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LITHIUM/METAL SULFIDE BATTERY DEVELOPMENT

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LITHIUM/METAL SULFIDE BATTERY DEVELOPMENT

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ABSTRACT

Lithium/metal sulfide batteries are being developed by Argonne National Laboratory and industrial contractors for electric-vehicle propulsion and for stationary-energy-storage applications such as load leveling. The battery cells consist of lithium-aluminum or lithium-silicon negative electrodes, iron sulfide (FeS or FeS_2) positive electrodes, and molten LiCl-KCl electrolyte. The cells are enclosed in a thermally insulated jacket to maintain an operating temperature of 400-500°C. A 40-kW-hr electric-vehicle battery consisting of 120 Li-Al/FeS cells is currently being fabricated and is scheduled for laboratory and in-vehicle testing in 1979.

INTRODUCTION

Lithium/metal sulfide batteries are being developed by Argonne Laboratory and several subcontractors for electric-vehicle propulsion and for stationary energy-storage applications such as load leveling. The use of a large number of electric vehicles would result in a significant decrease in the consumption of petroleum fuels [1,2], since the energy for charging the batteries could be provided by coal, nuclear, hydroelectric, or other sources; a side-benefit would be decreased air pollution in congested urban areas. Load-leveling batteries on electric-utility systems could conserve petroleum by reducing the need for gas turbines to meet peak power demands [3,4]. The stationary batteries may also find applications in systems using solar, wind, or other cyclic or intermittent energy sources.

In the initial stages of this program, attempts were made to develop battery cells using elemental lithium as the negative electrode, elemental sulfur as the positive electrode, and molten LiCl-KCl as the electrolyte. The electrochemical reaction that occurs during the discharge of this type of cell

$$2Li + S \rightarrow Li_2S \qquad (1)$$

has a very high theoretical specific energy of about 2600 W-hr/kg [5] and an emf of 2.2 V at 400°C. Although the thermodynamic properties of the lithium/sulfur system are very favorable for high-performance applications, several practical difficulties have discouraged the development of a practical cell [6]. The lithium metal, which is liquid at the operating temperature, attacks most ceramic materials that might be used as insulator or electrode separators, and it becomes difficult to retain in the porous metal electrode during extended cycling of the cell. Lithium also dissolves in the LiCl-KCl electrolyte to the extent of about 0.13 mol % at 400°C [7,8], which results in self-discharge of the cell. The metallic lithium also reacts with KCl in the electrolyte to form potassium vapor having an equilibrium partial pressure of 0.05 kPa at 425°C [9].

The elemental sulfur electrode also poses a number of practical problems. In addition to its corrosive behavior toward most metals, the sulfur tends to react with the Li_2S reaction product to form polysulfides that are soluble in the LiCl-KCl electrolyte [6], thereby providing a mechanism of sulfur escape from the electrode. Sulfur also has a rather high vapor pressure of 77 kPa at 425°C [10].

In the cells currently under development, these problems have been overcome by using Li-Al or Li-Si alloys, rather than lithium in the negative electrode [11,13] and iron sulfides (FeS or FeS_2), rather than sulfur in the positive electrode [14,15]. The lithium alloys and iron sulfides are solid materials at the cell operating temperature. These systems consist of two solid phases (electrodes) and one liquid phase (electrolyte), rather than three liquid phases, which is a much more favorable situation in the fabrication of a practical cell.

LITHIUM-ALLOY/METAL SULFIDE CELLS

Although the substitution of lithium alloys for elemental lithium and metal sulfides for sulfur has resulted in a practical cell system, it invokes a serious penalty in the theoretical specific energy and the cell voltage. The most technically advanced cell of this type is the LiAl/LiCl-KCl/FeS system, which involves the following overall electrochemical reaction:

$$2LiAl + FeS \rightleftarrows Li_2S + Al + Fe \qquad (2)$$

This is a two-electron reaction with a theoretical specific energy of 458 W-hr/kg and an emf of 1.33 V. The reaction at the Li-Al electrode is relatively straightforward, since the electrode is operated over a range from about 10 to 48 at. % lithium, which is within a two-phase field in the Li-Al phase diagram (α + βLiAl) [16]. The result is that the same two phases are always present with a change only in their relative amounts, which results in a constant potential of the Li-Al electrode (+ 294 mV *vs* Li at 427°C) [17]. Reaction 2 is actually much more complex than shown; for example an intermediate compound, $LiK_6Fe_{24}S_{26}Cl$, is formed by a reaction with KCl in the electrolyte [16], and intermediate ternary compounds such as Li_2FeS_2 have also been identified [18]. Further studies have shown that as many as six electrochemical reactions and four chemical reactions may be involved in the charging and discharging of the FeS electrode [18]. Overcharging of the FeS electrode appears to result in the formation of elemental sulfur, $FeCl_2$ (as K_xFeCl_{x+2}), and possibly FeS_2 [19]. Overcharging is avoided in the operation of LiAl/LiCl-KCl/FeS cells by limiting the charge cutoff potential to about 1.65 V.

The Li-Al/LiCl-KCl/FeS_2 and Li-Si/LiCl-KCl/FeS_2 systems are considered to have a long-range potential for higher performance than can be achieved with FeS positive electrodes. The overall reaction for a Li-Al/LiCl-KCl/FeS_2 cell is:

$$4LiAl + FeS_2 \rightleftarrows 2Li_2S + 4Al + Fe \quad (3)$$

This is a four-electron reaction with a theoretical specific energy of about 650 W-hr/kg. The voltage *vs* capacity curves show two voltage plateaus at 1.67 and 1.33 V, respectively. The Li-Al/LiCl-KCl/FeS_2 cells are often designed to operate only on the higher voltage plateau; these are referred to as "upper-plateau" cells. Reaction 3 also involves a number of steps and various intermediates (generally ternary compounds of lithium, iron and sulfur), some of which have not yet been fully identified. The overcharge products of the FeS_2 electrode are sulfur and $FeCl_2$ (K_xFeCl_{x+2}) [19], and the charge cutoff potential of Li-Al/LiCl-KCl/FeS_2 cells is usually set at 2.1 V. Two major problems that have slowed the development of cells having FeS_2 electrodes are a loss of cell capacity on cycling and the lack of metallic materials that are compatible with the FeS_2 at cell operating temperatures. Both of these problems are under active investigation.

Although the Li-Al electrode is used in the more advanced lithium alloy/metal sulfide cells at the present time, the Li-Si system is also under serious consideration and is being used in some experimental cells. From a theoretical standpoint, the fully charged Li-Si electrode corresponds to the compound Li_5Si, and the fully discharged electrode is elemental silicon. Four intermediate lithium-silicon compounds appear to be formed as the electrode is charged and discharged; however, there is some disagreement as to the exact compositions of these compounds [20,21]. In practice, the composition range that can be used satisfactorily falls between Li_4Si (charged) and LiSi (discharged). Unlike the Li-Al electrode, the Li-Si electrode shows several voltage plateaus between about +45 and +330 mV *vs* Li as a result of the lithium-silicon intermediate compounds. The Li-Si electrode has about twice the capacity of the Li-Al electrode (1.44 *vs* 0.70 A-hr/g), which gives it an advantage in specific energy and volumetric energy density. Several practical problems associated with its use, however, have not been fully resolved. One such problem is its corrosiveness toward iron, nickel and chromium, which are used for cell housings and electrode current collectors. Also, it is not compatible with BN electrode separators, which are usually used in cells of this type. Further development work will be required to take advantage of the favorable theoretical characteristics of the Li-Si electrode.

CELL DESIGN AND PERFORMANCE

Up to about a year ago, nearly all of the cells that had been built and tested were of a rectangular, prismatic bicell design with a central positive electrode and two facing negative electrodes. The more recent cells are of a multiplate design with two or more (usually three) positive electrodes and facing negative electrodes. The two outside electrodes in the cell stack are normally of half-thickness and are grounded to the cell housing. The positive electrodes are connected by a bus bar to the positive terminal that extends through the top of the cell housing via an insulating feedthrough. The multiplate cell design permits a significantly higher specific energy, specific power, and volumetric energy density than a bicell design with the same electrode loadings.

In all of the cell designs, porous separator sheets between the electrodes serve as electronic insulators, while at the same time providing a path for the migration of lithium ions through the LiCl-KCl electrolyte absorbed in the separator material. Most of the cell designs employ BN fabric or felt as the separator material, although powder separators formed by pressing or vibratory compaction of MgO, AlN, Si_3B_4, or other particulate materials, have been used successfully in experimental cells [22]. Since the negative and positive electrodes both consist basically of particle beds or porous structures of the active materials (*e.g.*, Li-Al, FeS), metallic screens are usually used to prevent the escape of particulate material from the electrodes into the separator. Metallic current collectors are normally placed in the electrodes to provide a low-resistance current path from all areas of the electrode to the terminal.

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

Representative performance data from several Li-Al/LiCl-KCl/FeS cells are presented in Table I [23]. The data are mean values from several cells of similar or identical design. The I-series are bicells fabricated by Eagle-Picher Industries, Inc. The M-series are bicells fabricated at Argonne; the PW-series were also fabricated at Argonne, but with MgO-powder rather than BN-fabric separators. The EPMP series are multiple-electrode (three positive, four negative) cells fabricated by Eagle-Picher. The improvement in specific energy and specific power that results from the use of multiple-electrode cells is evident from these results. The energy efficiencies (W-hr discharged/W-hr charged) for cells of this type generally fall in the range of 80-85%.

BATTERY GOALS AND STATUS

In general, the electric-vehicle battery must have a high specific energy to permit an adequate driving range, and a high specific power to maintain normal highway speeds and to provide sufficient power for passing and hill climbing [2]. The volumetric energy and power densities must also be high because of the limited space available in most vehicles for installation of the battery. For large-scale application in electric vehicles, the battery will probably have to have a maximum cost of $40-50/kW-hr and a minimum lifetime of 1000 equivalent deep-discharge cycles. The performance and lifetime goals for the electric-vehicle battery are presented in Table II [22]. The progression of performance goals shown in the table is based on specific improvements that are anticipated in the cell and battery designs as the technology is developed.

A significant event in the development of the electric-vehicle battery has been the initiation of a contract with Eagle-Picher Industries, Inc. for the development, design, and fabrication of a 40-kW-hr battery, designated Mark IA, which is scheduled for an in-vehicle test in early to mid-1979. The Mark IA battery will consist of multiplate Li-Al/FeS cells, and will be tested primarily to evaluate the technical feasibility of the lithium/metal sulfide system for use in electric vehicles. The Mark II battery will also consist of multiplate Li-Al/FeS cells, but will have somewhat higher performance than Mark IA. The primary purpose of the Mark II battery is to develop materials and fabrication methods that have a low cost in mass production. The Mark III program, which is aimed at a high-performance battery for passenger automobiles, is expected to begin in 1981. The type of cells for the Mark III battery has not yet been determined, but they will probably be multiplate Li-Al/FeS_2 cells.

The goals for the stationary energy-storage battery are listed in Table III [3,4]. The specific-energy and specific-power requirements for this application are less demanding than those for the electric-vehicle battery, but low cost (about $40-50/kW-hr) and long lifetime are essential. Most of the recent effort on the stationary energy-storage battery has involved conceptual design studies of a 100-MW-hr energy-storage plant. These studies, which were conducted as a cooperative effort between the Energy Systems Group of Rockwell International and ANL, have provided a general basis for design of a multiplate LiSi/FeS cell with a capacity of 2.5 kW-hr.

[illegible] CONCLUSIONS

At the present time, performance data have not yet been obtained on full-scale batteries using lithium/metal sulfide cells. Information from tests of individual cells and small groups of cells has indicated that the batteries should meet the program goals. The first full-scale battery to be evaluated will be the Mark IA electric-vehicle battery, which is scheduled for laboratory and in-vehicle testing in 1979.

A major objective of this program is to transfer the technology to industrial firms as it is developed, with the ultimate goal of competitive, self-sustaining industry for the production of lithium/metal sulfide batteries. This technology transfer is implemented primarily by the use of industrial participants and the subcontracting of development work to industrial firms.

The first commercial production of batteries will probably be for limited (low volume, high cost) markets such as postal vans, buses, mining vehicles, and submarines [2]. In these near-term (1982-1990) markets, the relatively high price of the batteries should be offset by their favorable performance characteristics. In the longer range, it is anticipated that batteries suitable for passenger automobiles will be developed, which could constitute a very large market. In the case of stationary-energy-storage batteries, it is more difficult to forecast future markets; however, planned tests of these batteries in the BEST facility should provide information useful for marketability, as well as technical feasibility evaluations.

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Table I. Performance Data on Li-Al/FeS Cells

Cell Type	No. of Cells	Specific Energy,[a] W-hr/kg	Specific Power,[b] W/kg	Energy Efficiency, %	Cycles
I	5	62	23	82	336
M	3	53	68	81	337
PW	3	41	30	84	328
EPMP	10	99	54[c]	80	275

[a] At 4-hr discharge rate.

[b] Measured as 15-sec power pulse at 50% state of charge.

[c] Specific power of EPMP cells subsequently increased to 95 W/kg by design changes to decrease resistance.

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

	Mark IA	Mark II	Mark III	Range
Specific Energy,[a] W-hr/kg				
Cell (average)	80	125	160	200
Battery	60	100	130	155
Energy Density,[a] W-hr/L				
Cell (average)	320	400	525	650
Battery	100	200	300	375
Peak Power, W/kg				
Cell (average)	60	125	200	250
Battery	45	100	160	200
Heat Loss through Jacket, W	400	150	125	75-125
Lifetime				
Deep Discharges[b]	200	500	1000	1000
Equivalent Distance, km	20,000	60,000	150,000	200,000
Target Dates				
Battery Test	1979	1981	1983	-
Pilot Manufacture	-	1983	1985	1990

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

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

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

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

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

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