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DEVELOPMENT OF PROTOTYPE SEALED BIPOLAR LITHIUM/SULFIDE CELLS

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ABSTRACT

Development of a prototype bipolar battery containing 13-cm dia cells for electric-vehicle propulsion is underway at Argonne National Laboratory (ANL). Both Li/FeS and Li/FeS_2 cells have been tested with LiCl-LiBr-KBr electrolyte and MgO powder separators for electrolyte-starved cell operation at 400 to 425 °C. These cells achieved the high performance and stability needed for the intended application. An innovative feature of this bipolar battery is a metal/ceramic bonded peripheral seal for each cell. The development of corrosion-resistant sealant materials at ANL has led to metal/ceramic bonds about 10 times stronger than obtainable with commercially available sealants for service at over 300 °C. This peripheral seal promotes long battery life by eliminating electrolyte loss and prohibiting transport of electrolyte from one cell to the next in a bipolar stack. Fabrication facilities have been recently constructed that enable development of 13-cm I.D. peripheral seals. The initial tests of prototype bipolar Li/FeS and Li/FeS_2 cells indicate improved performance as a result of scale-up. The 7-mm thick, 13-cm dia cells have total weight of 0.25 kg (cell density 2.8 g/cm^3). These cells are operated at 425 °C. The Li/FeS_2 cell exhibits 180 Wh/kg at a 30 W/kg discharge rate and the Li/FeS cell delivered 130 Wh/kg at a 25 W/kg rate. The low internal impedance of these cells enables high peak specific power capability: 400 W/kg for Li/FeS_2 and 240 W/kg for Li/FeS at 80% DOD.

INTRODUCTION

The objective of this effort is the development of a prototype bipolar battery that will attain high performance (~200 Wh/kg and 500 W/kg) and long cycle life (>1000 cycles) with the potential for low-cost fabrication. Lithium/sulfide (Li/FeS_2 or Li/FeS) cells with molten-salt electrolyte are well suited to the development of a bipolar battery. Long strings of series-connected cells are practical since cells always fail in a short-circuit condition. In a bipolar battery, cells form a series-connected stack with adjacent cells sharing a current-collector, the bipolar plate. To maintain the electrolyte molten, cells are normally operated at temperatures of 375 to 425 °C. The high-temperature bipolar battery operation provides advantages, as well as engineering and materials development challenges.

An improved Li/FeS_2 cell has exhibited the high performance and long life needed for the electric vehicle application. This high performance and stability resulted from a change of molten-electrolyte composition from LiCl-KCl eutectic to 25 mol% LiCl-37 mol% LiBr-38 mol% KBr (m.p. 322 °C) and use of a densely loaded FeS_2 electrode that is only operated on the upper voltage plateau (U.P.).[1] Electrolyte-starved (ES) cell operation[2] yields high performance and enables application of a low-cost MgO powder separator to replace the BN felt separator. These cells are over-discharge tolerant[3] and overcharge tolerant (OCT),[4] both of which are important for practical operation of the bipolar battery. This improved electrochemistry is currently being applied to the Li/FeS cell.

The development of a fabrication method for 13-cm I.D. peripheral seals in the bipolar lithium/sulfide cell is a key element of the scale-up effort. Our advanced metal/ceramic seal technology has shown superior bond strength. Additionally, new ceramic materials, which are chemically stable to the molten-electrolyte cell environment, have been engineered to match thermal expansion coefficients (CTE) of metal components. Our innovative design approach,[5] in which each cell in the bipolar stack is hermetically sealed, promises to provide long-term stability (capacity and coulombic efficiency) and overcharge tolerance.[6] A unique feature of the bipolar battery is that the positive and negative electrodes share a common current collector. Because of this arrangement, measures have to be taken to avoid the appreciable self-discharge that would result from an electrolyte path connecting the negative and positive electrodes. Earlier work on bipolar batteries concentrated on forming gaskets between the two electrode assemblies to retain the electrolyte; these batteries were short-lived. In our present bipolar cell design, a peripheral seal for each cell is formed prior to cell/battery assembly. A 500-cycle test of a stack of four 3-cm-dia bipolar cells has demonstrated the extended cycle-life capability of a bipolar Li/FeS_2 battery with this peripheral seal. Continued success in the fabrication and testing of sealed bipolar lithium/sulfide cells (3-cm dia) has led to the development of prototype (13-cm dia) bipolar cells (Fig. 1).

Prototype bipolar cells and seal components are being tested. New equipment has been designed and placed in operation within an argon glovebox to facilitate the bipolar battery scale-up. The necessary metal and ceramic hardware components have been designed and procured for the initial prototype (13-cm I.D.) seal development. Both prototype bipolar Li/FeS and Li/FeS_2 batteries are being developed. The bipolar Li/FeS cell will have a steel/ceramic/steel peripheral seal, whereas the bipolar Li/FeS_2 cell will have a steel/ceramic/molybdenum peripheral seal, which is more technically challenging. Coated-steel materials, such as TiN-coated steel, are candidates to replace molybdenum as the positive current collector. Such material would reduce the cost and bond strength requirements of the bipolar seal for the Li/FeS_2 battery.

MOLTEN SALT ELECTROCHEMISTRY

Improved cell electrochemistry has been demonstrated for both Li/FeS and Li/FeS_2 couples. Improvements came about from electrolyte modification that allowed "electrolyte-starved" cell operation with an MgO powder separator.[7] Earlier, costly BN fiber had been used as the separator material. The MgO powder separator is not physically stable under flooded electrolyte conditions; therefore, it must be used with limited amounts of electrolyte in the cell to fill pores of high-surface-area particles without fluidizing them. Besides low cost, the MgO powder separator, has thermodynamic stability to withstand near unit activity of lithium in the cell conditions of overcharge tolerance.

To increase the ionic conductivity of the electrolyte-starved cell, which is normally about 30% lower than that of the flooded cell, the electrolyte composition was shifted off-eutectic to a LiCl-rich composition (in mol%, 34 LiCl-32.5 LiBr-33.5 KBr), which has a 25% higher ionic conductivity than that of the LiCl-LiBr-KBr eutectic at 425 °C. This higher electrolyte conductivity approximately compensates for the reduced electrolyte content of the electrolyte-starved cell. Therefore, the

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area specific impedance (ASI_t) of the electrolyte-starved cells is comparable to that of the flooded cell. The capacity utilization of the electrolyte-starved cells is now slightly greater than that of the flooded cell.

Use of LiCl-LiBr-KBr electrolyte allows Li/FeS cell operation at considerably lower temperature (400-425°C) than with other electrolytes (LiCl-KCl, LiF-LiCl-LiBr). Electrolyte-starved Li/FeS cells with LiF-LiCl-LiBr are generally operated at 475°C; and corrosion reactions may limit cycle life. Thermal management of the Li/FeS battery operated at 475°C requires an active heating and cooling system, whereas at 425°C greater temperature fluctuations would be tolerated to minimize the active control. The Li/FeS discharge reaction proceeds as follows:

$$2LiAl + (FeS) \rightarrow 2Al + (Li_2S + Fe)$$

Small bipolar cells (5-cm^2 separator area, 30 wt% MgO powder-Maglite-S, 2-mm thick) were tested to determine the performance of the electrolyte-starved Li/FeS cell with LiCl-LiBr-KBr electrolyte at 425°C. Capacity utilization of the 1-mm-thick FeS electrode (625-mAh theoretical capacity) was evaluated at current densities ranging from 25 to 200 mA/cm^2. Electrodes were held within steel cups with a ceramic insulating ring at the periphery of the separator layer. As shown in Fig. 2, FeS electrode capacity utilization up to 100 mA/cm^2 was approximately 70%. Beyond 70% utilization of FeS electrode capacity, increasing Li_2S discharge product results in increasing internal electrode impedance. The Li/FeS cells are generally designed such that the LiAl electrode limits cell capacity. Eliminating excessive FeS electrode expansion from Li_2S generation at high-capacity utilization (>70%) promotes long cycle life. Additionally, the overcharge tolerance is related to two voltage plateaus, LiAl and LiAlFe, of the negative electrode. The discharge voltage capacity exhibiting an initially higher voltage (~0.2 V) relates to the overcharge tolerance, which will be described later in this section.

The electrochemistry of the Li/FeS_2 cell has been investigated to a greater degree than that of the Li/FeS cell. Operation at a low temperature, 390-435°C, with LiCl-LiBr-KBr electrolyte is beneficial to cycle-life stability. Also, cycle life was extended ten-fold by the use of upper-plateau FeS_2 electrode operation.[3] The overall Li/FeS_2 cell reaction is as follows:

$$2LiAl + FeS_2 \rightarrow 2Al + (Li_2FeS_2)$$

The discharge product of the FeS_2 electrode, Li_2FeS_2, is much denser than Li_2S. Therefore, a densely loaded FeS_2 electrode (about 50 vol%) was developed. As with the FeS test cell described above, the performance of the Li/FeS_2 cell (5 cm^2 area) having a MgO powder separator (2-mm thick) was evaluated. The 1-mm-thick FeS_2 electrode was housed in a molybdenum cup versus a LiAl + LiAlFe electrode in a steel cup. The two current-collector cups were separated by a ceramic ring at the periphery of the MgO separator layer. Capacity utilization of the U.P. FeS_2 electrode (625-mAh theoretical capacity) was evaluated at discharge current densities ranging from 50 to 200 mA/cm^2 at 425°C. As seen in Fig. 3, utilization of about 90% can be expected at about 100 mA/cm^2 for the electrolyte-starved U.P. FeS_2 electrode. Even at 200 mA/cm^2, 70% utilization of U.P. FeS_2 electrode capacity utilization is obtained. The relatively stable cell capacity with increased discharge current density indicates that the low internal cell impedance is little changed even at 80% depth of discharge.

Overcharge tolerance for lithium/sulfide cells was accomplished by an innovative application of a non-destructive self-discharge mechanism, the "lithium-shuttle mechanism."[4] In general, the lithium-shuttle mechanism involves diffusion of lithium metal species across the separator to chemically discharge the positive electrode. The chief controlling element of the mechanism is the lithium activity of the negative electrode, while the cell operating temperature and electrolyte composition are also contributing factors. With this design, lithium shuttle rates of ≥2 mA/cm^2 develop at Li-alloy electrode potentials of -150 to -200 mV (vs. $\alpha + \beta$ Li-Al reference electrode) in LiCl-LiBr-KBr electrolyte at 400°C. A Li-Al_5Fe_2 alloy with a potential of -260 mV (vs. $\alpha + \beta$ Li-Al reference electrode) has been applied to engineering development of overcharge-tolerant cells. Altering the electrolyte composition (e.g., LiCl-KCl or LiF-LiCl-LiBr) and cell operating temperature (>400°C) imposes new limits upon the lithium-shuttle rate, up to 10 mA/cm^2. Generally, the lithium shuttle rate is sufficient for charge equalization by a trickle-charge procedure without the need for electronics.

Extensive measurements of lithium transport rates using a potentiostated Li-AlFe electrode have provided evaluation of parametric effects for overcharge tolerance in Li/FeS_x cells. These lithium transport rates vs. reciprocal temperature for a given molten-salt electrolyte composition (Fig. 4) have been fit to Arrhenius expressions. We found that the Arrhenius rate expressions agree well with available physical data for lithium solubility, including dimerization of lithium for the respective molten-salt compositions. That is, Li_2^+ would be formed in the all-Li^+ ion electrolyte (LiF-LiCl-LiBr), whereas LiK^+ would be formed in the K^+-ion containing molten salts (LiCl-KCl, LiCl-LiBr-KBr).

Based on these fundamental understandings, a model of overcharge tolerance rate has been formulated.[8] Electronic conductivity of dissolved lithium in molten salt can be thought to short circuit lithium transport near the positive electrode, while the dimerization effectively removes electronic conductivity at the negative electrode side of the electrolyte layer. These concepts suggest a rather complicated model of the overcharge tolerance rate, with lithium diffusion constant, D, and electronic conductivity, κ, varying across the thickness of the molten-salt electrolyte layer. As a result, measurement of D and κ is difficult due to their interrelation.

A semiempirical model has been developed for the overcharge tolerance rate based on measured rates. An expression of lithium diffusion plus electronic conductivity was developed using the inputs of lithium activities at the respective electrodes. Overcharge tolerance rates for the three electrolytes of interest have been fit to this model with ≥90% agreement. This general agreement suggests the ability to predict and modify overcharge tolerance rates for battery cells. The ability to charge/equalize bipolar batteries without electronics is a key development objective.

BIPOLAR SEAL DEVELOPMENT AND TESTING

Our effort has been directed toward developing new ceramic materials that can be used in hermetic seal formation for the Li/FeS_2 cell.[9] A hermetic seal in the Li/FeS_2 cell has certain chemical and mechanical requirements that must be met by the component materials used in forming the peripheral seal for a bipolar cell. For long-term operation, the seal must maintain an electrically insulating, gas-tight bridge between the metal components, usually molybdenum at the positive side and steel at the negative side. Structural integrity requires coefficients of thermal expansion (CTE) for ceramic and metal components to be sufficiently matched to tolerate a temperature range of 750 to 1000°C for seal formation and room temperature to 450°C for cell assembly and operation. Ceramic sealants have been specially formulated to accommodate the differences in CTE between steel and molybdenum by forming a "graded" ceramic seal. Our sealants were found to exhibit greater than 95% coverage and wetting angles that approach 0° for both steel and molybdenum. An apparatus was developed to test the fracture strength of our composite ceramics used in the bipolar ring seal. The test determines relative strengths of the various compositions that we are developing. To date in this effort, we have achieved a six-fold increase in fracture strength by changing the composition of this ceramic material.

To evaluate the effectiveness of our ceramic sealant material, the bond strength of ceramic/ceramic and metal/ceramic seals is being determined. These physical data have provided a basis for developing the 13-cm ID peripheral seal needed for a prototype Li/FeS_2 bipolar battery. Test samples are prepared from two strips with 0.5 to 2.0 cm^2 bond areas. The bonded strips are mounted in a fixture that measures the shear force required to rupture the bond. There are no generally accepted test procedures of this type; therefore, our measurements are relative values. In these studies, over two dozen bond couples were formed, and the sheer strength tested.

As shown in Table 1, bond strengths with our standard sealant are outstanding. The substrate ruptures many times before the ceramic bond. For the molybdenum bond, the strength is improved by more than seven times by forming an intermetallic at the molybdenum surface prior to bond formation. A cataloging of various bond strengths aids our scale-up of the bipolar peripheral seal and will help develop optional approaches to seal formation. In comparison to commercially available bonding agents for high-temperature application (e.g., borosilicate glass, Aremco products), the standard sealant materials exhibit bond strengths approximately ten times greater. The chemical stability of the sealants developed at ANL makes them ideally suited for high-temperature battery applications. Additionally, as a result of the excellent wetting properties for these sealants, bond formation does not rely on a thermal/compression process; thus, the bonding is not unidirectional.

To date, we have fabricated over twenty-four 2.5-cm I.D. peripheral seals and evaluated them as housings for bipolar Li/FeS_2 cells. With emphasis upon ceramics research and seal assembly procedures, we were able to develop a seal with a graded CTE that approximately matches the CTEs for both steel and molybdenum housings. With the objective of establishing long-term stability and reproducibility, we then prepared six improved seals for the bipolar cell with similar ceramic compositions and processing methods. One seal was successfully leak-checked at a vacuum of 100 μm -- the vacuum limit of our test fixture. Another seal was used to build a sealed bipolar Li/FeS_2 cell (3-cm dia), which operated over 450 cycles and 2000 h and retained >90% of its initial capacity. The area-specific impedance for this small-scale cell was 0.55 Ω cm^2, which indicates the potential for high power with this technology. The remaining four seals were used to fabricate sealed bipolar Li/FeS_2 cells for a four-cell stack.

A number of the sealed bipolar cells, both Li/FeS and Li/FeS_2, underwent post-operative metallographic analysis to identify areas for improvement. The metallographic findings support the chemical/physical stability of our seal technology. In general, there is no indication of electrolyte escape from the sealed bipolar cells. The bipolar cell assembly methods will continue to be improved.

The four-cell stack was operated for >500 cycles (2500 h) with >98% coulombic efficiency,[10] as shown in Fig. 5. Three of the four cells were employed throughout the tests, while one initially weak cell was replaced at 150 cycles. Bipolar stack capacity (0.45 Ah) was at least 90% that of individual cells. The stack was operated at 425°C with 4-h charge and 2-h discharge rates and with charge and discharge cutoff voltages of 8.2 and 5.4 V, respectively. The average stack discharge voltage of approximately 6.5 V greatly exceeds the decomposition voltage of the molten-salt electrolyte at 3.2 V. Thus, this stack demonstration served as an excellent test of our seal technology. This initial bipolar cell stack was assembled from four individual cells stacked with nickel felt pads and voltage leads between the cells. The stack impedance at 0.7 ohm cm^2 of cell area is within 130% that of individual cells, in spite of the added intercell contact resistance. Improvements in stack integration may reduce stack impedance to less than that of cells, because of greater uniformity in intercell contact.

A special cycler was built to monitor the individual cells in the stack and determine the efficacy of the overcharge tolerance for the Li/FeS_2 cells. Voltages for the individual cells were well matched during normal cycles without the need for cell-to-cell charge equalization. During stack lifetime, the voltage and capacity of individual cells with repeated recharging were sufficiently well matched that charge equalization was needed only every 20th cycle rather than every cycle. Charge equalization was achieved without electronic equipment by use of an overcharge-tolerance mechanism for molten-salt cells, "the lithium-shuttle mechanism," which involves a simple trickle charge of the stack, as shown in Fig. 6. By cell design, lithium transport near the end of charge safeguards strong cells from overcharging, while weaker cells continue to accept charge capacity. The battery is effectively charge equalized when all the battery cells have reached the overcharge capacity state.

The molybdenum current collector for the FeS_2 electrode presents difficulties for seal scale-up, as well as of bipolar cells into a stack integration. Apparent commercial interest in the Li/FeS bipolar battery has provided support for the development of the less technically challenging peripheral seal of steel/ceramic/steel. This eliminates the problem of the CTE difference between steel and molybdenum in the Li/FeS_2 bipolar cell. A current collector of TiN-coated steel is an attractive alternative to molybdenum for the positive current collector in the Li/FeS_2 bipolar cell. A 3-cm-dia bipolar Li/FeS_2 cell was built to demonstrate the stability of a TiN-coated steel for the FeS_2 current collector. The cell was operated 40 cycles (200 h) at 415°C with >97% coulombic efficiency at current densities up to 100 mA/cm^2. The U.P. FeS_2 electrode capacity utilization was about 85% at 50 mA/cm^2. (Attack of the steel substrate would have degraded electrode utilization.) Thermal cycles were also tolerated. These results are encouraging because coatings with pinholes typically exhibit rapid degradation. This coating was prepared at high temperature using multilayer chemical vapor deposition (Richter Precision Inc., East Petersburg, PA). The TiN-coated steel current collector was visually examined after the 40-cycle test. No pin holes were seen. Even exposed edges, which are particularly susceptible to crack failures, showed no attack. Metallographic examination in cross section confirmed the stability of TiN-coated steel collector. This is a promising development for low-cost Li/FeS_2 battery and ease of scale-up.

PROTOTYPE BIPOLAR CELL DEVELOPMENT

The scale-up effort has required the acquisition of new equipment for a facility to handle fabrication of a 13-cm I.D., metal/ceramic seal. The new facility contains a 200-ton hydraulic press (Tee Tool, Joplin, MO), a large 1100°C processing oven, ceramic powder preparation equipment, welding capability, and bipolar stack testing facilities within a high-purity argon glovebox. (This facility was developed for materials research and applications under a jointly funded project of DOE and the State of Illinois.) In our current bipolar seal design, the metal current-collector components are attached to each other with a 2-mm thick, 135-mm I.D. ceramic ring. This ceramic ring is formed from pressed powders of our corrosion-resistant sealant material. Our two-year project objective is to develop reproducible procedures for bipolar seal fabrication to enable testing of a 36 V bipolar Li/FeS_2 battery containing 22 cells.

The initial prototype bipolar seals are designed to permit flexibility of materials selection. We intend to investigate options for stack integration and coated steels as a replacement for the molybdenum at the FeS_2 electrode. The seal components, as shown in Fig. 7, are designed for a simple stacking assembly method. The metal components are each bonded to the ceramic ring (an insulator) via parallel horizontal surfaces. A ceramic ring (MgO, Ozark Technical Ceramics) is used to "fixture" the assembled components. The metal components are custom designed and fabricated by stamping 5-mil sheet metal (Meyer Tool, Oak Lawn, IL). The seal is formed in a single thermal processing at 1100°C. Subsequent thermal cycle testing (25 to 400°C) evaluates the seal

mechanical durability. Metal/ceramic interfaces prepared in this way have been found to remain crack free after thermal cycling.

Initial tests of prototype bipolar lithium/sulfide cells without seals indicate their high performance capabilities. These bipolar cells have 13-cm dia electrodes, are 7-mm thick, and have a total weight of 0.25 kg (including the weight of two full current collectors). The electrode materials account for 48% of the total bipolar cell weight. The cell thickness breakdown is as follows: iron sulfide electrode, 2.2 mm; MgO powder separator, 1.8 mm; Li-alloy electrode, 3.0 mm. The separator of these initial cells is thicker than desired to aid handling of the 13-cm-dia pressed powder pellets. Electrodes and separator pellets were pressed at 400 tons using SAFT-America (Cockeysville, MD) equipment. The 13-cm dia pellets have very good handling properties. Future of prototype bipolar cells will increase the proportion of electrode materials and thin down the separator layer. This should further increase both specific energy and specific power.

These first prototype cells are exhibiting approximately 30% increased specific energy and more than doubled specific power over earlier monopolar cells. Both Li/FeS and Li/FeS_2 bipolar cells are operated at 425 °C with the LiCl-rich LiCl-LiBr-KBr electrolyte. The Li-alloy electrode consists of LiAl + LiAlFe to provide overcharge tolerance. As shown in Fig. 8, both cell types deliver about 25 Ah at a 5A discharge rate. These capacities translate to about 90% utilization of the U.P. FeS_2 theoretical capacity and 70% utilization for the FeS electrode cell. This utilization is similar to that of the 3-cm dia bipolar cells.

The scale-up generally has led to performance enhancement. The bipolar Li/FeS_2 cell delivers a specific energy of 180 Wh/kg at a 30 W/kg discharge rate, while the Li/FeS cell delivers 130 Wh/kg at a 25 W/kg discharge rate. The bipolar cell scale-up also indicates improved specific power as a result of lower internal impedance. (It was generally more difficult to provide uniform surface contact to the 3-cm-dia bipolar cells.) Bipolar cell impedance is evaluated through an IBM PC-based system with a Keithley 570 interface. Cell impedance is measured by a current-interrupt method with voltage relaxation recorded from milliseconds to about 15 s. This method indicates electronic and ionic contributions to cell impedance. As shown in Fig. 9, the impedance of the Li/FeS cell is impressively low, with only 0.4 ohm cm^2 values at up to 50% of the discharge capacity, which is equivalent to ~360 W/kg peak specific power. As is characteristic of Li/FeS cells, impedance climbs at higher depths of discharge (DOD), to 0.7 ohm·cm^2 at 80% DOD (240 W/kg). Superior specific power was achieved for the bipolar Li/FeS_2 cell because of its high average discharge voltage and impedance stability to 80% DOD. As shown in Fig. 10, this first prototype cell had a cell impedance of 0.5 to 0.6 ohm·cm^2. This indicates a peak specific power in excess of 400 W/kg.

Outstanding power density (~1000 W/L) of the bipolar lithium/sulfide cells is an important feature for electric vehicle batteries. Additionally, significant entropic cooling[11] of the Li/FeS_2 battery in discharge allows development of a dense monoblock battery, such as the bipolar battery, without extensive thermal management. The bipolar Li/FeS_2 battery is unique in its ability to provide outstanding electric vehicle performance in a small, cost-effective package.

SUMMARY

Electrolyte-starved cell operation with MgO powder separators was developed for both Li/FeS and Li/FeS_2 cells. Excellent performance was obtained at 425 °C with a LiCl-rich LiCl-LiBr-KBr electrolyte composition. A 1000-cycle life expectancy has been established for the Li/FeS_2 cell. The reduced temperature operation (425 °C as opposed to 475 °C for a LiF-LiCl-LiBr electrolyte) for the Li/FeS cell should extend its cycle life and improve thermal management of the battery. These cells use a "lithium shuttle" mechanism for overcharge tolerance. An understanding of lithium dimer formation has explained the influence of electrolyte composition upon lithium shuttle rates.

Bipolar seal development has identified high-strength metal/ceramic bond couples and higher strength ceramic structural materials. Over twenty-five 3-cm dia. seal components were evaluated to test fabrication methods and materials compositions as sealed bipolar cells tests. Long-term bipolar seal stability was demonstrated in a 500-cycle (2500 h) test of a four-cell bipolar stack. This 6.5 V stack, which exceeds the 3.2 V decomposition voltage of the molten electrolyte, provides a proof-of-concept that these bipolar seals will retain molten salt. Stack coulombic efficiency was >98% throughout the test.

A scale-up effort for bipolar lithium/sulfide cells is underway. The first prototype bipolar peripheral seals (13-cm dia I.D.) have been fabricated using newly designed equipment and hardware components. This large-diameter metal/ceramic seal has successfully undergone thermal cycling. The initial prototype seal design uses a simple stacked assembly, which allows for testing of a number of current-collector materials options. We designed the seal to facilitate bipolar cell integration into a stack through a simple steel/steel weldment. A successful test of TiN-coated steel for the FeS_2 current collector suggests its potential as a substitute for the expensive molybdenum in the Li/FeS_2 cell.

The initial tests of prototype bipolar Li/FeS and Li/FeS_2 cells indicate improved performance as a result of scale-up. These are 7-mm thick, 13-cm dia cells, have a total weight of 0.25 kg (cell density 2.8 g/cm^3), and are operated at 425 °C. The Li/FeS_2 cell exhibits a specific energy of 180 Wh/kg at a 30 W/kg discharge rate, and the Li/FeS cell delivers 130 Wh/kg at a 25 W/kg rate. The low internal impedance of these cells yields high peak specific power: 400 W/kg for Li/FeS_2 and 240 W/kg for Li/FeS at 80% DOD. Outstanding power density for the bipolar battery is particularly attractive for the electric vehicle application, especially hybrid vehicles. The design options of a lithium/sulfide bipolar battery for an electric car are explored in "Modeling of Lithium-Sulfide Batteries for Electric Vehicles and Hybrid Vehicles" by Nelson and Kaun in this symposium.

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Table 1. Tensile Strength of Bonded Surfaces

Bond Couple	Surface Area (cm^2)	Fracture Load (kg/cm^2)
Mo/standard sealant/Mo	2.0	3.2
Mo/standard sealant/Mo (Mo intermetallic used)	0.5	23.0
Mo/borosilicate glass/Mo	0.5	3.47
Al_2O_3/standard sealant/Al_2O_3	0.72	19.76
MgO/standard sealant/MgO	0.4	52.87
Steel/standard sealant/MgO	0.48	>35.6*
TiN-coated steel/standard sealant/TiN-coated steel	0.5	>16.7*
Steel/Aremco 565/MgO	1.5	1.4**

*Substrate ruptured before bond.
**Other Aremco bonding agents failed before load test.

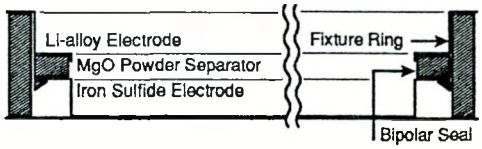

Fig. 1. Cross section of a sealed bipolar lithium/sulfide cell, i.e., one repeating element of the bipolar stack.

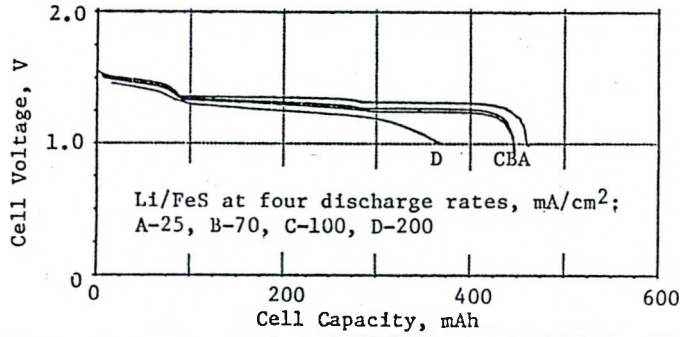

Fig. 2. Voltage/capacity plot of a bipolar Li/FeS cell (5 cm^2 area, 625 mAh theoretical capacity) operated at 425°C.

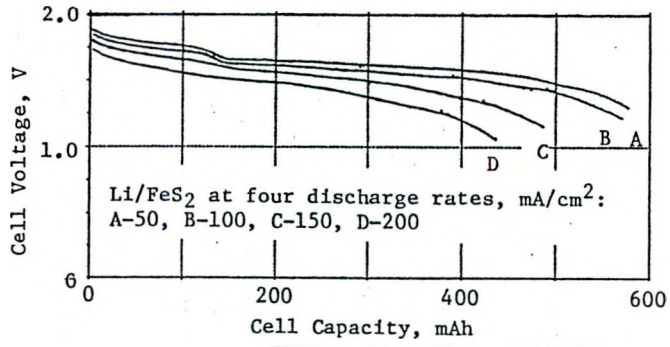

Fig. 3. Voltage/capacity plot of a bipolar Li/FeS_2 cell (5 cm^2 area, 625 mAh theoretical capacity) operated at 425°C.

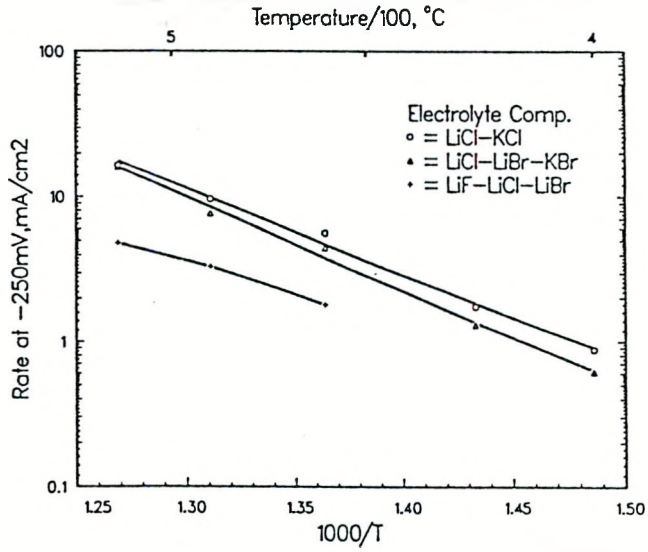

Fig. 4. Effect of temperature upon lithium shuttle rates at about -250 mA vs. LiAl reference electrode.

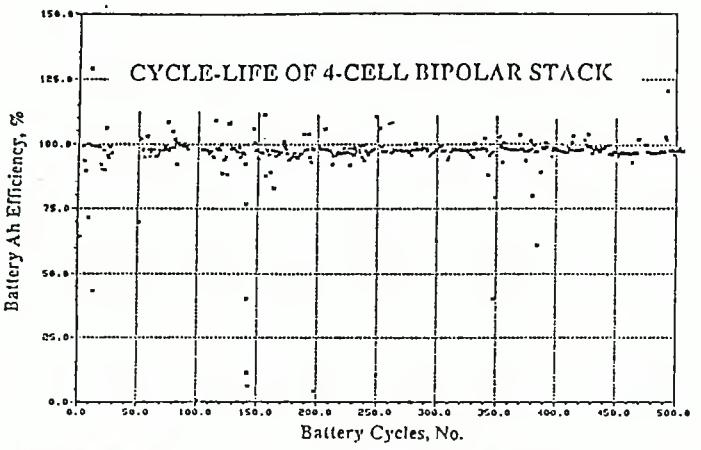

Fig. 5. Coulombic efficiency of a four-cell bipolar Li/FeS_2 stack during a 500-cycle test.

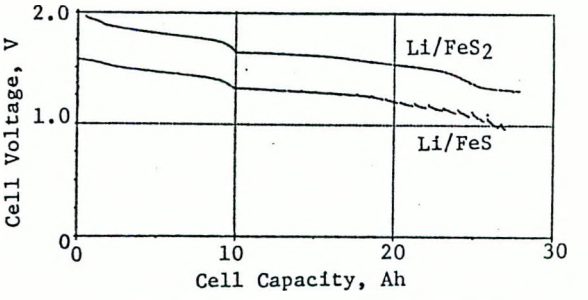

Fig. 8. Voltage/capacity plots of prototype bipolar Li/FeS_2 and Li/FeS cells at 425 °C. Both cells weigh about 0.25 kg.

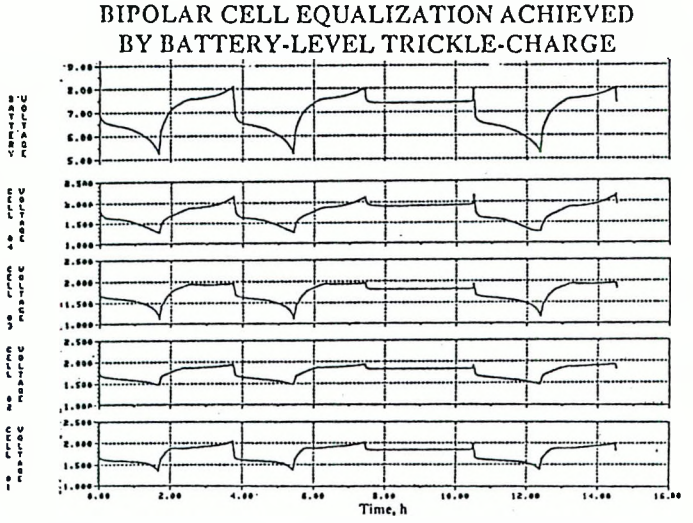

Fig. 6. Battery and cell voltage/time plots over three cycles with a trickle-charge period during the second cycle (cycle no. 402).

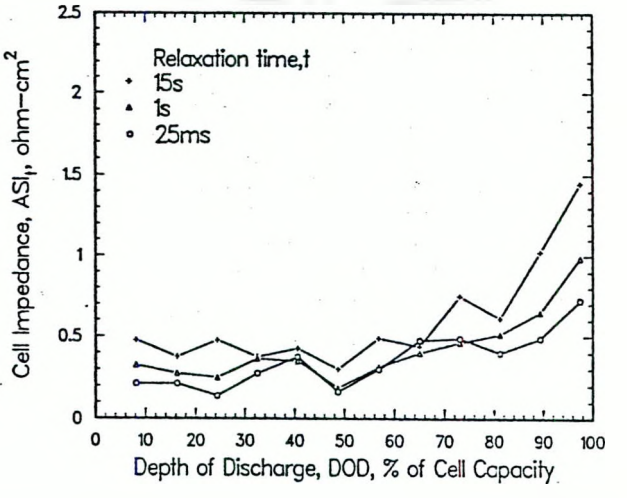

Fig. 9. Cell impedance (ASI_t) vs. depth-of-discharge for a prototype bipolar Li/FeS cell at 425 °C.

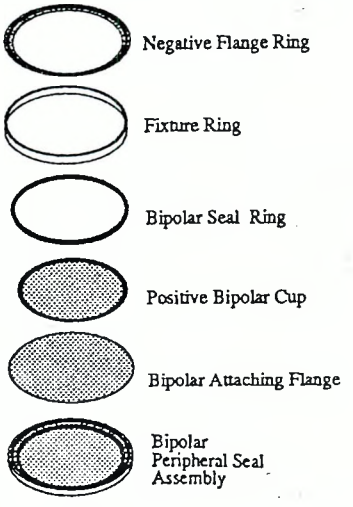

Fig. 7. Exploded view of a bipolar peripheral seal along with an assembled component.

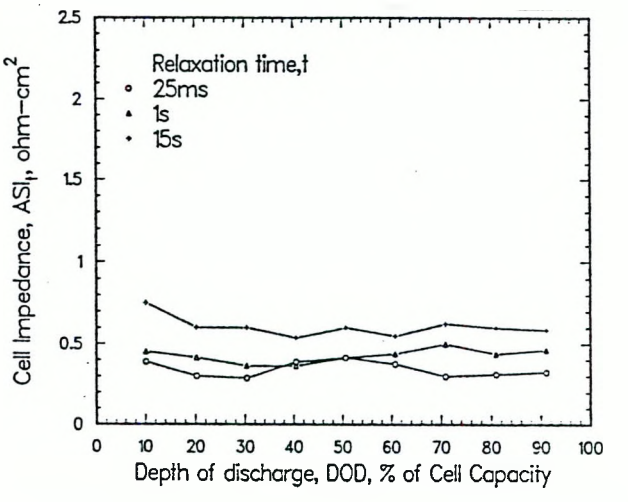

Fig. 10. Cell impedance (ASI_t) vs. depth-of-discharge for a prototype bipolar Li/FeS_2 cell at 425 °C.