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HIGH-PERFORMANCE BATTERIES FOR OFF-PEAK ENERGY STORAGE

Progress Report for the Period
January-June 1973

by

P. A. Nelson, W. J. Walsh, R. K. Steunenberg,
J. E. Battles, M. L. Kyle, K. M. Myles,
H. Shimotake, N. P. Yao, J. R. Birk,
W. D. Tuohig, D. S. Webster, and L. Burris

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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Chemical Engineering Division

March 1974

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ABSTRACT

This report is the first in a series of semiannual reports on a program to develop high-specific-energy lithium/sulfur batteries for off-peak energy storage in electric utility networks. The design goals for the battery include a specific energy of 150-200 W-hr/kg, a specific power of 25-50 W/kg, and a life-time of 5 years and more than 1250 charge-discharge cycles.

The cell design that has been selected for the initial studies has upper and lower negative electrodes of a lithium-aluminum alloy, a central positive electrode containing sulfur and additives to lower the sulfur vapor pressure, and a molten LiCl-KCl eutectic electrolyte (mp, 352°C). The cell operating temperature is about 400°C. Initial cell tests have been directed toward development of (1) a Li-Al alloy electrode, formed by electrochemical deposition of lithium on a porous substrate of aluminum fibers and (2) a sulfur electrode consisting of a mixture of a sulfur-arsenic alloy and finely divided carbon. The cell development effort is supported by Laboratory studies, in which problems associated with cell reactions are investigated, and by materials studies, in which cell components are fabricated and new materials of construction are identified and tested to determine their corrosion resistance to the cell environment.

SUMMARY

This program, which was recently undertaken for the U. S. Atomic Energy Commission, is directed toward the development of high-specific-energy lithium/sulfur batteries for off-peak energy storage in electric utility networks. The batteries would be recharged by the base-load generating stations during low-use periods (at night) and discharged into the utility network during the day, when the demand for energy is highest.

Cell Development

Design studies were performed to guide the developmental effort toward the most practical cell designs for the off-peak energy storage application. After considering the various alternatives, a bicell design was selected for the early work in this program. The cell has Li-Al alloy negative electrodes at the top and bottom and a central positive electrode consisting

of a sulfur-arsenic-carbon mixture. Other components tentatively selected include a boron nitride fabric separator, LiCl-KCl electrolyte, a centrally located feedthrough, and a stainless steel cell housing. The cell has an operating temperature of about 400°C. This cell design appears capable of achieving a specific energy of 150 to 200 W-hr/kg, which is the goal for off-peak energy storage.

An experimental effort was undertaken to develop a full-scale, high-performance Li-Al electrode for use in large (150 A-hr) sealed cells. The initial work was directed toward improving the slow and tedious electrode formation procedure which had hampered Li-Al electrode development efforts at other laboratories. A major improvement was achieved in the electrochemical formation of Li-Al electrodes through the use of a porous aluminum substrate. Structural constraints were found to be effective in reducing electrode expansion and deformation. The electrical performance of the Li-Al electrode was highly encouraging: the design goal of 0.4 A-hr/cm² at 0.1 A/cm² was achieved in several cells. The ampere-hour efficiency was generally about 100% and current densities of 0.1 to 0.2 A/cm² were achieved without significant polarization. Boron nitride fabric separators were found to be compatible with Li-Al electrodes. No deterioration of the Li-Al electrode was observed in any of the tests performed. Additional improvements are needed with respect to the geometry control of Li-Al electrodes.

The positive electrodes tested consisted of sulfur-arsenic alloys mixed with finely divided carbon to improve current collection. These electrodes showed good short-term electrical performance, with the design goal of 1.0 A-hr/cm³ being achieved. Erratic performance and short electrode lifetimes in the early tests were traced to incomplete alloying of the sulfur and arsenic because of surface oxides on the arsenic powder. A major improvement in lifetime and cell stability resulted when well-alloyed S-As mixtures were used in the electrodes. The feasibility of using molybdenum current collectors in the S-As-C electrodes was demonstrated through the use of charge cutoff voltages of less than 2.7 V (above this voltage, molybdenum reacts with the molten-salt electrolyte). Additional improvements are needed in the lifetime and current collection of S-As-C electrodes.

A full-scale (13-cm-dia) sealed cell (Cell No. W-1) was constructed near the end of this reporting period. Major components included upper and lower Li-Al electrodes (rated capacities, 75 A-hr each), a central S-As-C electrode (rated capacity, 150 A-hr), a 0.15-cm-thick separator of boron nitride fabric surrounding the S-As-C electrode, a housing of E-Brite 26-1 stainless steel, and a compression feedthrough having a molybdenum conductor and boron nitride insulation. Cell No. W-1 is the first hermetically sealed, welded cell developed in this program.

Supporting Laboratory Studies

Supporting laboratory studies are conducted to solve chemical problems that arise in the cell development work, to investigate the chemistry of the cell reactions, and to explore new electrochemical systems that may lead to improvements in the development of lithium/sulfur cells.

Soluble additives such as arsenic and selenium have been used to suppress the vapor pressure of sulfur and thereby decrease its loss through vaporization in lithium/sulfur cells. The effect of these additives on the vapor pressure of sulfur can be expressed by a modified form of Raoult's law that takes into account the polymerization of sulfur in the vapor phase. Experimental results, together with literature data, have indicated that partial discharge of a lithium/sulfur cell results in a mixture of Li_2S and sulfur which forms intermediate species such as S_2^- and S_2^{2-} . Since these species are somewhat soluble in the electrolyte, they represent a possible path for the transfer of sulfur from the sulfur electrode to the lithium electrode in a cell.

Various techniques for avoiding this type of transfer have been under investigation. Four lithium/sulfur-arsenic cells were operated at temperatures of 375-400°C to study the characteristics of the sulfur-arsenic electrode. The results showed that a diffusion barrier is required to confine the sulfur-arsenic mixture in the positive electrode and that AsCl_3 can be formed at charge cutoff voltages above about 2.9 V. An attempt to operate a lithium/sulfur-arsenic cell at lower temperatures of 305 to 330°C with LiCl-KCl-CsCl eutectic as the electrolyte proved unsuccessful in decreasing the transfer of sulfur to the lithium electrode.

The use of sulfides, rather than sulfur, as the active material in the positive electrode was investigated by operating a lithium/ Sb_2S_3 cell. Although this type of cell probably would not be suitable for practical application because of the high equivalent weight of antimony, this test demonstrated the feasibility of using sulfides as the active material in the positive electrode of lithium/sulfur cells. Preliminary tests of lithium/ FeS and lithium/ FeS_2 cells have shown that these cells exhibit very consistent electrical performance with high coulombic efficiencies (95-100%) and high utilization (80-90%) of the FeS or FeS_2 . Further studies of iron sulfides as the active material in the positive electrode are in progress.

Two sodium/sulfur cells having beta-alumina solid electrolytes were tested to provide a comparison with the performance of lithium/sulfur cells. The results suggest that the liquid-electrolyte lithium-sulfur cells are inherently capable of higher power densities than solid-electrolyte sodium/sulfur cells. A brief experimental study has been initiated to investigate the feasibility of operating a sodium/sulfur cell having a molten alkali-halide electrolyte.

Oxidation potential measurements have indicated that E-Brite 26-1 (a ferritic stainless steel) cannot be used at the sulfur electrode potential in the presence of LiCl-KCl electrolyte. However, it should be a suitable material for parts such as cell housings, which are maintained at the lithium potential.

Materials Testing and Fabrication

The development of hermetically sealed cells requires an electrical feedthrough constructed of materials that are compatible with the cell environment and are also lightweight and inexpensive. A compression-type feedthrough has been fabricated and is being evaluated in operating cells.

This feedthrough has several unique advantages; these include ease of construction, absence of a ceramic-to-metal braze, and elimination of the need for materials with matching coefficients of thermal expansion. The primary disadvantages are cost, weight, and size.

An impervious ceramic with improved mechanical properties is being sought to replace the lower boron nitride insulator in compression-type feedthroughs. Techniques have been developed for fabricating high-density [$>96\%$ of theoretical density (TD)] CaZrO_3 bodies using a pressure-sintering or hot-pressing process. Helium leak-detector tests have shown that CaZrO_3 bodies with densities greater than 95% of TD are impermeable to helium. In contrast, specimens with densities less than 91% of TD were grossly permeable to air. If the higher-density CaZrO_3 proves to be suitable for in-cell use, an effort will be made to produce equally suitable CaZrO_3 insulators by the less expensive technique of cold-pressing and sintering.

The fabrication of auxiliary cell components, such as cell housings, lithium-electrode current collectors, and sulfur-electrode current collectors is discussed. The cell housings (13-cm OD by 5 cm high) are fabricated from 20-mil E-Brite 26-1 stainless steel sheet, either by welding or by spinning. The sulfur-electrode current collector, which is in the shape of a basket, is fabricated from expanded molybdenum mesh. The current collectors for the Li-Al electrodes are fabricated by spot-welding stainless steel screens to stainless steel rings, thereby forming an enclosure to contain the Li-Al electrode.

Electrode separators are made from a boron nitride fabric woven from 30-mil, two-ply yarn. Compatibility tests in lithium at 400°C (cell operating temperature) have shown that a high-temperature (1700°C) treatment of the BN material in nitrogen effectively removes a residual B_2O_3 impurity; without this treatment, lithium reacts with the B_2O_3 , thereby resulting in deterioration of the BN fabric. The treatment is also effective in preventing the formation of a conductive surface layer on solid BN upon exposure to lithium. Although these test conditions are more severe than are encountered with Li-Al electrodes, the nitrogen treatment may be necessary for obtaining optimum performance from BN separators.

Corrosion tests of cold-rolled and annealed tungsten sheet in a mixture of S-10 at. % As and LiCl-KCl electrolyte revealed that the cold-rolled sheet experienced severe delamination and disintegration. The annealed tungsten was unaffected. Also, samples of cold-rolled sheet with electron-beam-welded edges were relatively unaffected.

I. INTRODUCTION

This is the first semiannual report on a program that has been undertaken by Argonne National Laboratory for the U.S. Atomic Energy Commission on the development of lithium/sulfur batteries for the storage of off-peak electrical energy. In various parts of the United States, electrical power shortages are developing during the peak load periods that occur during a few hours of the day. The use of secondary (electrically rechargeable) batteries may be an attractive alternative to the present methods of providing power during peak-demand periods.¹ In order to generate electrical power at the lowest cost and with the least pollution, the utilities normally use their newer, more efficient fossil fuel and nuclear generating stations to meet the base-load demand. During periods of high demand, the older fossil-fueled plants may be brought on line, and finally such supplemental sources as gas turbines or diesel engines can be activated. In some locations, pumped hydroelectric storage is used to provide supplemental power during periods of high demand. In this case, surplus power from the base-load plants is used to pump water to a storage reservoir during off-peak periods and the potential energy is recovered by a hydroelectric generator and fed to the power grid during the periods of high demand. The use of pumped hydroelectric storage, however, is limited to those areas having a suitable topography.

Secondary batteries, particularly those such as the lithium/sulfur battery, which is expected to have a high specific energy of about 150 to 200 W-hr/kg, have several potential advantages over the present methods of meeting peak-power requirements. A battery of this type would be modular in construction, quiet, emit no pollutants, and require no on-site fuel storage. These features would permit the batteries to be distributed throughout a utility network near the points of power use. The battery installations would be charged during the 4- to 8-hr daily off-peak period and discharged into the network as the demand increased.

The use of batteries for off-peak energy storage has several potential advantages,¹ including the following:

- (1) Lower transmission costs. The location of batteries throughout a utility network would tend to even the load on the transmission system, which would no longer need to be sized to accommodate peak loads. Since about 38% of the capital cost of providing power to a customer is in the transmission and distribution system, this could result in a significant saving.
- (2) Modular peaking capacity. Since the battery installation would consist of modular units, the number of modules would be determined by the local demand.
- (3) Short lead-time. Once the batteries are produced commercially on a large scale, individual modules would be available on short notice. This feature, combined with the modular nature of the battery installation, would allow great flexibility in siting and planning.
- (4) Low capital investment. Because of the modular nature of the batteries, it would be possible to purchase and install only the capacity that would be required at a site in the immediate future, thereby avoiding capital charges on unused excess capacity.

(5) Conservation of petroleum fuels. Batteries could reduce or eliminate the need for peaking plants such as gas turbines, which require relatively high grade petroleum fuels.

(6) Elimination of dispersed sources of pollution. The reduced need for supplemental fossil-fuel units such as gas turbines, would decrease the pollution caused by the combustion of fossil fuels. Thermal pollution problems would be transferred to the more efficient base-load units where they could be handled more effectively.

Although the use of secondary batteries appears highly attractive as a means of responding to load variations in an electric utility network, there appear to be no commercially available battery systems at the present time that would be capable of meeting the cost, lifetime, and performance requirements for this application. An analysis of these requirements¹ has indicated that a battery cost of \$12-15/kW-hr (at a 10-hr discharge rate) and lifetimes of 5 years and 1500 charge-discharge cycles would be competitive with existing peak power systems. Lead-acid batteries for such service would cost about \$50/kW-hr and nickel/cadmium batteries are much more expensive. Various other battery systems such as zinc/air, nickel/zinc, and sodium/sulfur, and molten-salt batteries, including lithium/sulfur, are currently under development, but none of these have reached the stage of commercial development where their economics and performance for large-scale energy-storage applications are known.²

It appears that the most difficult problem associated with batteries for this application will be to meet the lifetime requirement while maintaining high electrical performance. Since most of the high-performance batteries that are under development³ (e.g., lithium/sulfur,⁴⁻¹² sodium/sulfur,¹³⁻²⁴ lithium/chlorine²⁵⁻³²) operate at temperatures of 300-700°C, corrosion of the cell components is a significant problem. At present, the lifetimes of these high-temperature battery systems have been limited to less than a year.

Several considerations must be taken into account in the selection of a battery system for off-peak energy storage. The active materials that are used in the cells must have a low cost per kilowatt-hour of energy-storage capacity, and they must be sufficiently abundant to meet the needs of a large-scale energy-storage industry. These requirements probably rule out certain battery systems such as nickel/cadmium, silver/zinc, lithium/selenium, and lithium/tellurium. The zinc/air battery³³⁻³⁶ appears to meet these requirements, and it approaches the necessary specific energy, but it is not electrically rechargeable at its current stage of development. The specific-power capability of a battery is also a consideration in the off-peak energy-storage application. Although high specific power is not an absolute necessity if the battery is to be discharged at a 10- to 14-hr rate, it is desirable if the battery is to be recharged rapidly, and it provides more flexibility of operation for emergencies or unusual situations.

The performance goals that have been tentatively adopted for the program at Argonne on the development of lithium/sulfur batteries for off-peak energy storage are given below:

Specific energy	150 to 200 W-hr/kg
Specific power	25 to 50 W/kg
Lifetime	5 yr and >1250 cycles

Cost (as produced commercially)	\$15/kW-hr
Discharge time	10-14 hr
Charge time	4-8 hr
W-hr efficiency	>70%

These performance goals are being reviewed as the work progresses, and may be subject to revision, particularly the cost and the rate of charge and discharge.

The present program complements an existing effort at Argonne National Laboratory on the development of lithium/sulfur batteries for electric automobile propulsion, which is supported by the National Science Foundation.^{8,9} Although both programs are concerned with the development of lithium/sulfur batteries, the two types of batteries have significantly different operational requirements. The electric automobile requires a low-cost, high-specific-energy (200 W-hr/kg), high-specific-power (200 W/kg) battery that is designed for rapid discharge (at the 1-hr rate) and rapid charge acceptance. The off-peak energy storage battery, on the other hand, probably would be designed for a 10-14 hr discharge and a 4-8 hr charge. The longer charge and discharge periods make the energy-storage capability of the off-peak energy battery relatively more important and the specific power requirement relatively less important. The weight of the off-peak energy storage battery is less important, but the lifetime should be at least 5 yr, whereas a 3-yr life for an electric automobile battery may be adequate.

The developmental efforts in the two programs are coordinated under a common management at ANL to avoid overlap or duplication. Where appropriate, the benefits to the AEC program that might be gained from the complementary efforts in the NSF program are indicated.

The only types of batteries currently under investigation that show promise of meeting the criteria for both of the above applications are those that require elevated operating temperatures (lithium/sulfur, sodium/sulfur and lithium/chlorine). All of these systems employ (1) lithium or sodium negative electrodes, which have the desirable characteristics of low electro-negativity, low equivalent weight, and high exchange-current density, (2) a molten-salt or electrolytically conductive solid ceramic electrolyte, and (3) a chalcogen or halogen positive electrode. These materials are all relatively abundant and inexpensive.¹

The lithium/sulfur cell, under development at Argonne National Laboratory³⁻¹⁰ and at the Atomics International Division of North American Rockwell,^{11,12} and the sodium/sulfur cell being investigated at the Ford Motor Co.¹³⁻¹⁵ and various other laboratories¹⁶⁻²⁴ both show promise of meeting or exceeding the requirements for off-peak energy storage. The lithium/chlorine cell under study at General Motors Corp.,²⁵⁻³¹ and elsewhere,³² is capable of meeting the specific-energy requirement, but cannot be operated as an electrically rechargeable cell at its current state of development. At the present time, all of these high-temperature cells can probably be best characterized as being in the advanced laboratory to early development stages.³

A schematic representation of a lithium/sulfur cell, showing the processes that occur within the cell in simplified form, is presented in Fig. 1.

Fig. 1. Schematic Representation of a Lithium/Sulfur Cell

The overall electrochemical reaction that takes place as the cell is discharged can be written as follows:

In the initial stages of the discharge, the cell reaction product is soluble in the sulfur in the positive electrode. As the discharge progresses, however, the Li_2S product precipitates as a solid. The individual reactions occurring at the electrodes can be represented as

At the negative electrode, lithium metal is oxidized to lithium cations which migrate through the molten-salt electrolyte (*e.g.*, LiCl-KCl) to the positive electrode. The electrons from Reaction 2 pass through the external circuit. At the positive electrode, the electrons returning from the external circuit, the lithium cations in the electrolyte, and the sulfur in the electrode undergo Reaction 3. Information in the literature suggests that Reaction 3 occurs in at least two steps and involves various intermediate sulfur-bearing species (*e.g.*, S_2 , S_2^{2-} , S_4^{2-} , and S_3).³⁷⁻⁴² If the cell is discharged to completion, the sulfur is converted entirely to Li_2S (assuming that no excess sulfur is present). The cells, however, are not normally discharged to this point. When the cell is recharged by applying sufficient voltage to cause a current to flow in the opposite direction in the external circuit, the above reactions are all reversed. The open-circuit (no load) voltage of a lithium/sulfur cell at its normal operating temperature of 400°C is approximately 2.4 V.

The current experimental effort on this program involves (1) the engineering development, evaluation, and scaleup of individual lithium/sulfur cells, (2) the development of a 10 kW-hr battery, (3) the development and corrosion testing of cell components, (4) safety studies, and (5) supporting laboratory studies.

II. CELL DEVELOPMENT (W. J. Walsh)

A. Cell Design Studies

During the first few months of the program to develop lithium/sulfur batteries for the storage of off-peak electrical energy, design studies were performed to guide the developmental effort toward practical cell designs for this application. Data obtained in other programs on lithium/chalcogen cells at ANL were evaluated, and features of cell design that most strongly affect specific energy and specific power were identified. Electrodes were tentatively selected, and a preliminary cell design was prepared. Computer calculations were carried out to estimate the expected cell performance for various cell sizes, electrode compositions, separator designs, and other parameters.

1. Selection of Electrodes (W. J. Walsh, H. Shimotake)

A review of the previous battery programs at ANL revealed that the highest performance attained with a sulfur electrode ($>1.0 \text{ A-hr/cm}^3$ of electrode volume) was accomplished with an electronically conductive semisolid paste electrode.⁴³ This electrode consisted of a mixture of sulfur, an additive (*e.g.*, selenium or thallium) to retain sulfur in the electrode, and carbon black to provide electronic conductance and rigidity. A limitation of this electrode was the use of high-cost, low-abundance additives such as selenium and thallium; these additives are considered impractical for the off-peak energy storage application. Recent experiments in the NSF program⁹ have indicated, however, that arsenic, which is abundant and has a relatively low cost ($\sim \$0.50/\text{lb}$), is effective in retaining sulfur in the electrode. Consequently, the early work in the present program has been directed toward the development of a semisolid sulfur-arsenic-carbon electrode system.

Most of the cell development work at ANL has involved negative electrodes consisting of liquid lithium confined in porous stainless steel or nickel Feltmetal.* However, a Li-Al alloy electrode [developed by Sohio for a Li-Al/ TeCl_4 (carbon) battery⁴⁴] was tested in the course of a previous program⁴⁵ at ANL. The Li-Al electrode has several advantages, including relative ease of containment in the electrode structure and compatibility with a variety of ceramic materials (*e.g.*, boron nitride). Moreover, such an electrode is particularly suited for low-power-density applications (*e.g.*, off-peak energy storage) in which sustained current densities in excess of 0.2 A/cm^2 are not required. The principal disadvantage of a Li-Al electrode, relative to a liquid lithium electrode, is the loss of 0.3 V (emf *vs.* sulfur), which results in a reduction of $\sim 17\%$ in the average voltage; however, substantially longer battery lifetimes may be achievable because of reduced corrosion. After considering the various characteristics of the two systems (see Table I), a negative electrode consisting of a porous Li-Al alloy was selected for the early work in this program.

* A product of the Brunswick Corp.

TABLE I. Comparison of Liquid Lithium Electrode and Solid Lithium-Aluminum Electrode

	Lithium- 10 vol % Porous Metal	46 at. % Li- 54 at. % Al Alloy
Composition, wt %		
Lithium	33	15
Aluminum	0	72
Stainless Steel	60	8
Electrolyte	7	5
Physical State	Liquid + Solid	Solid
Current Density Capability	High	Moderate
Emf vs. Sulfur, V	2.3	2.0
Corrosiveness to Ceramics	High	Moderate
Lithium Containment	Under Study	Satisfactory
Materials Cost	Moderate	Moderate

2. Li-Al/S Bicell Design
(W. J. Walsh, P. A. Nelson)

The preliminary cell design developed for the off-peak energy storage application is shown in Fig. 2. This design, which has top and bottom

Fig. 2. Lithium/Sulfur Bicell Design.
ANL Neg. No. 308-3304 Rev. 1

Li-Al electrodes and a central sulfur electrode, and is thus referred to as a bicell design, was selected to allow the use of stainless steel cell housings, to minimize the current density requirements for the Li-Al electrode, and to maximize the utilization of the cell reactants. The LiCl-KCl eutectic (58.5 mol % LiCl-41.5 mol % KCl) was tentatively selected as the electrolyte because of its low density, relatively low cost, and high dissociation potential (~ 3.7 V). A boron nitride cloth infiltrated with liquid electrolyte was selected as the separator between the positive and negative electrodes. The central feedthrough design minimizes the amount of current collector required and allows direct stacking of the cells. This cell design appears capable of achieving a specific energy of ~ 200 W-hr/kg, which is the goal for off-peak energy storage. However, the design is considered to be very preliminary and improvements are anticipated during the course of the work in this program.

3. Cell Performance Calculations (P. A. Nelson, H. Tsai)

Calculations of the expected performance of cells of the basic configuration shown in Fig. 2 were carried out by computer for various combinations of design parameters. The primary design parameters used in these calculations are shown in Table II.

TABLE II. Design Parameters of Li-Al/S Cell

Average Cell Voltage, V	1.5
Sulfur Electrode	
Thickness, cm	0.8
Diameter, cm	12.5
Composition of Type I, ^a wt %	
Sulfur	68
Arsenic	17
Carbon (Vulcan XC-72R)	15
Composition of Type II, wt %	
Sulfur	48
Arsenic	12
Carbon (felt, cloth or powder)	40
Electrolyte Content, ^b wt %	20
Lithium-Aluminum Electrode	
Lithium Utilization, %	80
Composition, vol %	
Aluminum-45 at. % Lithium	93
Electrolyte (LiCl-KCl) ^b	5
Stainless Steel	2
Separator	
Boron Nitride Cloth, ^b vol %	30
Thickness, cm	0.2
Stainless Steel Housing	
Thickness, cm	0.38
Feedthrough	
Tungsten-Terminal Diameter/Sulfur-Electrode Diameter	0.04
Insulator Diameter/Sulfur-Electrode Diameter	0.08

^aType I electrode has a tungsten screen current collector.

^bLiCl-KCl electrolyte is assumed to be present in both electrodes and in the open spaces in the separator cloth. In addition, a sufficient amount is present above the upper lithium-aluminum electrode to provide for a change in volume of $0.7 \text{ cm}^3/\text{g}$ of lithium reacted.

Two types of sulfur electrodes were considered. Type I is a mixture of 68 wt % sulfur-17 wt % arsenic-15 wt % carbon impregnated with electrolyte. (For the calculations, the amount of electrolyte was assumed to be equal to 20 wt % of the electrode mixture.) This electrode would require a current collector of tungsten, or other material of high electrical conductivity, in the form of a screen, or perhaps some other geometry. The size of the current collector was calculated for each cell on the basis of a resistance loss in the current collector of 0.01 V when the cell was discharged at the 10-hr rate. The Type II sulfur electrode has a higher carbon content (40 wt %, electrolyte-free basis) than Type I. The carbon is in the form of felt, cloth, or powder and the overall electrode has a relatively high electrical conductivity. Consequently, no current collector, other than the carbon and graphite materials included in the mixture, would be required for the Type II electrode.

The lithium electrode is a lithium-aluminum alloy containing 45 at. % (17.4 wt %) lithium confined in a stainless steel screen enclosure. The electrode was assumed to contain 5 vol % electrolyte in the fully charged condition.

The separator for the cell was assumed to consist of a boron nitride cloth of 30% bulk density.

The electrolyte in the cell was assumed to fill all the voids in both electrodes and in the separator. In addition, a sufficient quantity of electrolyte was provided in the space above the top of the upper lithium electrode during the volume reduction that occurs on cell discharge.

Design calculations were performed to determine the effects on cell performance of variations in sulfur utilization, sulfur-electrode thickness, sulfur-electrode diameter, and separator thickness. The results are shown in Figs. 3, 4, 5, and 6, respectively, for both types of sulfur electrodes. In each of these calculations, the design parameters given in Table II were held constant except for the parameter being studied.

In Fig. 3, the calculated specific energy, current density, and cell weight are shown as functions of sulfur utilization. Assuming that the utilization of lithium is 80% and Li_2S is the final reaction product, it can be seen that for a cell with a Type I sulfur electrode 0.8 cm thick, the 200 W-hr/kg design goal can be reached with only 60% sulfur utilization. For a cell with a Type II sulfur electrode 0.8 cm thick, a utilization of 80% would be required to reach the same design goal. The current density corresponding to the 10-hr discharge rate increases with sulfur utilization, as expected. The cell weight is also affected by the sulfur utilization, because the cells were designed for 80% lithium utilization; therefore, the size and weight of the lithium electrode increase with increasing sulfur utilization.

The calculated effects of sulfur-electrode thickness on specific energy, current density, and cell weight are illustrated in Fig. 4. In general, the specific energy is quite high even for sulfur electrodes as thin as 0.6 cm. Also, the actual sulfur utilization would be expected to increase with decreasing electrode thickness because of reduced diffusion resistances and decreased interelectrode distances. Therefore, in a practical cell, the specific energy would probably be less affected by sulfur-electrode thickness than is shown in Fig. 4, which arbitrarily assumes a constant sulfur utilization of 70%. A thin sulfur electrode has the additional advantage of a lower current density.

Fig. 3. Effect of Sulfur Utilization on Specific Energy, Current Density, and Cell Weight

at a given charge-discharge rate, as illustrated in the middle plot of Fig. 4. Cell weight is also strongly affected by the sulfur-electrode thickness for a given cell diameter.

The effect of the sulfur-electrode diameter on the cell performance is shown in Fig. 5. The energy delivered (W-hr) increases quadratically because it is proportional to the sulfur-electrode area. The cell weight also varies approximately quadratically with the sulfur-electrode diameter. The specific energy (W-hr/kg) is therefore not strongly affected by the sulfur-electrode diameter. It can be seen that for cells with Type I sulfur electrodes, a maximum in the specific energy occurs at a sulfur-electrode diameter of 15 cm. This effect occurs because, for the same IR-drop requirement (0.01 V at a 10-hr discharge rate), the current collector of a larger cell has to be thicker; the increased thickness, in turn, affects the cell weight significantly owing to the high specific weight of the current collector. For a cell with a Type I sulfur electrode, it appears that a cell diameter greater than 15 cm is not desirable from the standpoint of performance. This is also believed to be true for the Type II sulfur electrode.

Fig. 4. Effect of Sulfur Electrode Thickness on Specific Energy, Current Density, and Cell Weight

The effect of the separator thickness on cell performance was also studied. A thin separator decreases the interelectrode distance and the weight of the cell. However, the separator must be thick enough to maintain its structural integrity and compact enough to result in effective separation of the electrode materials. Shown in Fig. 6 are the calculated cell characteristics as a function of separator thickness. Owing mainly to the increased weight of the separator, the specific energy of the cell decreases rather sharply with increasing separator thickness. For example, for cells employing Type I sulfur electrodes, the specific energy drops from 264 W-hr/kg for a 0.1-cm separator thickness to 190 W-hr/kg for a 0.5 cm separator thickness.

4. Heat Removal from Disk-Shaped Cells (P. A. Nelson, H. Tsai)

In the lithium/sulfur cells, part of the energy generated by the electrochemical reaction is released as heat. As a result, the temperature at the center of the cell will be higher than that at the outer boundary, where the heat is removed. Calculations (previously described in Ref. 9, pp. 19-20) were performed to determine the temperature difference for typical Li-Al/S cell

Fig. 5. Effect of Sulfur Electrode Diameter on Specific Energy, Current, and Cell Weight

conditions, as described below.

For a cell delivering a specific energy of 0.420 W/cm^3 (about 220 W/kg) and operating at an energy efficiency of 80% during the discharge portion of the cycle, the heat generation rate would be 0.105 W/cm^3 . A conservative estimate of the average thermal conductivity of the entire cell indicated a value of about $0.15 \text{ W/(cm)(}^\circ\text{C)}$ [about $9 \text{ BTU/(ft)(}^\circ\text{F)}$] for Li-Al/S cells. For these values of heat generation rate and thermal conductivity (both assumed to be uniform throughout the cell), the calculated temperature difference between the center and the circumference of a cell of the design shown in Fig. 2 would be about 7°C for a cell 12.5 cm in diameter and 18°C for a cell 20 cm in diameter. These values are considered to be higher than would be expected in an operating cell because the thermal conductivity value used was conservatively low and the assumed heat generation rate was higher than expected for sustained operation of the batteries. Therefore, the temperature differential expected for cells up to 20 cm in diameter should be small enough that the cells can be operated with both the center and the perimeter of the cell at temperatures within the acceptable operating range (370 to 410°C).

Fig. 6. Effect of Separator Thickness on Specific Energy, Cell Height, and Cell Weight

B. Lithium-Aluminum Electrode Studies (N. P. Yao, J. D. Arntzen)

1. Goals

The overall goal of these studies is to develop a practical lithium-aluminum electrode for off-peak energy storage application. Design studies (see Section II.A) indicate that a Li-Al/S battery should be capable of achieving the goal for the off-peak energy application, namely, a specific energy of 200 W-hr/kg at the 10-hr rate. On this basis, an experimental effort was undertaken to develop a practical Li-Al electrode for use in Li-Al/S cells. It is believed that the electrode must be capable of delivering a minimum capacity density of 0.4 A-hr/cm² and a capacity per unit volume of 0.7 A-hr/cm³ at a current density of 0.1 A/cm² for repeated cycles over thousands of hours for this application. The immediate objective is to develop a high-performance lithium-aluminum electrode having a diameter of 12.8 cm for use in 150 A-hr sealed cells.

2. Previous Work on Li-Al Electrodes

A lithium-aluminum alloy⁴⁶ has been utilized as the solid negative electrode in Sohio's Li-Al/TeCl₄(carbon) battery.⁴⁴ Excellent electrochemical performance has been reported⁴⁷⁻⁵⁰ for electrochemically prepared lithium-aluminum alloys (composition range, 5 to 30 wt % Li) in molten salt systems. It has also been reported⁵¹ that, in the temperature range from 300 to 380°C, the emf of the lithium-aluminum alloy electrode was constant, about 0.3 V versus a Li°/Li⁺ reference electrode, and was independent of the lithium concentration up to about 45 at. % (17.4 wt %) Li in the alloy. (With increasing lithium concentration above 45 at. %, the Li-Al electrode voltage approached that of the Li°/Li⁺ electrode.) The alloy electrode also exhibited relatively constant discharge and charge voltages.

Previous developmental efforts⁴⁷⁻⁵¹ on the Li-Al alloy electrodes have been based on electrochemically depositing lithium onto a substrate of solid aluminum metal. The use of a solid aluminum substrate required repeated electrical cycling at gradually increasing current densities to achieve a porous, electrochemically active surface; thus, the electrode preparation (or formation) procedure was very slow and tedious. The resultant porous structure of the Li-Al alloy was often dendritic and was subject to gradual structural disintegration with discharge-charge cycling. To overcome these difficulties, Chilenskas *et al.*⁴⁵ investigated Li-Al alloy formation on a substrate of high-surface-area aluminum Feltmetal (53% porosity). This procedure yielded a lithium loading in the alloy corresponding to a capacity density of about 0.2 A-hr/cm² at 0.1 A/cm² current density during the first two formation cycles. The ampere-hour efficiency was between 56 and 71%. The results of this work suggested that the tedious Li-Al alloy preparation could be substantially abbreviated by use of porous aluminum substrates; however, improvements in the capacity density and ampere-hour efficiency of the electrode would be needed to achieve the goals for off-peak energy storage applications.

Our effort in this task has been directed toward achieving this improvement. The procedures for electrode formation and tests of the resulting electrodes are described below.

3. Electrode Materials and Designs

Four types of commercially available, porous aluminum were obtained for inspection and testing: fiber disks, wire disks, foam, and sintered powder plaques. Of these, the fiber and wire disks were judged to have the best quality in appearance and in strength. Initial tests were conducted using the fiber disks as substrate material. The other forms of porous aluminum will be investigated in future tests and the performance of the electrodes will be compared with that of electrodes utilizing the fiber disks.

The aluminum fibers (Brunswick Experiment Fibers, 1100 grade, 99% purity), which are available in various diameters from 38 to 127 μ m, are produced by a proprietary process of the Brunswick Corporation. The fibers used in the disks were made from single fibers reported to have a minimum continuous length of about 2 ft. The apparent surface areas for fibers having diameters of 51 and 127 μ m were calculated to be 77 and 39 cm²/g, respectively. The fiber disks, which were supplied by the Brunswick Corp., were made by compacting the loosely packed aluminum fibers at room temperature in a die. The porosity

of the disks, which varied from ~ 30 to $\sim 55\%$, was controlled by the weight of aluminum and the size of the disks. Figure 7 shows a 7-cm-dia aluminum fiber disk made by loose-fiber compaction. Scanning electron micrographs showed that the fibers were randomly oriented with some surface deformation due to compaction (Fig. 8) and the fiber surface consisted of many fine grain boundaries (Fig. 9).

Fig. 7. Aluminum Fiber Disk (diameter, 7 cm; thickness, 0.48 cm; porosity, 50%; fiber diameter, 51 μm)

Four types of electrode structures have been tested using the fiber disks as the substrates. The designs of the electrode structures are shown schematically in Fig. 10. The Type A structure consisted of a bare aluminum fiber disk and several stainless steel wires. The wires were passed through small holes drilled in the disks to limit electrode expansion during the initial Li-Al formation; the wires also served as current collectors. For the electrode formation process, Type A structures were generally placed at the bottom of a stainless steel cell and the current-collector wires were spot-welded to the cell case. A 0.32-cm-dia stainless steel rod welded to the cell case served as the current lead. The Type A electrode had sufficient current collection, but the wires were inadequate in constraining the electrode expansion during the Li-Al alloy formation. The electrodes expanded (in an irregular shape) to as much as three times the original volume of the fiber disk, and gradual disintegration and loss of Li-Al alloy fines occurred.

Fig. 8. Scanning Electron Micrograph of Aluminum Fiber Disk Showing Random Orientation of Fibers (fiber diameter, $38\text{ }\mu\text{m}$; 200X). ANL Neg. No. 308-3250

Fig. 9. Scanning Electron Micrograph of Aluminum Fiber Surface Showing Fine Grain Boundaries (fiber diameter, $38\text{ }\mu\text{m}$; 1000X). ANL Neg. No. 308-3251

Fig. 10. Electrode Structures for Formation of Li-Al Electrodes

The design of the electrode structure was, therefore, modified for better containment of the Li-Al alloy. In the Type B design, the fiber disk was covered by a fine-mesh, stainless steel wire screen (40 by 40 mesh, 0.25-mm-dia wire). Stainless steel wires were again woven through the disk for electrode constraint and current collection. Both the screens and the wires were rigidly spot-welded to the cell case. This electrode structure significantly reduced the electrode expansion and resulted in improved containment of the electrode material. Lithium-aluminum electrodes prepared in this manner retained their physical integrity and electrical performance throughout the testing periods (up to 700 hr).

In the Type C and D designs the aluminum disk was totally enclosed in a screen basket. The electrode structure was attached to a stainless steel rod (0.32-cm-dia) with nuts, and this rod served as the electrode terminal. In the Type D structure, the screen basket was bent 90° upward at the periphery (for welding to the cell housing) to save space in the radial direction (see Fig. 10).

4. Experimental Procedures

The assembly of the electrochemical cells (except for the electrode-structure assembly), the formation of the Li-Al electrode, and the performance tests were conducted in a high-purity helium-atmosphere glovebox (O_2 , <2 ppm; H_2O , <5 ppm; N_2 , <10 ppm). Monitoring of the cell electrical performance and the control of automatic cell cycling were carried out by a means of a recorder console located outside the box. The electrical connections between the cell and the console were made at a feedthrough which was sealed into the glovebox wall. A data-acquisition system was used to automatically record the cell voltage, current, and temperature at frequent intervals on a paper tape, which was later processed for data reduction and printout.

A typical cell for the electrochemical formation of a Li-Al alloy electrode, namely that of cell LA-5, is shown in Fig. 11. The porous aluminum fiber disk served as the positive electrode. In all cells except Cell LA-3, the negative electrode consisted of liquid lithium and a nickel Feltmetal current collector confined within a BeO cup. In Cell LA-3, the Li-Al electrode of Cell LA-2 served as the negative electrode. The two Li-Al electrodes were used to test the compatibility of a boron nitride separator fabric with the Li-Al alloy in the absence of liquid lithium, which may attack the BN cloth. The electrolyte used in the cells was either 3.5 mol % LiF-56.0 mol % LiCl-40.5 mol % KCl or 58.5 mol % LiCl-41.5 mol % KCl.

The Li-Al alloy formation procedure involved electrically discharging and charging the Li(Al)/Li cell either at gradually increasing current or at constant current. During the cell discharge, lithium was deposited onto the aluminum substrate, forming a Li-Al alloy on the surface. Lithium was removed from the alloy during the cell charge. All the cells were operated at temperatures between 400 and 450°C.

Six electrochemical cells using different aluminum fiber disks as the starting materials were tested to obtain the requisite data for the development of an effective Li-Al electrode suitable for use in full-size Li-Al/S cells.

Fig. 11. Typical Li-Al Formation Cell (Cell LA-5)

Table III summarizes the physical characteristics of the aluminum fiber disks, the type of electrode structure, and the duration of cell tests. The disks tested were either 2.54 or 7.0 cm in diameter with thicknesses ranging from 0.32 to 1.01 cm. The maximum lithium capacity for these electrodes varied between 2.7 and 39.5 A-hr (based on a 45 at. % Li-Al alloy).

TABLE III. Description of Aluminum Fiber Disk Electrodes and Duration of Cell Tests^a

Cell No.	LA-1	LA-2	LA-3	LA-5	LA-6	LA-7
Physical Characteristics of Al Disks						
Diameter, cm	2.54	2.54	2.54	7.0	7.0	7.0
Thickness, cm	0.43	0.35	0.41	0.32	1.01	0.63
Weight, g	3.2	3.3	4.0	15.6	47.1	32.0
Fiber Diameter, μm	38	38	127	50	64	64
Porosity, %	45	31	28	53	55.5	51.1
Max. Li Capacity ^b						
Grams of Li	0.674	0.695	0.843	3.29	9.92	6.74
A-hr	2.61	2.69	3.26	12.7	38.3	26.1
Electrode Structure Type ^c	A	B	C	B	B	B
Total No. of Cycles	18	10	39	23	20	8
Total Hours of Test	380	80	310	360	700	320

^a Tests were performed with ternary LiF-LiCl-KCl or binary LiCl-KCl eutectic molten-salt electrolytes at temperatures of 400 to 450°C. Counterelectrodes were liquid Li with nickel Feltmetal current collectors for all cells except LA-3, in which the Li-Al electrode of Cell LA-2 served as the counter-electrode.

^b Based on a Li-Al alloy containing 45 at. % (17.4 wt %) Li.

^c The electrode structures are shown in Fig. 10.

In the experimental procedure, the cell, which contained the aluminum disk and the salt electrolyte, was evacuated at room temperature. The salt was then melted under a vacuum and the porous aluminum disk was allowed to soak overnight. The BeO cup and lithium electrode were then introduced into the cell and appropriate electrical connections made to the external circuit.

5. Results

In cells LA-1 through LA-3, which had 2.54-cm-dia electrodes, the main objectives were to investigate alloy-formation characteristics and the capability for rapid alloy formation, to obtain electrical-performance data, to test the compatibility of BN with the Li-Al electrode, and to test the effects of structural constraints during the formation process. The principal results obtained from operation of the three cells are as follows:

1. In Cell LA-1, an alloy having a composition of 43 at. % lithium was formed at a current density of 0.12 A/cm² within 1 to 2 cycles.

2. The maximum capacity density achieved (in Cell LA-1) was greater than 0.4 A-hr/cm^2 at 0.1 A/cm^2 current density. The capacity density of the Li-Al electrode in Cell LA-3 showed a decrease from 0.38 to 0.32 A-hr/cm^2 over a period of 310 hr and 39 cycles. The capacity loss was attributed to a loss of electrode material rather than to electrochemical processes. The ampere-hour efficiency of the Li-Al electrodes in long-term performance was nearly 100%. The electrodes could support a current density of 0.2 A/cm^2 without polarization.

3. Separators of boron nitride fabric appear to be chemically compatible with Li-Al electrodes. The presence of the BN fabric did not interfere with the electrode performance in the 310-hr test of Cell LA-3.

4. The use of an enclosure made of stainless steel wire screen (Type C electrode structure, Fig. 10) improved the mechanical integrity of the Li-Al electrode and reduced the volume expansion. The screen constraints had no effect on the electrochemical performance of the electrode.

The volume expansion of a Li-Al electrode during the electrochemical formation process occurs as a result of an expansion in thickness; the diameter remains unchanged. In these tests, the expansion was very irregular and produced an uneven surface. The volume-expansion factor for electrode structure Type B (Cell LA-2) was about 1.5 to 2.5, and that for electrode structure Type C (Cell LA-3) was about 1.3 to 1.7. Although the mechanical integrity of the electrodes was improved by the use of an enclosure made of stainless steel wire screens, additional constraints on the electrode are required to minimize the volume expansion, and thus maximize the capacity per unit volume of electrode (A-hr/cm^3).

Cells LA-5 through LA-7 had 7-cm-dia Li-Al electrodes; the electrodes were formed from aluminum fiber disks having porosities of 51 to 56%. These cells were operated to test the formation of intermediate-sized electrodes; to investigate the relationships between achievable capacity density, current density, diffusional overvoltages, and electrode thickness; and to further examine the problem of volume expansion during the formation process. These were the first tests of Li-Al electrodes of a practical size. The results provided important design information for full-size (12.8-cm-dia) Li-Al electrodes and clearly identified the critical areas which need further development.

The results obtained for Cells LA-5, LA-6, and LA-7 are given in Figs. 12 through 14. Figure 12 shows the capacity density (A-hr/cm^2) that was achieved as a function of the current density and the original thickness of the aluminum fiber disks. (As stated above, the thickness of the electrode expands considerably during Li-Al formation.) For all three cells, the capacity density decreased with increasing current density; this decrease is attributed to the ionic diffusional overvoltage within the porous Li-Al structure. The achieved capacity densities at 0.1 A/cm^2 current density and 0.2 V diffusional overvoltage were 0.33 , 0.41 , and 0.48 A-hr/cm^2 , respectively, for the 0.32 -, 0.63 -, and 1.01 -cm-thick Li-Al electrodes. Therefore, to meet the design goal of 0.4 A-hr/cm^2 at 0.1 A/cm^2 , the electrode thickness must be at least 0.6 cm .

Figure 13 shows the capacity per unit volume of electrode (A-hr/cm^3) that was achieved as a function of current density and the electrode thickness. The solid lines correspond to the capacity per unit volume of the three

Fig. 12

Current Density vs. Capacity Density for Li-Al Electrodes of Different Thicknesses (electrode areas, 38.4 cm²; temperature, 425°C; diffusional overvoltage, 0.2 V)

Fig. 13

Current Density vs. Capacity per Unit Volume for Li-Al Electrodes of Different Thicknesses

electrodes based on the original volumes of the aluminum fiber disks. The expansion factors were about 2.5, 2.2, and 1.7, respectively, for the 0.32-, 0.63-, and 1.01-cm-thick aluminum disks. When the data are normalized to the final expanded Li-Al electrode volume, the capacities per unit volume (dashed line in Fig. 13) are approximately the same for the three disks. The normalized capacity per unit volume at 0.1 A/cm² current density is about 0.3 A-hr/cm³, which is substantially lower than the design goal of 0.7 A-hr/cm³. These results clearly show that further developmental effort is needed to prevent an increase in thickness during electrode formation. Typically, to achieve the design goal of 0.7 A-hr/cm³ (0.4 A-hr/cm²) at 0.1 A/cm² current density, the thickness of the initial electrode structure must be about 0.6 cm for a disk with an initial porosity 50 to 55%, and the electrode must exhibit little or no expansion during the Li-Al alloy formation. The volume expansion

Fig. 14. Current Density *vs.* Percent Utilization for Li-Al Electrodes of Different Thicknesses (100% utilization corresponds to 45 at. % Li)

of the Li-Al electrode significantly decreases the capacity per unit volume of electrode and also increases the extra void volume in the electrode that must be filled with electrolyte. This results in an increase of overall weight and size, and a decrease in the specific energy and specific power of the cell.

Figure 14 shows the percent utilization of the Li-Al electrode as a function of current density for different electrode thicknesses. (An electrode utilization of 100% corresponds to 45 at. %, or 17.4 wt %, Li in the alloy.) Electrode utilizations at 0.1 A/cm² current density were about 62, 71, and 96%, respectively, for electrode thicknesses of 1.01, 0.63, and 0.32 cm. These results are consistent with the expectation that the useful electrode thickness is limited by the ionic diffusion within the porous electrode. Improvement in the percent utilization for thick electrodes would probably require electrode structures of short ionic paths.

As indicated above, electrode volume expansion was the limiting factor in achieving the design goal of 0.7 A-hr/cm³. Recent results on 12.8-cm-dia (129-cm²-area) Li-Al electrodes, which were placed in a full-size cell (see Section II.D), showed that rigid confinement of the aluminum disk between two stainless steel rings and two wire screens (electrode structure similar to Type D in Fig. 10) reduced the average expansion in electrode thickness to a factor of about 1.3-1.5. Further investigations of means to control volume expansion are now under way.

6. Conclusions

The following are conclusions drawn from the experiments to investigate

the formation and performance of Li-Al electrodes having diameters of 2.54 and 7 cm.

1. Porous aluminum disks (porosities, 28 to 55%) compacted from continuous aluminum fibers (fiber diameters, 38 to 127 μm) provided excellent starting materials for Li-Al electrode formation.

2. The use of porous aluminum fiber disks allowed the electrochemical formation to be completed in one or two cycles at an initial current density of 0.1 A/cm². This represents a reduction in formation time of at least an order of magnitude compared with the time required in previous formation methods using nonporous aluminum as the starting material.

3. Good reproducibility in the capacity and voltage performance of Li-Al electrodes has been achieved at 400 to 450°C in cells of the type Li-Al/LiCl-KCl/Li. Cell LA-3 was operated for 39 cycles and 310 hr and Cell LA-6 was operated for 20 cycles and 700 hr before the cell tests were voluntarily terminated. Ultimately, the cycle life of the electrode may be influenced strongly by the method of containing the Li-Al fines within the screen structure.

4. Boron nitride fabric, used as a separator, appeared to be chemically compatible with the solid Li-Al electrode when the materials were in direct contact.

5. Of the electrode structures tested (Fig. 10), Types C and D yielded the best constraints on the electrode volume expansion, but an improved electrode structure for the Li-Al electrodes needs to be developed.

6. The results obtained to date suggest that a Li-Al electrode having a diameter of 12.8 cm, a thickness of 0.6 cm, and a capacity density of 0.4 A-hr/cm² (capacity per unit volume, 0.7 A-hr/cm³) at a current density of 0.1 A/cm² will meet the cell requirements for off-peak energy storage.

7. The relationships between the capacity density, electrode thickness, and the current density for the Li-Al electrodes have been experimentally defined. The Li-Al electrodes prepared by the present techniques have met the design goal of capacity density (0.4 A-hr/cm²) but not the capacity per unit volume, i.e., only 0.3 A-hr/cm³ was achieved compared with the design goal of 0.7 A-hr/cm³ at 0.1 A/cm² current density. This clearly points out the need to improve geometry control to minimize the Li-Al volume expansion that takes place during the electrochemical formation.

8. Continued development work is needed in the following areas: optimization of electrode structures to minimize volume expansion; the development of a compact full-size (12.8-cm-dia) electrode; the evaluation of other porous aluminum substrates, such as drawn-wire disks, sintered powder plaques, and foam; the evaluation of Li-Al electrode performance in the presence of sulfur and sulfur-bearing species; and the evaluation of long-term (>1000 hr) electrode performance and the determination of cycle life.

C. Sulfur Electrode Studies (H. Shimotake, J. W. Allen)

1. Goals

The development of long-lived, high-performance sulfur electrodes is a major objective of this program. Lithium/chalcogen cells developed in the course of previous battery programs at ANL had exhibited good electrical performance but gradually lost their capacities due to sulfur losses from the sulfur electrode (Ref. 9, p. 29). The initial work in the present program has concentrated on the development of a semisolid sulfur electrode⁴³ consisting of a mixture of sulfur, arsenic (to prevent losses of sulfur from the electrode), and carbon black (to provide electronic conductance and rigidity). The goal of this work is to develop a long-lived, compact, and inexpensive sulfur electrode for use in light-weight, high-performance cells. For the off-peak energy application, it is believed that the electrode must be capable of delivering a capacity per unit volume of 1.0 A-hr/cm³ at a current density of 0.1 A/cm² while maintaining good mechanical integrity and minimum change in the shape of the electrode. The immediate goal is to develop a high-performance sulfur electrode having a diameter of 11 cm for use in sealed cells.

2. Electrode Design and Testing

The experimental efforts to date have concentrated on the design and testing of (1) small-scale sulfur electrodes (electrode area, ~5 cm²) having all-carbon construction except for a small amount of tungsten screen used for current collection and (2) intermediate-scale sulfur electrodes (electrode area, ~30 cm²) having molybdenum current collectors. In all tests, mixtures of S-10 at. % As or S-20 at. % As with carbon black were used as the electrode material. The electrodes were tested in cells with negative electrodes of lithium-impregnated nickel or stainless steel Feltmetal. Electrical performance tests were conducted to determine the voltage-capacity density characteristics, lifetime, and sulfur retention of the various electrodes. The physical properties of cells with both types of sulfur electrodes are summarized in Table IV. The tests of the cells are described below.

a. Cells Having Sulfur Electrodes with Carbon Structures and Tungsten-Screen Current Collectors

In the course of the NSF program on lithium/sulfur batteries⁹ it had been found that a significant capacity can result from electrochemical reactions involving molybdenum or niobium structural materials. Therefore, initial sulfur electrode studies in the present program were directed toward the testing of electrodes with all-carbon structure except for a limited amount of tungsten as the current collector. [Tungsten had previously been shown (Ref. 9, p. 58) to be resistant to electrochemical oxidation at potentials below about 3 V vs. Li⁺/Li⁰.]

A typical cell configuration, namely, that of Cell C-1 (see Table IV) is shown in Fig. 15. For Cells C-1, C-2, and C-3, the components included (1) a pellet of S-10 at. % As plus carbon enclosed in (2) a porous carbon cup, (3) tungsten-screen current collectors, (4) a nickel Feltmetal electrode impregnated with liquid lithium, and (5) a molten-salt electrolyte (LiF-LiCl-KCl eutectic). These components were placed in alumina crucible, which, in turn, was placed in a furnace tube attached to a glovebox containing high-purity helium.

TABLE IV. Physical Properties of Sulfur-Electrode Cells

Cell No.	C-1	C-2	C-3	A-1	A-2
Sulfur Electrode					
Area, cm ²	5	5	5	30	30
Thickness, cm	0.3	0.3	0.5	0.3	0.3
Weight, g	3.8	3.8	4.1	13.6	11.0
Composition, ^a wt %					
Sulfur ^b	68	68	68	68	54
Arsenic ^c	17	17	17	17	31
Carbon ^d	15	15	15	15	15
Current Collector	W screen	W screen	W screen	Mo screen	Mo screen
Housing	PG-60 graphite	ATJ graphite	ATJ graphite	Mo	Mo
Separator	PG-60 graphite	None	Carbon cloth	Zirconia cloth	Zirconia cloth
Lithium Electrode					
Area, cm ²	5	5	5	30	30
Weight of Lithium, g	3.2	3.2	3.2	6.2	6.2
Current Collector					
Material ^e	Ni	Ni	Ni	SS	SS
Thickness, cm	0.64	0.64	0.64	0.3	0.3
Electrolyte	LiF-LiCl-KCl	LiF-LiCl-KCl	LiF-LiCl-KCl	LiCl-KCl	LiCl-KCl
Interelectrode Distance, cm	1	1	1	1	1
Theo. Capacity Density, ^f A-hr/cm ²	0.86	0.86	0.93	0.51	0.32
Temperature, °C	400	400	400	380	380

^aThe sulfur-to-arsenic atom ratio was 9:1 for all cells except A-2; for Cell A-2 the ratio was 8:2.

^bSulfur:sublimed grade, Merck and Co.

^cArsenic: 99.5%, powder, City Chemical Corp.; for Cells A-1 and A-2, the arsenic was further purified by a vacuum-sublimation treatment to remove oxides.

^dCarbon black (Vulcan XC-72R, Cabot Corp.) was used in all cells except C-3, in which carbon flakes (Superflake, Superior Graphite Co.) were used.

^eLithium electrode current collector was either nickel or stainless steel Feltmetal of 90% porosity and 60- μ m pore size.

^fTheoretical capacity densities refer to the sulfur electrodes.

Fig. 15. Lithium/Sulfur Cell with Carbon Structure and Tungsten Current Collector (Cell C-1)

A pellet consisting of the sulfur, arsenic, and carbon was made as follows. The degassed carbon black was stirred into a previously prepared S-As liquid alloy at $\sim 250^{\circ}\text{C}$. To insure homogeneity, the S-As-C mixture was cooled to room temperature and pulverized with a mortar and pestle, and the powder was well mixed. The S-As-C pellet was made in a helium-atmosphere box with a 2.5-cm-dia die and a hydraulic press. The finely divided mixture was placed in the die and the pellet was formed under a pressure of 1.3×10^7 kg/cm² for 10 min at room temperature. The pressed pellets were estimated to have a porosity of 20 to 40%.

The tungsten screens and the S-As-C pellet were attached to the porous graphite cup (which previously had been impregnated with the salt) using two 0.5-mm tungsten wires sewn through four 0.8-mm holes provided in the pellet and the cup. The ends of the tungsten wires were fastened to the sulfur-electrode current lead to promote efficient current collection. The sulfur-electrode assembly and then the lithium-Feltmetal assembly were immersed in a molten-salt bath contained in an alumina crucible at $\sim 400^{\circ}\text{C}$.

The cells were charged and discharged at constant current with the aid of a dc power supply. Short-term voltage-current measurements were taken occasionally by (1) charging the cell to predetermined IR-free cutoff voltage, (2) placing the cell briefly on open circuit, and (3) recording the cell voltage within a few seconds after closing the switch in the current-

carrying circuit.

The electrical performance results are summarized in Table V. The cell experiments are discussed individually below.

Cell C-1 was operated to determine the performance of an electrode mixture consisting of S-10 at. % As and Vulcan XC-72R carbon black.* The entire sulfur electrode was enclosed in a porous carbon structure which had been impregnated with the electrolyte prior to the assembly. (The structure comprised the carbon cup and carbon sheath; see Fig. 15.) The initial performance of the cell was excellent; a capacity density of 0.73 A-hr/cm^2 (1-V cutoff) at a current density of 0.1 A/cm^2 was achieved. However, the cell operation was very brief because a furnace malfunction resulted in the inadvertent freezing of the cell.

Cell C-2 was similar to Cell C-1 except that no porous carbon sheath between the sulfur and lithium electrodes was used. A sulfur utilization of 45% (based on conversion to Li_2S) was achieved on the first discharge, but the cell failed during recharging. Post-test examination of the cell indicated that a large part of the sulfur had been lost during this brief test.

Cell C-3 was designed to test the use of a carbon cloth separator and carbon flakes** instead of carbon black in the S-As-C mixture. Again, a high sulfur utilization (71%) and an excellent capacity density (0.66 A-hr/cm^2 to a 1-V cutoff) were achieved. However, the cell capacity decreased rapidly after a few cycles, and the cell could not be effectively charged. When the cell was disassembled and inspected, it was found that most of the S-As-C mixture had escaped from the sulfur electrode.

In all experiments, the tungsten screens were effective in lowering the internal resistance of the cells. Corrosion of the tungsten was minimal.

In summary, sulfur electrodes using the carbon structure with tungsten-screen current collectors achieved excellent capacity density and sulfur utilization in short-time tests. However, in these early cells, sulfur retention was poor (resulting in declining cell capacities with time). It was subsequently found that complete alloying of the S-As mixtures had not occurred because of surface oxides present on the arsenic. Consequently, the sulfur vapor pressure had not been decreased, as expected, and sulfur was rapidly lost from the electrode. In subsequent cells (described below), the electrodes were prepared with purified arsenic.

b. Cells Having Electrodes with Molybdenum Housings and Current Collectors

The sulfur electrodes of Cells A-1 and A-2 were designed with molybdenum cell housings and molybdenum current collectors. Although it had

* A product of Cabot Corp.

** Superflake, a product of Superior Graphite Co.

TABLE V. Electrical Performance^a of Lithium/Sulfur-Arsenic Cells

Cell No.	Discharge Current Density, A/cm ²	Av. Discharge Voltage, V	Discharge Time, hr	Capacity Density, A-hr/cm ²	Energy Density, W-hr/cm ²	Capacity per Unit Vol. of S Electrode, ^b A-hr/cm ³	Sulfur Utilization, ^c %	No. of Discharge Cycles	Testing Period, hr
C-1	0.1	1.7	7.25	0.73	1.24	1.0	85	2	24
C-2	0.1	1.6	3.9	0.39	0.62	0.78	45	7	30
C-3	0.1	1.8	6.6	0.66	1.19	0.94	71	1	14
A-1	0.1	1.8	3.8	0.38	0.68	0.76	75	50	336
A-2	0.05	1.6	17	0.29	0.46	0.58	90	80	500

^aResults represent maximum values obtained during the "best" cycle for each cell.

^bCalculation based on final sulfur electrode volume without separators.

^cBased on Li₂S as the final cell product.

previously been determined in the NSF program⁹ that an electrochemical reaction occurs between molybdenum and the LiCl-KCl electrolyte at potentials ≥ 2.7 V, molybdenum might be a useful material of construction if the charge cutoff voltage could be kept below this potential. Molybdenum is cheaper and more abundant than tungsten (the other metallic current collector being considered) and provides more effective current collection than carbon or graphite. The objectives of these tests (Cells A-1 and A-2) were to determine (1) the electrical performance of cells operating at a charge cutoff voltage below 2.7 V, (2) the resistance of molybdenum to corrosion and electrochemical attack under these operating conditions, and (3) the effect on sulfur retention of using oxide-free arsenic in the sulfur-electrode mixture.

The procedure used to purify the arsenic involved the removal of surface oxides by vacuum sublimation. The arsenic was heated in a quartz chamber at 300°C and 10^{-4} Torr for 3 hr (the vapor pressure of As_2O_3 at 370°C is 200 Torr, compared with 1 Torr for pure arsenic). At the end of the 3-hr treatment, it was observed that the arsenic oxide had deposited in a cold zone of the quartz chamber. Mixtures of sulfur, purified arsenic, and carbon were then prepared for use in Cells A-1 and A-2.

The electrode design for Cells A-1 and A-2 is shown in Fig. 16. As discussed above, molybdenum was used as the material for the cell housing (or cup) and for the sulfur-electrode current collector. A piece of expanded molybdenum mesh, slightly larger than the molybdenum cup, was pressed tightly into the bottom of the cup, and the S-As-C pellet was placed on the molybdenum mesh. A separator consisting of zirconia cloth sandwiched between two pieces of expanded molybdenum mesh was then placed on top of the S-As-C electrode.

Fig. 16. Lithium/Sulfur Cell with Molybdenum Current Collector

Other cell components included a BeO insulator, LiCl-KCl eutectic electrolyte, and a negative electrode consisting of lithium contained in stainless steel Feltmetal. The startup procedure for these cells was similar to that for the carbon-structure cells. The electrical performance testing was also similar to that of the previous cells, except that the charge cutoff voltage was

maintained below 2.7 V and a reference electrode was inserted to provide additional information on the electrode processes. The electrical performance data are summarized in Table V.

Cells A-1 and A-2 achieved high cell capacity per unit volume of electrode and greatly improved sulfur retention and cell lifetime. The maximum capacity density achieved was 0.38 A-hr/cm² for Cell A-1 (corresponding to a capacity per unit volume of electrode of 0.76 A-hr/cm³) at a current density of 0.1 A/cm². The maximum sulfur utilization achieved was about 90% (based on the formation of Li₂S) for Cell A-2. Utilizations of over 30% were maintained for both cells during their testing periods, namely, 336 and 500 hr, respectively, for Cells A-1 and A-2. At the end of these periods, operation of the cells was voluntarily terminated so that the cells could be examined. Figure 17 shows typical curves of capacity density vs. voltage at various current densities for Cell A-1. Other cell-performance data are given in Fig. 18 as a function of cell cycle and cell life.

Greatly improved sulfur retention and cell lifetime were achieved in these tests, apparently as a result of the removal of oxide from the arsenic prior to the S-As alloying step. Upon disassembly and inspection of the cells after the tests, the molybdenum-mesh current collectors were found in excellent condition, with no detectable corrosion or electrochemical oxidation. Thus, it appears that maintaining the charge cutoff voltage below 2.7 V prevented the electrochemical interaction between the molybdenum and the molten-salt electrolyte. Preliminary chemical analysis of the disassembled cell components indicates that most of the sulfur was still present in the sulfur electrodes of both cells at the conclusion of the tests. Better sulfur retention would be expected in Cell A-2 (S-20 at. % As) than in Cell A-1 (S-10 at. % As); however, at present, data are insufficient to determine the effect of the increase in arsenic content.

3. Summary of Sulfur Electrode Development

The results obtained during this period are summarized as follows:

(1) The S-As-C electrodes showed good short-term electrical performance: a capacity density of 0.73 A-hr/cm² (corresponding to a capacity per unit volume of 1.0 A-hr/cm³) at a current density of 0.1 A/cm² was achieved in Cell C-1. This electrical performance appears to be satisfactory for the development of cells that meet the goals for off-peak energy storage.

(2) The use of oxide-free arsenic resulted in a complete alloying of the arsenic and sulfur and provided increased sulfur retention in the S-As-C mixtures. Cells C-1, C-2, and C-3 (with unpurified arsenic) had limited sulfur retention, whereas Cells A-1 and A-2 (with purified arsenic) had significantly improved sulfur retention and, therefore, improved cycle life. Cells A-1 and A-2 were operated for 336 and 500 hr, respectively. These cells showed marked improvements in stability and lifetime, with a leveling of the capacity at a sulfur utilization of about 30 to 50%. Additional improvements in cell lifetime are required, however.

(3) The well alloyed S-As-C mixtures in Cell A-1 and A-2 appeared to retain their physical integrity despite some volume expansion (which was expected) during the cell-cycling operations.

Fig. 17. Cell Voltage vs. Capacity Density for Cell A-1 (theoretical capacity density, 0.51 A-hr/cm²; temperature, 380°C)

Fig. 18. Capacity Density vs. Number of Cycles for Cell A-1 (theoretical capacity density, 0.51 A-hr/cm²; charge cutoff voltage, 2.6 V; temperature, 380°C)

(4) From the results obtained to date on Cell A-1 (S-10 at. % As) and Cell A-2 (S-20 at. % As); no definitive statement can be made on the effect of added arsenic on sulfur retention. Preliminary analyses indicate that sulfur retention was good for both cells. Further work is needed to determine the optimum concentration of arsenic in the electrode.

(5) After 336 hr of operation (Cell A-1) and 500 hr of operation (Cell A-2) at a temperature of 380°C and a charge cutoff voltage below 2.7 V, the molybdenum mesh current collectors were in excellent condition and showed no evidence of corrosion or electrochemical attack. Thus, molybdenum appears to be suitable for use in sulfur electrodes under these conditions, and molybdenum current collectors will be used in the next phase of the cell-development program.

D. Development of Full-Scale, Sealed Cells

(H. Shimotake, H. C. Tsai, W. J. Walsh, N. P. Yao, J. W. Allen, J. D. Arntzen)

A full-scale (13-cm-dia) sealed cell (Cell W-1) was constructed near the end of this reporting period. This cell, which is shown schematically in Fig. 19, is the first hermetically sealed, welded cell developed in this program. Major components include upper and lower Li-Al electrodes (rated capacities, 75 A-hr each), a central S-As-C electrode (rated capacity, 150 A-hr), a 0.15 cm-thick separator of BN fabric surrounding the S-As-C electrode, a housing of E-Brite 26-1 stainless steel,* and a compression feedthrough having a molybdenum conductor and boron nitride insulation.

Figure 20 shows the upper and lower Li-Al electrodes of Cell W-1. Both Li-Al electrodes had top and bottom stainless steel screens which were taut and securely spot-welded to stainless steel rings. In addition, stainless steel

Fig. 19. Schematic Diagram of Full-Scale, Sealed Lithium/Sulfur Cell

* A ferritic stainless steel developed by Airco Vacuum Metals Division, Air Reduction Co., Inc. Composition: Fe-26 wt % Cr-1 wt % Mo.

a.

b.

Fig. 20. Lithium-Aluminum Electrode Assemblies for Cell W-1

- a. Top electrode
- b. Bottom electrode

wires (Type 302, 0.79-mm dia) were sewn through the electrodes in an attempt to minimize electrode expansion during the electrochemical formation step. The lower Li-Al electrode assembly was directly spot-welded to the outer housing of the test cell in which the electrode was electrochemically formed. The upper Li-Al electrode included a central hole to allow passage of the feedthrough terminal and insulator. The upper electrode was formed in a separate cell and was later transferred to the test cell for assembly.

Figure 21 shows the sulfur-electrode assembly. The outer molybdenum expanded mesh basket and feedthrough terminal connection are described in Section IV.D of this report. The sulfur electrode consisted of a disk (11.0 cm in diameter and 0.8 cm thick) of S-20 at. % As mixed with Vulcan carbon black (12 wt % loading) having a layer of molybdenum wire mesh in the center; the disk was formed in a die at $\sim 200^{\circ}\text{C}$. A small hole was drilled through the S-As-C disk to allow penetration of the feedthrough, and the edges of the interior molybdenum mesh near the central hole were scraped clean to insure a good electrical contact with the feedthrough terminal. The sulfur electrode assembly was enclosed in a single-piece, knitted BN cloth with the edges sewn together (after assembly) using BN yarn.

The first step in assembling the cell was the electrochemical formation of the lower Li-Al electrode *in situ* in the E-Brite 26-1 stainless steel cell housing by a technique similar to that described in Section II.B of this report. The sulfur electrode assembly, the upper Li-Al electrode, and the cell cover-feedthrough assembly were then loaded into the cell at 400°C . The open-circuit voltage was found to be stable at 2.13 V, thereby indicating that the assembly operations had been accomplished without loss of integrity of the separator. After the cell was cooled to room temperature, the cell cover was heliarc-welded to the cell housing and the feedthrough seal was effected.

Figure 22 shows Cell W-1 after completion of the welding operation. As

Fig. 21. Sulfur Electrode Assembly for Cell W-1.

Fig. 22. Full-Scale, Sealed Lithium/Sulfur Cell (Cell W-1).

shown in the figure, two voltage leads and two current leads were attached by spot welding to the periphery of the cell. An off-center fitting at the top of the cell was incorporated into this first cell to allow occasional introduction of a reference electrode, leak-testing, adjustment of the electrolyte level, and venting operations. This fitting will not usually be used in future prototype full-scale cells.

During the construction and assembly of this first full-scale cell, difficulties were encountered with the geometry control of some components, especially the Li-Al electrodes. As a result, it was necessary to increase the height of Cell W-1 to about 4.5 cm instead of the design value of 3.2 cm, with an accompanying increase in the cell weight from ~900 to ~1250 g (because of the additional electrolyte needed to fill the cell). The theoretical maximum specific energy of the cell was about 150 W-hr/kg. It is believed that a 30 to 50% increase in the capacity will be possible when improvements are made in the individual cell components. At this writing, the operation of Cell W-1 had just begun and no electrical-performance results are available.

III. SUPPORTING LABORATORY STUDIES (R. K. Steunenber)

The laboratory studies are aimed primarily toward the solutions to specific problems that arise in the development work, but also include investigations of the chemical and electrochemical reactions occurring in the cells, determinations of thermodynamic and physical properties of pertinent materials, and experimental evaluations of other electrochemical couples that might be used in the cells (for example, the use of sulfur compounds, rather than sulfur, as the active material in the positive electrode). The results of these studies are expected to lead to innovations and improvements in the design of lithium/sulfur cells.

A. Investigations of Sulfur Electrode (J. R. Birk*)

In the development program on lithium/sulfur cells, the cell lifetime has frequently been limited by losses of sulfur from the positive electrode. Such losses result in decreasing capacity and sometimes interfere with the operation of the negative electrode, presumably through the formation of a sulfide film on the surface of the lithium. The losses of sulfur probably result from its vaporization (vapor pressure, 410 Torr at 400°C), its tendency to form soluble species in the molten-salt electrolyte, or both. Vaporization of the sulfur appears to be largely a cell start-up problem that may be solved by the use of additives and by modifications of the start-up procedures. The formation of sulfur-bearing species that are soluble in the electrolyte, and can therefore migrate to the lithium electrode, is a more fundamental chemical problem. However, there are indications that this problem may be avoided by modifications of the chemical makeup of the positive electrode.

1. Effect of Additives on Vapor Pressure of Sulfur

The effect of a soluble additive upon the vapor pressure of sulfur can be expressed by a modified form of Raoult's law that takes into account the polymerization of sulfur in the vapor phase:

$$P_S = (X_S)^n P_S^0 \quad (1)$$

where P_S is the vapor pressure of sulfur over the solution, X_S is the atom fraction of sulfur in the solution, n is the average number of sulfur atoms in a molecule of vapor, and P_S^0 is the vapor pressure of pure sulfur. At 400°C, the value of n is approximately 6.1.⁵² For this value of n , 10 at. % soluble additive would lower the vapor pressure of sulfur by about 50%, and 20 at. % additive would lower it by about 75%. In the cell development program, arsenic and selenium have been used as additives to the sulfur. Data from the literature indicate that sulfur-arsenic⁵³ and sulfur-selenium⁵⁴ mixtures behave nearly ideally in accordance with Eq. 1 for arsenic and selenium concentrations up to about 20 and 10 at. %, respectively. Thus, relatively small additions of these elements are quite effective in suppressing the vapor pressure of sulfur.

* Industrial Participant, Atomics International Division of Rockwell International Corporation.

2. Solubility of Sulfur-Bearing Species in Electrolyte

As a lithium/sulfur cell is discharged, a mixture of sulfur and the reaction product, Li_2S , is formed in the positive electrode. Phase-diagram studies have shown that two liquid phases, designated L_1 and L_2 , occur in the sulfur-rich region of the Li_2S -sulfur system. The composition of L_1 at 400°C is reported to be ~ 99.8 mol % sulfur (~ 0.2 mol % Li_2S) and that of L_2 , 68.4 mol % sulfur (31.6 mol % Li_2S).⁵⁵ Another source gives the composition of L_2 as 73.7 mol % sulfur (26.3 mol % Li_2S).⁵⁶ In the solid region of the Li_2S -sulfur system, the only phases observed are Li_2S and sulfur.

During the discharge of a lithium/sulfur cell, it appears that intermediate sulfur species can be formed in the presence of the molten-salt electrolyte:

The presence of the intermediate hypersulfide (S_2^-) and supersulfide (S_2^{2-}) ions in LiCl-KCl electrolyte has been observed by various investigators.³⁷⁻⁴² In addition to the species shown in Eq. 2, S_4^{2-} (a dimer of the hypersulfide) and S_3^- have been reported.^{37,38} On the basis of electrochemical studies,⁴² it appears that the last step of the reduction indicated by Eq. 2 is slow. The intermediate species, S_2^- and S_2^{2-} , appear to be quite soluble in the molten-salt electrolyte of a lithium/sulfur cell, and therefore represent a possible path for the transfer of sulfur from the positive electrode to the lithium electrode. The possibility of this type of sulfur transfer might be avoided or greatly decreased by (1) the use of sulfur compounds, rather than sulfur, as the active material in the positive electrode, (2) a change in the composition of the electrolyte to decrease the solubility of the intermediate sulfur species, (3) a decrease in the operating temperature to lower the solubility of the intermediates, or (4) the use of a catalyst to accelerate the last step shown in Eq. 2. Several of the cell tests described below were conducted as an initial effort to investigate some of these possibilities.

3. Cell Tests

(J. R. Birk, Z. Tomczuk, H. Shimotake)

a. Lithium/Sulfur-Arsenic Cells

Four lithium/sulfur-arsenic cells were operated to investigate the electrical and chemical characteristics of the sulfur-arsenic electrode. The cells were of a generally similar design, the active material in the positive electrode being a sulfur-10 at. % arsenic mixture to which 15 wt % Vulcan XC-72R carbon black was added to improve current collection. This mixture was contained in ATJ graphite or PG-60 porous graphite,* and no metal parts were used in the electrode. The negative electrode was a pool of molten lithium metal. The electrolyte was the LiF-LiCl-KCl eutectic (3.5 mol % LiF -56.0 mol % LiCl -40.5 mol % KCl), and the cells were operated at 375 - 400°C . The following observations were made during these tests:

* A product of Union Carbide Corp.

(1) A diffusion barrier is required to confine the sulfur-arsenic mixture in the positive electrode.

(2) A reference electrode proved to be highly useful in monitoring the performance of the individual working electrodes.

(3) The presence of a small amount (~1-5 ppm) of moisture, present as an impurity in the helium atmosphere over the cell, caused a stream of particulate solid to escape from the cell. This material, which was identified as KOH, probably resulted from the reaction

(4) When a cell was overcharged, the voltage reached a plateau at 2.95 to 3.15 V (IR-free). Material that had volatilized and condensed on cool portions of the apparatus was shown by X-ray fluorescence analysis to contain arsenic. These results were not unexpected, since thermodynamic data⁵⁷ indicate that the reaction

should occur at a potential of 2.9 V vs. the lithium electrode. These data indicate that the charge cutoff potential for lithium/sulfur-arsenic cells should be limited to about 2.85 V to avoid the formation of AsCl_3 .

In considering the discharge of a lithium/sulfur-arsenic cell containing excess lithium in the negative electrode, the question arises as to whether additional capacity will be obtained from the reaction of lithium with arsenic after all the sulfur is converted to Li_2S . A Li/LiCl-KCl/As cell was operated at about 400°C to investigate this possibility. The open-circuit potential of the cell was about 1.1 V, and the capacity obtained during discharge was 1.07 A-hr (0.4 V IR-free cutoff), compared with a theoretical value of 0.73 A-hr, assuming that the product is Li_3As . Because of the low potential at which the lithium-arsenic reaction occurs, this reaction should not contribute significantly to the capacity of lithium/sulfur-arsenic cells, which are normally discharged to a cutoff voltage of about 1 V. Furthermore, it is suspected that an additional reaction, such as the formation of lithium carbide, might have been involved (the arsenic was contained in a graphite electrode). In polarization tests, a current plateau was found at 2.99 V, which confirms the previous indications that AsCl_3 is evolved at potentials above about 2.9 V.

The possibility of using a lower cell operating temperature was investigated by testing a lithium/sulfur-arsenic cell at temperatures of 305 and 330°C. The electrolyte was the LiCl-KCl-CsCl eutectic (57.5 mol % LiCl-13.3 mol % KCl-29.2 mol % CsCl; mp, 260°C). The sulfur electrode consisted of the sulfur-10 at. % arsenic mixture plus 15 wt % carbon black in an ATJ graphite housing. The lithium electrode was stainless steel Feltmetal soaked with liquid lithium. When an attempt was made to operate the cell, sulfur escaped rapidly from the positive electrode, imparting a yellow color to the electrolyte and forming a solid crust on the lithium electrode. Although this test was unsuccessful in reducing the transfer of sulfur to the lithium electrode by decreasing the temperature, it does not necessarily rule out the possibility that this reduction might be accomplished with another electrolyte system.

b. Lithium/Metal Sulfide Cells

The electrochemical discharge mechanism (Reaction 2) indicates the presence of polysulfide and hypersulfide intermediates, which appear to be soluble and thus represent a source of sulfur loss from the positive electrode. Chemical studies have shown that these intermediates are formed not only electrochemically but also directly from sulfur and sulfide (Reactions 5 and 6):

One approach to avoiding formation of these soluble species is to shift the equilibria of these reactions to the left by stabilizing the sulfur. One method of doing this is to use sulfur in the form of compounds (*e.g.*, As_2S_3 , Sb_2S_3 , etc.) rather than in the form of elemental sulfur.

A Li/LiF-LiCl-KCl/ Sb_2S_3 cell was tested to investigate the feasibility of this approach. The Sb_2S_3 was mixed with crushed PG-60 porous graphite. The cell was operated at a temperature of about 405°C for 360 hr and 41 cycles. The electrical performance was poor during the first few cycles, but then improved greatly, giving capacities of 54, 65 and 73% of the theoretical value at current densities of 220, 112, and 56 mA/cm², respectively, with an IR-free discharge cutoff voltage of 1.3 V. The theoretical capacity is based on the reaction

When the IR-free discharge cutoff voltage was decreased to 0.8 V, however, a capacity greater than the theoretical value based on Eq. 7 was obtained, thereby suggesting that further reduction of the antimony can occur:

Although the Li/LiF-LiCl-KCl/ Sb_2S_3 cell probably would not be suitable for practical applications because of the high equivalent weight of antimony, it was considered useful in demonstrating the fact that sulfur compounds can be used as the active electrode material in lithium/sulfur cells.

Arsenic sulfides are of interest since they may be present in the positive electrodes of lithium/sulfur-arsenic cells. Accordingly, tests were conducted to determine whether As_2S_3 and the Li_2S formed as a product of the discharge reaction would combine to form a ternary compound. Equimolar amounts of Li_2S and As_2S_3 were heated in an evacuated quartz ampul, first at 385°C, and then at 482°C, for a total period of 5 hr. X-ray diffraction analysis showed that little, if any, of the reactants were present, and that a new compound had formed. Its composition has not been determined, but it is postulated to be LiAsS_2 . An analogous reaction of Na_2S and Sb_2S_3 has been reported in the literature.⁵⁸ Visual observations indicated that the reaction product of Li_2S and As_2S_3 has a low solubility in molten LiCl-KCl at 400°C.

Preliminary experiments were conducted very recently on the use of iron sulfides (FeS and FeS_2) rather than sulfur, as the active material in the positive electrode of lithium/sulfur cells. The testing of iron sulfides

was based on the premise that these materials might eliminate the problems of sulfur volatility and solubility in the molten-salt electrolyte. Tentative results from tests of lithium/FeS and lithium/FeS₂ cells indicate very consistent electrical performance with high coulombic efficiencies (95-100%) and high utilization (80-90%) of the FeS or FeS₂. These preliminary results indicate that a concerted effort on the use of iron sulfide and other metal sulfides as positive electrode materials is warranted.

c. Sodium/Sulfur Cells

Two sodium/sulfur cells employing beta alumina (Na₂O·11Al₂O₃) as a solid electrolyte were constructed and operated to obtain a comparison of the performance of sodium/sulfur and lithium/sulfur cells. The solid electrolyte in both cells was a beta-alumina tube* 11.5 cm long and 0.9 cm ID with a wall thickness of about 0.1 cm. The sodium electrode consisted of sodium metal inside the beta-alumina tube, with an initial active area of 2.9 cm² in the first cell and 8.0 cm² in the second one. The sulfur electrode in the first cell was carbon felt impregnated with sulfur, and in the second one, a mixture of sulfur and ground PG-60 porous graphite. The cells were operated at temperatures of 293 and 297°C, respectively. In both cells, the capacity was limited by the amount of sodium present. About 75% of the theoretical capacity was achieved with the first cell and approximately 100% with the second one. In both cases, the open-circuit potential was 2.08 V. The short-circuit current densities were about 600 and 500 mA/cm², respectively, for the two cells. These data indicate that the ionic conductivity of the beta-alumina electrolyte was in the range from 0.02 to 0.03 ohm⁻¹ cm⁻¹.

The following conclusions were reached from these tests:

(1) Smooth electrical performance was maintained as the cells were charged and discharged. At a current density of 300 mA/cm², the discharge capacity density was typically about 0.59 A-hr/cm² (1-V cutoff), with an average terminal voltage of 1.6 V, which corresponds to a power density of 0.5 W/cm².

(2) The current density during charge appeared to be limited to about 200 mA/cm², which is consistent with data in the literature.¹⁷

(3) The ionic conductivity of the beta-alumina electrolyte (0.02 to 0.03 ohm⁻¹ cm⁻¹) is in reasonable agreement with the literature.¹⁷

(4) The self-discharge rates of the cell were low. However, sulfur losses were observed, apparently because of an inadequate seal around the beta-alumina tube.

(5) The ampere-hour efficiencies of the cells were near 100%.

According to the above results, the solid-electrolyte sodium/sulfur cell has a lower average terminal voltage than that of the lithium/sulfur cell (1.6 V vs. 1.8 V at a discharge current density of ~300 mA/cm²), and a relatively low short-circuit current density of ~0.6 A/cm², compared with

* Fabricated by the Toshiba Electric Co., Japan.

several amperes per square centimeter for the lithium/sulfur cell. In terms of performance, it appears that lithium/sulfur batteries will be capable of considerably higher specific power than sodium/sulfur batteries. However, further development work is needed on both systems before a final judgement can be made as to their relative merits.

All the sodium/sulfur cells currently under development¹³⁻²⁴ employ beta alumina or a glass as a solid electrolyte for sodium-ion conduction. It is possible that a liquid electrolyte might offer some advantages in terms of higher current densities and the elimination of cracking, which often occurs after extended cycling of beta alumina. A brief test was performed with a sodium/sulfur cell employing 53.5 mol % LiCl-8.5 mol % NaCl-38.0 mol % KCl (mp, $\sim 350^{\circ}\text{C}$) as a liquid electrolyte. The negative electrode was Type 302 stainless steel Feltmetal containing liquid sodium, and the positive electrode was a sulfur-10 at. % arsenic mixture plus 15 wt % carbon black, contained in ATJ graphite. The cell had an open-circuit voltage of about 2.5 V and a short-circuit current density of $\sim 650 \text{ mA/cm}^2$. However, the capacity densities were low, about 15 to 25 mA-hr/cm², and the cell exhibited a high rate of self-discharge. Subsequent analysis of the negative electrode indicated that lithium rather than sodium, had been deposited on the electrode when the cell was charged. Although this initial test of a sodium/sulfur cell with a molten-salt electrolyte (53.5 mol % LiCl-8.5 mol % NaCl-38.0 mol % KCl) was not successful, it is possible that a suitable electrolyte can be found, *e.g.*, an electrolyte having a considerably higher sodium-ion content and a melting point low enough for practical cell operation.

B. Oxidation Potential of E-Brite 26-1 Stainless Steel

A brief test was conducted to determine the potential at which E-Brite 26-1 stainless steel begins to undergo anodic oxidation in molten LiCl-KCl electrolyte. The measurements were made with a cell in which one electrode was Type 302 stainless steel Feltmetal containing lithium and the other one was a flat plate of E-Brite 26-1. The LiCl-KCl eutectic was used as the electrolyte and the cell was operated at a temperature of 397°C . Current density-*vs.*-voltage curves showed a distinct break at 2.1 V. When the cell was charged at constant current, the open-circuit potential remained at 2.1 V, thereby confirming the current density-*vs.*-voltage measurements. These results indicate that E-Brite 26-1 cannot be used at the sulfur electrode potential in lithium/sulfur cells. However, it should be satisfactory as a cell housing, provided that the housing is maintained at the lithium electrode potential. (A description of the cell housing is given in Section IV.C.)

IV. MATERIALS TESTING AND FABRICATION (J. E. Battles)

The development of various cell components such as cell housings, current collectors, insulators, interelectrode separators, and electrical feedthroughs are important to the successful development of lithium/sulfur batteries for load-leveling devices. The materials of construction must be resistant to corrosive attack by various combinations of lithium, LiCl-KCl electrolyte, and sulfur (plus additives) which make up the cell environment. Hence, the effort in this phase of the program involves not only corrosion testing of many materials under various conditions, but also component design and fabrication. For containment of active cell materials, the cell assembly will need to be hermetically sealed by welding, brazing, or other techniques.

The cell housing and the current collectors will probably be metallic. Attack of metallic materials of construction is most likely to occur when the metal is at the sulfur electrode potential in the presence of the electrolyte and sulfur. These conditions result in electrochemical attack on most metals, depending on the cell voltage. An electrical feedthrough with an insulator is required for isolating at least one electrode from the metallic cell housing. The principal components of a feedthrough are the electrical conductor, the insulator, and the sleeve, which is attached to the cell body. The design of the feedthrough is dependent on the choice of materials for the conductor, insulator, and cell housing.

Non-metallic cell components include the electrical insulators and interelectrode separator. In general, the use of oxide ceramic materials as electrical insulators is limited to those oxides which are thermodynamically more stable than lithium oxide (Li_2O). When lithium-aluminum electrodes are employed the lithium is less reactive toward insulator materials because the activity of lithium is significantly reduced. The development of a porous interelectrode separator compatible with the cell environment will permit closer spacings of the electrodes and a reduction in the amount of electrolyte required. Since the properties of ceramics can be influenced by the preparative method, fabrication process, and purity of the material, considerable effort is directed toward developing process parameters for obtaining ceramics with the properties required for optimum cell performance.

A. Electrical Feedthrough Development (K. M. Myles, J. W. Downey, J. E. Battles)

The development of hermetically sealed cells requires an airtight electrical feedthrough constructed of materials that are compatible with the cell environment and are also light weight and inexpensive. Two basic designs are currently being developed; a compression type for immediate-term use and a braze type for the ultimate cell configuration. The major development efforts of the braze-type feedthrough are being conducted in the NSF battery program (Ref. 9, p. 66). The compression-type feedthrough is discussed below.

A schematic representation of the compression-type feedthrough is shown in Fig. 23. The essential components are the electrical conductor (currently Mo or W), the insulator (BN), and the body, which is brazed to the cell housing. The hermetic seal is obtained by crushing a lava (MgSiO_3) plug against the conductor and the wall of the body by applying pressure to the metal

Fig. 23. Schematic Representation of Compression-Type Electrical Feedthrough for Lithium/Sulfur Cells

pressure ring. Corrosion of the lava by molten lithium is prevented or minimized by the protective layer of CaZrO_3 or Y_2O_3 powder placed between the lava plug and the lower BN insulator. The feedthrough body is brazed to the E-Brite cell housing using a braze filler metal with the composition (in wt %) 81.5 Ni-15 Cr-3.4 B.

Because of the rather simple design, the compression-type feedthroughs have several unique advantages over other types of feedthroughs; these include ease of construction, absence of a ceramic-to-metal braze, and elimination of the need for materials with matching coefficients of thermal expansion. Thus, the feedthrough can be constructed using any materials that are compatible with the cell environment. The primary disadvantages are cost, weight, and size. Several of these feedthroughs have been fabricated and are being evaluated. Thus far, the feedthroughs appear to meet all near-term expectations with regard to leak tightness and corrosion resistance.

B. Development of Ceramic Insulators (W. D. Tuohig)

The lower insulator for the compression-type feedthrough (see Fig. 23) is currently machined from boron nitride stock, which is expensive and has poor mechanical properties. Hence, it would be desirable to find a replacement material for boron nitride for use as an insulator. Not only must the fabricated insulator have good mechanical and corrosion-resistance properties, but it must also be impervious to the electrolyte to prevent corrosion at the

grain boundaries and subsequent disintegration of the insulator. An impervious body would also be ideal for a braze-type feedthrough.

The technique of fabricating ceramic insulators by pressure sintering (or hot-pressing) is being studied for several reasons: (1) Hot-pressing allows the fabrication of fine-grained, high-density bodies without the extensive development effort that might be required to obtain similar materials by conventional techniques. (2) The mechanical properties of hot-pressed bodies are generally superior to conventionally produced counterparts made from the same starting material. (3) The effects of process variables (initial particle size, calcining, additives, etc.) are readily evaluated under controlled conditions. If the hot-pressed bodies prove to have suitable properties, an effort will be made to produce equally acceptable components by cold-pressing and sintering, a technique that would reduce the cost of mass-produced components.

Pressure sintering or hot-pressing may be defined as the application of external pressure to a powder compact at elevated temperature. The synergistic effect of pressure and temperature on the dynamics of consolidation has received increased attention in recent years, and has led to commercial fabrication of materials which cannot be produced by any other technique.⁵⁹ Hot-pressing provides an improved method of controlling microstructure, in that the driving force for densification is increased without a commensurate increase in the driving force for grain growth. As a result, densities very close to theoretical values have been achieved for a number of materials.⁶⁰

The mechanism of densification during pressure sintering has been the subject of studies by Vasilos and Sprigge,⁶¹ Coble and Ellis,⁶² Rossi and Fulrath,⁶³ and Murray *et al.*⁶⁴ Although simple models based on sphere-sphere and sphere-plate geometries are inadequate to describe the process, most workers are of the opinion that, under generally employed conditions (pressures less than 4×10^7 N/m² and temperatures below 1800°C), densification occurs predominantly by a diffusional mechanism.

The plastic flow model proposed by Murray *et al.*⁶⁴ and by McClelland⁶⁵ may, however, be applicable to soft materials such as Cu, Pb, and NiO.² Coble and Ellis⁶² studied neck growth between single-crystal Al₂O₃ spheres under an applied load and concluded that only the very early stage of neck growth was the result of flow at contact points. Deformation occurred only until the effective stress dropped below the yield stress. Neck growth continued, however, by a diffusion-controlled process.

Nadler and Fitzsimmons⁶⁶ have studied the preparation and properties of CaZrO₃. They report densities as high as 4.5 g/cm³ [94% of theoretical density, (TD)] obtained by cold pressing and firing at 1800°C in vacuum. These specimens exhibited appreciable absorption despite their relatively high density, thereby indicating appreciable open porosity. No reference to pressure sintering of CaZrO₃ was found in the literature.

Our preliminary attempts to hot-press CaZrO₃ were made with as-received -325 mesh material from Zircoa Corp., Solon, Ohio. A commercial GCA Vacuum Industries hot-press unit, coupled with a Tocco induction generator, was employed. All experiments were carried out in a vacuum below 10⁻⁴ Torr. The initial experiments, summarized in Table VI, revealed that hybrid dies of TZM

TABLE VI. Summary of Experiments on Hot-Pressing of CaZrO_3

Expt. No.	Die Material	Ram Material	Temp., °C	Time, min	Pressure, N/m^2	% TD	Remarks
HPCZ-1	G ^a	G	1600	20	2×10^7	85	Extensive reaction with graphite; reaction layer spalled off on heating in air.
HPCZ-2	G ^b	G ^b	1450	20	2.7×10^7	92	Increase in density at lower temperature than in HPCZ-1; reaction minimized and die-wall friction reduced.
HPCZ-3	TZM ^c	G	1350	-- ^d	--	75	Terminated inconclusively.
HPCZ-4	TZM	G	1430	20	3.3×10^7	95	Discoloration due to carbon disappeared on heating in air; excellent impervious body.
HPCZ-5	TZM	TZM	1375	20	3.3×10^7	-- ^e	Unable to extract punches; may have exceeded usable limits of TZM.
HPCZ-6	TZM	G ^f BN	1390	20	3.3×10^7	93	No reaction with BN; apparently BN may be satisfactory as die material below $3.3 \times 10^7 \text{ N/m}^2$.

^aG = graphite^bBN aerosol spray used to minimize carbon diffusion.^cTZM = Mo-Ti-Zr high temperature alloy (Climax Molybdenum Co.).^dPunch failed as load was applied.^ePunch seized.^fBN spacers incorporated between specimen and punch.

and graphite were satisfactory for the hot-pressing operation.

The presence of a liquid phase at the grain boundaries has been observed⁶⁷ in specimens prepared by conventional sintering of as-received CaZrO_3 powder. Corrosion tests in molten lithium have indicated that this phase was preferentially attacked; its presence was, therefore, unacceptable in cell components. An electron-microprobe analysis revealed that the phase consisted predominantly of Ca and Si. It was concluded that this phase, probably CaSiO_3 , was formed by a reaction between SiO_2 (an impurity in the starting material) and remnant CaO . In an effort to eliminate the CaO , the powder was treated by leaching in 1*N* HCl , followed by repeated rinsing, ball milling, and drying. The product cake was crushed and passed through a No. 400 sieve. Sinterings prepared from the treated material showed no evidence of the grain-boundary phase. This material was then used for all subsequent hot-pressings.

It has been reported that LiF promotes densification during pressure sintering of MgO .⁶⁸ Therefore, tests were performed to study the effect of LiF additions, up to 2 wt %, on the pressure sintering of CaZrO_3 . Appreciable subsidence* was found to occur in the presence of LiF below 1000°C ; this is approximately 200°C lower than the temperature at which subsidence is otherwise observed. Examination of the resulting microstructure indicated, however, that this densification consisted primarily of particle rearrangement, and that little actual sintering had taken place. It was concluded that LiF actually inhibited material transport and produced lower ultimate densities than could otherwise be attained.

Additional experiments were performed wherein the powder was heated in the die prior to the application of the load. Densities exceeding 4.63 g/cm^3 (97% of TD) were obtained at temperatures below 1400°C . Figure 24 illustrates schematically the process which presently appears to be optimum. A number of right cylinders have been prepared by this process and tested with a standard Veeco leak detector. It was found that specimens having densities greater than 4.54 g/cm^3 (95% of TD) were completely impermeable to helium and readily supported a vacuum of 10^{-6} Torr. In contrast, specimens with densities below 4.35 g/cm^3 (91% of TD) were grossly permeable to air--to the extent that they were unable to support a vacuum of 10^{-4} Torr. The microstructure of a pressure-sintered CaZrO_3 body having a density of approximately 96% of theoretical is compared in Fig. 25 with that of a CaZrO_3 body (92% of TD) produced by Coors Porcelain Co. by conventional pressing and sintering. Relative differences in pore size, grain size, and density are apparent and these should be reflected in observed physical properties.

High-density, impermeable feedthrough insulators are being prepared routinely by pressure-sintering of right cylindrical blanks and subsequent diamond core drilling to produce the central conductor hole. Attempts to press an annular configuration directly were unsuccessful because a suitable mandrel material could not be found. Additional specimens for mechanical test and corrosion experiments are also in preparation.

* Subsidence is a measure of the linear compaction of the powder.

Fig. 24. Optimum Conditions for Pressure Sintering of CaZrO_3

- a. Temperature profile as a function of time
- b. Resulting densification at the given temperature and pressure

C. Fabrication of Cell Housings (K. M. Myles)

To meet the performance specifications imposed on a Li/S cell, the cell housing must be light weight, inexpensive, and corrosion resistant. A material that appears to meet all of these requirements is E-Brite 26-1, a ferritic stainless steel (Fe-26 wt % Cr-1 wt % Mo). The properties of this material, that are particularly attractive for use as cell housings are the very low levels of carbon, nitrogen, and tramp impurity elements and the lack of nickel without the usual decrease in weldability. E-Brite is an economical stainless steel (just slightly more expensive than Type 304 stainless steel) that combines excellent fabricability with good general corrosion resistance and also good pitting corrosion resistance and immunity to chloride stress-cracking. Also, because of its extremely low carbon content (<0.005 wt %), E-Brite is less subject to sensitization as a result of welding or thermal treatments.

a.

b.

Fig. 25. Microstructures of CaZrO_3 Produced by Different Sintering Techniques
a. Pressure sintered at ANL (96% TD; 200X)
b. Conventionally pressed and sintered by Coors Porcelain Co. (92% TD; 200X)

Nine cell housings (three with an ID of 8.25 cm and six with an ID of 13 cm) have been fabricated using 0.5-mm-thick sheet which was cold rolled from 1.5-mm-thick sheet and then annealed. The flat sheet was formed into tubes about 5 cm long and heliarc welded. A shallow cup was then welded to one end of each tube. For each housing, a feedthrough body was brazed to a second shallow cup to form the top of the housing. (This assembly is welded to the top end of the housing after the electrodes are inserted.) Although this forming technique was satisfactory, future cell housings are being fabricated by spinning by an outside vendor to reduce cost.

D. Lithium Electrode
(K. M. Myles)

As discussed in Section II.B, lithium-aluminum electrodes have been prepared by an electrochemical reaction of lithium with porous aluminum disks made from 2- to 5-mil dia aluminum fibers. Disks formed from knitted aluminum wire (6- to 10-mil diameter) mesh* are also being tested for use as electrode structures. These disks have the advantages that the aluminum wire is a single, continuous filament and may be less expensive than the fibers in large-volume production. Evaluation tests of electrode structures made from the wires are under way.

As the LiAl intermetallic compound forms in the electrode structure, the volume of the disk increases considerably. To restrain this growth, the aluminum disk is tightly sandwiched between two 40 by 40 mesh stainless steel screens (wire diameter, 0.010 in.). Good electrical conductivity is assured by spot welding the screens onto stainless steel rings that are, in turn, spot welded to the inside wall of the cell housing. This technique also provides a convenient method of positioning the lithium-aluminum electrode within the cell.

E. Sulfur Electrode
(K. M. Myles)

Because of the low electrical conductivity of the sulfur-electrode mixture of sulfur, arsenic, and carbon, it is necessary that a metallic current collector be added to the structure. Electrochemical measurements have indicated that molybdenum is nonreactive in the LiCl-KCl electrolyte at potentials less than ~ 2.7 V (Ref. 9, p. 54). Also, preliminary cell tests have indicated that molybdenum does not react when the charge voltage is maintained below 2.7 V. Accordingly, the sulfur electrode of the first full-scale cell (see Section II.D) was fabricated using expanded molybdenum mesh as the current collector. The 0.020-in.-thick mesh is fabricated from 0.005-in. molybdenum sheet. A basket arrangement is then formed from the mesh with the top and bottom layers overlapping along the outer edge of the electrode. The centers of both the top and bottom layers of mesh are recessed inward and punched with a 1/8-in.-dia hole. The complete current collector consists of these two layers and a third flat, middle layer that are fastened together with a threaded molybdenum electrical conductor, and two molybdenum nuts which fit in the recessed area.

*Produced by Otto H. York Co., Inc., Parsippany, N. J.

F. Interelectrode Separators (J. E. Battles)

A porous separator material, such as a cloth or paper, that is resistant to the cell environment would permit closer spacing of the lithium and sulfur electrodes and would help to reduce the overall weight and volume of the cells. Ceramic cloths of boron nitride* and Zircar** (zirconia stabilized with CaO or Y_2O_3) have undergone preliminary testing in operating test cells, and the initial results have been encouraging. However, work in other battery programs at ANL has indicated that the corrosion resistance of ceramic materials to molten lithium is affected by the purity of the material and the fabrication method. Accordingly, further testing of BN is being undertaken.

A BN separator was prepared (by knitting) from 30-mil two-ply yarn; the fibers are fully dense (100% of TD) and contain less than 2% B_2O_3 . The material was vacuum-outgassed at about 500°C before being placed in a Li-Al/S test cell, which was operated for about 350 hr at 400°C before the test was terminated. Examination of the BN separator revealed no apparent deterioration or change in resistivity, and only a slight discoloration was observed. Encouraging results have also been obtained with BN cloth exposed to lithium at 400°C in static compatibility tests of about 300-hr duration.

Previous results at ANL⁶⁹ with commercial hot-pressed BN in static tests and in operating cells containing lithium had shown that the material darkened and became conductive in less than 100 hr. Since BN is thermodynamically more stable than Li_3N , this type of behavior would not be expected. The conflicting results obtained in the various tests lead to the hypothesis that the poor performance of BN might be due to the reduction of B_2O_3 by lithium. (Normal BN stock contains about 5-6 wt % B_2O_3 , whereas high-purity stock material contains about 2 wt % B_2O_3 and the cloths and yarns made from BN fibers contain less than 2 wt % B_2O_3 .) If this hypothesis is correct, it may be necessary to remove all or most of the B_2O_3 from the BN.

Samples of BN cloth have, therefore, been subjected to several types of treatments to remove the B_2O_3 , and these materials have been tested for compatibility with lithium. The samples were given the following treatments: (1) solution in methanol for 0.25 hr, (2) vacuum outgassing at 400°C for 15 hr, and (3) heating in N_2 at 1700°C for 1.5 hr. The treated samples, along with a sample of as-received BN, were submerged in lithium maintained at 400°C for 300 hr and then examined after removing the lithium by dissolution in methanol. The sample pretreated with N_2 remained intact with no appreciable deterioration, discoloration, or change in resistivity. The remaining samples were badly deteriorated. Although the conditions of these compatibility tests of BN cloth are more severe than the actual cell environment, especially in cells utilizing Li-Al electrodes, the results indicate that a high-temperature pretreatment with N_2 may be necessary for obtaining optimum performance from BN separators.

G. Materials Evaluation (J. E. Battles, F. C. Mrazek)

Nine samples of tungsten were examined visually and metallographically

* A product of the Carborundum Co.

** A product of the Union Carbide Co.

after exposure to a mixture of S-10 at. % As and LiCl-KCl electrolyte at 400°C for 336 hr. The samples included cold-rolled and annealed sheet, wire screen, elox-cut disks from cold-rolled sheet, and disks cut from cold-rolled sheet that subsequently were treated by electron-beam-welding the edges. The purpose of this experiment was to identify the types of tungsten stock and pretreatments that would yield the maximum corrosion resistance to the sulfur-electrode material.

Careful examination of the samples, after removal from the mixture and cleanup, indicated that all samples had experienced severe delamination and disintegration except the annealed sample and the two disks with electron-beam-welded edges. For an understanding of the behavior of the tungsten samples, it is helpful to consider the microstructure of cold-rolled and annealed tungsten. Cold-rolled tungsten has a laminar-type structure with severely deformed and elongated grains as shown in Fig. 26, whereas annealed tungsten has randomly oriented grains. Thus, it appears that failure resulted from selective reaction starting at the exposed edges and proceeding along the highly oriented laminar structure of the cold-rolled material. Apparently the product formed by this reaction generated sufficient pressure to force the layers apart, thereby causing delamination and breakup of the cold-rolled sheet and wire. These results indicate that only annealed tungsten and possibly cold-rolled tungsten with electron-beam-welded edges are compatible with the sulfur-electrode mixture.

Fig. 26. Typical Microstructure of Cold-Rolled Tungsten Sheet (etched with $\text{H}_2\text{O}_2\text{-NH}_4\text{OH-H}_2\text{O}$; 300X)

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