by this mode), and it coincided with changes in methods of cell assembly and pretreatment of BN-felt separators. (Present BN felts are saturated with magnesium acetate or nitrate, compressed, and then pyrolyzed before assembly; previous felts were untreated and compressed during cell assembly.) Although the mechanism for the formation of Li-Al protrusion has not been completely elucidated, recent studies have shown that they can be prevented by simple mechanical design changes. The MTTF for the Group IX cells was significantly extended over that of the Group VI cells (see Section 5.2); this was accomplished by reducing the

*These electrodes did not have retainer screens such as those used in present cell designs.

Table 2.5. Failure Analysis of Eagle-Picher Group I, III, VI, and IX Cells

Failure Mechanisms	Number
Li-Al Protrusions across BN Felt Separator	26
Extrusion of Active Material from Ruptures in the Electrode Edge Retainers	9
Short Circuit in Feedthrough	1
Assembly Difficulty	3
Other	3
Not Identified	3
Not Examined	<u>5</u>
Total	50

Fig. 2.10. Penetration of BN-Felt Separator by a Li-Al Protrusion

size of the openings in the photoetched retainer screens (from 0.33- to 0.23-mm dia). Post-test examination of the Group IX cells showed that, although the failures were caused by protrusions, the number of protrusions was considerably less than that observed in the Group VI cells.

The second major cause of short-circuit failures in Eagle-Picher status cells was the extrusion of active material at the edge of the electrodes. An example of this failure mode is shown in Fig. 2.11, where the positive electrode material has extruded through a rupture in the edge retainer and contacted the negative electrode. This failure mode, which was caused by inadequate mechanical restraint at the electrode edges, was the predominant cause of short-circuit failures in Group I cells (9 of the 14 cells in this group failed by this mode). No additional extrusion failures occurred after a U-shaped channel was added to reinforce the mechanical restraint at the edges of both electrodes in the Group III cells. The formation of Li-Al protrusions was observed in Group I cells, and three cell failures were caused by these protrusions.

Fig. 2.11. Example of Cell Failure Caused by Extrusion of Positive Material through a Rupture in the Electrode Retainer

A Group III status cell was deep cycled for 1717 cycles (16,800 h) before failure due to a short circuit. Microscopic examination showed that the failure mode in this cell was migration of positive electrode material through the BN-felt separator and contact with the negative electrode. This condition was aided by iron deposits in the separator. The migration of positive electrode material into the separator can be prevented

by reducing the size of the openings in the photoetched retainer on the electrode face to about 0.12-mm dia. The iron deposits can be reduced or eliminated by lowering the charge cut-off voltage.

Post-test analysis was also done on the five Li-Al/FeS multiplate cells (Group X) that were fabricated by Eagle-Picher for the U.S. Army MERADCOM and tested for life cycle at ANL. The mean time to failure for the five cells was 1023 cycles (range: 849-1319 cycles). These cells had a fine mesh screen (200 mesh) in support of the normal electrode retainers to prevent the formation of Li-Al protrusions across the BN-felt electrode separators. Metallographic examination confirmed that the addition of the fine mesh screen had effectively prevented the formation of Li-Al protrusions.

In this group of five cells, the failure mechanism was the deposition of metallic iron in the electrode separator. The iron eventually bridged the space between the electrodes. Iron deposition, which had been observed in previous examinations of cells that had been overcharged, is known to be dependent on the charge cutoff voltage. Solutions to this failure mechanism are to reduce the charge cutoff voltage, to increase the electrode separation, and to add overcharge protection to the positive electrode.

The results of extensive cell failure analysis as discussed above indicate that the short-circuit failures are of mechanical origin. Appropriate changes have been made in the cell designs to correct those mechanical deficiencies. The post-test examinations have shown no indications of an intrinsic failure mode in the Li-Al/FeS system. Careful examination of the electrode microstructures, current collector materials, and BN-felt separator indicates that cell life greater than 2.5 y and 1000 cycles can be expected.

2.1.8.3 Stability of Electrode Microstructures

Extensive metallographic examinations were conducted to determine the electrode microstructure and the long-term stability of this structure. These studies also included determination of material distribution, lithium concentration gradients, reaction products, phase identification, and volume fraction of active materials vs. electrolyte. These latter studies are discussed in detail in ANL-80-130;⁵ the microstructure and microstructure stability are discussed below.

Important to the electrode morphology studies is the determination of the typical microstructure for a Li-Al electrode from a cell subjected to the normal test procedures (i.e., deep cycling at a 4-h discharge rate). Of equal importance is whether or not this typical microstructure is favorable for high utilization of active material (lithium) at the fast reaction rates necessary for a high-performance cell. Metallographic examinations of many cells (>200) demonstrated that the microstructure shown in Fig. 2.12 is common to all Li-Al electrodes and, hence, is considered typical. The Li-Al (white phase) forms a connected porous or skeletal structure within the electrolyte matrix (dark). The microstructure appears to have been formed in a random manner, without evidence of a directional growth pattern. The cell examinations included small test cells, engineering-scale bicells, and large

Fig. 2.12. Typical Microstructure of Li-Al Electrode

(400 Ah) multiplate cells. The Li-Al electrodes were fabricated in the charged, semicharged, and discharged states with thicknesses from about 4 mm to more than 10 mm. The electrodes were fabricated from (1) Li-Al powder, (2) aluminum wire plaques electrochemically charged with lithium, (3) cast solid plates of Li-Al, or (4) lithium foil combined with aluminum wire. This skeletal Li-Al structure has been confirmed by optical microscopic and scanning electron microscopic examinations. From an areal analysis of Fig. 2.12, the volume fraction of Li-Al was determined to be 0.5 to 0.6, with the remainder being electrolyte. This microstructure appears ideal for high utilization of the active material at high reaction rates because of the open, high surface area and small size of the skeletal structure. The open structure allows access of ample electrolyte to all parts of the electrode, and the small size of the skeletal structure (and high surface area) reduces the diffusion time for lithium into and out of the aluminum base.

This porous microstructure is formed early in the life of the cell, <25 cycles, and it remains relatively stable through the life of the cell as shown in Figs. 2.13 to 2.15. The composite photomicrograph in Fig. 2.13 shows a representative cross section of a Li-Al electrode from an Eagle-Picher status cell that was operated for 260 deep discharge cycles. The Li-Al alloy appears white, and the electrolyte appears gray in these photographs. The black areas are voids caused by incomplete filling of electrolyte. As shown, the center portion of this electrode was not fully utilized, as evidenced by some agglomeration (sintering) and unreacted particles of Li-Al. These cells (status cells) were fabricated with a 30% excess lithium capacity and, hence, some material would be expected to remain unreacted. The typical porous microstructure is evident except in the center portion of the electrode.

The composite photomicrograph in Fig. 2.14 shows the representative microstructure of the Li-Al electrode from a cell that was operated for 696 deep discharge cycles. This microstructure appears very similar to that observed in the cell operated for only 260 cycles (Fig. 2.13). The typical Li-Al microstructure observed in a cell operated for 1031 cycles is shown in Fig. 2.15. Comparison of the microstructures from these three cells, which were operated for 260 to 1031 cycles, demonstrates that the porous Li-Al structure remains relatively stable.

The microstructure of the positive electrode is much less complex than that of the negative electrode. However, this electrode is more complex in terms of the number of sulfide phases formed and the number of possible reaction paths. The reactions of the FeS positive electrode on charge and discharge are discussed in Section 1.3.2.

The typical positive electrode consists of solid particles (sulfide and metal) dispersed within a liquid matrix of the electrolyte. No evidence has been found to indicate that the sulfide particles are connected to form a permanent skeletal structure such as that found in the negative electrode. This is true whether the electrode is fully charged, partially charged, or fully discharged. The typical microstructure of an FeS electrode in the charged state is shown in Fig. 2.16. In the charged state, the electrode contains the least amount of solids (about 40 to 50 vol %); the opposite prevails in the negative electrode. The as-fabricated FeS electrodes are normally about 45-50 vol % FeS.

50X

200X

Fig. 2.13. Typical Microstructure of Eagle-Picher Li-Al Electrode after 260 Cycles

50X

200X

Fig. 2.14. Typical Microstructure of Eagle-Picher Li-Al Electrode after 696 Cycles

50X

200X

Fig. 2.15. Typical Microstructure of Eagle-Picher Li-Al Electrode after 1031 Cycles

Fig. 2.16.

Microstructure of an Electrode
Containing Mostly FeS (500X)

Figure 2.17 shows the microstructure of $\text{Li}_2\text{S} + \text{Fe}$ in a fully discharged electrode. Microscopic areal examinations indicate that the typical positive electrode is about 80-85 vol % solids ($\text{Li}_2\text{S} + \text{Fe}$) at full discharge. The volume fraction of solids is increased by almost a factor of two when an FeS electrode is discharged to $\text{Li}_2\text{S} + \text{Fe}$. The complete discharge (100% utilization) of an as-fabricated electrode with 50 vol % FeS, in the absence of any expansion, would lead to a fully dense electrode (i.e., no electrolyte). The formation of a dense layer of $\text{Li}_2\text{S} + \text{Fe}$ at the face of the electrode would seriously hinder the transport of lithium to the remainder of the electrode and thus limit the electrode utilization. In practice, this undesirable condition is largely avoided by expansion of the electrode. Microscopic examinations of numerous cells have shown no evidence that the microstructure of the positive electrode undergoes any changes with cycle life that would indicate instability.

The in-cell corrosion of current collector materials has been characterized using metallography, X-ray diffraction, and electron microprobe analyses. In FeS electrodes, intergranular corrosion of the low-carbon steel current collectors is initially very rapid, but it diminishes to a low value after 200-300 days. Studies have shown that the rapid intergranular corrosion can be eliminated by the addition of excess iron powder to the FeS electrode. (See Section 4.0.) In the negative electrode, examinations have shown that aluminum reacts with iron and nickel current collectors to form brittle, intermetallic compounds. This reaction occurs by the galvanic deposition of aluminum at the end of discharge, when the Li-Al alloy is depleted of lithium. This relatively slow reaction ($\sim 20 \mu\text{m}/\text{y}$) becomes diffusion limited after the initial stage, which is limited by the transport of

Fig. 2.17.

Microstructure of an Electrode
Containing only Li_2S and Fe
(500X)

aluminum to the surface of the current collector material. Studies have shown that this reaction can be reduced by maintaining excess Li-Al in the electrode. Also, protective coatings have been investigated as a means of preventing this corrosion reaction. Microscopic examinations of BN-felt separators have shown no detectable reaction with the BN after 2.5 y of normal cell operation. An unidentified reaction has been observed with the BN separator from cells operated in reversal. However, cell reversal occurred after the cell had developed a short circuit and cycling in a series array was continued.

2.2 Gould Cells

2.2.1 Electrode Composition

The composition for the as-built electrodes in recent Gould cells (12 Group II status cells and four development cells) is shown below in Tables 2.6 and 2.7. The values given are for the materials which are mixed and then cold pressed to make the electrode plaques and are for a single pressed plaque with dimensions of 12.45 by 17.0 cm (4.9 by 6.7 in.). Two of these plaques are required per electrode, one on each side of a center-line current collector. The positive materials are mixed, and then the material is heated to fuse the electrolyte. After cooling, the material is ground and ball-milled, and the electrodes are cold pressed from -40 mesh material. The negative materials are mixed, ground, and screened to -40 to +200 mesh powder, which is cold pressed to form the electrode plaque. The electrolyte composition is 68.4 wt % LiBr-22.0% LiCl-9.6% LiF.

Table 2.6. Composition of Positive Electrode in Gould Cells

	Group II Status Cells	Development Cells
Weight, g		
FeS	79.9	64.6
Fe	5.2	4.5
Mo	3.6	2.7
Electrolyte	39.2	16.3
Capacity, Ah	48.7	39.4
Pressed Thick., cm	0.188	0.132
No. Needed per Cell	4	6

Table 2.7. Composition of Negative Electrode in Gould Cells

	Group II Status Cells	Development Cells
Weight, g		
LiAl	65.6	41.8
LiSi	16.4	11.9
Al	—	2.6
Electrolyte	44.2	30.3
Li Composition, wt %		
LiAl	20.0	19.3
LiSi	43.6	47.5
Capacity, Ah	78.6	53.1
Pressed Thick., cm	0.394	0.259
No. Needed per Cell	4	6

2.2.2 Current Collector Design

The major electrodes of the cell are divided in half by a nickel sheet current collector (10-mil thick) in the center plane of the electrode. One pressed plaque, which contains no internal current collector structure, is placed on either side of the central current collector sheet to form the complete electrode. Fig. 2.18 shows the complete current collector, which consists of the collector plate and a current collector bus welded to the top edge of the collector plate on both sides, so that the plate is sandwiched between the collector bus. The tabs on the collector bus are located to match and mate with the bus bar of the cell feedthrough terminal. The thickness of the collector bus is approximately the same as that of the pressed electrode plaque to be used in the particular electrode.

The outer negative electrodes are half-thickness electrodes. The current collector sheet forms the back of the electrode, and the current collector bus is only on one side of this sheet, the same side as the pressed electrode plaque.

Fig. 2.18. Gould Current Collector (dimensions in inches)

2.2.3 Particle Barrier Design

Fig. 2.19 shows the particle barrier design used in Gould Group II status cells. Only one-half of the complete particle barrier is shown. The other half is essentially the same except for the x- and y-dimensions, which are each increased 0.089 cm (0.035 in.) so that the two halves slip together to encase the two electrode plaques and the center-plane current collector sheet. The edges of both halves are properly notched to accommodate the tab of the current-collector bus bars. The overlapped edges of the particle barrier halves on the completed electrode assembly are spot welded together. This prevents particle migration from the electrode edges. The inside dimensions of the particle barrier are 12.51 x 17.59 cm (4.925 x 6.925 in.). The x-dimension of the electrode plaque is 12.45 cm (4.900 in.), which allows 25 mils for tolerance match and slip fit of the electrode with the inner particle barrier half. The sum of the y-dimension of the electrode plaque (17.02 cm) and the current collector bus bar height (0.508 cm) allows 25 mils in the y-direction; this allowance also accommodates the fit between the particle barrier case and the electrode plaque. The holes in the face of the particle barrier are photoetched and are approximately 12 mils in diameter. In some of the more recent Gould cells, a 200-mesh stainless steel screen was added under the photoetched particle barrier.

2.2.4 Separator Investigations

The powder separators used in Gould cells are made by mixing MgO powder with crushed electrolyte at room temperature and then fusing the mixture. After cooling, the material is reduced in size, screened, and cold pressed. An attempt is made in the powder separator design to balance these factors in manufacture so that high-performance separators (i.e., low resistance to ion transport with long cycle life) that will not crack during cell assembly are produced.

Fig. 2.19. Gould Particle Barrier Design (dimensions in inches)

Table 2.8 shows the volume fraction of powder, electrolyte, and void in powder separators used in two recent cells: Cell P-82, a Group II status cell, and P-174, a development cell. The separator as-built thickness and weight were the same for both cells. In the cold as-fabricated state, the separators have a true void of around 25 vol % for the mixes used and for the 450-ton pressing force with 12-s pressing time. The solids used in the Group II cells were 72 wt % electrolyte and 28 wt % MgO. This combination gave an as-built separator of 19 vol % MgO and 57 vol % electrolyte. When this separator is heated to operating temperature, the electrolyte expands and fills most of the manufacturing void so that only about 5% residual void is left, assuming no overall expansion of the separator. In the development cell, the solids (MgO) content was increased to 35 wt % and the electrolyte was reduced to 65 wt %. This gave a higher density separator, 22 vol % MgO. The void volume at room temperature was about the same as that of the Group II cells, 25 vol %, so that the increase in MgO was compensated for by a decrease in electrolyte from 57 to 52 vol %. This decreased electrolyte leaves a larger "residual void" after heating. The residual void is a measure of the amount of electrolyte that can seep into the separator when it is in contact with the electrodes in the cell. This electrolyte would come from the cell electrodes. If the as-manufactured void were decreased by increasing the amount of electrolyte in the pressing mix, then on heating a cell, salt would flow out of the separator into the electrodes since the residual void would be less than zero. Ideally, the residual void should be zero. The higher percentage of MgO used in the development-cell separator was expected to increase the cycle life. This number was not increased more since a number much greater than 20 vol % solids in the separator will start to decrease cell performance.

Table 2.8. Volume Distribution in Gould Powder Separator Cells

Separator Comp. ^a	Temp.	Volume Fraction of Component	
		Group II Status Cell (P-82)	Development Cell (P-174)
MgO Powder	Room	0.19	0.22
Solid Electrolyte	Room	0.57	0.52
Manufactured Void	Room	0.24	0.26
MgO Powder	Operating	0.19	0.22
Liquid Electrolyte	Operating	0.76	0.69
Residual Void	Operating	0.05	0.09

^aSeparator size is 6.9 x 5.1 x 0.055 cm (2.7 x 2.0 x 0.022 in.); weight is 75 g.

2.2.5 Feedthrough Experimentation and Cell Assembly

Positive feedthrough parts for Gould cells are assembled as shown in Fig. 2.20. After proper alignment of component parts, a temporary spacer is placed between the terminal housing and the bus bar, and the terminal sleeve is forced into the bus bar. This compresses the BN powder. While under load, the terminal sleeve is welded to the bus bar, so the compressive force on the powder seal is retained after the external force on the sleeve is released. The temporary spacer which fixes the position of the terminal housing relative to the bus bar is removed to complete the positive feedthrough assembly.

Cell assembly starts by the fabricator stacking electrodes and cell separators as shown in Fig. 2.21. This creates a multilayered sandwich. Pressed MgO-electrolyte sheets are added to the bottom and side edges of the electrode-separator sandwich, and the assembly is slipped into the cell can. The sheets at the edges and bottom of the electrodes are similar to the pressed separators except for thickness, which is 75 mils for the edge insulators and 145 mils for the bottom insulator (separators are 55-mil thick).

The assembly containing the positive feedthrough and can cover is set in place, and the tabs of the positive electrodes are welded to the bus bar. The negative bus-bar terminal assembly is welded to the tabs of the negative electrodes. The other part of the cell can cover is slipped into place over the negative terminal, and then the entire can cover is seal welded into place. The negative terminal is seal welded to the can cover. The assembly of the cell is shown in Fig. 2.22. The cell is heated to degas the assembly, and then the exhaust tube is pinched off and welded shut to seal the cell. No liquid electrolyte is added during assembly of the Gould cell. The description given above is for the Group II status cells. The assembly of later development cells was slightly different because they had seven electrodes instead of five.

Fig. 2.20. Gould Positive Feedthrough

Fig. 2.21. Electrode-Separator Assembly for Five-Plate Gould Cell

2.2.6 Cell Design

Table 2.9 shows the weight breakdown for a typical Gould Group II status cell. The cell is assembled "dry" with no electrolyte added as liquid. However, electrolyte powder is pressed with other electrode materials in making the electrode. The total electrolyte in the cell is about 656 g, which is about 26% of the total weight. The total active material weight (FeS, LiAl,

NOTE: COVER WELDS MUST BE LEAK TIGHT

Fig. 2.22. Assembly of Gould Group II Status Cell

LiSi) is 648 g, which is also about 26% of the total cell weight. Table 2.10 shows the weight breakdown for Gould development cell P-174. The total electrolyte in this cell is 668 g, which is 22% of the total weight (this seven-plate cell is heavier than the five-plate Group II status cell). The total active material weight (FeS, LiAl, LiSi) in this development cell is 710 g, which is 23% of the total cell weight. Cell weight per unit of theoretical capacity was 12.86 g/Ah for the five-plate status cell, and this was increased to 13.08 g/Ah in the seven-plate development cell, P-174.

The Gould cells are built in an electrolyte deficient state. Table 2.11 shows the amount of void in the electrodes for both the frozen- and molten-electrolyte condition for the Group II status cells and the P-174 development cell. The significant difference is in the positive electrode, where the amount of electrolyte has been cut from 44 vol % in the status cell to 26 vol % in the development cell.

The Gould cells are built in the fully charged state so that the negative electrodes have the minimum void volume in the as-built state. The positive electrode, however, has the maximum void volume in the as-built state, and this void volume decreases as lithium moves into the positive electrode when the cell discharges. Table 2.12 gives the electrolyte distribution and the initial electrolyte loading in the cells for the as-built (charged) condition. The volume available does not indicate the total electrolyte in the cell, since about 9% of the total electrolyte is in an inactive portion of the cell (the electrode edge insulator). Table 2.13 gives the distribution for electrolyte as the cell discharges to 80, 85, and 90% of the sulfide theoretical capacity. Volume available for electrolyte may actually contain

Table 2.9. Weight of Components in Gould Group II Status Cell (194 Ah)

	Component Wt., g
Positive Electrodes ^a	736
Current Collectors with Attached Bus Bar	144
Pressed Materials	523
Particle Retainers	69
Negative Electrodes ^b	769
Current Collectors with Attached Bus Bar	224
Pressed Materials	505
Particle Retainers	40
Separators	303
Electrode Edge Insulators	89
Cell Can	362
Positive Feedthrough & Cover Assembly	108
Negative Terminal & Bus	44
Cell Cover	37
Electrolyte Powder Addition	40
MgO Powder Added to Top	6
Total Cell Weight	2,494
Electrolyte in Cell	
Positive Electrode	157
Negative Electrode	177
Separators	218
Electrode Edge Insulators	64
Powder Addition	40
	656

^aFour electrode plaques, two electrode assemblies.

^bFour electrode plaques, one inner and two outer assemblies.

either electrolyte or void because insufficient electrolyte is available to fill the void. The values given in these tables are based on the total volume in the active portion of the cells. Assuming no change in the electrode and separator dimensions during cycling, Table 2.13 shows that on the initial discharge electrolyte is forced out of the positive electrode. For instance, in the positive electrodes in the as-built status cell, there is 70.8 cm³ electrolyte in an available volume of 89.6 cm³. At 80% discharge, the available volume is reduced to 37.2 cm³; thus 33.6 cm³ of electrolyte must have been displaced from the electrode. The negative electrodes could accommodate this electrolyte. Initially, they contained 79.6 cm³ of electrolyte, and at 80% discharge, the available volume was 162.3 cm³, which is greater than the sum of the excess electrolyte from the positive electrode and the initial electrolyte loading for the negative electrode, 113.2 cm³. This transfer of electrolyte may be the only cycle of forced transfer of electrolyte, because

Table 2.10. Weight of Components in Gould Development Cell P-174 (236 Ah)

	Component Wt., g
Positives Electrodes ^a	862
Current Collectors with Attached Bus Bar	212
Pressed Materials	544
Particle Retainers	106
Negatives Electrodes ^b	944
Current Collectors with Attached Bus Bar	353
Pressed Materials	518
Particle Retainers	73
Separators	440
Electrode Edge Insulators	91
Cell Can	391
Positive Feedthrough & Cover Assembly	180
Negative Terminal & Bus	80
Cell Cover	51
Electrolyte Powder Addition	43
MgO Powder Added to Top	6
Total Cell Weight	3,088
Electrolyte in Cell	
Positive Electrode	98
Negative Electrode	182
Separators	286
Electrode Edge Insulators	59
Powder Addition	43
	668

^aSix electrode plaques, three electrode assemblies.

^bSix electrode plaques, two inner and two outer assemblies.

thereafter the space available for electrolyte in the electrodes is sufficient to handle displaced salt with cycling. Transfer of electrolyte by capillary action may occur, in which case there could again be forced transfer of electrolyte on cycling when the available space for electrolyte is less than the displaced electrolyte during cycling.

Development Cell P-174 had three positive electrodes and two full and two half-thickness negative electrodes. The Group II status cells had two positive electrodes and one full and two half-thickness negative electrodes. The feedthrough of the status cell is shown in Fig. 2.20. In the development cell, the copper core was increased to 1.3 cm (1/2 inch) dia. The size of the electrodes are the same in both cells, 12.45 by 17.0 cm (4.9 by 6.7 in.); thus for the same current, the current density in the development cell is two-thirds the value in the status cell. This lower current density is expected to increase utilization and more than compensate for the less favorable weight distribution in the development cell.

Table 2.11. Volume Fractions in As-Built Electrodes for Gould Cells

	Component Volume Fraction ^a			
	Status Cell		Development Cell P-174	
	Hot	Cold	Hot	Cold
Positive Electrode				
Active Solids	0.44	0.44	0.51	0.51
Electrolyte	0.44	0.33	0.26	0.20
Void	0.12	0.23	0.23	0.29
Negative Electrode				
Active Solids	0.62	0.62	0.64	0.64
Electrolyte	0.24	0.18	0.25	0.19
Void	0.14	0.20	0.11	0.17

^aThe designation "hot" is used to indicate the cell operating temperature range of 455 to 475°C; "cold" indicates the range of 25 to 300°C.

Table 2.12. Distribution^a of Electrolyte in As-Built Gould Cells (Charged State)

	Vol. Available for Electrolyte, cm ³			
	Status Cell		Development Cell P-174	
	28°C	460°C	28°C	460°C
Positive Electrodes	89.6	70.8	82.8	44.0
Negative Electrodes	126.0	79.6	118.8	81.8
Separator	103.8	97.9	144.2	128.6
Total	319.4	248.3	345.8	254.4

^aThe assumption was made that the dimensions of the electrodes and separator do not change with cycling. In practice, changes do occur. The data in this table provide a comparison of the electrolyte distribution under the condition of no volume changes in the electrodes and separator.

Table 2.13. Distribution^a of Electrolyte in Discharged Gould Cell as a Function of FeS Utilization

	Vol. Available for Electrolyte, cm ³					
	Status Cell			Development Cell P-174		
	80%	85%	90%	80%	85%	90%
Positive Electrodes	37.2	34.0	30.8	20.6	16.6	12.8
Negative Electrodes	162.3	167.2	171.6	168.7	174.5	180.2
Separator	103.8	103.8	103.8	144.2	144.2	144.2
Total	303.3	305.0	306.2	333.5	335.3	337.2

^aThe assumption was made that the dimensions of the electrodes and separator do not change with cycling. In practice, changes do occur. The data in this table provide a comparison of the electrolyte distribution under the condition of no volume changes in the electrodes and separator.

2.2.7 Cell Performance

Lifetime testing was completed for the second group of Gould status cells with MgO-powder separators. These cells were built with MgO pressed powder separators, instead of BN felt; were electrolyte deficient; used an all-lithium electrolyte (22 mol % LiF-31% LiCl-47% LiBr); and contained a mixture of lithium-silicon and lithium-aluminum for the negative electrode material. The test results are shown in Fig. 2.23 for operating temperatures of 455-475°C. The MTF at 455°C operation (the operating temperature recommended by Gould) was 268 cycles (Weilbull slope 3.1). The average specific energy for the 12-cell group was 80 Wh/kg at the 4-h rate. Standard deviation in the 4-h capacity (avg., 157.6 Ah) was $\pm 3.2\%$. Subsequent operation at higher temperature increased the MTF to 330 cycles (Weilbull slope 2.9). All cells at this initial operating temperature, 455°C, showed a 20% capacity loss. Increasing the temperature restored capacity to less than 20% capacity loss in all but two cells; in one of these two cells, short circuiting (coulombic efficiency dropped to <95%) coincided with the 20% capacity loss at 455°C. In ten cases out of eleven, raising the temperature restored capacity to a degree that added cycles were logged, the range being 5 to 260 added cycles. A 5°C temperature increase from the base temperature (455°C) was just as effective in restoring cell capacity as a 10°C increase; when capacity again declined after the initial temperature change, subsequent temperature change had little effect. The abnormal temperature sensitivity of these cells is attributed to the use of the high melting point (445°C) electrolyte. The average capacity loss rate at 455°C was 0.08% per cycle. When cycles were added by raising the temperature, the average fading rate decreased to 0.06% per cycle.

Figure 2.24 gives the results of specific energy measurements for the Group II status cells and the development cell P-174. A modest increase in specific energy (3.75% at 4-h discharge) was achieved in the

Fig. 2.23. Test Results for Group II of Gould Status Cells

Fig. 2.24. Specific Energy for Recent Gould Cells as a Function of Discharge Rate

development cell, which had seven plates instead of five and a larger feed-through (copper core of 1.3-cm instead of 0.63-cm dia) than the status cells did. Analysis of data from the Group II status cell and the development cell showed a 6% gain in utilization of active material for the latter at a 4-h discharge rate, but the poorer loading ratio (cell weight/theoretical capacity) prevented the full potential of this improvement to be reflected in increased specific energy.

2.2.8 Post-Test Cell Examinations

The facilities and procedures for the post-test examinations of Gould cells were the same as those discussed in Section 2.1.8 for the Eagle-Picher cells. The results of the post-test examinations on early development cells were discussed in the topical report ANL-80-130.⁵ The results of the cell failure analysis for the D-series cells and two groups of status cells from the Mark II program are presented below.

The Gould D-series cells used BN-felt separators and were assembled in the half-charged state, in which the negative electrodes are pressed from a blend of Li-Al alloy and Al powders are used for pressing the negative electrodes. The theoretical capacity of these multiplate cells (two positive and three negative plates) was about 200 Ah. The negative electrodes of LiAl + Al were pressed to a capacity loading density of about 1.3 Ah/cm³, based on the fully charged state (and no expansion). Post-test examinations showed that cell failure (short circuits) was caused by the formation of large, localized Li-Al agglomerates that severely compressed the opposing positive electrode. The stress and distortion caused by these agglomerates, in turn, caused the BN-felt separator to rupture. A typical example of this short circuit failure mode is shown in Fig. 2.25. As shown in the photomicrograph, the Li-Al is agglomerated and has pushed the retainer screen ahead of the protrusion. This behavior has been observed only in Gould D-series cells assembled in the half-charged state. Although the mechanism for the formation of these protrusions is unknown at this time, it appears that aluminum segregation within the as-fabricated electrode may be involved. A metallic support structure within the positive electrode would be expected to reduce the compression of this electrode, thereby reducing the growth of the protrusions and the subsequent rupture in the BN separator. This recommendation was incorporated into a new group of Gould D-series cells.

The cycle life for the twelve cells in this group of D-series cells ranged from a low of 42 to a high of 152 deep discharge cycles. The cells all failed because of short-circuit formation. Microscopic examination showed that the major cause of failure (7 cases) was the extrusion of positive electrode material either at the electrode edge or at the top of the positive electrode through a gap in the electrode retainer frame at the terminal. The longest-lived cell (152 cycles) failed because of a Li-Al protrusion such as that shown in Fig. 2.25. This occurred in spite of the honeycomb structure placed in the positive electrode of these cells and illustrates the significant force exerted by the formation of these Li-Al protrusions. The excessive expansion exhibited by the negative electrodes is discussed later.

Following the D-series cells, major design changes were incorporated in the Gould cells; namely, the BN-felt separator was replaced with an MgO-powder separator, the electrodes were pressed in the fully charged

Fig. 2.25. Example of Short Circuit Caused by Nonuniform Expansion of the Negative Electrode (which ruptured the BN-felt separator)

state, the negative electrodes were Li-Al-Si, and the "electrolyte-starved" concept was used. Two groups of 12 such cells each were fabricated and tested. The electrolyte-starved condition of these cells made it very difficult to conduct post-test examinations because of the severe breakup of the electrodes as the cells were dissected.

Post-test examination of the two groups of Gould status cells with MgO-powder separators showed only a single mechanism for the internal short-circuit failures. The failure modes are summarized in Table 2.14. Electrolyte leakage was observed in the feedthroughs of all cells. Two cell failures were caused by short circuits in the electrical feedthroughs. Although all of the cells in the first group and most of the cells in the second group failed because of capacity loss, cell operation was continued to the point of short-circuit failure (coulombic efficiency decline) except for two cells in the first group. In these cells, the predominant failure mode was short circuits caused by complete penetration of the MgO-powder separator by active material from the positive electrode, as shown in Fig. 2.26. The material from the positive electrode compressed the MgO powder, and its irregular advance resulted in numerous localized penetrations, which eventually contacted the negative electrode (300-500 cycles). This failure mode occurs because the mechanical properties of the present MgO-powder separators are inadequate for the containment of the positive electrode material. Elimination of this failure mechanism requires substantial improvements in the mechanical properties of the powder separator/retainer system. The compressive strength of the powder separator can be improved by increasing the

Table 2.14. Failure Analysis of Two Groups of Gould Status Cells with MgO-Powder Separators

Failure Mechanism	Number
Separator Penetrated by Positive Electrode Material	13
Short Circuit in Feedthrough	2
Capacity Decline	2
Not Examined	7
Total	<u>24</u>

Fig. 2.26.

Penetration of MgO-Powder Separator by Active Material from the Positive Electrode. (Major cause of short-circuit failures in Gould status cells.)

density of the fabricated separator and by using a blend of particle sizes rather than using all submicron particles. Also, the migration of active material from the positive electrode can be reduced significantly by using retainers with smaller openings, such as 0.1- to 0.2-mm rather than 0.33-mm diameter. It is important to recognize that the separator and retainer must be designed to complement and support each other.

Metallographic examination indicated that the capacity loss exhibited by these cells was probably caused by coalescence of the electrolyte into the positive electrode, the separator, and localized areas of the negative electrode. A net movement of electrolyte from the negative electrode to the separator and positive electrode appears to have occurred. Large areas of the negative electrode appeared isolated because the surrounding areas were essentially devoid of electrolyte. The microstructure of a Li-Al-Si electrode with 429 cycles is shown in Fig. 2.27. This area was better filled with electrolyte than most other areas. As shown in Fig. 2.27, the electrode has a duplex microstructure of the typical Li-Al porous structure with a dispersion of nodules. The porous structure was confirmed by X-ray diffraction and scanning electron microscopy/energy dispersive X-ray analyses to be a Li-Al alloy. Silicon, if present, was below the detection limit. Examination of the nodules, with secondary ion mass spectrometry, indicated that they are a Li-Si alloy possibly containing some aluminum. Also, X-ray diffraction analysis indicated a possible Li-Al-Si ternary alloy.

In summary, the data from the post-test examinations of both the Eagle-Picher and Gould cells showed that the failure mechanisms are of mechanical origin and can be easily corrected by design changes. Further, the microscopic examinations of the Li-Al and FeS electrodes from long-lived cells have shown that the electrode microstructures are stable with cycle life and that corrosion of the current collector materials is not a serious problem. Most important, these examinations have shown no indication of intrinsic behavior that would be expected to limit the cycle life of Li-Al/FeS cells.

50X

200X

Fig. 2.27. Microstructure of Li-Al-Si Electrode from Gould Cell P-88, 429 Cycles

3.0 CELL DEVELOPMENT

(E. C. Gay, T. D. Kaun, and F. J. Martino)

3.1 Objectives

This effort is directed primarily toward the development of engineering-scale Li-Al/FeS cells capable of meeting the requirements of electric automobile batteries. A major part of the cell development effort is the design, construction, and testing of engineering cells in a continuing effort to increase electrical performance and reliability and yet reduce the cost and complexity of the cells. In support of this effort, a number of research activities were devoted to studying problems encountered in the engineering cells and to testing possible improvements in components or procedures.

The cell development program includes the following: cell capacity-stabilization studies, cell and electrode characterization studies, resistance mapping studies, cell-polarization measurements, cell-swelling studies, cell-failure analyses, and cell post-test examinations.

3.2 Reactions of FeS Electrodes in LiCl-KCl Electrolyte

Five phases have been identified in the positive electrode of Li-Al/FeS cells with LiCl-KCl electrolyte.³²⁻³⁸ These phases are FeS, $\text{Li}_6\text{Fe}_{24}\text{S}_{26}\text{Cl}$ ("J-phase"), Li_2FeS_2 ("X-phase"), Li_2S , and Fe. The FeS phase corresponds to a fully charged electrode, the J- and X-phases are present at intermediate states of charge or discharge, and the Li_2S and Fe phases correspond to the fully discharged electrode.

Since the formation of J-phase is diffusion limited and the discharge of J-phase occurs at lower voltage than the discharge of X-phase, suppressing these reactions and accentuating the X-phase reaction is desirable for high electrode performance. One method found for suppressing the J-phase was to use an electrolyte with a high LiCl-to-KCl ratio.^{4,6} Discharge of FeS in LiCl-saturated (68 mol % LiCl) electrolyte at 425°C showed 80% thinner J-phase surface layers than discharge of FeS in eutectic electrolyte.⁴ Cell tests³⁹ also established the beneficial effects of LiCl-rich electrolytes on cell performance.

Phase studies were conducted with cells having eutectic electrolyte at temperatures of 480-500°C.³⁵ For a 20% discharged cell, X-phase was in equilibrium with J-phase and iron at 500°C. For a 43% charged cell at 490°C, X-phase and iron were dominant; only traces of J-phase were found. Near full charge at 490°C, FeS, J-phase, and iron were still the dominant phases. These high-temperature studies showed that increased temperature was not as effective in suppressing J-phase as was electrolyte with a high LiCl-to-KCl ratio.

In summary, high LiCl concentrations in the LiCl-KCl electrolyte tend to improve cell performance by suppressing the adverse effects of the J-phase. The required mole ratio of LiCl to KCl is approximately 2:1. This electrolyte accentuates the X-phase reactions, which are more reversible than the J-phase reactions.

3.3 Cell Fabrication Techniques

3.3.1 Eagle-Picher and Gould Cells

Cell designs and fabrication techniques for state-of-the-art Eagle-Picher and Gould cells are presented in Section 2 of this report.

3.3.2 High-Specific-Power Cell Designs

Cell designs and fabrication techniques required for high power cells are presented in Section 5 of this report.

3.3.3 ANL Electrode Fabrication

3.3.3.1 Negative Electrodes

The Li-Al electrodes evaluated at ANL generally contained 48 to 50 at. % Li and were prepared by (1) electrochemical formation in a substrate of compressed aluminum fibers, (2) pressing of powdered mixtures of electrolyte and pyrometallurgically prepared Li-Al, (3) vibratory loading of Li-Al powder into a porous metallic structure, and (4) slurry formation with Li-Al powders.

The initial porosities of the aluminum substrates used in the electrochemical formation were 40-80%, and the volume fraction of electrolyte in the Li-Al electrodes in the fully charged state was 0.20-0.70. Constraining plates are required during electrode formation to provide controlled dimensions and shape. Some electrodes of this type have shown poor utilization of the Li-Al farthest from the positive electrode; i.e., the wire form of the original substrate was retained after many cycles, but the Li-Al nearest the positive electrode was a highly porous, spongy structure.⁴⁰ With electrode thicknesses of about 0.3 cm, this electrode has shown high performance, but this fabrication technique is not considered to be practical for the preparation of large numbers of electrodes for charged cells. The electrochemical process may be used, however, for an uncharged cell that contains a porous aluminum structure as the negative electrode. The charged electrochemical Li-Al electrodes have provided a useful experimental tool for evaluation of various positive electrodes with a well-characterized negative electrode.

The pressing technique entails pressing mixtures of electrolyte and Li-Al powder to form plaques of the desired dimensions and electrolyte content. Metallic wire and honeycomb structures⁴¹ have been used as current collectors in these electrodes. The major advantage of this and other fabrication techniques in which pyrometallurgical Li-Al is used is the initial homogeneous loading of lithium in the electrode. However, large volume expansions have been observed after cycling with electrodes of this type when the electrolyte volume fractions were less than about 0.3.

In the vibratory loading technique, the Li-Al powder is ground to give an average particle size of 40-50 mesh, with less than 10% passing through a 100-mesh sieve. A porous (93-95%) iron structure is used, Retimet Type 30 Fe4.* Similar porous nickel structures have also been used.

*Dunlap Ltd., Aviation Div., England.

Vibratory loading of the Li-Al powder into the facial surfaces of flat, porous structures has been much more effective than edge loading, which has resulted in some segregation according to particle size differences. This effect has not been observed for facial loading. A typical vibratorily loaded negative electrode contains 49 vol % Li-Al, 6 vol % Fe, and 45 vol % void. This electrode is vacuum filled with electrolyte before operation of the cell. The high electrolyte content of this electrode (the originally 45 vol % void is replaced with electrolyte) accounts for good volume control during cycling. Slurry-formed Li-Al electrodes are discussed in Section 3.3.3.3.

The negative electrodes prepared by vibratory loading of Li-Al powder into a porous metallic structure have demonstrated the best current collection and volume control of all the negative electrodes evaluated. An example of the volume control that can be achieved is shown in the data published for Cell S-63.⁴⁰ The electrode in this cell was initially loaded with 44 vol % Li-Al alloy (pyrometallurgically prepared); the volume percent of Li-Al alloy in the negative electrode after cycling, as determined from computer scans, was 46.5 vol %.

3.3.3.2 Positive Electrodes

Charged and uncharged FeS electrodes have been fabricated at ANL by pressing, carbon-bonding, and vibratory-loading techniques. The different physical characteristics of the active materials and current collectors have required variations in the fabrication procedures. Some techniques that have appeared promising for charged positive electrodes have not been satisfactory for uncharged electrodes.

Since the iron sulfides have poor electrical conductivity, current collectors must be added to meet the power density requirements for an electric-vehicle propulsion battery and to obtain high utilization of the active material. Improvements in current collection have been sought by adding other metal sulfides that have good electrical conductivity.⁴² Additional current collection is provided by using porous current collector structures, screens, or plates as described below.

The vibratory loading technique for iron sulfide electrodes has been described previously.⁴³ This technique is similar to that described above for vibratorily loaded Li-Al electrodes. Attempts by an industrial contractor, Gould Inc., to develop suitable manufacturing techniques for electrodes of this type for ANL have met with limited success, as determined by performance of the electrodes.⁴¹ This result was in contrast to the high performance measured with similar electrodes fabricated at ANL. The major differences were in the techniques adopted by Gould, which were projected to be low-cost fabrication procedures. Gould used edge loading for the porous structures, whereas facial loading was used at ANL. Gould cells had problems with the containment of the iron sulfide powders in the positive electrode, and short circuited due to bridging of carbon cement between the electrodes. Steps were taken in the assembly of the ANL cells to reduce the chances for these problems occurring. As a result of these efforts, Gould recommended that the development of pressed or paste-type electrodes, which may be more suitable for manufacture of large numbers of cells, be pursued. Therefore, efforts were terminated on the development of vibratorily loaded positive electrodes.

Carbon-bonded positive electrodes appear to provide the high performance of vibratorily loaded electrodes fabricated at ANL and to have the potential of much easier manufacture. The carbon-bonded electrode⁴⁴ is formed from a three-component paste of active electrode material, a volatile, noncontaminating material, and a carbon cement. After the carbon cement is cured and the volatile material is driven off, a rigid, porous structure is formed in which the active material is held in a lattice of carbon. The carbon typically occupies about 10 vol % of the structure. Porosity is controlled uniformly to nearly any desired level by the quantity of volatile material in the paste. The material cost for this technique is low and fabrication is simple. Charged iron sulfide electrodes fabricated by this technique have demonstrated the potential for meeting the performance goals for off-peak energy storage and electric-vehicle propulsion batteries.

Fabrication techniques for pressed uncharged and charged iron sulfide electrodes have been described previously.^{45,46} These techniques generally involve preparation of a homogenous mixture of active material and electrolyte and compaction of this mixture onto a metal current collector. Uncharged FeS electrodes fabricated by this technique have attained high performance.⁴⁷

3.3.3.3 Fabrication of Improved Performance Electrodes

Prismatic test cells were fabricated with electrodes that have an area of 12.5 x 17.5 cm (5 x 7 in.) and thickness of 0.7-1.4 cm (0.3-0.5 in.). The active materials were contained within enclosures of steel perforated sheet (0.45-mm thick, 45% open area), which also served as the current collectors.⁴⁸ The Li-Al electrodes were fabricated by spreading a mixture of Li-Al (149-420 μ m dia particles) and carbon powder additive (3-5% of electrode volume) slurried with an organic solvent (e.g., petroleum ether, toluene) into the current collector.⁴⁹ The solvent was removed by vacuum before cell assembly. Capacity densities were 0.9 Ah/cm³ for the Li-Al and 1.4 Ah/cm³ for the FeS electrodes. These electrodes were assembled into cells with BN-felt separators (Kennecott Corp.). Molten-salt electrolyte (54 wt % LiCl-KCl, Anderson Physics Lab.) was introduced by vacuum infiltration in a helium-atmosphere glovebox. The improved performance demonstrated by these electrodes is discussed in Section 5 of this report.

3.4 Negative Electrode Development

Lithium is attractive as a negative electrode material for high performance batteries⁵⁰⁻⁵² because of its low weight per unit of electricity delivered, low affinity for electrons, and high electrochemical reactivity. However, containment of liquid lithium in the negative electrode over a large number of cycles has proven to be a problem because, in time, uncontained lithium bridges to the positive electrode, forming electrical short circuits. Another problem in cells with liquid lithium is that the ceramic separators and electrical feedthroughs have high corrosion rates. These problems can be avoided by the use of solid Li-Al alloys. In previous work by other investigators, excellent electrochemical performance of electrochemically prepared Li-Al alloy (composition range 17-62 at. % Li) in molten-salt systems was reported.⁵³⁻⁵⁵ The emf of a Li-Al alloy electrode is constant, about 0.3 V vs. a Li reference electrode, and independent of lithium concentration up to about 45 at. % Li in the alloy. The single voltage plateau enables the system to deliver good power throughout the discharge.

Metallographic examinations of many (>200) cells demonstrated that the microstructure shown in Fig. 2.28 is common to all Li-Al electrodes and, hence, is considered typical.⁵⁶ The Li-Al (white phase) forms a connected porous or skeletal structure within the electrolyte matrix (dark). The microstructure appears to have been formed in a random manner, without evidence of a directional growth pattern.

Metallographic examinations have shown that some degree of agglomeration of Li-Al occurred in multiplate cells of 150 to 400 Ah capacity. Agglomeration of Li-Al is a rare occurrence in bicells with negative electrodes less than about 6-mm thick. The agglomeration was classified according to the appearance of the microstructure. The agglomeration shown in Fig. 3.1 was classified as moderate. The center portion of the electrode has undergone densification and depletion of lithium. Both faces of the electrode show the typical microstructure, and the tarnished appearance indicates the charged state (i.e., β -LiAl). This type of agglomeration was observed in the inner negative electrode of many Mark IA multiplate cells, which had BN fabric separators. (Later Mark II cells had BN felt separators, which are more compressible than the fabric and thereby allow slightly more electrode expansion. As a result, little agglomeration was observed in the Mark II cells.)

Fig. 3.1. Negative Electrode Showing Complete Agglomeration in the Center of Electrode. (BN-fabric separator shown on each side of electrode is deficient in electrolyte.)

3.4.1 Mechanisms of Li-Al Agglomeration

A number of mechanisms have been proposed for Li-Al agglomeration in multiplate cells.

One hypothesis relates agglomeration to the initial loading of Li-Al in the electrode.⁵⁷ This hypothesis is based on the observation that the major difference between the negative electrodes in the bicells and multiplate cells is the density of the as-fabricated electrode--55 to 60 vol % LiAl in the bicell electrodes and 70 to 75 vol % LiAl in the multiplate electrodes. This dense loading of the electrode in the multiplate cell means that additional space is required to accommodate the electrode expansion as the typical microstructure of 50 to 60 vol % Li-Al is formed. The expansion of the Li-Al electrode is opposed by the previously expanded positive electrodes and by the restrainer hardware used to prevent expansion of the cell. This condition keeps the negative electrode under compression, which is conducive to sintering of most powder materials. However, out-of-cell experiments to initiate sintering in β -LiAl were unsuccessful, and out-of-cell sintering tests were therefore repeated with aluminum and with a two-phase (α -Al plus β -LiAl) material containing 7.5 wt % Li. Microscopic examinations showed significant sintering in the aluminum sample, but only a minor amount of sintering in the other sample. This behavior is consistent with the microscopic examination, which shows the agglomerated areas of the multiplate electrodes to be depleted of lithium.

Other hypotheses on the cause of Li-Al agglomeration have been proposed,⁵⁸ but none has been proven experimentally.

3.4.2 Effect of Li-Al Agglomeration on Cell Performance

Agglomeration in the Li-Al electrodes of Mark IA multiplate cells is believed to be a contributing factor to the greater capacity decline observed in these cells compared to bicells. However, the available data on capacity decline with cycling in Li-Al/FeS bicells indicated that, although agglomeration in the Li-Al electrode is believed to be a factor in capacity decline with cycling in the multiplate cells, the proposed mechanisms of agglomeration do not appear to apply to the tested bicells, which differed from the multiplate cells with respect to degree of cell restraint, Li-Al composition, and electrode arrangement.

The initial loading of Li-Al in the electrodes of the multiplate cells was suggested to be an important factor in agglomeration. Agglomeration was observed in multiplate cells with Li-Al loading densities of 70 to 75 vol %. The data shown in Table 3.1 indicate that Li-Al/FeS bicells with loading densities of 69-77 vol % Li-Al had low capacity decline rates (<0.03 % capacity decline per cycle). Thus, a high initial Li-Al loading density does not necessarily lead to high capacity decline rates in bicells. It was concluded that, although Li-Al agglomeration is believed to be a factor in increased capacity decline rates in multiplate cells, other factors must also play an important role.

3.4.3 Performance Characteristics of Li-Al Electrodes

Investigations were conducted⁵⁹ to determine the effects on performance of volume fraction of electrolyte in the electrode, electrode thickness, fabrication technique, lithium concentration in the Li-Al alloy, and type of current collector in the electrode. The solid lithium-aluminum electrodes were prepared by four processes: (1) electrochemical formation in

Table 3.1. Specific-Energy Decline Rate vs. Negative Loading Density in Li-Al/FeS Bicells

Cell Designation ^a	Vol. Frac. Li-Al in As-Fabricated Neg. Electrode	Specific Energy, Wh/kg	Discharge Rate, h	No. of Cycles Operated	% Decline in Specific Energy Per Cycle
M-8	0.69	59	3.7	180	0.02
KK-5	0.75	60	5	400	0.03
1A6	0.69	54	8	95	0.03
I3B2	0.70	65.6	10	163	0.08
I3B1	0.70	64.2	10	504	0.03
I3C2	0.77	62.4	9	504	0.004
1B4	0.60	60.9	9	1168	0.015

^aThese are all Li-Al/FeS bicells of different designs.

a substrate of compressed aluminum fibers, (2) electrochemical preparation of the Li-Al electrode by direct contact with lithium, (3) pyrometallurgical preparation of the Li-Al and pressed Li-Al and electrolyte powder electrodes, and (4) vibratory loading of pyrometallurgically prepared Li-Al powder into a porous metallic structure. The Li-Al electrodes tested had lithium compositions of 50-60 at. %, electrolyte volume fractions of 0.2-0.7, and thicknesses of 0.32-1.62 cm. The range of theoretical capacity density for the cells was 0.43-1.55 Ah/cm².

Improved utilization was achieved in Li-Al electrodes with nickel Retimet current collectors. Nickel Retimet porous foam electrodes vibratory loaded with Li-Al powder (electrolyte volume fraction of 0.46 and thickness of 0.8 cm) achieved 78 % and 66 % utilization at discharge current densities of 64 and 200 mA/cm², respectively. Electrochemically formed Li-Al electrodes (electrolyte volume fraction of 0.40 and thickness of 0.6 cm) with no metallic current collector achieved only 70% and 40% utilization at 64 and 200 mA/cm², respectively.

The effects of electrolyte content (20, 46, and 70%) on the performance of 0.32-cm thick electrochemically formed Li-Al electrodes were the following: (1) the electrode that contained 20 vol % electrolyte showed the highest utilization (86-83%) at current densities ranging from 64 to 190 mA/cm², (2) the capacity densities for the electrode containing 46 vol % electrolyte were about 27% lower than those of the electrode with 20 vol % electrolyte, and (3) the capacity densities for the electrodes with 70 vol % electrolyte were 66.5% lower than those of the electrode with 20 vol % electrolyte.

3.4.4 Testing of Cells with Negative Electrode Additives

Cells have been operated to evaluate the effects of the addition of a third metal to Li-Al alloy electrodes.⁶⁰ These cells contained negative electrodes in which pyrometallurgically prepared Li-Al and an additive were loaded into iron Retimet current collectors.

The elements added to the Li-Al electrode (85-90 Ah) included 5 wt % In, 8 wt % Ca, 8.6 wt % Sn, and 5 wt % Zn. The relative performance of electrodes containing these additives compared to a Li-Al baseline cell is shown in Table 3.2. Utilization and percent capacity decline per cycle were used as performance criteria. Electrodes with Ca and Sn showed higher utilization than the baseline Li-Al electrode. However, the capacity decline rate was unacceptably high for the Ca-additive electrode. Based on utilization and capacity decline rate, the Sn additive was the only one with promise for the development of an improved negative electrode.

Table 3.2. Performance of Li-Al-M/FeS Cells (discharge current density, 27 mA/cm²)

Negative Electrode Description	Theor. Capacity, Ah	Negative Util., %	Capacity Decline per Cycle, %/cycle
Li-Al	85	61	0.01
Li-Al-5 wt % In	85	57	0.04
Li-Al-8 wt % Ca	90	71	0.21
Li-Al-8.6 wt % Sn	86	73	0.035
Li-Al-5 wt % Zn	85	63	0.035

Negative electrodes of Li-Al-Fe have shown the greatest potential for improved performance in Li-alloy/FeS cells.⁶¹ The composition Li₅Al₅Fe₂ exhibits an electrode potential of about 0.2 V greater than that of Li-Al alloy electrodes. It was proposed that this negative electrode material would show reduced propensity for corrosion of iron cell components. These electrodes also showed evidence of a tendency to recharge uniformly with lithium, without generating high lithium concentrations at the negative electrode face.

3.4.5 Development of High-Performance Li-Al Electrodes

Studies have shown that capacity loss occurs in cells that utilize more than 60-65 % of the available lithium in Li-Al alloy electrodes. In an attempt to develop improved-performance Li-Al electrodes, bicells were built with central Li-Al electrodes of 65-Ah capacity and FeS electrodes of 120-Ah capacity.⁶² Carbon or AlFe powders (about 3-5 vol %) were added to the negative electrodes. A utilization of 82 % was measured with stable capacity for the

Li-Al electrode with carbon powder.⁶³ Addition of AlFe powder to the negative electrode did not enhance lithium utilization but did produce greater capacity stability than the Li-Al electrode with no additive.

Tests of bicells of the same design were used to compare the performance of slurry-formed LiAl electrodes (in Cells WR-9, -10, and -11) with the standard cold-pressed electrodes (in Cell WR-1). The results of these tests are illustrated in Fig. 3.2. The slurry-formed Li-Al electrodes (prepared with toluene or petroleum ether) all provided about 80% utilization with a 0.9 Ah/cm^3 loading. Additives of carbon or MgO powder showed further improvement in utilization and capacity stability. The slurry-formed Li-Al electrode with carbon powder additive was used for engineering development of negative-electrode-limiting cell designs (see Section 5.2).

Fig. 3.2. Cell Capacity and Utilization vs. Cycle Number of Cells with Slurry-Formed Li-Al Electrodes

3.4.6 Major Shorting Mechanisms for Li-Al Electrodes

The major short-circuiting mechanisms for the negative electrodes in Li-Al/FeS cells tested to date have been extrusion of active material from ruptures in the electrode edge retainers and Li-Al protrusions across BN-felt separators. As discussed in Sections 2.1.8 and 2.2.8, extrusion of active material from the electrodes was eliminated by encasing the electrode edges with a U-shaped channel frame. The Li-Al protrusions were eliminated by incorporating a fine mesh (100 mesh or lower) wire screen inside the normal negative electrode retainer.

The major emphasis in the development of the negative electrode has been improved performance rather than cycle life. Nevertheless, with the above mechanical design improvements, the Li-Al electrode has been operated for over 1000 cycles with good capacity stability.

3.5 Positive Electrode Development

A number of investigators at ANL have contributed to the development of positive electrodes for Li-Al/FeS cells. Shimotake reported on the development of uncharged positive electrodes.⁴⁷ He reported that the assembly of FeS electrodes in the uncharged state was desirable to reduce the volume expansion of the positive electrode on cycling.⁴⁵ Gay published work on the development of positive electrodes with porous-metal and porous-carbon current collectors.⁶⁴ Development of carbon-bonded positive electrodes was reported by Kaun.⁶⁵ Pressed positive electrode development with various types of current collectors (including sheet metal, honeycomb, wire and carbon powder, or metal powders) was also reported.⁶⁶ The reaction sequence in FeS electrodes operated in LiCl-KCl electrolyte was reported by Tomczuk.^{6,7,67} This result was determined by combining the data from phase studies, cyclic voltammetry experiments, and emf measurements. Reported below are the tests conducted to improve FeS electrode performance and lifetime.

3.5.1 Effect of Capacity Loading Density

The effects of positive-electrode loading density on cell capacity, specific energy, and specific power were investigated.⁶⁸ While maintaining the same electrode and cell dimensions and fabrication techniques, the theoretical capacity density of the positive electrode was increased by reducing the initial electrolyte volume fraction. The theoretical capacity density of the Li-Al negative electrodes was held constant, with an initial value of 0.9 Ah/cm³ (~30 vol % electrolyte).

Bicell test data indicated that cell performance was sharply affected by the initial theoretical capacity density of the positive electrode (Fig. 3.3). Utilization and achieved capacity are both important variables for improved specific energy. The highest achieved capacity (see Fig. 3.4) and specific energy (70 Wh/kg) were obtained with a theoretical capacity density of 1.4 Ah/cm³ in the positive electrode.

3.5.2 Effect of Additives

Interaction of FeS with the potassium in the LiCl-KCl eutectic, earlier found to have detrimental effects on cell performance, was reduced by the addition of Cu₂S to the FeS electrode.⁶⁹ Concentrations of up to 20 mol % Cu₂S have been used. However, post-test examinations of these cells indicate a movement of copper through the electrode separator,^{5,70} which created a short circuit.

Tests were conducted on bicells with additives of NiS (M-5) and carbon powder (M-6) as substitutes for the Cu₂S. For comparison, a baseline cell with a Cu₂S additive in the positive electrode (M-9) and a cell with LiCl-rich electrolyte (54 wt % LiCl-KCl) and no additive (M-8) were also operated. These tests were conducted in a compact cell design with BN-felt separator and hot-pressed electrodes.

Table 3.3 summarizes the design for the above cells. The cells were operated with a discharge cutoff voltage of 0.9 V and a charge cutoff of 1.69 V. The operating temperature was 450°C. Table 3.4 presents a summary of the performance data.

Fig. 3.3. Effect of Initial Positive-Electrode Capacity Density on Electrode Utilization

Fig. 3.4. Effect of Initial Capacity Density on Achieved Electrode Capacity

Table 3.3. Design of Li-Al/FeS Cells with Different Electrode Compositions

	M-5	M-6 (uncharged)	M-8 ^a	M-9 ^b
Positive Electrode Comp.	FeS-50 mol % NiS	FeS-16 mol % Cu ₂ S-C	FeS	FeS-16 mol % Cu ₂ S
Half Thickness, cm				
Positive	0.31	0.63	0.27	0.31
Negative	0.38	0.63	0.47	0.63
Theoretical Cap., Ah				
Positive	105	128	113	145
Negative	139 (55 at. % LiAl)	158 (55 at. % LiAl)	115	175
Theor. Cap. Den., Ah/cm ³	1.18	0.68	1.40	1.62
Cell Wt., kg	1.62	1.80	1.52	1.52
Cell Vol., cm ³	510	674	514	514

^aAll cells had LiCl-KCl eutectic electrolyte except M-8, which had 54 wt% LiCl-KCl (LiCl-rich) electrolyte.

^bThis cell had an improved current collector design over that of M-6, which incorporated a "wishbone terminal" in the positive electrode.

Table 3.4. Test Results from FeS-Electrode Additive Study

Cell Designation ^b	Additive	Disch. Rate, h	Temp., °C	Specific Energy, Wh/kg	Power Density, ^a W/cm ²	Specific Power, ^a W/kg
M-5	NiS	7	450	59	0.36	63
		4.5		43		
		4.5	500	54		
		2.5		48		
M-6	Carbon/Cu ₂ S	4	450	56	0.48	75
			500	67		
M-8 ^c	None	4	450	58		
		8		69		
M-9 ^d	Cu ₂ S	4	450	65	0.48	76
		2		50		

^a50% depth of discharge.^bAll of the cells contained LiCl-KCl eutectic electrolyte except cell M-8.^c54 wt % LiCl-KCl electrolyte (LiCl-rich).^dImproved current collector design.

Cell M-5 (NiS additive) shows no improvement in performance over FeS electrodes without additives. Improved performance at elevated temperature was expected, based on the smaller amount of J-phase present at temperatures around 500°C.

A comparison of the performance of Cells M-6 and M-9 shows that the benefits from the carbon additive were similar to those of a "wishbone terminal" current collector design in the positive electrode. The latter cell, while maintaining high power, attained higher specific energy.

The data obtained for Cells M-6, M-8, and M-9 were insufficient to determine whether cells with the LiCl-rich electrolyte perform as well as cells with the Cu₂S additive. A detailed study of the effect of the LiCl-rich electrolyte on the performance of the FeS electrode is presented in Section 3.11.

3.6 Capacity Stabilization

As mentioned earlier, the average decline in specific energy per cycle for a number of Eagle-Picher Mark IA multiplate cells was greater than that measured for bicells. The objective of these studies was to identify the causes of the higher energy-decline rate and to minimize this decline.

Table 3.5 presents the average performance of four series of bicells tested during 1978-79.⁷¹ The R- and M- series cells had BN-felt separators; the PW-series cells had MgO-powder separators; and the G-series cells had BN-fabric separators. Table 3.6 shows the average performance of four series of Li-Al/FeS multiplate cells and the production cells fabricated by Eagle-Picher for the Mark IA battery program. As can be seen by comparing Table 3.5 with Table 3.6, the average decline in specific energy for the multiplate cells was over four times higher than that for the bicells (0.25% per cycle vs. 0.06% per cycle.)

3.6.1 Capacity Loss Studies

The objective of this work was to determine how the electrochemical characteristics of the positive and negative electrodes of the Mark IA multiplate cells affect their capacity retention.⁷² The first step in this investigation was the development of a satisfactory reference electrode to permit measurement of the electrode potentials. This reference electrode utilizes the Ni/Ni₃S₂/S²⁻ half-cell.⁷³

A reference electrode was inserted into a Li-Al/FeS bicell (EPRE-1) with Mark IA electrodes. The theoretical capacities for the positive and negative electrodes of this cell were 97 and 108 Ah, respectively (negative-to-positive capacity ratio of 1.1). The measurements made with the reference electrode indicated that the capacity of the cell was limited by the positive electrode during charge and by the negative electrode during discharge. This cell showed a capacity decline rate of 0.15% per cycle. In a subsequent test, reference electrodes were used in a Li-Al/FeS bicell identical in design to EPRE-1 except that the theoretical capacity of the negative electrode was 216 Ah, a negative-to-positive capacity ratio of 2.2. This cell showed very little capacity decline over 55 cycles. The reference electrode

Table 3.5. Performance of Li-Al/FeS Bicells

Cell Designation	No. of Cells	Average Specific Energy, ^a Wh/kg	Average Discharge Rate, h	Average No. of Cycles Operated ^b	Percent Decline in Specific Energy	Percent Decline in Specific Energy Per Cycle
M-series ^c	6	54.3	3.5	252	24	0.09
R-series ^c	14	52.9	4.0	235	12	0.05
PW-series ^c	8	47.2	7.0	328	18	0.05
G-series ^d	7	55.8	7.6	107	5	0.05
Total	35	54.2	5.3	250	14	0.06

^aTypical value determined within the first 20 cycles.

^bReasons for termination include cell failure (short circuit or declining coulombic efficiency), as well as the end of scheduled testing.

^cFabricated at ANL.

^dFabricated at Gould Inc.

Table 3.6. Performance Summary for Li-Al/FeS Mark IA Multiplate Cells

Cell Designation	No. of Cells	Average Specific Energy, ^a Wh/kg	Average Discharge Rate, h	Average No. of Cycles Operated ^b	Percent Decline in Specific Energy	Percent Decline in Specific Energy Per Cycle
A-series	7	95.4	5	97	20	0.21
B-series	18	100.5	4	100	23	0.23
C-series	13	102.4	4	111	36	0.32
D-series	24	97.2	4	119	28	0.24
Mark IA Production Cells	21	100.7	4	122	26	0.24
Total	83 ^c	99.2	4	110	27	0.25

^aTypical value determined within the first 25 cycles (4-h rate).

^bReasons for termination include cell failure (short circuit or declining coulombic efficiency), as well as the end of scheduled testing.

^c65 cells tested at Eagle-Picher; 18 at ANL.

indicated that (1) the negative electrode was essentially unpolarized during cycling, and (2) essentially all the polarization developed by the cell was present in the positive electrode. Based on these observations, it was concluded that the negative electrode utilization is a factor in the capacity decline of multiplate cells.⁷⁴

Some of the 50 Mark IA cells tested for capacity stability were cycled with limited depth of discharge. The rate of capacity decline was correlated to the depth of charge--or more directly to the percent utilization of the negative electrode. Beyond 60% utilization of the Li-Al (46 at. % Li) electrode, the rate of capacity decline increased significantly, to 0.25% per cycle. Therefore, a direct approach to reducing the rate of capacity decline in multiplate cells is to increase the relative Li-Al electrode capacity to the positive electrode so that its percent utilization is limited. Increasing the negative-to-positive capacity ratio from approximately 1.0 for Mark IA cells to 1.3 produced this change. The next-generation multiplate cells, Mark II, were designed with a 30% increase in Li-Al electrode capacity--for a 1.3 negative-to-positive capacity ratio. Consequently, the rate of capacity decline for the Mark II cell was an acceptable $\leq 0.02\%$ per cycle, as shown in Fig. 3.5. With contributions from other modifications (i.e., LiCl-rich electrolyte and an increase from 46 to 50 at. % Li), as well as reduced negative utilization, the negative electrodes of Mark II cells exhibited stable capacity for utilizations up to 68% of the theoretical capacity of the Li-Al electrode.

Fig. 3.5. Negative Electrode Capacity Stability Related to the Extent of its Initial Utilization in Mark II Multiplate Cells

3.6.2 Parametric Studies of Capacity Stability

Parametric studies were conducted with Li-Al/FeS bicells (12.7 x 17.8 cm) to determine the effects of design variables such as electrode thickness, capacity-loading density, and negative-to-positive capacity ratio on capacity stability in bicells. It was hoped that these tests, conducted over a wide range of variables, would produce typical capacity decline rates such as observed in the multiplate cells and thus provide clues as to the causes of their capacity decline. Tests of the bicells were favored because of the greater ease of fabrication and lower cost of the experiments.

3.6.2.1 Effect of Capacity Loading Density and Electrode Thickness

To simulate the end-of-test conditions for electrodes in Li-Al/FeS cells, bicell MEXPl was constructed with electrode thicknesses approximating those of terminated M-series bicells.⁷⁵ The positive electrode was 0.9-cm thick with 1.05-Ah/cm³ loading density, and the negative electrode had a 1-cm half-thickness with 0.55-Ah/cm³ loading density. The negative-to-positive capacity ratio was 0.86. Testing of this cell provided information on the effect of lower loading density (typically 0.9 Ah/cm³ for the negative electrode and 1.4 Ah/cm³ for the positive electrode) and greater electrode thickness (typically 0.3-cm thick for the positive electrodes and 0.3-cm half-thickness for the negative electrodes) on the capacity stability of Li-Al/FeS bicells. Another major change in this cell was the use of LiCl-rich electrolyte instead of the LiCl-KCl eutectic. Finely powdered electrolyte added to the BN-felt surface was the only wetting agent used in this cell.

A plot of the data for positive-electrode utilization of Cell MEXPl at current densities of 37, 56, 74, 110, and 148 mA/cm² was found to be nearly linear, with a maximum of 69% and a minimum of 50%. Post-test examination of this cell revealed a separator that was electrolyte deficient. In spite of this deficiency, Cell MEXPl demonstrated stable capacity, with less than 0.015% decline per cycle. The results of this test indicated that the increased electrode thickness and lower loading density for Cell MEXPl had no significant effect on the capacity stability compared with the Mark IA bicells and multiplate cells, in spite of the poor electrolyte wetting of the separator.

3.6.2.2 Effect of Negative-to-Positive Capacity Ratio

Stable capacity is achieved in Li-Al/FeS bicells with negative-to-positive capacity ratios of about 1.3 and LiCl-rich electrolyte (54 wt % LiCl-46 wt % KCl).⁷⁶ Cell MNPl was operated to investigate the effect on capacity stability of a negative-to-positive capacity ratio of 1.0. A similar cell (M8NOHN) but with a negative-to-positive ratio of 1.4 was also operated.

Although both cells were discharged at 74 mA/cm², Cell MNPl showed about 30% lower utilization. This lower utilization was due to two factors: the negative electrode was limiting capacity on discharge, and Cell MNPl had less negative-electrode capacity than did cell M8NOHN. The cells had identical positive-electrode capacity. However, the capacity

stability of Cell MNPl over 160 cycles was less than 0.01% per cycle, with 73% utilization of the negative electrode. This capacity stability is an improvement over that observed for the Mark IA multiplate cells and bicells, which showed a capacity decline of about 0.15% per cycle at 73% negative electrode utilization. This improved performance is attributed to use of the LiCl-rich electrolyte in Cell MNPl.

3.6.2.3 Effect of Cycle Life

A study was conducted to determine the rate of capacity decline in Li-Al/FeS cells as a function of cycle life.⁷⁷ The effects of the electrolyte composition, the negative-to-positive capacity ratio, the electrode thickness, and the electrode capacity density were considered in this study. Thirty-three cells (18 bicells and 15 multiplate cells) were used in a multiple regression analysis of the cell specific energy. The range of cycle life used in this analysis was 28-1300 cycles. The following conclusions were drawn from this study:

- (1) A 50% decrease in the negative-electrode thickness resulted in a 50% decrease in the specific-energy decline at 200 cycles and a 25% decrease in the specific-energy decline over 800 cycles.
- (2) Changes in the positive-electrode loading density had little effect on the specific-energy decline with cycling.
- (3) A 40°C temperature increase resulted in a 50% decrease in the rate of specific-energy decline at less than 200 cycles.
- (4) Negative electrodes with 30% excess lithium capacity (negative-to-positive capacity ratio of 1.3) decreased the specific-energy decline by 15% over 800 cycles.

3.6.2.4 Nature of Capacity Loss With Cycling

A performance summary of the longest-operating bicell fabricated by ANL is presented in Table 3.7. At 350 cycles, nearly all of the cell's 6% capacity loss with cycling was recovered through the use of a lower constant current charge. The charge current density had been reduced from 37 mA/cm² (8-h rate) to 18 mA/cm² (16-h rate). The implication is that the lower charge rate may reduce lithium concentration at the surface of the negative electrode; the result is recovered capacity and more completely charged electrodes. Alternative cell charging methods, such as the use of a constant-voltage, current-limited charge, also resulted in successful capacity retention in this cell, earlier bicells, and a multiplate cell. As shown in Table 3.7, a return to the original constant-current charge, 37 mA/cm², resulted in the loss of 3% capacity (50% of the recovered capacity) by 500 cycles.

3.7 Resistance Mapping Studies

Resistance mapping measurements were made for state-of-the-art Li-Al/FeS cells to determine the resistance of the various current-carrying elements of

Table 3.7. Cycle Life Summary of Cell SM8F10

Cycle No.	Capacity, ^a Ah	Energy, ^a Wh	Coulombic Eff., %	Capacity Decline, %
50	74	87	98	3
150	74	88	98	3
200	74	87	98	3
250	75	89	99	2
300	72	85	98	6
350	77	91	99	0 ^b
400	75	89	99	2
450	75	89	99	2
500	74	88	98	3

^aRecorded at a discharge rate of 4 h (74 mA/cm²) and a charge rate of 8 h (37 mA/cm²); 460°C.

^bResult of charging at 16-h rate (18 mA/cm²) during cycles 343-362.

the cell. These measurements were expected to aid in the development of improved designs of these components that would provide lower cell resistance. Higher power cells with the lower resistance cell components could then be fabricated and tested.

Results of the resistance measurements for EPI Cell 111 (fabricated by Eagle-Picher) are shown in Table 3.8. The total cell resistance was 1.31 mΩ. About 49% of the cell resistance was external to the electrode stack. Of this resistance, about 18% was in the positive interelectrode connectors, 9% was in the negative interelectrode connectors, 9% was in the negative terminal, and 13% was in the positive terminal.

Results of the resistance measurements for an improved cell design (LCMP-8) with lower resistance components are shown in Table 3.9. This cell was designed and fabricated at ANL and has about the same capacity as EPI Cell 111. The objective was to reduce the cell resistance external to the electrode stack. This objective was accomplished. Of a total cell resistance of 0.47 mΩ, only 0.08 mΩ (17%) was external to the electrode stack. These improvements were made by (1) increasing the size of the cell terminals and using copper-cored negative and positive terminals, (2) using nickel interelectrode connectors and electrode tabs instead of steel as was used in EPI Cell 111, and (3) increasing the width of the electrode tabs from 1.0 to 6.4 cm. These improvements were later used in cells fabricated by Gould and Eagle-Picher.

3.8 Cell Polarization Measurements

The electrode performance of Li-Al/FeS cells has been characterized by using the dc-pulse technique and the dc-current-interruption, potential-relaxation technique.⁷⁸ The Ni/Ni₃S₂/S²⁻ couple was found to possess the best long-term stability for use as reference electrodes in Li-Al/FeS cells.⁷³ To investigate the potential distribution in engineering-scale

Table 3.8. Resistance Mapping Measurements on EPI Cell 111

Cell Component ^a	Resistance, m Ω
1 to 2	0.175
4 to 5	0.110
3 to 4	0.115
2 to 6	0.230
Electrode Stack (50% DOD)	<u>0.680</u>
Total	1.310

^aThe resistance measurement points are: 1. Positive Cell Terminal (6.3-mm-dia copper core). 2. Positive Inter-electrode Connector (3.2-mm-thick steel). 3. Negative Electrode Housing (9.9-mm-wide tab). 4. Negative Inter-electrode Connector (3.2-mm-thick steel). 5. Negative Cell Terminal (6.3-mm-dia steel). 6. Positive Electrode Housing (9.9-mm-wide tab).

Table 3.9. Resistance Mapping Measurements on ANL Cell LCMP-8

Cell Component ^a	Resistance, m Ω
1 to 5	0.05
2 to 4	0.03
Electrode Stack (50% DOD)	<u>0.39</u>
Total	0.47

^aThe resistance measurement points are: 1. Positive Cell Terminal (9.5-mm-dia copper core). 2. Positive Inter-electrode Connector (4.8 mm-thick nickel). 3. Negative Electrode Housing (6.3-wide nickel tab). 4. Negative Inter-electrode Connector (4.8-mm-thick nickel). 5. Negative Cell Terminal (1.3-mm-dia copper core). 6. Positive Electrode Housing (6.4-cm-wide nickel tab).

(>100 Ah capacity) cells, a Li-Al/FeS bicell was equipped with reference electrodes in six locations.⁷⁹ Large potential gradients were found across the faces of the electrodes of the cell, probably caused by nonuniform current distribution on the electrode surfaces developed during operation. These nonuniform current distributions create activity gradients, which cause local currents to develop within the working electrode. The presence of these local currents complicates the electrochemistry of the cell.

Electrode polarization measurements designed to study the voltage-loss processes that limit the specific power and energy of the Li-Al/FeS cell showed that cells with 30% excess negative-electrode capacity were limited on both charge and discharge by the electrochemical overpotential that develops in the positive electrode. Typical voltage-loss values during discharge and charge of intermediate-size bicells (theoretical capacity, 38 Ah; separator area, 106 cm²) are shown in Figs. 3.6 and 3.7, respectively.

Fig. 3.6.

Discharge Characteristics of Intermediate-Size Prismatic Bicell (LCS-4). (Lower two curves refer to the negative electrode, and upper two to the positive electrode. The dashed lines indicate a 1-ms relaxation, and the solid lines indicate a 15-s relaxation. The symbols η , I , and ASR are the potential, current, and area specific resistance, respectively.)

3.9 Thermal Cycling of Li-Al/FeS Cells

Thermal cycling studies were initiated to characterize the effects of temperature changes (room temperature to 460°C) on cell performance.⁸⁰ A summary of these results is presented in Table 3.10. The cells were of identical construction except for the treatment of the BN-felt separator with wetting agents. Numerous thermal (freeze-thaw) cycles were conducted over successive deep-discharge cycles. With the exception of the baseline cell containing the untreated felt (MFT0), the cells exhibited good performance stability, with as many as 68 thermal cycles for one cell (MFT2). The overall capacity losses were no greater than those shown by similar cells not subjected to repeated thermal cycling. The higher capacity loss observed for the cell with untreated BN felt indicates that poor wetting of the separator was a contributing factor to the capacity decline observed in the earlier Mark IA cells.

Fig. 3.7.

Charge Characteristics of Intermediate-Size Prismatic Bicell (LCS-4). (Lower two curves refer to negative electrode, and upper two to positive electrode. The dashed lines indicate a 1-m-s relaxation, and the solid lines indicate a 15-s relaxation.)

Table 3.10. Summary of Thermal (Freeze-Thaw) Cycling Tests of Li-Al/FeS Bicells

	Cell No.			
	MFT0	MFT1	MFT2	MFT3
BN felt treatment	Dusted with powdered LiCl-KCl	LiAlCl ₄	MgO	MgO
Thermal cycles	27	38	68	16
Deep discharge cycles	227 ^a	217 ^b	440	101 ^c
Capacity loss/cycle, %	0.095	0.034	0.020	0.027

^aVoluntary termination; test completed.

^bTerminated as a result of cycler malfunction.

^cTermination due to short circuit between electrodes (identified later by post-test examination).

Post-test examinations of the thermally cycled cells showed the following: (1) the BN-felt separators in cells which used wetting agents were completely filled with electrolyte, (2) there were no differences in the physical appearance of cells thermally cycled and not thermally cycled, (3) no cell failures

were caused by failures in the BN-felt separators, and the BN felt retained its integrity during thermal cycling, and (4) the electrode morphology of thermally cycled cells appeared to be the same as that for cells with no thermal cycling.

3.10 Cell Expansion Studies

Compact Li-Al/FeS cells require constraint on the faces and edges of the cells to prevent volumetric expansion of the electrodes. Studies were conducted to determine the magnitude of the restraining forces required and to determine the causes of cell swelling.

3.10.1 Experimental Cells

Elliot and Cooper⁸¹ studied the cell volume change by dilatometry. The maximum volume increase occurred on the first discharge. Electrode expansion studies were also conducted, and the maximum volume increase of the positive electrode occurred on the first discharge. In earlier reports, the phase associated with the large initial expansion was erroneously attributed to J-phase, which had been identified by metallographic and X-ray techniques.⁸² Later results showed that the expansion was due to formation of the voluminous Li_2S , which is the final discharge product.

Anderson and Shimotake studied the effect of restraining force on the expansion of small button-type (41 Ah) electrodes during cycling.⁸³ The apparatus used for these studies was described in an earlier report.⁸⁴ An applied load was varied from 19 kPa (2.7 psi) to 110 kPa (16 psi), and expansion and contraction of the electrodes were measured with a linear voltage differential transformer (LVDT).

Positive-electrode expansion tests were operated at discharge current densities of 15 and 50 mA/cm^2 , and the maximum expansion occurred during the first discharge. The extent of the expansion was found to be a function of both the discharge current density and the applied load. At a discharge current density of 50 mA/cm^2 , the minimum load required to restrain the electrode was 110 kPa (16 psi). When the discharge current density was reduced to 15 mA/cm^2 , the minimum restraining load was 69 kPa (10 psi).

Negative-electrode expansion tests were operated at discharge current densities of 15 mA/cm^2 . The negative electrode contracted during the first discharge, and a slight volume increase was observed after a few cycles.

3.10.2 Engineering-Scale Cells

A cell-swelling test apparatus was built by Eagle-Picher according to ANL specifications. Results of tests on Eagle-Picher multiplate (EPI) cells using this apparatus are shown in Fig. 3.8. The shapes of the curves for swelling force as a function of depth of discharge differed for the two cells shown (Mark IA and Mark II cell designs), but the magnitude of the peak force was about the same. The peak force is about 750 kg. Thus, for a 323- cm^2 electrode area, the pressure is 2.3 kg/cm^2 (32.9 psi).

No force data were available for the first discharge of the EPI cells during the break-in cycles. Thus, no data were available for comparison with results from the experimental cells described above (Section 3.10.1).

Fig. 3.8. Swelling Force of EPI Multiplate Cells Plotted as a Function of State of Charge

Conclusions drawn from post-test observations of the EPI cells and analysis of force data are as follows: (1) Cell edge forces were reduced by perforated metal containers and edge frames on the electrodes. (2) Face forces in the cells are at a maximum when the available electrolyte in the negative electrode is at a minimum and the negative electrode expansion is at the maximum (end of charge). (3) The maximum force is not at the end of discharge, as might be expected based on calculations. (4) There is no detectable effect of temperature on cell forces.

3.10.3 Post-Test Examination of Electrode Expansion

Electrode expansion has been observed in the post-test examinations of all bicells and multiplate cells. The electrode expansion within a given cell can be divided into three classes:

1. negative electrode expansion and positive electrode compression,
2. positive electrode expansion and negative electrode compression, and
3. expansion of both electrodes.

Class three behavior is most common; class one behavior occurs next most frequently. Class two is a rare occurrence and appears to be associated with porous negative electrodes such as those fabricated from pressed aluminum wire

and lithium foil. Obviously, the amount of electrode expansion depends upon a number of factors; however, the most important factors appear to be the as-fabricated electrode loading density (Ah/cm^3 or volume fraction of active material), percent utilization of the active electrode material, compressibility of the separator, and the degree of cell restraint used during its operation.

Engineering-scale cells have been examined to obtain quantitative data on the expansion of the electrodes. The data are summarized in Table 3.11 for Li-Al/FeS multiplate cells fabricated by Eagle-Picher for the Group I cells. The state of charge for each cell is indicated by the phases present in the positive electrode ($\text{Li}_2\text{S} + \text{Fe}$ for full discharge and FeS for full charge). The electrode expansion is reported as percent increase in thickness over the as-fabricated thickness for all electrodes (i.e., the positive electrodes, the inner negative electrodes, and the outer negative electrodes, which are normally one-half the thickness of the inner negative electrodes). The cells listed in Table 3.11 showed reasonable uniformity in electrode thicknesses. The data show that more expansion occurred in the outer negative electrodes than in the inner electrodes. This finding is consistent with the metallographic observation that the outer negative electrodes show less agglomeration than do the inner negative electrodes. This difference may be related to the fact that the outer electrodes are in contact with the cell can; consequently, they have better current collection. The data show a trend in the electrode expansion according to the state of charge; this is to be expected since the volume of the active material increases by almost a factor of two when the positive electrode discharges from FeS to $\text{Li}_2\text{S} + \text{Fe}$. Similarly, the volume of the negative electrode active material decreases during discharge. The data have been normalized, and the results are presented graphically in Fig. 3.9. The electrodes of the Eagle-Picher multiplate cells exhibited class three behavior, i.e., both the positive and negative electrodes expanded.

A similar analysis of the electrode expansion data for the D-series multiplate development cells fabricated by Gould Inc. showed that the electrodes exhibited class one behavior. As discussed in Section 2.2.8, these cells were assembled in the half-charged state with a high capacity loading density in the negative electrodes ($\sim 1.3 \text{ Ah/cm}^3$). The electrode expansion data are summarized in Table 3.12, and a graph of the normalized data is shown in Fig. 3.10. The positive electrodes showed a slight compression at full charge, but the negative electrodes exhibited severe expansion (60-70%). This electrode expansion is accommodated by the compression of the BN-felt separators. Post-test examinations have shown that the electrode expansion is related to the loading density of the as-fabricated electrode. For example, the Gould cells with the higher loading density (1.32 Ah/cm^3 , near 100% solids at full charge) showed excessive expansion (60-80%), whereas the Eagle-Picher cells with a lower loading density ($\sim 0.92 \text{ Ah/cm}^3$) showed moderate expansion (20-30%).

Cell examinations have shown that the negative electrodes can expand to occupy the available space, which results in electrodes containing a much lower volume fraction of Li-Al than that observed in electrodes from cells operated with mechanical restraint. Further, cell examinations have shown that continued operation after removal of the restrainer hardware results in significant cell expansion, as shown in Fig. 3.11. Two cells were fabricated identically and subjected to the same testing for the first 247

Table 3.11. Summary of Electrode Expansion and Cause of Failure in Eagle-Picher Group I Multiplate Cells

Mark II Cell No.	Cycles	Cause of Failure	Separator Thickness, mm ^a	Electrode Expansion						State at Termination of Operation
				Outer Neg.		Inner Neg.		Positive		
				cm, ^b	%	cm, ^b	%	cm, ^b	%	
-032	238	Protrusion	1.6	0.40	25	0.83	30	0.32	3	Charged
-033	696	Extrusion	1.5	0.38	19	0.69	8	0.43	39	Discharged
-036	1031	Iron sulfides across separator	1.3	0.50	56	0.82	28	0.38	23	Charged
-037	292	Protrusion	1.3	0.42	31	0.72	13	0.41	32	Discharged
-038	356	Extrusion	1.6	0.42	31	0.73	14	0.42	35	Discharged
-039	263	Extrusion	1.6	0.40	25	0.71	11	0.41	32	Discharged
-040	508	Extrusion	1.2	0.40	25	0.78	22	0.42	35	Semicharged
-041	804	Extrusion	1.4	0.41	28	0.86	34	0.36	16	Charged
-043	323	Extrusion	1.6	0.42	31	0.84	31	0.34	10	Semicharged
-046	559	Wrinkle in corner of electrode frame that cut separator	1.4	0.39	22	0.81	25	0.40	29	Charged
-049	263	Extrusion	1.5	0.41	28	0.72	13	0.40	29	Semicharged

^aThe separators were compressed to a 2.5-mm thickness in the as-assembled cell.

^bThe reported thickness is an average of the measured minimum and maximum thicknesses. As-fabricated thicknesses are: outer negative, 0.32 cm; inner negative, 0.64 cm; positive, 0.31 cm.

Table 3.12. Summary of Electrode Expansion and Cause of Failure in Gould D-Series Development Cells

Gould Cell No.	Cycles	Cause of Failure	Separator Thickness, mm ^a	Electrode Expansion						State at Termination of Operation
				Outer Neg.		Inner Neg.		Positive		
				cm, ^b	%	cm, ^b	%	cm, ^b	%	
D-76 ^c	75									
D-77	80	Extrusion	1.1	0.44	19	0.83	48	0.48	-9	Semicharged
D-78 ^c	42									
D-79 ^c	80									
D-80	99	Extrusion	0.9	0.48	78	0.95	69	0.52	-2	Charged
D-81	96	Extrusion	0.8	0.44	63	0.80	43	0.56	6	Semicharged
D-82	66	Extrusion	0.9	0.50	85	0.91	63	0.51	-4	Charged
D-83	152	Protrusion	0.9	0.43	59	0.82	50	0.56	6	Discharged
D-84	117	Extrusion	0.9	0.46	70	0.89	59	0.57	8	Discharged
D-85 ^c	66									
D-86	92	Extrusion	1.1	0.43	59	0.91	62	0.50	-6	Semicharged
D-87	50	Extrusion	0.9	0.44	63	0.85	52	0.56	-6	Semicharged

^aThe separators were composed of two layers of 2.0-mm-thick felt. The in-cell thickness is 1/4 of the original; the separator density increased to 32%.

^bThe reported thickness is the average of the measured minimum and maximum thicknesses. The as-fabricated thicknesses are: outer negative, 0.27 cm; inner negative, 0.56 cm; positive, 0.53 cm.

^cCell was not examined after testing.

Fig. 3.9. Electrode Expansion as a Function of Depth of Discharge for Eagle-Picher Group I Cells

Fig. 3.10. Electrode Expansion as a Function of Depth of Discharge for Gould D-Series Cells

a. Vertical Section of a Bicell Operated under Restraint for 247 Cycles

b. Vertical Section of a Bicell Operated under Restraint for 247 Cycles and Without Restraint for 20 Additional Cycles

Fig. 3.11. Effect of External Restraint on Cell Expansion

cycles with cell restraint (Fig. 3.11a). Restraint hardware was then removed from one cell and the operation of that cell was then continued for an additional 20 cycles (Fig. 3.11b). A comparison of the cross sections of the two cells showed that the negative electrodes expanded after the restraint hardware was removed. Prior observations had suggested that cells reach a steady-state condition of expansion early in cycling and remain constant at that state. These results, however, indicate that the expansion reaches a steady state only if a constant degree of restraint is maintained.

3.11 Effect of Electrolyte Composition on Cell Performance

3.11.1 Engineering-Scale Cells (>60 Ah Capacity)

Early Mark IA and ANL test cells used eutectic LiCl-KCl electrolyte and the metal sulfide additive, Cu_2S , in the positive electrode to improve electrode bed conductivity and to reduce the detrimental effects of J-phase formation.⁶⁹ Although the performance of the positive electrode was improved, the cells were limited in cycle life by copper deposition in the electrode separator, which eventually bridged the electrodes and created a mechanism for short circuits.⁸⁵ Electrolyte containing excess LiCl (68 mol % LiCl; 425°C liquidus) resulted in improved performance of small (15 cm²) cells.⁸⁶ Tests of a number of engineering-scale bicells demonstrated the benefits of LiCl-rich electrolyte.⁸⁷ Table 3.13 shows design characteristics of several Li-Al/FeS cells with LiCl-rich electrolyte; shown for comparison are a Li-Al/FeS cell with eutectic electrolyte (M-10) and one with eutectic electrolyte and 16 mol % Cu_2S in the positive electrode (M-12). The effect of current density on utilization in these cells is shown in Fig. 3.12. The cells with the eutectic electrolyte show about a 50% decrease in the positive electrode utilization as the discharge current density is increased from 40 to 110 mA/cm². The cell with the LiCl-rich electrolyte showed a decrease in utilization of only 10% over the same range of discharge current density. Thus, performance of Li-Al/FeS cells shows a large improvement in utilization at higher discharge current densities when the LiCl-rich electrolyte is substituted for the LiCl-KCl eutectic.

3.11.2 Small-Scale Cells (<10 Ah Capacity)

These studies were designed to investigate the effects of electrolyte composition and temperature on the utilization of the FeS electrode. The capacity of the FeS electrodes used in this study was about 6.7 Ah. Details of this work have been published in the literature.⁸⁶ The approximate electrolyte compositions (in mol % LiCl) investigated were 53, 58 (eutectic composition), 65, and 68 and are shown in Table 3.14.

The results of small-cell tests with these electrolyte compositions (Tables 3.15-3.17) indicated that, at a given current density, the utilization of the FeS electrode (1) increases with the LiCl content of the electrolyte, (2) is dependent on temperature when the electrolyte composition is equal to or less than 58.6 mol % LiCl, and (3) appears to be nearly independent of temperature when the LiCl concentration in the electrolyte is equal to or greater than 64.8 mol %. The effect of current density on the FeS electrode utilization is quite small except in the 52.9 mol % LiCl electrolyte system. Positive electrode utilizations as high as 90 % of theoretical were obtained at 450°C with electrolyte containing 67.8 mol % LiCl-32.2 mol % KCl.

Table 3.13. Design Characteristics of Selected Li-Al/FeS Bicells^a

	M-10	M-12	M-8	M-11	M-13	M-15	Status & M8NP
Active Material	FeS	FeS-Cu ₂ S	FeS	FeS	FeS	FeS	FeS
Thickness, ^b cm	0.61	0.62	0.59	0.63	0.63	0.63	0.63
Theor. Cap., Ah	115	121	113	132	105	88	120
Theor. Cap. Density, Ah/cm ³	1.40	1.41	1.40	1.61	1.29	1.0	1.40
Electrolyte Vol. Fraction ^c	0.50	0.43	0.50	0.42	0.56	0.62	0.50
LiCl Conc., wt %	44	44	54	54	54	54	54

^aFabricated in the charged state.

^bRefers to total electrode thickness; each negative electrode is typically 0.63-cm thick.

^cAll Li-Al negative electrodes contained 30 vol % electrolyte.

Fig. 3.12. Effect of Electrolyte Composition on Positive Electrode Utilization as a Function of Current Density

Table 3.14. Composition of LiCl-KCl Electrolytes Studied

Electrolyte System	Approximate Electrolyte Composition		
	wt % LiCl	mol % LiCl	Ratio of Li ⁺ /K ⁺
KCl Rich ^a	39	53.0	1.13
Eutectic	44	58.2	1.38
LiCl Rich ^b	51	64.0	1.77
LiCl Rich ^a	54	67.5	2.08

^a425°C liquidus.

^b400°C liquidus.

Table 3.15. Performance of Li-Al/FeS Cell EC-1

Electrolyte Composition, mol % LiCl	Current Density, mA/cm ²		Utilization, %	
	Charge	Discharge	450 °C	500 °C
58.2 ^a	50	50	47	66
	50	100	36	47
	100	50	41	58
	100	100	40	52

^aComposition determined by wet chemical analyses.

Table 3.16. Performance of Li-Al/FeS Cell EC-2

Electrolyte Composition, mol % LiCl	Current Density, mA/cm ²		Utilization, %	
	Charge	Discharge	450 °C	500 °C
67.3 ^a	50	50	86	90
	50	100	84	85
	100	50	78	80
	100	100	80	82

^aComposition determined by wet chemical analyses.

The findings that the positive electrode utilization in Li-Al/FeS cells is improved by increasing the LiCl content of the electrolyte have been confirmed by tests on cells of between 60 and 350 Ah capacity.⁸⁸ In these larger capacity cells, increasing the temperature above 450 °C improved utilization of the FeS electrode, even when the electrolyte contained about 67.5 mol % LiCl. This difference in performance from the smaller capacity cells of this study may be caused by precipitation of a solid-salt phase during cycling in the larger cell.⁸⁹

3.12 Cell Vibration Testing

Cell vibration tests were conducted at Eagle-Picher to determine the ability of lithium/iron sulfide cells for electric vehicles to withstand road vibrations.⁹⁰ The cell chosen for the vibration tests was a Li-Al/FeS₂ bicell. This cell contained the following design features to prevent the escape of active material from the electrodes: a positive particle barrier of 150-mesh molybdenum screen, FeS₂ sieved to -40 to +150 mesh, Y₂O₃-felt particle barriers on both positive and negative electrodes, a BN-fabric separator, and particle barriers of 115-mesh stainless steel screen on the negative electrodes. Of particular interest in this test were the effects of vibrations on the molybdenum-to-molybdenum weld joints of the positive electrode. The possibility of embrittled molybdenum weld joints made this a more severe test than would be the case for Li-Al/FeS cells in which the molybdenum is replaced with low carbon steel.

Table 3.17. Performance of Li-Al/FeS Cell EC-3

Electrolyte Composition, ^a mol % LiCl	Current Density, mA/cm ²		Utilization, %	
	Charge	Discharge	450 °C	500 °C
52.9	50	50	25	46
	50	100	16	28
	100	50	14	50
	100	100	14	40
58.6 ^b	50	50	53	70
	50	100	39	53
	100	50	43	61
	100	100	44	55
64.8	50	50	74	77
	50	100	73	74
	100	50	68	70
	100	100	68	71
67.8	50	50	91	90
	50	100	90	89
	100	50	83	84
	100	100	85	86

^a Compositions determined by wet chemical analyses.

^b Near eutectic composition.

Equipment used in the vibration testing included a Ling Model 275A Exciter, a Ling Model PP60/80 power supply, and an instrumentation console for controlling and monitoring the vibration levels. The cell was under constant surveillance with a charge/discharge cyler and voltage and current recorder during vibration testing.

The cell was placed in the test fixture and bolted to a mounting plate (Fig. 3.13). Under the mounting plate were three layers of Transite for heat insulation between the oven and shaker head.

The cell (designated EP-035) was vibrated at a level of 0.63-cm (0.25 in.) displacement amplitude (5-16 Hz) and 1.5 g (16-50 Hz), with a sweep time of 7.5 min. This level was continued until 1.37×10^6 vibrational cycles were accumulated on the cell; this is equivalent to over 12 years of expected road life. Vibration was performed on a schedule of approximately a 4-h cell discharge and no vibration during the approximately 8-h charging mode. Table 3.18 shows the cell cycling schedules during vibration.

Fig. 3.13. Equipment for Cell Vibration Tests

Table 3.18. Cycling Schedule during Vibration Testing of Cell EP-035

Cycle No.	Capacity on Last Cycle, Ah	Vibration
1-34	67.75	No
35-36	66.6	Yes
37-89	55.9	No
90-92	57.6	Yes
93-100	65.3	No

The test results showed no harmful or undesirable effects of vibration on the cell's electrochemical performance. In addition, the cell hardware was able to withstand the vibration levels imposed upon the cell. The capacity decline rate for Cell EP-035 (see Table 3.18) was 0.036% per cycle. The range of capacity decline rates for cells of this type with no vibration was 0.03 to 0.26 % per cycle. Thus, it was concluded that the vibration had no detrimental effects on cell performance and that the lithium/iron sulfide cells will withstand the vibrations due to road usage.

3.13 Driving Profile Characteristics

Simulated driving profile discharges representing the SAE J227a(B), SAE J227b(C), and SAE J227a(D) driving profiles have been tested on lithium/iron sulfide cells. All of the cells used in these tests had lower capacity, specific energy, and peak specific power than the state-of-the-art cells.

One of the earliest simulated driving profile tests was conducted in 1978 on an Eagle-Picher Mark IA cell, EPMP-071, which was part of the D-series of development cells that were fabricated before construction of the Mark IA battery. In these cells, the separator was woven BN fabric rather than the present BN-felt separators, and the FeS electrodes contained some Cu_2S additive. Further, the D-series cell contained smaller diameter and poorer conducting feedthroughs, smaller interelectrode tabs, and poorer current collectors than the present cells. After 94 discharge-charge cycles, this cell was subjected to driving-cycle tests on discharge cycles 95 and 96. During discharge 95, the SAE J227a(B) driving cycle, shown in Fig. 3.14 as the dashed line, was used. This cycle involves 19 s of acceleration at constant power, followed by a 19-s cruise period at constant power and a rest period of 34 s. During discharge 96, the acceleration period was at constant acceleration, rather than constant power, which requires a significantly higher power pulse (about 250 W, as opposed to 145 W maximum). This regime is shown as the solid line in Fig. 3.14. The computer-controlled cycler was set to limit the maximum current to 300 A, which was the limit for the controller to be used for subsequent tests in an electric van.

Fig. 3.14.

The SAE J227a(B) Driving Cycle (Solid Curve) and a Modified Driving Cycle with Constant Power Acceleration (Dashed Curve). (Both driving cycles yield identical vehicle speeds 19 s after initiation of acceleration.)

In both tests, the discharge cutoff voltage was set at 0.7 V. The cell underwent over 300 driving cycles in discharge 95 before it reached the discharge cutoff voltage. With the higher power demand for the constant-acceleration cycle of discharge 96, the 300-A current limit was reached after

about 200 cycles. Although the driving cycles were continued until the cell reached the discharge cutoff limit of 0.7 V, the cell was not meeting the power-pulse requirement during approximately the last 100 cycles. One would not expect to see this limitation with the present Eagle-Picher cells, since they have a lower resistance than the Mark IA cells (about 1.0 vs. 1.5-2.0 mohm).

Another test of interest was conducted in 1979 on a small battery module consisting of five Mark IA cells. The cycling history of this module is summarized in Table 3.19.

The module, which had a capacity of approximately 290 Ah (1650 Wh), was fabricated at Eagle-Picher and operated through ten deep discharge cycles prior to shipment to ANL, where it was subjected to an additional 26 cycles consisting of constant-current discharges of 70 A followed by constant-current charges of 40 A. Starting at cycle 27, five deep discharges were conducted on the J227b(C) driving profile. In these tests, 0.75 V was used as the discharge cutoff voltage for the individual cells. In the first of these five discharges (cycle 27), the module had a capacity of 294 Ah (1,653 Wh), and it produced 605 driving cycles before reaching the cutoff voltage. In the last one (cycle 31), it had a capacity of 283 Ah (1,576 Wh) and produced 575 driving cycles.

Following these tests, the module was connected in series with the lead-acid batteries in a Volkswagen Transporter electric van. This test was conducted primarily because of some concern about the possibility that there might be capacitive or inductive effects from the module that would be incompatible with the chopper/controller system in the van. However, that turned out not to be the case. The van was operated in a road test for about one hour under road-load conditions without regenerative braking. The battery performed very well during the 4.85-Wh discharge. When regenerative braking was incorporated into the system, short-duration current peaks caused the cell voltages to exceed the desired cutoff voltage for periods of milliseconds.

Up to this point, the module had been recharged only in the "bulk" charge mode, i.e., no equalization of the individual cells. Beginning with cycle 35, equalization charging was initiated. In this mode, the module was charged at 40 A, tapering to 3.5 A, after which the individual cells were charged to the cutoff voltage (1.60 V) at 3.5 A. At cycle 54, bulk charging was resumed, with the cutoff occurring when any one cell reached 1.60 V, and this mode was continued to cycle 60. Equalization was then attempted, with the module capacity reaching about 250 Ah. However, the capacity dropped rapidly with further cycling and the test was discontinued. When the module was disassembled, short circuits were found in the feedthroughs of two of the cells as a result of electrolyte creepage through the BN powder seals. The leaks were attributed to the rigid intercell connectors, which stressed the positive terminals during operation of the module. This effect has been observed in other units with the rigid interconnectors, and the problem was solved by Eagle-Picher's subsequent development of flexible interconnectors. Despite this problem, which shortened the life of the module, it appears that the driving profile tests had little effect on the system.

Another series of tests was conducted in 1979 and 1980 on Li-Al/FeS bicells (12-cm square) having capacities ranging from 70 to 100 Ah. These cells were built and tested at ANL, primarily to investigate the effect of

Table 3.19. Cycling History of Mark-IA 6-V Module Test

Discharge No.	Type Charge ^a	Capacity, Ah	Energy, Wh	Remarks		
D-3	Bulk C.C. @40 A	283	1637	Robicon Cyclor		
D-25	Bulk C.C. @40 A	266	1531	Robicon Cyclor		
D-27	Bulk C.C. @40 A	294	1653	605 Cycles J277b Cycle "C" to 0.75 V/cell		
D-31	Bulk C.C. @40 A	283	1576	575 Cycles J227b Cycle "C"		
D-32	Bulk C.C. @40 A	36	205	In VW Van, 1-h road test w/lead-acid in series		
D-35	Bulk C.C. @40 A Taper to 3.5 A Equalize @3.5 A	258	1485	Computer control using ANL charger/equalizer		
D-39	Bulk C.C. @40 A Taper to 3.5 A Equalize @3.5 A	264	1501	"	"	"
D-40	Bulk C.C. @60 A Taper to 3.7 A Equalize @3.7 A	268	1521	"	"	"
D-48	Bulk C.C. @40 A Taper to 3.7 A Equalize @3.7 A	266	1512	"	"	"
D-48	Bulk C.C. @40 A Taper to 3.7 A Equalize @3.7 A	260	N/A ^b	"	"	"
D-53	Bulk C.C. @40 A Taper to 3.7 A Equalize @3.7 A	262	N/A	"	"	"
D-54	Bulk C.C. @40 A	240	N/A	"	"	"
D-60	Bulk C.C. @40 A	208	N/A	"	"	"
D-61	Bulk C.C. @40 A Taper to 3.7 A Extended Equalization	250	N/A	"	"	"

^aC.C. is the constant current.^bN/A means no data were available.

current-collector resistance on the behavior of the cells under a driving-cycle regime. Most of these cells contained the LiCl-rich LiCl-KCl electrolyte, but a few used the LiF-LiCl-LiBr salt. The driving profile was a modified J227a(D) cycle, which involved the following power pulses:

<u>Power Level, W</u>	<u>Time Increment, s</u>
48	28
15	50
7	10

The driving profile was stored in a computer that drove the battery cycler until a cell became incapable of delivering the highest level power pulse at a cell cutoff voltage of 0.9 V. The best performance was about 115 driving cycles for one discharge, which corresponds to about 110 miles of driving, assuming a car equivalent to the ETV-1.* During ten consecutive discharges on this driving cycle, the number of driving cycles per discharge dropped from 97 to 95. Thus, the capacity decline was about 2% in the ten consecutive discharges. Another observation of interest in this test was that a significant improvement in the performance occurred when the conductivity of the current-collector material was increased. Post-test examinations of the cells showed no differences between these cells and the ones that had been subjected to standard cycle-life testing.

*An electric automobile developed by Chrysler with DOE support.

4.0 MATERIALS DEVELOPMENT (J. A. Smaga)

Efforts in this phase of the program are directed towards the selection and development of cost-effective materials for hardware components, i.e., the current collector, electrode retainer, separator, electrical feedthrough, and cell can. The selection criteria vary for these components because of their differing functions within the cell. Extensive testing, both in-cell and out-of-cell, is done to determine whether component materials have the compatibility, as well as the mechanical and physical properties, required for the intended application. Corrosion reactions and other forms of thermally assisted degradation are identified; in addition, the mechanisms of these reactions are determined and their severity quantified. Alternative materials, improved fabrication procedures, or electrode modifications are developed to ensure that cell performance and lifetime are not limited by the cell hardware.

4.1 Current Collector Materials for Li-Al Electrodes

The construction materials used for negative electrode hardware are required to possess adequate mechanical strength at elevated temperatures, ease of fabrication into the desired component structures, low electrical resistivity for current-carrying components, and compatibility with the active materials in this electrode. To varying degrees, most iron and nickel-base materials successfully meet the first three requirements. Unfortunately, these materials are also susceptible to a detrimental reaction with the aluminum present in the negative electrode. This reaction has been well characterized, and several approaches to minimize it have been investigated.

4.1.1 Galvanic Reaction Mechanism

Early in the development of the Li-Al/FeS cells, metallic aluminide layers were found to form on both nickel⁹¹ and low carbon steel.⁹² The brittleness of these layers undermines the structural integrity of components made from such materials, and the high electrical resistivity of intermetallics impairs cell performance. The source of this layer is a galvanic reaction, which becomes activated when the electrode is in or near the discharged state. During this portion of a cycle, the Li-Al alloy is depleted of lithium but remains in physical contact with the electrode hardware. Aluminum ions generated within the electrode are transported by the electrolyte and deposited on the components, and subsequently diffuse into the metal substrate.

Figure 4.1 shows a typical example of this reaction for a low-carbon-steel current collector. The reaction rates were measured for collectors from a number of cells operated in the temperature range of 435-450°C⁵ and are plotted in Fig. 4.2. The dependence of the galvanic reaction on the square root of the duration of cell operation indicates that this reaction is diffusion controlled. For this current collector design, the honeycomb ribs have a thickness of 125 μm . Complete penetration of the honeycomb structure is projected to occur in slightly more than two years.

(a)

(b)

(c)

(d)

(e)

Fig. 4.1. Aluminum Intermetallic Reaction Layer Formed on a Low-Carbon-Steel Current Collector from a Li-Al-Mg Electrode: (a) 300X Photomicrograph, (b) 500X Electron Microprobe Specimen Current Image, (c) Iron $K\alpha$ Scanning Image, (d) Aluminum $K\alpha$ Scanning Image, and (e) Magnesium $K\alpha$ Scanning Image

In out-of-cell tests, this reaction was found to be highly temperature dependent for both iron- and nickel-base alloys.⁹³ On low carbon steel, $FeAl_2$ is the predominant compound formed; on nickel, Ni_2Al_3 is formed. For stainless steel, which is commonly used for screen retainers, the reaction layer is composed of an inner layer with the stoichiometric form, $MeAl$, and an outer layer of $MeAl_2$, where Me stands for Fe, Ni, and Cr. Other tests indicate that maintaining excess β -LiAl in a uniformly utilized electrode (no macro-segregation into regions of α -Al and β -LiAl on discharge) is effective in suppressing the galvanic reaction.⁹⁴

The formation of the Al-rich reaction layer has been studied extensively for low carbon steel (AISI 1008 or 1010). As shown in Fig. 4.3, the deposition of aluminum onto a steel substrate has been found to obey an Arrhenius temperature dependence:

Fig. 4.2. Corrosion of Low-Carbon-Steel Current Collector by the Negative Electrode ($\text{Fe} + 2\text{Al} \rightarrow \text{FeAl}_2$)

Fig. 4.3.

Arrhenius Temperature Dependence for Aluminum Deposition with Couples of Al/LiCl-KCl/AISI 1008 Steel. (Q is activation energy.)

$$\text{Deposition Rate} = DR_0 \exp(-Q/RT) \quad (1)$$

where the activation energy, Q , is $21.4 \text{ kcal} \cdot \text{mol}^{-1}$ and the rate constant, DR_0 , is $5.2 \times 10^8 \text{ mg} \cdot \text{cm}^{-2} \cdot \text{y}^{-1}$ or $1.65 \times 10^{-2} \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. The data for the galvanic deposition of aluminum onto nickel, though incomplete, indicate that the deposition is analogous to that of steel.

The deposition of aluminum has a linear dependence on time and controls the overall rate of reaction only for a short time during the initial stage of layer formation. Beyond a certain transition time, the diffusion of aluminum into the substrate metal controls the overall reaction, and the reaction rate has a square-root dependence on time. At 475°C , the diffusion coefficients for AISI 1008 steel and commercially pure nickel were found to be 2.7×10^{-11} and $3.4 \times 10^{-11} \text{ cm}^2/\text{s}$, respectively.⁹⁵ Chromium in stainless steel and nickel-base alloys reduces the diffusivity of aluminum, but the higher electrical resistivity of these alloys makes them ill suited for use as current collectors.

4.1.2 Coatings as Aluminum Diffusion Barriers

Coatings have been evaluated as a method of preventing the formation of detrimental intermetallic layers. In addition to serving as a barrier to diffusion of aluminum into the substrate metal, the coating must be easily applied, compatible with β -LiAl, adherent to the substrate without appreciable diffusion of the coating into the substrate, and potentially low in cost. A number of coatings have been evaluated for these qualifications. Coating performance is influenced by both the coating composition and the method of application.⁹⁶

Thin, conductive ceramic coatings of TiC and TiN/TiC applied by chemical vapor deposition hold the most promise.⁹⁷ These coatings are compatible with β -LiAl and, as shown in Fig. 4.4, are highly effective barriers to aluminum diffusion, preventing FeAl_2 formation for a diffusion couple tested at 475°C for 1000 h. These coatings remain adherent to low carbon steel in spite of the tendency to develop fine cracks through the full thickness (10-20 μm) of the coating.

4.1.3 Galvanic Reaction in Li-Si Electrode

The occurrence of the galvanic reaction is not restricted to the Li-Al electrode. Investigators of the Li-Si electrode report that metallic silicides form at an even faster rate than metallic aluminides.⁹⁸ These silicon intermetallic layers have the same detrimental consequences. Negative electrode additions such as FeSi_2 can reduce the reaction rate by a factor of two or more. Titanium coatings have also been used as a protective barrier to the formation of these layers.

4.1.4 Materials for Cell Cans

The cell can is at the negative electrode potential but is not in direct physical contact with the active material. As a result, the formation of brittle, intermetallic layers is greatly ameliorated. Furthermore, the cell can is not a major current-carrying component and its conductivity

STEEL/TiC/Al DIFFUSION
COUPLE AFTER 1000 h AT 475 °C

Fig. 4.4. Scanning Electron Microscopy/Energy Dispersive X-Ray of Chemically Vapor Deposited Coating of TiC on Low Carbon Steel

is not an important consideration. Type 304 stainless steel is currently favored for this application by the industrial contractors because it is readily welded, retains its stiffness at cell operating temperatures, and has excellent oxidation resistance for cell operation in air.

The design of a battery module calls for the operation of a series of cells held under constraint in a sealed container with an inert cover gas. Under these conditions, low carbon steel is a suitable low-cost alternative for the cell can. Low carbon steel is also less sensitive to localized corrosion failures, such as stress-corrosion cracking and intergranular corrosion. Cell cans of low carbon steel are routinely used without difficulty for engineering cells built at ANL. One final consideration for cells used in a module is the electrical insulation of individual cells, which could be accomplished by applying an insulating ceramic coating on the cell cans. These coatings must be easily applied, adherent to the cell can, and resistant to spalling with thermal cycling. At present, little attention has been devoted to identifying suitable coating materials and methods of application.

4.2 Current Collector Materials for FeS Electrodes

Positive-electrode hardware materials have the same mechanical and conductivity requirements as their counterparts in the negative electrode. However, the compatibility requirements for these two electrodes are markedly different. The metals used in the positive electrode must be resistant to sulfidation by the various sulfides formed in this electrode. Secondly, candidate materials are required to have an oxidation potential safely above the charge cut-off voltage so that anodic dissolution of the component is avoided.

4.2.1 Accelerated Corrosion Tests

The metal sulfides present in the fully charged electrode represent the most corrosive state of this electrode.^{24,99} As a result, accelerated corrosion tests are conducted by immersion of test materials into an equal volume mixture of LiCl-KCl eutectic and FeS powder. Table 4.1 summarizes the test results for a representative selection of materials.

Among the group of commercially pure metals, molybdenum, nickel, and niobium have excellent corrosion resistance over the temperature range of 400 to 500°C. The latter two metals (and several of the iron- and nickel-base alloys) develop slight weight gains because the predominant reaction is the deposition of iron. The iron deposition rate is moderately low, and the reaction has not been found to be detrimental. Its occurrence is probably related to a substoichiometric concentration of sulfur in the FeS used in these tests. The sulfidation of copper becomes excessive above 450°C. A high-temperature reaction involving Cu₂O precipitates in non-OFHC grades of copper also results in severe internal porosity. Intergranular attack of Armco Electromagnet Iron results in the fallout of individual grains. The high reaction rates for this material appear relatively insensitive to temperature.

All of the nickel-base alloys and most of the iron-base ones have acceptably low corrosion rates. The three iron-base alloys with an ANL designation are experimental alloys;¹⁰⁰ the first number is the approximate Mo

Table 4.1. FeS/LiCl-KCl Compatibility Test Results

Material	Corrosion Rate, ^a $\mu\text{m/yr}$			Major Reactions and Comments ^b
	400°C	450°C	500°C	
Metals (commercial grades):				
Aluminum	1300	>6400	>6400	1
Copper (ETP) ^c	16	150	6100	2, 1(500°C)
Copper (OFHC) ^c	--	110	--	-
Iron (Armco)	440	460	410	3
Nickel	+13	+10	+49	4
Niobium	+11	+26	+24	4, 5
Molybdenum	1.8	3.1	10	6
Titanium	4300	5200	>5500	1
Zirconium	4700	5200	16000	1
Fe-base Alloys:				
1008 steel	64	230	270	3
Fe-2.25Cr-1Mo	11	20	58	7
ANL-5-0	10	12	86	6, 5(450-550°C)
ANL-10-20	+29	+9.1	+40	4
ANL-15-30	+30	+18	+30	4
Type 304 SS	3.8	3.6	9.0	6
Kovar	+26	+23	+11	4
Ni-Base Alloys:				
Hastelloy B	1.8	2.5	+11	6, 8 (500°C)
Hastelloy C	1.1	0.9	+18	6, 8 (500°C)
Inconel 617	0.2	2.3	+18	6, 4 (500°C)
Inconel 625	0.9	2.7	+4.9	6, 4 (500°C)
Inconel 706	--	4.6	--	6
Inconel 718	--	5.0	--	6
Incoloy 825	--	2.1	--	6
52 Alloy	+24	+23	+16	4
MP-35N	+35	+25	+74	4
Coated Steel Substrates:				
60 μm E'plated Cr	28	2.8	20	6, 9, 10
15 μm " Ni	--	+100	--	4, 9, 11(450-500°C)
25 μm " Ni	--	+ 22	--	4, 9
15 μm E'less Ni	+17	+ 44	+1.8	4, 9
25 μm " Ni	+27	+ 55	+87	4, 9

^aFor most materials the listed corrosion rate is the average for two or more tests conducted for 500 hours or more. Values preceded by a ">" indicate that complete reaction of the sample occurred in less than 500 hours. Values preceded by a "+" indicate a net weight gain.

^bThe reactions corresponding to the code numbers are listed below. Unless a code number is specified with a particular temperature, the reaction occurred at all three temperatures (400, 450, 500°C).

1. Severe sulfidation	7. Internal sulfidation zone
2. Internal porosity	8. Adherent sulfide-metal layer
3. Intergranular attack	9. Good coating adherency
4. Iron deposition	10. Partial coating breaches
5. Embrittlement	11. Substrate attack
6. Minor attack	

^cETP and OFHC are electrolytic tough-pitch and oxygen-free high conductivity grades of copper, respectively.

concentration and the second stands for the Ni content. Only low carbon steel has a moderately high rate because of intergranular attack. According to unpublished results, the performance of steels with higher carbon contents (up to AISI 1040 steel) is comparable to that of low carbon steel. The apparently low rate for the Crolloy composition, Fe-2.25Cr-1.0Mo, is deceptive, since an extensive band of internal sulfidation was noted for this alloy. Both electroless and electroplated nickel coatings have good compatibility. The major reaction is iron deposition, but at higher temperatures the thinner electroless nickel coatings develop breaches that allow some substrate attack.

In general, the effect of temperature is to accelerate the corrosion rate by an order of magnitude over this temperature range. Higher temperatures also accelerate other detrimental effects such as embrittlement. More detailed descriptions of these accelerated tests are provided elsewhere.^{93,99,101} Corrosion tests have also been conducted with metal sulfides that have been used as additives or alternatives to the FeS electrode. The corrosiveness of these metal sulfides increases in the following order: FeS, Cu₂S, CuFeS₂, NiS, FeS₂, TiS₂, NiS₂, and CoS₂.^{101,102}

4.2.2 Oxidation Potential Measurements

Candidate materials must also have oxidation potentials sufficiently above the charge cut-off voltage, which is typically 1.6 V for FeS cells. Table 4.2 lists the oxidation potentials for some common metals and alloys. The measurements are at 450°C for the metals¹⁰³ and at 425°C for the alloys.^{100,104} The elements above chromium have acceptable oxidation resistance, but brazes or alloys containing a high percentage of the reactive elements listed below Cr would be suspect. All of the listed alloys are sufficiently noble for FeS electrode applications. The composition of the electrolyte also influences the measured oxidation potential. An increase in the oxidation potential by as much as 70 mV occurs when low carbon steel is tested in electrolytes which are higher in lithium ion concentrations than the eutectic.⁹⁷ The presence of Li₂S in the electrolyte dramatically lowers the oxidation potentials of metals and alloys^{34,105} because metal sulfides can now form. Fortunately, in an actual positive electrode, the formation of Li₂S always occurs in conjunction with fine iron particles, and the overwhelming surface area of these particles shields the hardware components from significant attack.

Table 4.2 also lists the apparent oxidation potentials at 450°C for steel substrates with both electroplated and electroless nickel coatings. These are average values for multiple tests. These coating potentials are lower than the potential for nickel and reflect the presence of defects or the development of breaches during testing, which allow substrate attack of the type shown in Fig. 4.5. The presence of 10% phosphorus in electroless nickel is an additional factor which lowers the apparent oxidation potential of this material. In tests of coating reliability, electroplated nickel protects 99.5% of the substrate, whereas electroless nickel offers a 98% protection level.¹⁰⁶

Table 4.2. Oxidation Potentials of Metals and Alloys
in Molten LiCl-KCl Eutectic

Metals	Oxidation Potential, V vs. β -LiAl ^a	Alloys	Oxidation Potential, V vs. β -LiAl
Gold	3.22	Hastelloy B	2.31
Molybdenum	2.41	Hastelloy C	2.31
Silver	2.27	Inconel 617	2.27
Nickel	2.21	Inconel 625	2.24
Niobium	2.21	Inconel 718	2.23
Copper	2.06	Incoloy 825	2.22
Cobalt	2.02	Inconel 706	2.20
Iron	1.84	ANL-10-20	2.18
Chromium	1.59	52 Alloy	2.15
Vanadium	1.48	Type 304 SS	2.14
Titanium	1.27	ANL-5-0	1.96
Aluminum	1.25	AISI 1008 Steel	1.83
Manganese	1.16		
Zirconium	1.15	Electroplated Ni	2.10
		Electroless Ni	1.92

^aThe potentials for the unalloyed metals and the Ni-coated substrates are for a temperature of 450°C. Those for the alloys are for a temperature of 425°C.

Fig. 4.5. Localized Failure of an Electroplated Nickel Coating and the Resultant Attack of the Low-Carbon-Steel Substrate after an Anodic Polarization Test

4.2.3 Low-Carbon-Steel Current Collectors

The majority of the Li-Al/FeS cells have used low-carbon-steel (AISI 1008 or 1010) current collectors in conjunction with Type 304 stainless steel retainers for the FeS electrode. Stainless steel has demonstrated the necessary corrosion resistance and mechanical strength for the retainer application. Current collectors of low carbon steel are favored because the resistivity of this material ($52 \mu\Omega\cdot\text{cm}$ at 450°C) is one-half to one-third that of highly alloyed materials.¹⁰⁷ As Fig. 4.6 shows, the marginal corrosion resistance of low carbon steel limits the effective lifetime of these collectors. These data are from the same cells mentioned in Section 4.1, and identical honeycomb structures were used in both electrodes. The attack was nonuniform and greatest near the interface, as reflected by a wide variation in the depth of penetration. Perforation of the $125\text{-}\mu\text{m}$ honeycomb ribs began in less than 225 days. Initially, the corrosion rate was approximately $90 \mu\text{m}/\text{yr}$ per side, and the corrosion was characterized by intergranular penetration between surface grains and subsequent grain fallout. After approximately 250 days, the corrosion rate slowed to $5\text{--}10 \mu\text{m}/\text{yr}$ per side, and little additional intergranular corrosion occurred.

Fig. 4.6. Corrosion of the Low-Carbon-Steel Current Collector in the Positive Electrode

An electrode modification was developed to suppress the initial stage of rapid corrosion.²² Excess iron powder was added to the active material mix used to form the positive electrode. The optimum concentration, as determined by the accelerated corrosion tests shown in Fig. 4.7, is 30 mol %, provided the powder size is under $150 \mu\text{m}$. Small test cells with low-carbon-steel collectors and retainers were operated for two months to test this modification. The results show a 70 to 75% reduction in corrosion with the excess iron powder addition.

Fig. 4.7.

Corrosion of Low Carbon Steel
Tested for 500 h at 450°C in
a Mixture of FeS and LiCl-KCl
Eutectic Modified with Dif-
ferent Concentrations of Iron
Powder

4.2.4 Nickel Current Collectors

Nickel has also been used for positive electrode hardware. With an electrical resistivity of $38 \mu\Omega \cdot \text{cm}$ at 450°C, nickel offers a further improvement in conductivity for current collectors, but at this temperature nickel is relatively soft and not well suited for use as an electrode retainer. The in-cell corrosion resistance of this material can be highly dependent on the assembled state of charge.²² Figure 4.8 contrasts the appearance of collectors from cells assembled in the fully charged (only FeS) and semicharged states. Negligible corrosion is typical for components from cells built in the fully charged condition. The major reaction is deposition of iron to a typical thickness of 4 to 6 μm . Intergranular corrosion occurs in cells assembled in semicharged or uncharged condition if coarse ($>100 \mu\text{m}$) iron powder is used in the positive electrode mix. Localized areas of severe attack appear like pits on cleaned components.

The intergranular attack occurs during the early charge cycles, when the nickel components serve as a partial substitute for the slowly reacting, large iron particles in the cell redox process. Fortunately, this detrimental reaction is avoided through the use of fine iron particles that more closely approximate the less than 5- μm dia particles that normally form during discharge of an FeS electrode. The use of fine iron particles improves iron distribution within the electrode and greatly increases the surface area of iron.

Low-carbon-steel components plated with nickel have also been evaluated as a corrosion resistant but more economical alternative to nickel. In small cell tests, iron deposition is the predominant reaction over most

Fig. 4.8. Photomicrograph Composites of Two Nickel Current Collectors: (a) Fine Iron Particles Deposited on the Collector Surface from a Cell Built in the Charged State, (b) Intergranular Corrosion of a Collector from a Cell Built in the Semi-Charged State, which Produced Localized Areas of Very Fine Ni Powder and Nickel Sulfides

of the component surface; however, breaches did develop in the 25- μm electroplated coatings.¹⁰⁸ The subsequent substrate attack results in a pitted appearance over as much as 20% of the component surface. Nickel-plated copper current collectors also have been tested as a means of reducing internal cell resistance even further. The performance of one cell (>500 cycles) indicates that this coating may provide satisfactory protection for copper.¹⁰⁹

4.3 Electrode Separator Studies

The requirements for electrode separators include the following: compatibility with both the positive and negative electrodes, maintenance of electrical insulation between electrodes that are closely spaced together, high but uniform porosity, and good wettability by the electrolyte.

4.3.1 Separator Compatibility Requirements

Compatibility with the $\beta\text{-LiAl}$ electrode places severe restrictions on the selection of candidate ceramic materials. Among the nonradioactive and nonhygroscopic oxides only MgO , Y_2O_3 , and BeO have the required thermodynamic stability. Similarly, the only nonconductive, commercially available nitrides that are more stable than LiN are AlN , BN , and Si_3N_4 .^{18,110}

However, in electrochemical cells BN can react to form lithium borides and Li_3N at potentials within 100 mV of liquid lithium. These potentials can be encountered in the Li-Si system.¹¹¹ Because of the reduced activity of lithium in $\beta\text{-LiAl}$, other ceramics with marginal stability have been considered. However, ceramics such as CaZrO_3 , MgAl_2O_4 , or SiC-2AlN become electrically conductive, disintegrate, or fragment after test exposures.^{19,99,112}

Impurities often reduce the corrosion resistance of a supposedly stable material. Weight losses for hot-pressed MgO samples are directly related to the concentration of SiO_2 present in the sample.⁹⁹ The preferential attack of impurities concentrated at the grain boundaries in Si_3N_4 bodies leads to intergranular cracking. Hot-pressed BeO has excellent long-term resistance to lithium attack, provided that the concentrations of both silicon and sulfur are kept below 30 ppm.¹¹³ Beryllia, however, is toxic in its powdered form. While Y_2O_3 is compatible with lithium, use of this material in cells has been discontinued because yttria reacts with the positive electrode to form conductive $\text{Y}_2\text{O}_2\text{S}$.^{114,115} For these reasons, the developmental effort has concentrated on the use of BN and MgO as separator materials. Different separator concepts have evolved because of the differences in the physical properties and fabrication of these two materials.

4.3.2 Boron-Nitride Felt Separators

Boron nitride felt, prepared under a proprietary process by the Kennecott Copper Co., is the successor to BN woven fabric, the first successful separator for lithium/metal sulfide cells. The felt allows closer electrode spacing and has more porosity than BN fabric. In addition to these technical advantages, BN felt represents a considerable cost savings over its predecessor.¹⁵ To form a felt, fibers of B_2O_3 are spun and subsequently converted to BN by a high temperature reaction with ammonia. Additional B_2O_3 fibers are mixed throughout the BN fibers prior to a second treatment at 1700°C in nitrogen, which forms the BN bonds between the individual fibers, as shown in Fig. 4.9. No more than 0.5 wt % B_2O_3 can remain after the conversion, or lithium reduction of B_2O_3 results in a conductive separator.¹¹²

The typical diameter of a fiber is 6-8 μm , and the average size of the openings in the felt is 25 μm . The felt thickness can be varied from 1 to 3 mm. A typical 2-mm-thick felt averages 35 mg/cm^2 in basis weight, 4.5 kPa/mm in burst strength, and 92% in porosity.¹¹⁶ Electrode expansion during cell operation compresses the felt to about one-half of its original thickness. Early problems with nonuniform fiber distribution within the felt have been minimized through the use of the Fourdrinier felt formation process. From the first successful demonstration, the BN-felt separator has been a reliable component, provided it is handled properly during cell assembly.

A major difficulty with the BN separator was its nonwettability by the electrolyte.¹¹⁷ Before the development of wetting agents, cells had to be repeatedly evacuated and repressurized to force electrolyte into the pore structure of the felt. A moderately successful method developed by Eagle-Picher entails soaking the separator in a solution of methyl alcohol containing dissolved electrolyte.¹¹⁸ A subsequent drying treatment leaves a salt residue embedded in the material.

Fig. 4.9. SEM Image of a BN-Felt Separator

Because this treatment produces a fairly rigid separator, the felt must be constrained in the desired geometry before drying. Dusting the felt with LiAlCl_4 ($\sim 7 \text{ mg/cm}^2$) has also been effective in promoting wetting of BN felt;¹¹⁷ however, this agent reacts to form aluminum deposits within the separator when in contact with the negative electrode. Excessive use of LiAlCl_4 or nonuniform distribution within the felt causes short circuits to develop in the cell.¹¹⁹

Other wetting treatments depend upon the incorporation of MgO within the felt to improve wettability. Both Gould and Eagle-Picher have worked on a magnesium acetate wetting treatment.¹²⁰ The felt is immersed in an organic solution containing $\text{Mg}(\text{C}_2\text{H}_3\text{O}_2)_2$. A subsequent heating step evaporates the solvent and ultimately decomposes the acetate to form a thin coating of MgO on the BN fibers. This coating stiffens the separator and enhances its wettability. Eagle-Picher has since developed a similar treatment which uses magnesium nitrate as the wetting agent. The $\text{Mg}(\text{NO}_3)_2$ process takes less than half the time and produces a separator that is considered more uniform in its wettability.¹²¹ Another wetting treatment involves the direct incorporation of fine MgO powder into the BN felt during the fabrication of the felt.¹²² The BN fibers and MgO powder are slurried together in kerosene before the felt is laid down and the BN bonds are formed. Felts with 0.3 g of MgO per square centimeter of felt showed improved wetting characteristics in initial tests.

4.3.3 Powder Separators

In the powder separator concept, the other cell components provide support and containment of a loose bed of insulating powder.¹⁶ A wider selection of lower-cost candidate ceramics is feasible with this concept, since most thermodynamically stable ceramics are available in a suitable powdered form. Furthermore, the structural integrity of this type of separator cannot be compromised by impurities in an inherently stable material. The MgO powder used in the first cell to successfully demonstrate this concept had a purity of only 94%. Magnesia has been used extensively in cells built at ANL, Rockwell International, and Gould, but other ceramics have also been tested. At Rockwell International, AlN and Si₃N₄ powders have been used because of the greater resistance of these ceramics to the formation of lithium borides when in contact with Li_xSi electrodes.¹²³ These investigators also studied lithium-ion conducting ceramics with varying ratios of Li₃PO₄ and Li₄SiO₄, in spite of some questions on their long-term stability. Calcium sulfide is also of interest because its density is less than 70% of MgO.¹²⁴

Vibratory compaction and various pressing techniques are used to form powder separators. For the vibratory compaction technique, the electrodes are pre-positioned within a cell can with spacers. The powder is then vibrated in place between the electrodes. With this method, screen retainers are needed on the faces of both electrodes to maintain a uniform electrode-separator interface during cell assembly. For one pressing technique, the separator is formed by hot pressing a blended mix of powdered ceramic and electrolyte directly onto a pre-pressed positive electrode plaque. This method eliminates the positive electrode retainers in cell designs where interfacial current collection is not critical. Comparison tests of these two methods of fabrication showed that they have little, if any, effect on cell performance.¹²⁵ Gould has used cold pressing to fabricate rigid, free-standing separators out of powdered MgO and electrolyte mixtures.¹²⁶

The thickness of powder separators is typically 2 to 3 mm, and the porosity ranges from 30 to 50%. The greater thickness and lower porosity in comparison to BN-felt separators result in higher internal resistances for powder separator cells. Cell performance was diminished because of the lower porosity, especially at high current densities, as is illustrated in Fig. 4.10. The findings for the powder separator cells of Gould indicate that improvements in the current collection system minimize this problem.¹²⁶ (See also Sections 2.2.4 and 2.2.7.) In early development stages, powder separator cells also had briefer lifetimes. Short circuits developed because of the displacement of the powder within the separator region due to the movement of active materials during cell operation. Cells built with a low volume fraction (~30) of fine ceramic powder were especially susceptible to this problem.

A final question is the optimum size distribution and volume fraction of powder in the separator. The work in this area is incomplete but indicates that powder which is too coarse (+100 mesh) or too fine (-250 mesh) fails to maintain active material separation.¹²⁷ Mixtures of fine and coarse powders reduce this tendency but also lessen separator porosity substantially.

Fig. 4.10. Electrode Utilization for Cells with BN Felt and MgO Powder Separators

4.3.4 Porous, Rigid Separators

For the fabrication of porous, rigid separators, thin ceramic plates are sintered from suitable ceramic powders. The rigid structure facilitates easier cell assembly, maintains uniform spacing between electrodes, and minimizes the movement of active materials into the separator region. Different ceramic powders have been fabricated into rigid separators, and these candidates have cost and/or wettability advantages over BN felt. Rockwell International has built cells with AlN and Si_3N_4 plates,¹²⁸ as well as plates formed from Li_3PO_4 - Li_4SiO_4 powder mixtures.¹²⁹ These separator plates are approximately 2 mm in thickness and range from 45 to 50% in porosity.

Alternative pre-sintering procedures have been employed to increase the porosity of rigid separators. Much of this work was done with Y_2O_3 powder prior to the discovery of yttria's in-cell reaction. Ceramic foams were made from aqueous suspensions of an oxide powder, foaming agents, and organic binders. Cured Y_2O_3 foams have porosities of 63 to 90%, depending on the processing parameters.¹³⁰ In another technique, cast plasters are made by mixing an oxide powder into a dilute nitric acid solution. Yttria separators prepared in this manner range in porosity from 55 to 70%, depending on the sintering treatment.¹³¹ The Y_2O_3 - HNO_3 plaster technique produces stronger plates, which have more uniform pores of smaller diameter ($<5 \mu\text{m}$) than those produced by the foaming method. However, severe shrinkage during firing results in serious warpage. Acceptably strong and flat plates have been formed by crushing ceramic structures prepared by these two methods and

then calcining the powder prior to sintering new plates. Both Y_2O_3 and MgO separators formed by the calcination/sintering treatment have been used successfully in small test cells.¹¹⁵ The MgO plates prepared in this manner are typically 40% porous, but porosities as high as 60% are believed to be achievable. Further optimization of strength, porosity, and pore size is required, and the fabrication of flat, full-sized separator structures remains to be demonstrated.

4.4 Electrical Feedthrough Development

The electrical feedthrough insulates the positive-electrode terminal rod from the cell can, which is at the negative electrode potential and completes the seal of the cell. This hardware component requires the use of compatible materials in leak-tight, lightweight, compact, and inexpensive designs. The feedthrough used in the construction of most cells relies on the compression of a powder to form the insulating seal. A second concept, which depends on a metallurgical bond to form the seal, has also been investigated.

4.4.1 Mechanical-Type Feedthrough

The most advanced design of the ANL mechanical feedthrough is the retainer ring type shown in Fig. 4.11. The retainer ring is pressed into the feedthrough housing as the BN sealant powder is compressed. When the powder is fully compressed, the retaining ring locks in a groove in the feedthrough housing. This design is easy to assemble and is more compact (<25 mm tall) and lighter than prior designs of mechanical feedthroughs.¹³² Maximum leaktightness in air is approximately $10^{-6} \text{ Pa}\cdot\text{m}^3/\text{s}$ and is achieved when a

Fig. 4.11. Schematic of the ANL Mechanical Feedthrough

pressure of about 100,000 kPa is exerted on the powder.¹³³ Beryllia is used as the lower insulator because of its superior combination of corrosion resistance, thermal shock resistance, and mechanical strength. Both low carbon steel and stainless steel have been used for the feedthrough housing.

This feedthrough meets cost goals and has generally proven reliable when properly assembled. An improper seal allows electrolyte penetration of the powder sealant to occur, and an electrochemical couple is established between the feedthrough housing and the positive terminal. The resultant anodic dissolution of the terminal rod and subsequent metallic deposition near the housing forms a metallic bridge across the insulator.¹³⁴ Modified versions of the ANL designed feedthrough are used in both Eagle-Picher and Gould cells (see Figs. 2.4 and 2.20, respectively). In both contractor designs, a copper-cored steel terminal is used to lower the overall cell resistance. A further reduction in cell resistance is possible by enlarging the feedthrough to accommodate a larger terminal. However, there is concern that increasing the terminal diameter from the present 6.4 mm to 12.7 mm will reduce the reliability of the seal.¹³⁵ The use of a glass solder seal on the top of the feedthrough is one way of improving the leak-tightness. In earlier work, secondary glass seals reduced the leak rate in air by four orders of magnitude, to 10^{-10} Pa·m³/s.¹³⁶

An alternative concept in mechanical feedthroughs is the ram type shown schematically in Fig. 4.12. A soft metal, such as copper or nickel, is plated on one end of a metal sleeve. As the ceramic body is inserted into the metal sleeve, the soft metal is smeared over the ceramic to form a hermetic seal. The metal sleeve must not undergo stress relief at cell operation temperatures or the high hoop stresses that hold the ceramic in compression will be lost. This concept was abandoned when efforts to produce smaller feedthroughs (6.4-mm dia terminals) were unsuccessful, but this technique is best suited for the fabrication of larger diameter components.

Fig. 4.12. Conceptual Design of a Ram Seal

4.4.2 Brazed Feedthrough

The brazed feedthrough design allows the use of lightweight, inexpensive, stamped-metal parts instead of the machined parts used in the mechanical design. This cost advantage and the pretested hermetic seal are major advantages of the brazed feedthrough. The principal problem encountered with this type of feedthrough is that most brazes for metal-to-ceramic bonds are not oxidation resistant at the FeS_2 positive electrode potential. This may not be a problem in cells with FeS electrodes. Reaction of the braze with metal sulfides in this electrode and galvanic corrosion because of the dissimilarity in the braze and adjacent metal parts are also concerns. The feedthrough designs shown in Fig. 4.13 make use of a long restrictive path to minimize electrochemical attack of the braze. Plating the exposed braze surfaces with a more noble metal may also have merit.

Brazed feedthroughs are tested by applying a constant potential across a sealed Li-Al/LiCl-KCl half-cell. Time to failure is determined by monitoring the resistance until it falls from the megohm range down below an ohm. Failure is due to the dissolution of the braze or one of its constituents and subsequent deposition as a metallic bridge.¹³⁷ At the time these tests were conducted, brazed feedthroughs were primarily intended for FeS_2 cells. The applied potentials were in the range of 1.8 to 2.0 V and the failure times were comparatively short. In FeS cells, such high voltages are never encountered, and several types of brazed feedthroughs should have significantly longer lifetimes. Among the more promising candidates are nickel-base braze to BeO insulators and nickel terminals.

Fig. 4.13.

Alternative Brazed Feedthrough Designs

5.0 TRADE-OFF STUDIES OF CELL POWER, ENERGY, AND CYCLE LIFE (E. C. Gay, T. D. Kaun, and F. J. Martino)

5.1 Performance Goals

The performance and lifetime goals shown in Table 5.1 were adopted. For the purposes of cycle-life testing, a deep cycle was defined as at least 80% of the theoretical cell capacity, and end of cell life was defined as either a 20% loss of the initial stable capacity or a drop in the coulombic efficiency to less than 95%.

Table 5.1. Program Goals for Li-Alloy/FeS
Electric-Vehicle Cells

Cell Capacity, Ah	150-350
Specific Energy, ^a Wh/kg	125
Energy Density, Wh/L	300
Peak Power, ^b W/kg	185
Lifetime (deep discharges) ^c	500 ^d

^aCalculated at the 3-h discharge rate and 8-h charge rate.

^bPeak power sustainable for 20 s at 0 to 50% state of discharge; at 80% discharge, the peak power is about 70% of the value shown.

^cEnd of life is defined as a 20% loss of the initial peak capacity or a decrease of coulombic efficiency to less than 95%.

^dMean-time-to-failure (MTTF) cycles based on statistical analysis of cycle-life data from status cells.

The goals for specific energy and specific power shown in Table 5.1 represent the upper limit believed achievable with the Li-alloy/FeS system, but the lifetime goal is believed to be far short of the capability of the system, as shown by results of state-of-the-art cells discussed below. The goal of 500 cycles represents a compromise for projections based upon the Gould and Eagle-Picher technologies, which were at different stages (early vs. mature) of development. That is, the Gould cells (MgO-powder separators) were at a relatively early stage of development when this goal was selected, and the Eagle-Picher cells (BN-felt separators) represented a much more mature technology.

5.2 State-of-the-Art Cell Studies

Development cells were built at Eagle-Picher, Gould, and ANL with the objective of demonstrating improved specific energy, specific power, and cycle life relative to the status cells, which were discussed in Sections 2.1 and 2.2 of this report. These cells were tested at ANL.

5.2.1 Specific Power

A summary of the performance of five ANL cells, which achieved up to 192 W/kg at 50% depth of discharge (DOD) and power-to-energy ratios up to 2.5, is presented in Table 5.2. The basic design of these cells included perforated-sheet electrode enclosures that also served as current collectors. Improved cell power was attained through reduced internal resistance by placing the current collector at the face of the electrodes.¹³⁸ With these cells, electrode terminal configurations and method of electrode terminal attachment were examined for their contributions to cell power. The highest power-to-energy ratio, 2.5, was achieved with cell LCMP-8, which used a low-resistance cell terminal/feedthrough component that had a resistance of 0.05 mΩ. This cell terminal contains a 0.95-cm-dia copper core attached (by silver brazing) directly to a nickel interelectrode bus bar. This cell also contained wide electrode terminals that were extended into the electrode to improve current distribution. These electrode terminals were attached to the perforated sheet enclosures by brazing.

Table 5.2. Performance of Recent Experimental
Li-Al/FeS Cells (1981-1982)

Cell No.	Specific Energy, ^a Wh/kg	Specific Power, W/kg		Power-to- Energy Ratio ^b	Number of Cycles Tested
		5% DOD	50% DOD		
LCMP-7	88	142	129	1.5	100
LCMP-8	77	233	192	2.5	94
LCMP-10	92	178	130	1.4	180
LCMP-16	98	208	161	1.6	106
LCMP-17	101 ^c	180	151	1.5	75

^a4-h discharge rate unless shown otherwise.

^bBased on specific power at 50% DOD.

^c3-h discharge rate.

For batteries that may power commuter vehicles, specific power at 80% DOD is an important measure of battery performance. Initially, cells with negative-to-positive capacity ratios greater than one were limited by the positive electrode on discharge, and the resistance of such cells more than doubled at 80% DOD and greater. Later, new fabrication techniques produced negative electrodes which provided up to 80% utilization and stable capacity with cycling; these electrodes permitted the fabrication of cells with negative-to-positive capacity ratios less than one which were limited by the negative electrode on discharge. These cells showed only about a 25% increase in cell resistance at 80% DOD. A negative-electrode-limiting cell (with approximately 18% excess FeS capacity) exhibits 70% increased peak power at 80% DOD (Fig. 5.1). Cells LCMP-16 and LCMP-17 have similar hardware configurations, but the former has the typical 30% excess Li-Al capacity and the latter has the negative-electrode-limiting design. The power density at 80% DOD was 0.22 W/cm^2 and 0.38 W/cm^2 for cells LCMP-16 and LCMP-17, respectively. In spite of the thinner electrodes of EP-111 (one-third as thick as electrodes of ANL cells), this Eagle-Picher cell produced only 0.1 W/cm^2 at 80% DOD. Cell LCMP-17 provided a peak power of 100 W/kg at 80% DOD.

Fig. 5.1. Effects of Cell Design on Area Specific Power as a Function of Depth of Discharge

5.2.2 Specific Energy

The performance of Li-alloy/FeS development cells built by Eagle-Picher, Gould, and ANL is shown in Table 5.3. The highest combination of specific energy and specific power was achieved with Cell LCMP-17. This cell had the negative-electrode-limiting cell design, as well as the improved

Table 5.3. Performance of Li-Alloy/FeS Development Cells

Cell Characteristic	Eagle-Picher Cell (EP-176)	Gould Cell (G-112)	ANL Cell (LCMP-17)
Specific Energy, ^a Wh/kg	87	72	101
Specific Power, ^b W/kg	104	130.5	151
Utilization, ^a %	85.3 ^c	80.0 ^c	76 ^d
Power-to-Energy Ratio	1.2	1.8	1.5
Cycle Life	109	110	75
Theoretical Capacity, Ah	394.8	194	370
Total Cell Weight, kg	4.793	2.693	3.325

^aMeasured at the 3.4-h discharge rate.

^bMeasured at 50% state of charge.

^cPositive-electrode-limiting design; positive electrode utilization is shown.

^dNegative-electrode-limiting design; negative electrode utilization is shown.

current collector, cell terminal, and interelectrode connector designs discussed above. Cells G-112 and LCMP-17, which showed the highest power, used larger diameter feedthrough terminals than were used in cell EP-176. A weight breakdown for these development cells is given in Table 5.4. The electrolyte-starved cell design used by Gould shows about 2-4% lower weight of electrolyte compared to the other designs. In addition, Li-Al-Si negative electrode material used by Gould because of its higher specific capacity than that of Li-Al shows about 2-3% lower weight. The percentage weight of cell housing was 3-7% lower for cell LCMP-17 than the other two cell designs.

5.2.3 Cycle Life

A summary of the cycle-life tests for two groups of Gould status cells and four groups of Eagle-Picher status cells is presented in Table 5.5. The design of these cells was discussed in Section 2. The highest mean time to failure was 410 cycles for the Eagle-Picher Group I cells and 330 cycles for the Gould Group II cells.

Based on a limited number of cycle-life tests for development cells delivered by Gould and Eagle-Picher to ANL in FY 1983, there appears to be improvement in the cycle life of these cells compared to the status cells. Cycle-life testing of five Li-Al/FeS development cells fabricated by Eagle-Picher (Group X) demonstrated over 1000 cycles. At the 4-h discharge rate to 100% DOD, the average specific energy of these cells is 77 Wh/kg. The

Table 5.4. Weight Breakdown for Li-Alloy/FeS Development Cell's

Cell Component	Percentage of Total Cell Weight		
	Eagle-Picher Cell (EP-176)	Gould Cell (G-112)	ANL Cell (LCMP-17)
FeS	13.5	12.3	21.7
Li-Al	15.5		14.1
Li-Al-Si		12.1	
Electrolyte	28.0	23.9	25.6
Current Collector	23.5	22.0	23.5
Cell Housing	12.3	15.4	8.9
Feedthrough Assemblies	4.3	9.8	4.1
BN Felt	2.9		2.1
MgO Powder		4.5	

Table 5.5. Test Results of Gould and Eagle-Picher Status Cells^a

	Gould		Eagle-Picher			
	I	II	I	III	VI	IX
No. of Cells	12	12	14	12	12	12
Avg. Peak Capacity, Ah	158	157	288	294	347	340
Mean Specific Energy, Wh/kg	74	80	71	81	94	90
Peak Specific Power, W/kg	70	70	55	55	74	80
Mean Time to Failure, ^b Cycles	c	330	410	362	138	345
No. of Cycles						
High	307	542	1031	908	201	>517
Low	14	158	238	23	100	193
Weibull Slope ^b	c	2.9	2.9	1.4	2.1	3.2
Avg. Capacity Loss, %/cycle	0.08	0.06	0.032	0.027	0.045	0.025

^aGould cells have MgO-powder separators; Eagle-Picher cells have BN-felt separators. Operating temperature ranged from 455 to 490°C.

^bEnd of life defined as 20% capacity loss or <95% coulombic efficiency.

^cBecause temperature was increased to improve performance, no data are available.

improved cycle life for these cells compared to the status cells is attributed to the use of a 200-mesh screen on the face of the negative electrode to prevent Li-Al protrusion growth, which was a major cause of failure in the status cells. Cycle-life testing of two Gould development cells continues. One cell has achieved 480 cycles and the other 347 cycles.

5.3 Experimental Cell Studies

A typical Mark II cell contains 20-35% excess Li-Al capacity. This capacity was necessary to provide stable capacity with cycling for conventional Li-Al electrodes.⁷⁴ Negative electrodes fabricated by a slurry process showed improved performance over the conventional cold-pressed Li-Al electrodes.¹³⁹ These electrodes were used in cell LCMP-17 to produce the highest combination of specific energy and specific power of any Li-Al/FeS cell tested in the Mark II program. A major benefit of this cell design is the extension of the high power capability to 80% DOD.

Performance results for Li-Al/FeS cells with excess FeS capacity have been published.¹⁴⁰ Cell resistivity as a function of DOD is presented in Fig. 5.2 for Cells EP-111, LCMP-16, and LCMP-17. Cells EP-111 and LCMP-16 have 30% excess Li-Al capacity, whereas cell LCMP-17 has 19% excess FeS capacity. Cell EP-111 has seven electrode plates, 1800-cm² separator area, and grid-type current collectors, whereas the LCMP cells have five electrode plates, 850-cm² separator area, and perforated-sheet current collectors.

Fig. 5.2. Cell Resistance due to Electrode Components as Influenced by the Capacity-Limiting Electrode (discharge capacity given after cell number)

To provide a better basis for comparison, Fig. 5.2 presents data on electrode-to-electrode resistance, with the terminal effects (determined from resistance mapping investigations) subtracted. Terminal effects accounted for 40% of the cell resistance for EP-111 and less than 10% for the LCMP cells. Cell EP-111 exhibits rather constant resistance up to 50% DOD, but the resistance increases from 1.3 to 2.0 ohm·cm² at 50-80% DOD. Power at 50% DOD is only 0.185 W/cm². Data obtained using a Ni/Ni₃S₂ reference electrode revealed that the resistance increase at 50% DOD is due chiefly to the FeS electrode. Cell LCMP-16 (260 Ah FeS vs. 340 Ah Li-Al) exhibits a resistance as a function of DOD that is quite similar to that of Cell EP-111, but is reduced about 0.5 ohm·cm² throughout the discharge. The improved current collector design of Cell LCMP-16 along with a low-resistance terminal resulted in a power of 0.5 W/cm² at 50% DOD. Cell LCMP-17 has cell hardware identical to that of LCMP-16, but the thicker electrodes (440 Ah FeS vs. 370 Ah Li-Al) provide 15% greater discharge capacity--280 Ah. The cell resistance for LCMP-17 as a function of DOD does not exhibit the extreme rise at 50% DOD that the other two cells do. In this negative-electrode-limiting design, the cell performance characteristics change to resemble those of the Li-Al electrode. Resistance increase for 50% to 80% DOD of LCMP-17 is less dramatic, 0.7 to 0.9 ohm·cm². This change in performance has improved the cell power at 80% DOD by 70%--from 0.22 W/cm² for LCMP-16 to 0.38 W/cm² for LCMP-17.

Along with the improved power in Cell LCMP-17, its specific energy was increased about 15%. The specific energy at a 3-h discharge rate is 101 Wh/kg for Cell LCMP-17 and 87 Wh/kg for LCMP-16. Improvement in specific energy was accomplished through thicker electrodes--building more capacity into the cell without proportionally increasing its weight. An equally important factor was the trade-off in electrode thickness (available capacity) and reduced utilization caused by the higher operating current density. Two bicells, LC-20 and LC-22, illustrate the different effect of current density upon utilization for the positive- and negative-electrode-limiting designs, respectively. Figure 5.3 shows the voltage vs. capacity curves at two current densities, 75 and 100 mA/cm². Cell LC-20 exhibits a 15% capacity reduction by an increase of current density from 75 to 100 mA/cm², whereas the capacity of LC-22 is reduced by less than 4%. The improved discharge kinetics of Cell LC-22 provides a basis for designing cells with high specific energy and power. A utilization of 75% is obtained from Li-Al electrodes of more than 1.0-cm thickness (0.9 Ah/cm²) at a current density of 100 mA/cm², while the utilization of FeS electrodes is less than 65% and thereby does not impart a resistive hindrance to power capability.

In summary, Cell LCMP-17 has demonstrated specific power of 151 W/kg at 50% DOD and 100 W/kg at 80% DOD, with a specific energy of 101 Wh/kg at the 3-h rate. This negative-electrode-limiting cell design exhibits a flatter curve for cell resistance vs. DOD, thereby yielding good power at 80% DOD. It is concluded that, in applications where power capability limits the useful extent of cell capacity, the electrode capacity ratio is a crucial design parameter. Also, the cell discharge kinetics are improved with the negative-electrode-limiting cell design.

Fig. 5.3. Voltage vs. Capacity Curves at Two Current Densities

5.4 Cell Modeling Studies

5.4.1 Electrochemical Modeling

Studies have been conducted to provide fundamental current-potential data on various cell elements;^{141,142} these data were then used with computer programs developed by Globe Union¹⁴³ to calculate the specific power and specific energy that can be achieved in a cell with various plate areas and various weights and configurations of current collectors.

Based on data from small-scale conventional cells (less than 40-Ah capacity cells with negative-to-positive capacity ratios greater than one), calculations were made to predict the performance of large cells with similar electrode beds (loading, thickness, and capacity ratio). These calculations show a conflict in the criteria for maximizing both specific energy and specific power. As the weight for the current collector, electrode connector, and terminal is increased, the specific energy goes through a maximum because the weight of these components begins to increase faster than the energy increases. At higher weights of these components, the specific power goes through a similar maximum. At even higher weights of these components, both the specific energy and the specific power decrease because the weight increase is no longer able to produce a corresponding increase in specific energy or power. The dependence of specific energy and power on the weight of the current-collector grid is shown in Fig. 5.4 for three plate sizes.

Fig. 5.4. Dependence of Specific Energy and Specific Power on Grid Weight for Three Plate Sizes (number in cm is both plate length and width)

5.4.2 Cell Design Modeling

Power and energy trade-offs may be made by varying the thickness of the electrode, as well as the size of the current collector, interelectrode connectors, and cell terminals. A computer program for the design and optimization of Li-alloy/iron sulfide cells has been developed to calculate voltage losses across all of the current-carrying elements of the cell. These losses can be distributed as desired across the electrode current collectors, interelectrode connectors, and cell terminals. In this manner, as the size and thickness of the electrodes are changed, the current collector, cell terminals, and interelectrode connectors can be sized to maintain the same voltage drop across these components. The objective of this analysis is to determine cell designs with desired specific-energy and specific-power characteristics. The program for cell design optimization was developed from tests of Li-Al/FeS cells, described below.

5.4.2.1 Performance Data

Five small-scale Li-Al/FeS cells (100-cm² electrode area, <30-Ah capacity) were tested to obtain data on utilization as a function of current density, electrode thickness, and electrode loading density. Electrode polarization measurements (15-s relaxation measurements) were also

made with these cells. The cell design consisted of facial current collectors of perforated iron sheet (0.025-cm thick, 45% open area, 0.096-cm dia hole size) with nickel terminals, BN-felt separator, 53 at. % Li-Al negative electrodes, and LiCl-rich electrolyte. The positive electrodes were formed from pressed powders, while the negative electrodes were either pressed or slurry formed. The design variables investigated included positive electrode thickness (0.3-0.4 cm) and theoretical loading density of the negative electrode (0.8-0.9 Ah/cm³). The volume fraction electrolyte in the positive electrode was 0.51, the positive loading density was 1.4 Ah/cm³, and the negative-to-positive capacity ratio was 1.2.

Results from performance tests of full-scale Li-Al/FeS cells (200-400 Ah capacity), which were conducted at ANL over the past two years,¹⁴⁴ were also used to obtain performance and lifetime data. These cells contained different designs for the current collector, interelectrode connector, and cell terminal.

5.4.2.2 Voltage Loss Data

The computer program for the design and optimization of Li-alloy/iron sulfide cells was developed from the test data of the small-scale and full-scale cells and from studies designed to investigate the voltage losses that occur within the electrode beds and separator of Li-Al/FeS cells.¹⁴⁵ The electrode bed polarization measurements were made using the DC pulse and/or the DC current-interruption, potential-relaxation (CIPR) techniques. In the former technique, the pulse duration was usually 15-30 s. With the CIPR technique, the cell voltage was measured principally for periods of 1 ms and 15 s. Ohmically and electrochemically related bed resistances were calculated from equations derived from area-specific-resistance measurements obtained from the electrode polarization studies. The resistance of different designs for the current collector and interelectrode connector was calculated based on resistance mapping studies. Calculated performance using the computer cell design program showed excellent agreement with the measured performance.

Electrode bed resistances were calculated from equations derived from area-specific-resistance measurements. The area specific resistance is nearly independent of the current density in the lower current range (0-200 mA/cm²) and includes both the ohmic and most of the electrochemically related resistances. An analysis of the data shown in Table 5.6 provided the following equations for the area specific resistance of FeS and Li-Al electrodes. For the FeS electrode,

$$ASR_{15s} = 0.0226 / (1 - U_p)(1 - e_{f*})T_p$$

where ASR_{15s} = area specific resistance at 15 s

U_p = positive electrode utilization

T_p = positive electrode thickness (cm)

e_{f*} = volume fraction electrolyte in the fully charged electrode

Table 5.6. Area Specific Resistance of Li-Al and FeS Electrodes

	Cell No.									
	LCS-2				LCS-3		LCS-4			
Discharge Current Density, ^a mA/cm ²	43		271		40		60		271	
Electrode	Pos.	Neg.	Pos.	Neg.	Pos.	Neg.	Pos.	Neg.	Pos.	Neg.
ASR _{15s} , ^b mohm-cm ²	480	70	620	120	410	70	250	60	380	120
Electrode Half-Thickness, cm	0.16	0.30	0.16	0.30	0.26	0.49	0.26	0.49	0.26	0.49
Loading Density, kC/cm ²	5.0	3.5	5.0	3.5	4.0	2.8	5.0	3.5	5.0	3.5

^aElectrode area was 106.9 cm².

^bMeasurements of 15-s area specific resistance were at 50% state of charge.

For the Li-Al electrode,

$$ASR_{15s} = 0.051/(1 - U_n)$$

where U_n is the negative electrode utilization. The calculated and measured area specific resistance showed excellent agreement, as demonstrated in Fig. 5.5. The largest deviation occurred near the end of discharge (80% DOD), where very high polarization was observed in the positive electrode for cells in which the positive electrode was limiting.

5.4.2.3 Cell Design Program

A modular approach was used in the development of the computer cell design program. This approach provides flexibility in changing active material and electrolyte compositions, type of separator, type of current collector, cell shape, and cell configuration. The variables are changed by merely replacing a data pack in the program.

The computer cell design program was used to calculate specific energy, specific power, volumetric energy density, and volumetric power density for Li-Al/FeS cells with usable capacity of 100-400 Ah, positive electrode thicknesses of 0.3-0.5 cm (0.1-0.2 in.), and electrode sizes of 17.5 x 20 cm (6.9 x 7.9 in.), 17.5 x 13 cm (6.9 x 5.1 in.), and 12.7 x 13 cm (5.0 x 5.1 in.). The cell terminals, interelectrode connectors, and electrode current collectors were sized to provide the desired power-to-energy ratio.

Fig. 5.5.

Calculated and Measured Area
Specific Resistances for
Li-Al/FeS Cells

For cells with one to three positive plates with electrode size of 17.5×20 cm, the design calculations revealed the following: (1) the specific energy and specific power showed about the same percentage increase (28 to 49%) with increased number of electrode plates at power-to-energy ratios between 0.7 and 2.0 h^{-1} ; (2) the highest specific power (about 163 W/kg at 50% state of charge) was achieved with the 0.5-cm -thick positive electrode and power-to-energy ratio of 2.0 h^{-1} ; and (3) the highest specific energy (108 Wh/kg at the 3-h discharge rate) was achieved with the 0.3-cm -thick positive electrode and power-to-energy ratio of 0.7 h^{-1} .

For cells with two to seven positive plates with electrode size of 12.7×13 cm, the design calculations revealed the following: (1) the specific energy and specific power showed about the same percentage increase (13 to 65%) with increased number of electrode plates at power-to-energy ratios between 0.7 and 3.2 h^{-1} ; (2) the highest specific power (about 236 W/kg at 50% state of charge) was achieved with the 0.5-cm -thick positive electrode and power-to-energy ratio of 3.2 h^{-1} ; and (3) the highest specific energy (110 Wh/kg at the 3-h discharge rate) was achieved with the 0.3-cm -thick positive electrode and power-to-energy ratio of 0.7 h^{-1} .

The 12.7×13 cm electrodes provided the highest specific energy and specific power over the range of variables used in these calculations. The calculated performance for cells with electrodes of this size is shown in Table 5.7. The percentage increase in the volumetric energy density and volumetric power density with increased number of electrode plates was only about 30% of the increase in specific energy and specific power.

Table 5.7. Calculated Performance of Li-Al/FeS Cells
(12.7 × 13 cm electrodes)

Usable Capacity, Ah	Pos. Elect. Thick., cm	No. Pos. Plates	Pos. Elect. Util., %	Power-to- Energy Ratio	Specific Energy, ^a Wh/kg	Specific Power, ^b W/kg	Vol. Energy Density, ^a Wh/L	Vol. Power Density, ^b W/L
200	0.3	3	85	0.7	102	72	279	195
200	0.3	3	85	1.5	90	135	272	410
350	0.3	6	85	0.7	110	77	282	198
350	0.3	6	85	1.5	96	144	275	413
200	0.5	2	66	0.7	92	64	245	165
200	0.5	2	66	3.2	68	220	232	740
350	0.5	4	66	0.7	98	70	248	170
350	0.5	4	66	3.2	73	234	235	750

^a3-h discharge rate.

^b50% state of charge.

5.5 Proposed Cell Designs

5.5.1 Conventional Negative Electrodes

As discussed earlier in Section 5, Cell LCMP-17 achieved the highest combination of specific energy and specific power of any Li-Al/FeS cell tested in the Mark II program. This cell design, with the modifications discussed below, shows the greatest potential of meeting the performance goals given in Table 5.1.

The computer calculations based on Cell LCMP-17 are presented in Table 5.8. In the cell design chosen for these calculations, the negative electrodes were grounded to the cell housing. This design has demonstrated long lifetimes (over 1000 cycles) for some cells. The design used in Cell LCMP-17 had the positive electrodes grounded to the cell housing. The results in Table 5.8 show that this design provides lower cell resistance for a given current collector weight, since the cell housing contributes to current collection in the electrode needed most--the positive electrode. However, since the cycle life of the positive-electrode-grounded cell design has not been determined, the design proven to yield long cycle-life (negative electrode grounded) was used for these calculations. As shown in Table 5.8 for the same cell weight and capacity, the positive-electrode-grounded cell design has a 0.8-mΩ cell resistance, which is lower than the 0.97 mΩ for the negative-electrode-grounded cell design. As a result, it has a higher specific power (151 vs. 132 W/kg) and power-to-energy ratio (1.5 vs. 1.3 h⁻¹).

Table 5.8. measured and Calculated Performance and Design Features of Cell LCMP-17

	Cell LCMP-17	Calculation from Computer Model
Positive Electrode Size, cm	12.5 × 17.5	13.2 × 17.5
Carbon Additive Weight, g	85	85
Theor. Capacity, Ah	440	440.6
Thickness, cm	0.70	0.70
FeS Weight, g	721	722
Active Material Loading Density, Ah/cm ³	1.4	1.4
No. of Parallel Electrodes ^a	3	2
Electrode Utilization, %	64	64
Negative Electrodes		
Theor. Capacity, Ah	370	370
Thickness, cm	1.0	1.0
50 at. % Li-Al Weight, g	468.3	468.5
Active Material Loading Density, Ah/cm ³	0.85	0.87
No. of Parallel Electrodes ^a	2 ^a	3 ^a
Negative-to-Positive Capacity Ratio	0.84	0.84
Carbon Additive Weight, g	81.7	82
Electrode Utilization, %	76.2	76.2
Electrolyte Weight (54 wt % LiCl-KCl), g	850	832.2
Current Collector		
Pos. Perforated Particle Retainer Thickness, cm	0.025 ^b	0.033 ^b
Neg. Perforated Particle Retainer Thickness, cm	0.046 ^b	0.033 ^b
Total Current Collector Weight, g	>755 ^c	857.9
Open Area of Perforated Plate	0.55	0.55
Terminal Diameter (neg), cm	0.95 (neg) ^d	0.94 (neg/pos)
Cell Resistance, mΩ	0.8	0.97
Cell Housing		
Thickness, cm	0.038	0.038
Weight, g	295	255.6
Total Cell Weight, kg	3.325	3.325
Specific Energy (3 h), Wh/kg	101	102
Specific Power (50% DOD), W/kg	151	132
Power-to-Energy Ratio, h ⁻¹	1.5	1.3

^aTotal number of electrode plates are the same in the two designs. The positive electrodes were grounded to the cell can in Cell LCMP-17; the negative electrodes were grounded to the cell can in the cell design of the computer model.

^bBased on the difference between the cell design of LCMP-17 and the model (positive electrode grounded vs. center electrodes), these are equivalent dimensions.

^cPositive electrodes were grounded to cell housing; the fraction of housing weight contributing to current collection for the positive electrode was not included in the current collector weight shown.

^dPositive grounded to cell can; center sheet of cell can was 70-g, 10-mil copper sheet covered with steel sheet.

Calculations were made to determine specific energy and specific power as a function of cell capacity and power-to-energy ratio. These results are presented in Fig. 5.6 and show that cells with the general characteristics of Cell LCMP-17 (capacity less than 400 Ah) are not capable of simultaneously delivering a specific energy of 125 Wh/kg at the 3-h discharge rate and a specific power of 185 W/kg at 50% DOD.

Fig. 5.6.

Specific Energy and Specific Power as a Function of Cell Capacity for Li-Al/FeS Cells (based on the LCMP-17 cell design)

A parametric study was conducted to determine if there were Li-Al/FeS cell designs that would meet the performance goals. The range of variables used in this study is shown in Table 5.9. Both negative- and positive-electrode-limited cell designs were used in this analysis.

Table 5.9. Range of Variables Used in Power vs. Energy Trade-Off Studies

Cell Theor. Cap., Ah	80-720
No. of Pos. Plates	1-7
Electrode Size, cm	12.7 x 12.0 to 17.5 x 20.3
Elect. Thickness, cm	0.3-0.7
Pos. Elect. Util., ^a %	64-85
Power-to-Energy Ratio, h ⁻¹	0.7-3.2

^aFor the 3-h discharge rate.

The effect of theoretical capacity on the performance of positive-electrode-limited cells is shown in Table 5.10. Above 435-Ah capacity, the payoff of percent increase in specific energy per ampere-hour of capacity is very small, 0.02%/Ah. The effect of plate size on performance is shown in Table 5.11. For the three electrode sizes examined, the highest combination of specific energy and specific power was achieved with the 12.7 × 12.0 cm size. For a five-plate cell of this size, with 263-Ah capacity at the 3-h discharge rate, a specific energy of 94 Wh/kg and a specific power of 140 W/kg at 50% DOD were calculated. The effect of electrode thickness on the performance of positive- and negative-electrode-limited cells is shown in Table 5.12. For the positive-electrode-limited cell designs, the highest specific energy and specific power were calculated for the 0.3-cm-thick positive electrode. However, the negative-electrode-limited cell with 0.7-cm-thick positive electrodes exceeded this performance. A similar result is shown in Table 5.13 over a capacity range of 188-371 Ah. For roughly the same usable capacity, the performance of the negative-electrode-limited cells exceeds that of the positive-electrode-limited ones.

Table 5.10. Effect of Capacity on Performance of Li-Al/FeS Cells

No. of Pos. Plates	Pos. Elect. Theor. Cap., Ah	Specific Energy, ^a Wh/kg	Percent Change	Peak Specific Power, ^b W/kg	Percent Change
2	290	99	--	130	--
3	435	105	6	136	4
4	580	108	3	142	4

^aAt the 3-h discharge rate.

^bAt 50% DOD.

Table 5.11. Effect of Plate Size on Performance of Li-Al/FeS Cells

Elect. Dimen., cm	No. of Pos. Plates	Discharge Cap., Ah	Specific Energy, ^a Wh/kg	Peak Specific Power, ^b W/kg
12.7 × 12.0	5	263	94	140
17.5 × 12.2	4	289	92	138
17.5 × 20.3	2	242	84	127

^aAt the 3-h discharge rate.

^bAt 50% DOD.

Table 5.12. Effect of Electrode Thickness on Performance of Li-Al/FeS Cells

Limiting Electrode	Pos. Elect. Thickness, cm	Pos. Elect. Util., %	No. of Pos. Plates	Specific Energy, ^a Wh/kg	Peak Specific Power, ^b W/kg
Pos.	0.3	85	4	94	122
Pos.	0.4	75	3	90	118
Pos.	0.5	66	3	87	115
Neg.	0.7	64	2	99	130

^aAt 3-h discharge rate.^bAt 50% DOD.

Table 5.13. Calculated Performance of Li-Al/FeS Cells

Limiting Electrode	Disch. Cap., Ah	Pos. Elect. Util., %	Specific Energy, ^a Wh/kg	Peak Specific Power, ^b W/kg
Pos.	200	85	90	135
Pos.	350	85	96	144
Neg.	188	64	96	144
Neg.	371	64	105	157

^aAt 3-h discharge rate.^bAt 50% DOD.

5.5.2 Advanced Negative Electrodes

The above calculations indicate that Li-Al/FeS cells of 150-450 Ah capacity can achieve a specific energy of 105-110 Wh/kg at the 3-h discharge rate and a specific power of 155-165 W/kg at 50% DOD. Based on cycle-life tests of state-of-the-art Li-Al/FeS cells, it is believed that cells of this performance level could be built with a cycle life of well over 600 cycles. A more specific upper limit cannot be determined because the cycle-life tests are not yet complete. Therefore, the strategy to reach the performance goals was to evaluate negative electrode materials with potential for higher performance than the Li-Al electrode. Our efforts were concentrated on the Li-Si electrode, which provides a greater loading (ampere-hour per gram) than that of Li-Al, and the Li-Al-Fe electrode, which has higher average discharge voltage than that of the Li-Al electrode.

The improved performance of Li-Al-Fe ternary alloys was first observed experimentally in the ANL cell development program.¹⁴⁶ Three compositions of Li-Al-Fe alloy were cycled to determine the effect of composition on the average discharge voltage. These compositions were: $\text{Li}_5\text{Al}_5\text{Fe}_2$ (12.3 wt % Li, 48.0 wt % Al, 39.7 wt % Fe), $\text{Li}_5\text{Al}_5\text{Fe}$ (15.4 wt % Li, 59.8 wt % Al, 24.7 wt % Fe), and $\text{Li}_4\text{Al}_4\text{Fe}_2$ (11.2 wt % Li, 43.6 wt % Al, 45.2 wt % Fe). The voltage vs. capacity curves for these electrodes are shown in Fig. 5.7. The $\text{Li}_5\text{Al}_5\text{Fe}_2$ electrode showed the greatest improvement compared to the Li-Al electrode, based on increased average discharge voltage per unit of increased weight due to the iron addition. The average voltage of this electrode was about 0.2 V greater than that observed for the Li-Al electrode.

Fig. 5.7. Voltage vs. Capacity for Li-Al-Fe/FeS Cells

Calculations were made to determine the specific energy and specific power of $\text{Li}_5\text{Al}_5\text{Fe}_2/\text{FeS}$ and $\text{Li}_{3.25}\text{Si}/\text{FeS}$ cells over a capacity range of 150–400 Ah. Some of these results are shown in Table 5.14. Over a capacity range of 186–371 Ah, a specific energy of 105–119 Wh/kg and a specific power of 157–179 W/kg were calculated.

The projected specific energy and specific power of the Li-alloy/FeS prismatic cells are shown in Table 5.15. Based on these calculations, the Li-Al-Fe/FeS and Li-Si/FeS cells show potential for achieving the performance goals. The cycle-life data for cells using these advanced negative electrodes are very limited. Thus, cycle-life data of these cells are needed to determine whether the cycle-life goal will be met.

Table 5.14. Calculated Performance of Li-Alloy/FeS Cells

Neg. Elect. Comp.	Discharge Cap., Ah	Specific Energy, ^a Wh/kg	Peak Specific Power, ^b W/kg
Li ₅ Al ₅ Fe ₂	186	109	164
Li ₅ Al ₅ Fe ₂	371	119	179
Li _{3.25} Si	186	105	157
Li _{3.25} Si	371	115	173

^aAt 3-h discharge rate.^bAt 50% DOD.

Table 5.15. Projected Performance of Li-Alloy/FeS Electric-Vehicle Cells

Cell Type	Specific Energy, Wh/kg	Peak Specific Power, ^b W/kg	Cycle Life
LiAl/FeS	105-110	157-165	>800 ^c
Li ₅ Al ₅ Fe ₂ /FeS	110-125	165-187	d
Li _{3.25} Si/FeS	105-120	157-180	d

^aAt 3-h discharge rate.^bAt 50% DOD.^cCycle-life tests of five development cells are continuing with no cell failures.^dThe cycle life of cells of this type with 150-450 Ah capacity has not been determined.

6.0 BATTERY DESIGN CONSIDERATIONS (A. A. Chilenskas)

6.1 Battery Design

6.1.1 Utility Load-Leveling Batteries

The design criteria for a stationary energy storage (SES) battery to be used for daily load leveling are as follows:

- (1) 100 MWh of electrical energy must be stored in about 7 h, which can be then discharged over a 5-h period at times of peak load (this cycle must be repeated five consecutive days per week).
- (2) The plant lifetime must exceed 20 years, although the cells can be replaced after 19 years.
- (3) The cost per kilowatt-hour should be in the range of \$45 to \$55 (1978 dollars).

In 1978, the first conceptual design of a 100 MWh SES battery having lithium/metal sulfide cells was developed as a result of a joint effort between ANL and Rockwell International.¹⁴⁷ In this design, the submodule, which is the basic replaceable unit for the battery, consisted of ninety-six 2.5 kWh cells. However, the cost for this battery was found to be too high, \$60-80/kWh, excluding the cells and converters. Therefore, three possible conceptual designs were investigated. Rockwell International proposed a design in which the submodule consists of four-hundred and eight 2.5 kWh cells. The other two proposed designs were developed at ANL; the submodule consists of one-hundred 1.2 kWh cells in one of them, and one 30 kWh cell in the other. The above designs are described more fully in an ANL report.¹⁴⁸ Under a separate contract, United Technologies Corp. conducted a study¹⁴⁹ of the interface between the SES battery and the converter. The major conclusion of this study was that the terminal voltage at the converter should be 2000 V.

The four conceptual designs represent a very broad range of engineering approaches, ranging from designs based on present-day hardware to designs which require significant advances in technology. Table 6.1 presents the costs projected for the four designs in the order of increasing technical advancement required. Of the four, the SCS and LCS systems appear to be the most technically practical and have acceptable costs.

For the 1978 reference design, the electronic equalization was the same as that used for electric-vehicle batteries and contributed to a relatively large portion of the overall battery cost. For the SCS and LCS designs, a new equalization scheme, which consists of a fixed resistance shunt of appropriate resistance for each cell, was proposed. This equalization scheme adds very little equipment cost to the battery; the sacrifice in coulombic and energy efficiency is about 4%.

The cell reliability required for an SES battery was assessed since there were no data on the mean time before failure (MTBF) of the cells that would be used in such a battery. The approach taken was to determine what MTBF would be required for a low maintenance battery. It appears that a

Table 6.1. Cost of Proposed SES Batteries

Designation	Capacity, kWh		Battery Hardware Cost, ^a \$/kWh	Energy Footprint, ^b kWh/ft ²
	Cell	Submodule		
1978 reference design	2.5	240	60-88	11
SCS	1.2	120	30-60	10
LCS	2.5	1020	22-37	8
LFSC	30	30	22-25	9

^aCell cost not included.

^bConverters excluded from this value.

MTBF of about 200 years* will be required over the cell's useful life of ten years. This may be difficult to achieve, although the cell reliability that will probably be required for the electric vehicle application is of the same order. This long MTBF favors smaller cells than might otherwise be optimum for this application.

6.1.2 Batteries for Electric Vehicles

6.1.2.1 Design Requirements

In design studies done by Toyota Motors Co. and ANL, battery requirements were developed for electric vehicle applications.^{150,151} A Toyota Carina converted to electric drive was used in computer simulations to model the performance of an electric passenger car. Similarly, a Toyota Hi-Ace van was used to model the performance of an electric van. A weight analysis for these two vehicles converted to electric drive is given in Table 6.2.

The volume available for the battery in the passenger car was found to be a maximum of 270 dm³; however, to maintain the proper axial weight distribution of 52% front and 48% rear, the volume was limited to about 190 dm³. The volume available for the van battery was found to be 261 dm³. The axial weight distribution was kept the same as for the ICV van by dividing the battery into three modules.

The battery power and energy requirements were calculated as a function of gross vehicle weight for both vehicles. The results are summarized in Table 6.3.

The power/energy (P/E) ratio of the battery was studied as a function of the desired vehicle range. An expression was derived that provides the P/E ratio of the battery as a function of vehicle range, R(km), which is independent of vehicle weight, W_V(kg), and battery weight, W_B(kg). This expression is

* A MTBF of 200 years can be considered as a failure rate of 0.5% of the total cells per year or 5% of the total cells in 10 years.

Table 6.2. Weight Analysis for Electric Vehicles

Items ^a	Weight, kg	
	Passenger Car	Van
ICV Curb Weight ^b	1110	1465
Surplus ICV Parts	245	275
EV Shell	865	1190
Conversion to EV Drive		
Reinforce Frame	40	55
Motor/Cooling Blower	80	100
Controller/Power Cable	43	45
Auxiliaries	40	40
EV, without battery	1063	1430

^aICV = internal combustion vehicle; EV = electric vehicle.

^bThe ICV "ready to go," without passengers.

Table 6.3. Battery Power and Energy Requirements^a

	Passenger Car	Van
Power, kW/kg (vehicle wt)		
Diesel Equivalent Accl.	0.030 ^b	0.025 ^c
Gasoline-Engine Equivalent Accl.	0.040 ^d	0.034 ^e
Energy, kWh/km·metric ton		
SAE J227 a/D with regenerative braking	0.120	0.135
SAE J227 a/D without regenerative braking	0.128	0.144

^aResults essentially independent of gross vehicle weight for the ranges studied.

^b0-48 km in 6 s and 0-100 km in 22 s.

^c0-48 km in 7 s and 0-100 km in 33 s.

^d0-48 km in 4.5 s and 0-100 km in 16 s.

^e0-48 km in 6 s and 0-100 km in 22 s.

$$P/E = \frac{1000C_1(W_V/W_B)}{V_E(W_V/W_B)R} = \left(\frac{1000C_1}{V_E R} \right)$$

where C_1 , a factor used in determining the acceleration of the vehicle, is proportional to battery power output divided by vehicle weight, P/W_V . The vehicle energy economy, V_E , is defined as battery output divided by the vehicle range times its weight (kWh/km-metric ton). A plot of the P/E ratio required for the passenger car and the van is given in Fig. 6.1. Two acceleration regimes (gasoline engine and diesel) were calculated for each vehicle. Only three curves are shown because the upper limit for the van with gasoline-engine acceleration coincides with the lower limit for the automobile with diesel-engine acceleration. As can be seen, designing a vehicle for a short range can significantly affect the battery design by requiring a high power output per unit battery weight. For example, a van with gasoline-engine acceleration requires a battery P/E ratio of 1.25 for a 200 km range but needs a battery P/E ratio of 2.5 for one-half this range (100 km). The impact of increasing P/E ratio upon the specific energy was discussed in Section 5.

The vehicle and battery specifications and projected performance are given in Table 6.4.

Fig. 6.1. P/E Ratio as a Function of Range

Table 6.4. Vehicle and Battery Requirements and Projected Performance

	Van	Automobile
Vehicle		
Curb Weight, kg	1,430	1,065
Battery Weight, kg	430	300
Payload, kg	<u>360</u>	<u>150</u>
	2,220	1,515
Acceleration Time, s		
0-48 km/h	6	4.5
0-100 km/h	22	16
Max Speed, km/h	154	136
Range		
Overnight Recharge, km	160	160
Overnight + Quick Charges, km	280	400
	(1 recharge)	(2 recharges)
Gradeability, %	38	38
Motor		
Max Power, kW	78	51
Max Torque, kg·m	15	16
Battery		
Capacity, kWh	44	27.5
Weight, kg	430	300
Volume, dm ³	261	183
Max Power, kW	78	55
P/E Ratio, h ⁻¹	1.8	2

6.1.2.2 Thermal Management Studies

6.1.2.2.1 Cell Heating Effects

The heating effect during the discharge or charge of a cell can be expressed as:

$$\dot{Q} = \dot{Q}_{IRR} \pm \dot{Q}_{REV}$$

$$\dot{Q} = \eta I + kI$$

where $\dot{Q}$ = heat generation (W)

$\dot{Q}_{IRR}$ = irreversible heat (W)

$\dot{Q}_{REV}$ = reversible heat (W)

η = overpotential (V)

I = current (A)

F = Faraday's constant

k = temperature dependent constant defined by

$$k = \frac{\dot{Q}_{REV}}{I} = \frac{-T\Delta S}{F}$$

Early work employing a combination of thermodynamic values and dE/dT measurements yielded a value of $k = 0.074$ to 0.118 W/A for a Li-Al/FeS cell at 465°C .¹⁵² An experiment which measured the heat output of a Li-Al/FeS-15% Cu_2S cell yielded a value of 0.104 W/A at 450°C , corrected to 0.106 at 465°C . Work based upon $\Delta E/\Delta T$ measurements¹⁵³ for the reaction $2\text{Li} + \text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe}$ gave the value of k as 0.048 to 0.052 for the temperature range 450 to 500°C . Thus, the heating effects in Li-Al/FeS cells at 470°C are:

$$\dot{Q} \text{ (Discharge)} = I(\eta + 0.05)$$

$$\dot{Q} \text{ (Charge)} = I(\eta - 0.05)$$

The open-circuit potential (OCP) of an Li-Al/FeS cell was measured in the temperature range of 450 - 500°C . An Eagle-Picher cell with a 360-Ah theoretical capacity (MK II-044) was charged at 40 A (7-h rate) and discharged at 70 A (4-h rate). In each case, the cycle was interrupted several times for periods of 1-24 hours to obtain the equilibrium OCP. The discharge and charge cutoff voltages were 1.0 and 1.6 V, respectively. The OCP measurements were conducted at cell temperatures of 450 , 465 , 480 , and 500°C . The resulting OCP values are shown on Fig. 6.2.

The heat generation rate of a cell as a function of current level was measured. Cell MK II-044 was cycled at 465°C at discharge currents of 40 - 200 A (~ 20 - 100 mA/cm²). In all cases, the charge current was kept at 40 A and cutoff voltages at 1.0 and 1.6 V. The increase in average heat-generation rates with current level is shown on Fig. 6.3. The change in heat-generation rate with the state of charge is given on Fig. 6.4 for each of the discharge currents applied.

An investigation into the feasibility of rapidly recharging Li-Al/FeS cells showed that the maximum heat-generation rate during rapid recharge (~ 1 -h rate) is approximately the same as that occurring during a 4-h discharge.¹⁵⁴ Thus, the heat generation during rapid recharge is reduced to a manageable level due to the entropy cooling effect.

Fig. 6.2. Open-Circuit Potential of a Li-Al/FeS Cell

Fig. 6.3.

Heat Generation Rate of a Li-Al/FeS Cell as a Function of Current Level

Fig. 6.4. Heat Generation Rate of a Li-Al/FeS Cell as a Function of DOD

Fig. 6.5. Li-Al/FeS Battery Temperature during Driving Cycle

6.1.2.2.2 Temperature Management during a Driving Cycle

The temperature cycle experienced by a 44-kWh van battery that undergoes a full discharge is shown on Fig. 6.5. Without cooling, the maximum temperature that is reached is about 500°C. To keep the battery within the desired operating temperatures of about 450 to 470°C, a cooling rate of 750 W would remove the 6-kWh heat accumulation due to the full discharge of the battery. For vehicles such as vans that are parked during the weekend (fleet operation), the temperature of the battery could be allowed to rise to 500°C on Friday and permitted to cool slowly during the weekend. This procedure would eliminate most, if not all, of the electrical energy needed to maintain the battery at operating temperature.

6.1.2.2.3 Efficiency and Heating Cost of the Battery

High-temperature batteries that are used to power vehicles will normally be kept at their operating temperatures continuously. The heat loss that results can be kept to a very low level by the use of high-efficiency thermal insulation developed especially for this purpose. As indicated above, the loss in system energy efficiency due to the heat loss can be reduced or eliminated by utilizing the heat generated by the internal resistance of the battery during charge and discharge.

Based upon energy balance calculations, the battery efficiency and the cost of the electricity used to maintain the battery at operating temperature have been determined for an automobile as a function of annual miles driven. The battery energy balance is given in Fig. 6.6. The system efficiency is defined as the fraction of total ac energy delivered by the battery to the motor/controller. The charge/discharge efficiency for this battery in a vehicle with regenerative braking is estimated at 75%.* For conditions where no ac energy is supplied to the battery for heating, the system efficiency is about 80%, i.e., 0.30 kWh of dc power is delivered to the motor/controller for 0.378 kWh of ac power from the wall plug. The efficiency assumed for the charger is 90%. In Fig. 6.7, the system efficiency is given as a function of annual mileage for two levels of battery heat loss, 75 and 150 W. The maximum efficiency for a battery with a 75-W constant heat loss is achieved after about 6000 miles are driven per year, while 12,000 miles per year need to be driven to achieve the maximum efficiency when the heat loss is 150 W. The cost of electricity for battery heating for the two cases is given in Fig. 6.8. For a car driven 6000 mi/y with a 150-W battery heat loss, the system energy efficiency is 60% and the cost for battery heating is about 1/2 ¢/mi. With a 75-W battery heat loss and the same annual mileage, the system energy efficiency is 80%, and the battery heating cost drops to zero. The main conclusion drawn from these calculations is that high system efficiencies and negligible battery heating

* Charge/discharge efficiencies for a single cell are about 83-88% at a 4-h discharge rate. The lower value used in the calculations discounts the efficiency for cell and battery connections and the more-severe driving cycle.

$$\text{EFFICIENCY} = \frac{E_{BO}}{E_C + E_H} \quad (\text{fraction of AC energy that is delivered to the motor/controller})$$

Fig. 6.6. Battery Energy Balance

Fig. 6.7. System Efficiency of Electrical Energy Use vs. Miles Driven per Year

Fig. 6.8. Cost of Electricity for Battery Heating vs. Miles Driven per Year

costs can be obtained for automobiles driven 6000 to 12,000 mi/y if high-efficiency insulation (discussed below) is used to reduce the battery heat loss to levels of 75-150 W.

6.1.3 Component Development

6.1.3.1 High-Efficiency Thermal Insulation

Union Carbide Corp. (Linde Division) is developing a load-bearing insulation for high-temperature batteries.¹⁵⁵ The requirements of such an insulation are that it be capable of withstanding pressures of 95 kPa (15 psi) and temperatures of 450°C, be lightweight (about 250 kg/m³), and have a thermal conductivity of 2.38×10^{-3} W/m·K (140 Btu/h-ft·°F) or lower. Three candidate insulation systems that have been tested appear promising: (1) an insulation board composed of fiberglass sheets compressed together, with no radiation foils; (2) Linde's Super Insulation (fiber glass and aluminum foil) with load-supporting glass fiber paper sheets (8% of total area) and 40 radiation foils; and (3) Linde's Super Insulation with Min-K 2000 peg supports and 120 radiation foils. The latter two insulations are illustrated in Fig. 6.9. Table 6.5 shows the results of the insulation tests for the three materials along with commercially available insulations.

The use of the first and third types of insulation for a small automobile battery using the Li-Al/FeS technology was examined further. The results obtained using the Linde board insulation are given in Fig. 6.10. A battery with a 1-in.-thick insulated case would lose about 106 W heat continuously at 450°C, with energy densities of 85 Wh/kg and 120 Wh/L. The results obtained with Linde peg-foil are illustrated in Fig. 6.11. For a case with 1/2-in. insulation thickness, the heat loss is 66 W, with energy densities of 87 Wh/kg and 150 Wh/L.

THICK-THIN AND PEG-SUPPORTED INSULATION SYSTEMS

NOTE: THICK-THIN SPACER IS PRODUCED IN A CONTINUOUS PAPER MAKING PROCESS.

Fig. 6.9. Load-Bearing Thermal Insulation

6.1.3.2 Charger

A charger/equalizer system capable of accommodating batteries of up to 16 cells has been designed. Figure 6.12 shows a block diagram of this system, which consists of three basic units: main charger, equalizer, and controller. The main charger is a programmable current-regulated power supply. Different power supplies may be used as needed to satisfy battery-voltage and charge-rate requirements. The equalizer contains voltage-monitoring and current-bypass circuitry to accommodate up to 126 cells; additional equalizers may be added to the system for batteries containing more than 16 cells. The controller is a microprocessor-based unit that establishes overall system operation. The controller continuously monitors cell voltage status, automatically adjusts battery charge current,

Table 6.5. Pressure-Supporting Vacuum Thermal Insulation

Description	Thermal Conductivity, ^a W/m·K	Density, kg/L	Percent Compression at 95 kPa Load
Glass Mat Board (no foils)	3.88×10^{-3}	0.35	7
Paper Spacer (40 foils)	1.64×10^{-3}	0.24	21
Min-K Pegs (120 foils)	1.75×10^{-3}	0.18	6
Min-K 2000 ^b	18.16×10^{-3}	0.32	7
Microtherm 20 CRC ^c	14.19×10^{-3}	0.32	2

^aMeasured at $T_H = 840^\circ\text{F}$ (450°C) and $T_C = 75^\circ\text{F}$ (24°C).

^bA product of Johns-Manville Co.

^cA product of Micropore International.

Fig. 6.10. Specific Energy (SPE) and Volumetric Energy Density (VED) as a Function of Thickness for Linde Glass Board Insulation

Fig. 6.11. Specific Energy (SPE) and Volumetric Energy Density (VED) as a Function of Thickness for Linde Peg Foil Insulation

Fig. 6.12. Block Diagram of ANL Equalizer/Charger ($i_{B \text{ REF}}$ is the reference signal or current from the control unit that governs the magnitude of i_B , the battery charge current)

and initiates current shunting. The controller is preprogrammed to provide a full bulk, taper and equalization charge, in the sequence shown in Fig. 6.13. For laboratory operation, the controller will also be programmed to allow user communication via a printer/keyboard terminal for charge parameter modification and operational status/performance reporting.

Fig. 6.13. Current Waveform for Battery Charging (I_{BK} = bulk current; I_{EQ} = equalization current)

A fully assembled equalizer/charger chassis has been successfully operated.¹⁵⁶ This unit has two types of printed circuit boards (PCB) to facilitate fabrication and maintenance. One PCB contains the individual cell voltage-monitoring and current-bypass circuitry, and the other provides the interconnector wiring for 16 of the cell-circuit PCB's. A microprocessor-based charge-control unit was fabricated and preprogrammed by the Omnibyte Corp. (West Chicago, IL) according to ANL specifications. A remotely programmable, current-regulating power supply (Electronic Measurements, Inc., Neptune, NJ) is used as the system's main charger. The output capability of the main charger permits the charging of up to 12 cells at a maximum rate of 120 A. A Texas Instruments printer/keyboard terminal is employed for user communication with the charger control unit.

6.2 State-of-the-Art Batteries

The thrust of the work in the past several years has been upon the assembly and testing of small laboratory-type batteries (five to ten cells), to gain experience in the electrical performance of series-connected arrays. Engineering development of the battery hardware, especially with regard to battery modules and components that are lightweight and compact, is at a very early stage.

6.2.1 Module Design and Testing

A chronological listing of the small battery tests carried out from 1977 to 1981 is given in Table 6.6. These tests were run in laboratory-type arrays that were provided with electrical resistance heaters to maintain the cells at operating temperatures in an insulating case of high-efficiency vacuum-foil or conventional insulation. Generally, no cooling systems were employed. Temperature control was maintained by regulating the power input to the resistance heaters located within the insulated case. Detailed description of a 10-cell battery test performed at ANL has been reported elsewhere.^{157,158} The main conclusions drawn were: (1) equalization charging

Table 6.6. Tests of Small Lithium/Iron Sulfide Batteries

Year	No. of Cells	Battery Voltage, V	Battery Capacity, kWh	Thermal Insulation	Cycle Life
1977	6	8.8	1.0	Vac-Foil	11
1979	10	5.9	3.7	Conventional	34
1979	5	5.6	1.6	Vac-Foil	70
1980	9	10.6	3.0	Conventional	72
1981	10	~12	2.5	Vac-Foil	71
1981	10	~12	2.5	Vac-Foil	~79
1981	10	11.6	3.8	Conventional	270
1981	10	11.8	4.0	Conventional	150

of individual cells is effective in maintaining high battery capacity, (2) charge termination of the battery should be based upon the status of individual cells, (3) discharge termination can be based upon total battery voltage, and (4) operating the battery with several cells shorted (failed) is possible. An energy output of 66% of the peak output was achieved even after 30% of the cells had been shorted. Failing cells were easily identified by their voltage patterns, which were monitored through the voltage sensing leads provided for each cell.

As noted, battery component development is at an early stage of development. One component developed in the module test programs that may find use in future full-scale batteries is the flexible connector developed by Eagle-Picher. The connector consists of multiple layers of copper foils (0.01-cm thick) that are welded at their ends, resulting in a flexible center section. A nickel insert is brazed into the intercell connector at either end. Cell terminals pass through the nickel inserts, and lock nuts complete the connection to the cell terminals. This type of connection has exhibited low resistance (0.02 to 0.04 m Ω) and permits rapid assembly and disassembly. Figure 6.14 shows some details of the connector.

6.2.2 Cell Expansion Forces

A major failure mechanism for lithium-aluminum/iron sulfide cells has been attributed to the extrusion of the active materials from the electrode structure. The extruded material causes bridging of the electrodes, which results in an electrical short circuit. The main cause of the extrusion is the force exerted by the expanding active materials, which undergo volume changes during the cell reaction. Various electrode-structure designs to contain the material have been developed. For example, a picture-frame-type structure has been used to constrain the electrode edges. Furthermore, a

Fig. 6.14. Intercell Connector

cell is generally tested with a set of external restraining plates attached to the cell can. Such mechanical methods of constraining electrode expansion have been successful in extending cycle life. However, to develop better structural design of a cell as well as a battery module, an accurate estimation of the electrode expansion force is needed. Several experiments have been run to measure the expansion force during the cell operation. In one such test, the expansion force was determined as a function of the depth of discharge by means of a force gauge attached to the surface of a full-size cell.¹⁵⁹ Interpretation of the force on individual electrodes was difficult because of the lump-sum nature of the experiment, which measured the sum of expansion force and deformation.

For a further understanding of the expansion effects, an apparatus (shown in Fig. 6.15) that consists of a small electrode directly attached to a sensor was built to allow in situ measurement of the dimension changes of the electrode. An analytical model describing the dynamic behavior of the cell during cycling under constraining force was also developed. The experimental results and the model were then used to estimate the force required to constrain the electrode.¹⁶⁰ Some of the experimental results showing the volume change of positive electrodes as a function of applied pressure and discharge current density are presented in Fig. 6.16. These results show excellent agreement with the behavior predicted by the model.

6.3 Engineering Characteristics

The engineering characteristics of the Li-Al/FeS battery have been studied in cell and small battery tests and have been reported elsewhere.¹⁶¹ The main conclusions drawn in that study were: (1) the battery provides very high volumetric and gravimetric energy storage; (2) high power can be designed into the system, if desired, by trading off energy density for power density;

Fig. 6.15.

Apparatus for Electrode Volume Change Measurements (LVDT = linear displacement transducer)

Fig. 6.16. Volume Change of the Positive Electrode

(3) the electrochemical reactions do not produce gases; (4) the battery can be sealed, which is a major safety advantage; (5) no maintenance is required; (6) the cells and battery are rugged and safe.*

Thermal management can be accomplished by the use of a high-efficiency insulation developed by the Linde Division of Union Carbide in the DOE program. Moreover, small battery tests in the laboratory indicate that the battery could have outstanding reliability. A ten-cell series-connected battery continued to operate at a reduced output with up to three failed cells.

* Electric-vehicle cells have been crushed in 30 mph crash-barrier tests without incident. Vibration and repeated thermal cycling have also been shown to have no effect upon cell performance.

7.0 CELL AND BATTERY COST PROJECTIONS (A. A. Chilenskas)

7.1 Cell Materials Cost

The materials employed in the construction of the Li-Al/FeS cell are shown in Table 7.1. Conventional materials of low cost are employed with the exception of the lithium and BN felt (developed specially for this technology). A low-cost separator consisting of a pressed mixture of MgO and electrolyte powders is under development.

Table 7.1. Cell Materials of Construction

Component	Materials
Active Materials	
Negative Electrode	50 at. % Li-Al
Positive Electrode	FeS
Electrolyte	67 mol % LiCl-33 mol % KCl
Separator	BN felt or MgO powder
Current Collector and Particle Retainer	Low-Carbon Steel, AISI 1008, 1010
Bus Bars and Terminals	Low-Carbon Steel and Copper-Cored Steel
Cell Housing	Low-Carbon Steel or Stainless Steel
Positive Terminal Feedthrough	
Insulators	Al ₂ O ₃ (upper), BeO (lower)
Sealant	BN Powder
Housing	Low-Carbon or Stainless Steel

At present, the BN felt is provided in laboratory-scale quantities and is priced at about \$2500/m², although the raw materials, B₂O₃ and NH₃, are abundant and inexpensive. Some process development that would lead to lower production costs has been completed by the felt manufacturer (Carborundum Corp.). The cost is projected by the manufacturer to decrease rapidly with increased volume of production and is expected to drop to about \$50/m² with a production volume sufficient for 3,400 vehicle batteries per year. Costs approaching \$10-20/m² have been projected by the manufacturer for high-volume production, e.g., 100,000 vehicle batteries per year.

Fabrication costs of the cells can be expected to be very low. The principal components of the cell, the negative and positive electrodes, are now fabricated by cold-pressing powders of the active materials mixed with the electrolyte.

7.2 Cell Manufacturing Cost

A manufacturing cost estimate for Li-Al/FeS cells to be used in stationary energy-storage (SES) applications was reported in 1976.¹⁶² These cost calculations were updated in 1979¹⁶³ and expanded to include Li-Al/FeS and Li-Al/FeS₂ cells designed for electric-vehicle applications. For a manufacturing plant producing about 40,000 electric-vehicle batteries per year, the analysis indicated that the manufacturing cost (in 1979 dollars) would be \$24 to 41/kWh for SES cells and \$31 to 55/kWh for electric-vehicle cells. The materials cost was found to be between 52 and 65% of the total manufacturing cost. The most expensive materials and components were lithium (metal and compounds), \$4.61 to 14.26/kWh; BN felt, \$4.0 to 8.50/kWh; feedthrough components, \$2.40/kWh; positive current collectors, \$1.48 to 2.20/kWh; and aluminum, \$1.43 to 1.66 kWh.

These costs, which include a 25% return on capital investment, are summarized in Fig. 7.1. Low and high estimates are made for each type of cell to allow for the uncertainties in materials and fabrication costs.

Fig. 7.1.

Estimates of Material and Manufacturing Costs for Li/MS_x Cells in 1979 Dollars (high and low estimates given)

7.3 Manufacturing Cost of Insulated Battery Enclosures

The cost of manufacturing battery enclosures¹⁵¹ with glass-board insulation was estimated by the Linde Division of Union Carbide for two production levels--1000 units and 200,000 units per year. These estimates are given in Table 7.2.

Table 7.2. Manufacturing Cost of Insulated Battery Enclosures

	Cost in 1981 Dollars	
	1000 unit/y	200,000 unit/y
Direct Material	363,000	14,200,000
Direct Labor ^a	563,700	8,634,900
Subtotal	926,700	22,834,900
Contingency at 20%	185,340	4,566,980
Subtotal	1,112,040	27,401,880
Warranty Expense at 2%	22,240	548,000
Product Overhead at 17%	189,050	4,658,320
Subtotal	1,323,330	32,608,200
Equipment Depreciation (12 y)	69,560	1,211,810
Building Depreciation (25 y)	7,000	262,000
Return on Investment	250,640	6,098,860
Total Cost	1,650,530	40,180,870
Cost/Unit	1,650	201

^aIncludes indirect material, indirect labor, service expenses, and manufacturing staff.

The enclosures are rectangular, with outer dimensions of 0.3 × 0.3 × 1.6 m. Assuming that the enclosed battery has a volumetric energy density of 150 Wh/L, the enclosures provide for 22-kWh storage and would cost \$75/kWh at 1000 units/y and \$9/kWh at 200,000 units/y.

7.4 Battery Manufacturing Cost

As noted, the ANL cost estimates show the cell manufacturing cost for electric-vehicle batteries to range from \$31 to 55/kWh. Cost estimates by the Linde Division of Union Carbide indicate a cost of \$9/kWh for the insulated battery enclosure. Including heating and cooling auxiliaries, ANL estimated that the manufacturing cost of a Li-Al/FeS electric-vehicle battery ranges from \$59 to 90/kWh (1979 dollars).

Other manufacturing cost estimates (1978 dollars) were made by industrial firms that participated in ANL's cell development program. For a pilot-plant producing 10,000 electric-vehicle batteries per year, the cost was estimated to be \$86-128/kWh by Gould and \$181/kWh by Eagle-Picher. For a first-generation manufacturing plant producing 70,000 electric-vehicle batteries per year, the costs were estimated as \$70-106/kWh by Gould and \$127/kWh by Eagle-Picher.

8.0 REMAINING PROBLEMS AND ISSUES

8.1 Battery Design

8.1.1 Thermal Management

Design and test work needs to be carried out on the light-weight and compact insulated cases for the battery using the high-efficiency insulating materials developed by Linde. Problem areas that need to be addressed include (1) dimensional changes in the inner case wall caused by thermal expansion and (2) heat loss from the battery caused by penetrations, case edge losses, etc.

8.1.2 Charger

A need exists for an inexpensive charger that provides the required charging and equalizing of the battery. The present charger design needs additional work directed to sizing the equalizing circuits for smaller currents and examining the impact of this change upon cost.

8.2 Manufacturing Costs

The outstanding issue for the Li-Al/FeS system is the manufacturing cost of BN felt. Present cost of the felt is high, although the materials that go into its manufacture are abundant and inexpensive. A low-cost alternative to BN felt, MgO powder, has been employed with considerable success.

The potential for cost reduction by fabricating the cells in a discharged state needs further exploration. The discharge product of the cell reaction, Li_2S , has been produced from Li_2CO_3 and H_2S in small batches. Because Li_2CO_3 is inexpensive relative to lithium metal, the potential for cost reduction appears real. Cells fabricated in the discharged state have been operated successfully.

8.3 Estimated Lifetimes for Cell Hardware

For state-of-the-art cells, no lifetime-limiting problems are foreseen for the ceramic components. The BeO insulators, as well as the BN felt and MgO powder separators, are inherently stable in Li-Al/FeS_x. However, boron nitride cannot be used with Li_4Si electrodes.

The performance of current collectors is readily influenced by such factors as collector design, material used for fabrication, electrode composition, operating temperature, and cycling conditions. The lifetime projections listed in Table 8.1 are based on the results of post-test cell examinations and corrosion tests. The lifetime values for the honeycomb current collectors estimate the time for complete reactions to occur. The perimeter framing and cross-members in this design will still provide mechanical support and some current collection beyond these projected lifetimes. The lifetime values for the flat sheet collectors represent 50 to 60% reaction of the collector. For these calculations, a minimum collector thickness of 0.010 to 0.013 cm was considered essential for electrode support and current collection. The stainless steel retainers used for both electrodes should remain serviceable for more than five years.

Table 8.1. Lifetime Projections for Current Collectors
in State-of-the-Art Cells

Cell Design ^a	Collector Design	Lifetime, y	
		Positive	Negative
EP Group IX	Honeycomb (5 mil, AISI 1010 Steel)	1.2	2.6
EP Group X	Honeycomb (5 mil, AISI 1010 steel)	1.2	2.4
EP Group XI	Flat Sheet (10 mil, AISI 1010 steel)	4.7	1.5
Gould Group II	Flat Sheet (10 mil, nickel)	>5	3.2
Gould Development	Flat Sheet (10 mil, nickel)	>5	2.2

^aEP = Eagle-Picher Industries, Inc.

The primary factors that limit the lifetimes of negative electrode collectors are: increased temperature, reduced electrode capacity, and the partial substitution of Li-Si for Li-Al. Adding excess iron powder to the positive electrode would increase the lifetime of low-carbon-steel collectors to meet design goals.

8.4 Cell Design

The projected specific energy and specific power of the Li-alloy/FeS cells are 105-120 Wh/kg at the 3-h discharge rate and 155-190 W/kg at 50% depth of discharge. The candidate negative electrodes include Li-Al, Li-Al-Fe, and Li-Si electrodes.

The Li-Al/FeS cells have been operated for over 1000 cycles and show promise of even longer lifetimes. Specific energies of greater than 110 Wh/kg at the 3-h discharge rate will require higher-performance cell designs. Bipolar cell designs with electrolyte-starved electrodes have shown promise of delivering higher performance while maintaining long cycle life.

The Li-Al/FeS cells with the longest cycle life have contained BN felt separators. Further efforts are needed to develop Li-Al/FeS cells with MgO powder separators that can attain 1000 cycles or greater. The longest-lived Li-Al/FeS cells require a fine mesh screen on the face of the negative electrode to prevent formation of Li-Al protrusions. To meet the cost goals of cells for electric-vehicle batteries, a more cost-effective means of extending the cycle life will be required.

The Li-Al-Fe/FeS and Li-Si/FeS cells show the greatest potential for attaining higher specific energy compared with Li-Al/FeS cells. The Li-Al-Fe/FeS cell also shows potential for higher specific power. Further efforts are needed to develop Li-Si electrodes with the high power of Li-Al electrodes. Development of higher performance electrodes will require studies of the corrosion of these electrodes on negative electrode current collectors and the separators. Cycle-life testing of these electrodes is also needed.

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