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RECHARGEABLE MOLTEN-ELECTROLYTE LITHIUM BATTERIES--
A STATUS REPORT

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KEY WORD LIST

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1	molten electrolyte conductivity rechargeable lithium cell
2	melting point conductivity Li-alloy FeS_2 Electrode
3	specific energy current-collector FeS electrode
4	lithium-limited driving profile LiCl-LiBr-KBr
5	upper plateau FeS_2 off-eutectic electrode impedance
6	overcharge tolerant lithium shuttle equalization
7	self-discharge polarization electrolyte-starved

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ABSTRACT

Lithium-alloy/metal sulfide cells with on molten-halide electrolytes, which are operated in a temperature range of 375-475°C, have undergone many improvements in recent years. Cycle life now exceeds 1000 cycles. The Li-alloy/LiCl-LiBr-KBr eutectic (25:37:38 mol%)/upper-plateau (U.P). FeS_2 cell operated at 400°C has shown excellence performance prospects: 200-Wh/kg specific energy and 200-W/kg specific power. Electrolyte composition has played a dominant role in attaining long-term stable electrochemical performance. A modified LiCl-LiBr-KBr composition (34:32.5:33.5 mol%) was found to exhibit 25% increased ionic conductivity over that of the eutectic. This higher-conductivity electrolyte approximately compensates for the reduced electrolyte content of the electrolyte-starved FeS_2 cell. Such a cell has attained of 95% utilization of U.P. FeS_2 electrode capacity at a comparable cell impedance (0.8-1.0 ohm-cm^2) to that of an the electrolyte-flooded cell. Advancements in cell design and materials application have reduced materials costs and increased battery durability. Both FeS and FeS_2 cell tests have demonstrated overcharge tolerance (3-5 mA/cm^2) for electrolyte-starved operation with MgO powder separators.

INTRODUCTION

Continuing development of rechargeable Li-alloy/metal sulfide batteries is being pursued to improve performance and cycle life and to decrease cost by substitution or application of low-cost materials. Cells using MgO powder separators, which have potential for lower cost than the previously used BN felt, must be operated in an electrolyte-starved condition. This has required changes in the cell electrochemistry. Only in recent years has an electrolyte (LiCl-LiBr-KBr) been identified which supports long cycle life and high performance for the upper-plateau (U.P.) FeS_2 cell ($FeS_2 + 2Li \rightarrow Li_2FeS_2$).[1] In addition, new overcharge-tolerant cells can be safely charged without electronic monitoring. The overcharge-tolerance also enables self-(electrochemical) charge equalization of cells in a battery. Cycle life of batteries is, therefore, expected to be similar to that of cells, i.e.,>1000 deep discharge cycles. This paper summarizes the status of FeS and FeS_2 battery-cell development.

Three Li-ion containing molten salts are dominant in lithium/metal sulfide battery development: LiCl-KCl, LiCl-LiBr-KBr, and LiF-LiCl-LiBr. We have recently determined their conductivities (by AC impedance technique) as a function of temperature for the eutectic compositions. The results are plotted in Fig. 1. Each of these molten salts has unique properties that dictate cell development. For example, the LiF-LiCl-LiBr (all Li-ion electrolyte) has the highest conductivity, about 3.0 S/cm at 450°C, but its higher melting point, 440°C, requires cell operation in excess of 450°C.[2] On the other hand, the LiCl-LiBr-KBr electrolyte, with its lower melting point at 320°C and broad liquidus for deviations of Li/K ion ratio from that of the eutectic, provides a stable operating environment at 400°C for the FeS_2 electrode[3] and has a conductivity of 1.3 S/cm at 450°C. The LiCl-KCl eutectic has a 354°C melting point with cells operated at 450°C and a conductivity of 1.4 S/cm at 450°C.[4] The LiCl-KCl has been the typical electrolyte used in primary thermal batteries and still serves as a baseline electrolyte for rechargeable cell electrochemical studies. The Li^+ ion and K^+ ion activities of these molten salts regulate solubilities of electrode charge/discharge products and electrode kinetics. As will be discussed later, self-discharge rates, cell performance, and cycle-life stability are strongly dependent upon the electrolyte properties.

An important feature of the Li-alloy/FeS_x cells is the high capacity density of their electrodes, 0.9 to 1.4 Ah/cm^3. In development of high specific energy cells, high energy density for the electrodes enables cells to be designed with rather low non-active material weight contribution; that is, voluminous electrodes require more weight contribution from cell support structure. Typically, battery cells of other electrochemistries attain about 20% of their theoretical specific energy, whereas molten-salt lithium cells can attain 30 to 50% of their theoretical specific energy. The molten-salt lithium cells, particularly the U.P. FeS_2 type, have dense discharge products (e.g., Li_2FeS_2, 2.85 g/cm^3), which require less electrolyte/separator and current collector for cell operation. A typical cell density is 3 g/cm^3. The Li-alloy performance should also be judged on effective capacity density, that is, usable capacity density. Some lithium alloys, such as LiSi, have a significant portion of Li capacity at low Li activity and high electrode impedance. This unusable lithium takes up significant volume. Consequently, such a negative electrode with high specific energy (Wh/g) may not have satisfactory volumetric energy (Wh/cm^3). Earlier assessments[5] showed that the conventional Li alloys (that is, Li-Si, Li-Al, Li-AlSi) have similar effective capacity densities of 1.17 ± 0.05 Ah/cm^3. The Li-Al alloy is generally preferred because of its stable potential and low impedance throughout its discharge capacity.

In spite of somewhat similar theoretical specific energies (460 to 475 Wh/kg), the U.P. FeS_2 cell has specific energy and power capabilities (200 Wh/kg and 200 W/kg) which are at least 50% greater than those of the FeS cell. The higher voltage, as shown in Fig. 2, and lower impedance of the U.P. FeS_2 electrode are combined with 50% greater utilization of theoretical capacity. The energy density of the U.P. FeS_2 electrode is about 1.90 Wh/cm^3, compared to about 1.05 Wh/cm^3 for the FeS electrode. In addition, cell power (V^2/R) for the U.P. FeS_2 cell is about double that of the FeS cell. Voltage for the U.P. FeS_2 cell is about 35% higher, and cell impedance at 80% depth of discharge (DOD) is about 80% of the FeS cell impedance. Therefore, the U.P. FeS_2 cell can achieve a much higher fraction of theoretical energy than the FeS cell based on similar supporting structure weight and cell volume.

The other distinction between FeS and FeS_2 cells is the current-collector material. The FeS electrode uses iron or nickel current-collector. The higher sulfur activity of the U.P. FeS_2 electrode requires the higher oxidation potential and greater corrosion resistance that is afforded by molybdenum current collectors. Molybdenum has excellent corrosion life, but it is costly and has limited working properties for welding and forming. Coatings, such as TiN/TiC, on low-cost base metals have shown promise for the U.P. FeS_2 electrode current collector. Alternatively, the bipolar cell configuration enables application of less molybdenum or of coated steel.

FeS CELL DEVELOPMENT

The FeS cells demonstrated stable performance and long cycle life much earlier in their development than did the FeS_2 cells. Additionally, the ability to design cells with an iron current collector for the positive and negative electrodes made FeS cell development somewhat easier. As a result, the FeS version has undergone engineering development to the stage of small battery tests. The FeS electrode kinetics has been improproved with use of Li^+-rich electrolyte compositions, such as Li-rich LiCl-KCl and LiF-LiCl-LiBr, to achieve greater utilization of cell theo-retical capacity. Present FeS cell development is led by Westinghouse Oceanic Division (formerly Gould)[6] which is testing LiAlSi/LiF-LiCl-LiBr (MgO)/FeS cells that are operated at 475°C. These cells are designed for electrolyte-starved cell operation, which enables practical application of an MgO powder separator (instead of the more expensive BN felt used previously). The LiF-LiCl-LiBr electrolyte (all Li^+ ion) does not polarize under high current flow, as would K^+-ion containing electrolytes (e.g., LiCl-KCl). Thus, high performance (specific energy at C/3, 100 Wh/kg;

specific power, 100 W/kg) was maintained with a limited amount of electrolyte in the cell, which is required to avoid fluidization of the MgO powder separator.

A low cycle life of 300-500 cycles was observed for some of these cells and may be explained by a mild overcharge of the FeS electrode. However, recent development of overcharge-tolerant cells (discussed later) is expected to extend the FeS battery cycle life.

Earlier FeS cells had a capacity decline problem due to Li-Al electrode agglomeration. Inert particle (carbon, MgO) additions to the LiAl powder-bed electrode and use of a slurry fabrication method, rather than cold-pressing, helped it retain an open sponge structure.

The FeS cell capacity stability and performance were subsequently improved by a lithium-limited cell design[7] which employs a deep-dischargeable Li-Al electrode. The capacity of the positive electrode relative to that of the negative (Li-Al) electrode influences the internal cell impedance as a function of depth of discharge. Generally, for power-demanding applications (e.g., electric vehicles), usable capacity is limited by the ability of the battery to meet the power pulse required for a satisfactory vehicle acceleration. When the battery can no longer provide the required power for a 30-s acceleration, the cell is considered fully discharged. The lithium-limited cell design has demonstrated 10% higher specific energy for constant-current discharge and nearly double specific power at 80% DOD compared with the FeS-limited cell design. Battery specific energy under an electric vehicle driving profile (SAE J227 a/D) is increased by 50%. With the lithium-limited design, the FeS electrode impedance increases by 100% at about 50% to 80% of theoretical capacity, whereas the Li-Al impedance is relatively unchanged in this capacity range. Therefore, the Li-Al electrode capacity is sized relative to that of the FeS electrode so that it is exhausted before the FeS electrode begins its upswing in electrode impedance. The optimal active material utilization occurs at about 80% for the Li-Al electrode and about 70% utilization for the FeS electrode.

FeS_2 CELL DEVELOPMENT

Two innovations in the electrochemistry for the FeS_2 cell have transformed it into a stable-capacity, high-performance secondary cell.[8] First, a significant capacity decline problem was overcome with a change of electrolyte from LiCl-KCl eutectic to LiCl-LiBr-KBr eutectic and lower temperature operation. High performance was attained at 400°C, or 50°C lower than the operating temperature with the LiCl-KCl electrolyte. The cycle life of the FeS_2 cell was extended 10 fold, to 1000 cycles. This result indicates that both time- and cycle-related capacity loss mechanisms had been overcome in the FeS_2 cell with LiCl-LiBr-KBr electrolyte. Second, specific energy and power were improved by operating the cells exclusively on the upper of the two discharge voltage plateaus (the second plateau is similar to the discharge curve for FeS). The loading density of the FeS_2 electrode was increased from 1.5 Ah/cm^3 for a two-plateau FeS_2 cell to 2.4 Ah/cm^3 for an upper-plateau FeS_2 cell. The higher capacity density reduced the internal cell impedance by about 50%. Also, it yielded a virtually flat curve for cell internal impedance versus discharge capacity. Thick FeS_2 electrodes (8-mm thick) were operated with high utilization (80-90%) of the U.P. FeS_2 capacity. As shown in Fig. 3, FeS_2 cell capacity and discharge voltage were improved by 50% and 10%, respectively, compared with those of earlier two-plateau FeS_2 cells having comparable weight and volume. In addition, cell power at 80% DOD was doubled due to 0.3-V increased discharge voltage along with lowered cell impedance.

Ongoing electrolyte development for the FeS_2 cell at Argonne National Laboratory indicated that off-eutectic compositions of LiCl-LiBr-KBr have higher conductivity than that of eutectic composition. Lithium chloride additions (Fig. 4) to the LiCl-LiBr-KBr eutectic enhanced ionic conductivity by 25 to 37% with liquidus $\leq$400°C. Current U.P. FeS_2 cells have 34 mol% LiCl-32.5 mol% LiBr-33.5 mol% KBr electrolyte, which has a liquidus transition at 360°C. Addition of lithium fluoride to LiCl-LiBr-KBr has also been examined, but lesser increases in ionic conductivity are obtained. Based on the LiF-LiBr-KBr phase diagram,[9] the eutectic composition contains only a few mole percent LiF. Further increases in electrolyte conductivity with LiF addition seems rather limited.

Currently, the U.P. FeS_2 cell effort is focused on development of separators to facilitate overcharge tolerance and reduce materials cost. Application of the LiCl-rich, LiCl-LiBr-KBr composition to electrolyte-starved U.P. FeS_2 cells with MgO powder separator (~75 vol % electrolyte) results in performance levels comparable to those of flooded cells with BN felt separator (~95 vol % electrolyte). The higher Li^+ ion content and higher conductivity for this electrolyte approximately compensate for the reduced electrolyte content. As shown in Fig. 5, 95% utilization of theoretical U.P. FeS_2 electrode capacity is attained at up to 100 mA/cm^2 with 425°C operation. A drawback to the LiCl-rich electrolyte is that the U.P. FeS_2 electrode capacity utilization is more sensitive to operating temperature and current density. The electrode impedance of 0.8-1.0 $\Omega\text{-cm}^2$ is comparable to that for the flooded cell operation.

As seen in Fig. 6, the curve for the positive area-specific impedance (ASI) as a function of DOD is virtually flat out to 80% DOD. The impedance values at 45 ms relaxation indicate that approximately 50% of the electrode impedance is electronic rather than ionic. Such low cell impedance is highly desirable for power-demanding applications such as the electric vehicle. Cell engineering development and cycle-life testing of the electrolyte-starved U.P. FeS_2 cells are progressing in conjunction with development of overcharge tolerant cells (described below).

DEVELOPMENT OF OVERCHARGE TOLERANT CELLS

The recent development of overcharge-tolerant Li-alloy/FeS and Li-alloy/ FeS_2[10] cells was accomplished by an innovative application of a nondestructive self-discharge mechanism, based on a "lithium-shuttle mechanism." In general, the lithium-shuttle mechanism involves diffusion of lithium metal species across the separator to discharge the positive electrode. The chief controlling element of the mechanism is the Li activity of the Li-alloy electrode; cell operating temperature and electrolyte composition are contributing factors. With this design, self-discharge rates of ≥ 2 mA/cm^2 develop at Li-alloy electrode potentials of -150 to -200 mV vs. an $\alpha + \beta$ LiAl reference electrode at 0 mV. A Li-Al_5Fe_2 alloy with a potential of -260 mV vs. the LiAl reference electrode has been applied to engineering development of overcharge-tolerant cells.

The design of an overcharge-tolerant cell is based on use of a lithium-alloy electrode with two distinct states of lithium activity, which establish appreciably different rates of self-discharge for the cell. The higher rate is associated with the cell's overcharge capacity. This design approach is tied to the Li-alloy electrode and, therefore, is relevant for cells with either FeS or FeS_2 electrodes. The capacities and compositions of the Li-alloy and metal sulfide electrodes are matched such that the Li-alloy electrode attains high lithium activity before there is any excessive polarization (i.e., beyond theoretical capacity) of the metal sulfide electrode. In addition, during normal operation at "rated capacity," the cell's self-discharge rate must remain rather low to attain an energy efficiency $\geq 85\%$ and coulombic efficiency $\geq 98\%$. In the overcharge state, the cell's self-discharge rate must be compatible with equalization rates of 2-3 mA/cm^2 trickle charge. It is also desirable to have design flexibility for adjusting portions of the overcharge capacity, as well as the potential attained by the Li-alloy electrode in the overcharge state.

Tests of overcharge-tolerant FeS_2 cells (25 Ah capacity) with reference electrodes (Ni/Ni_3S_2) have verified that the lithium-shuttle mechanism provides sufficient levels of overcharge tolerance and overcharge protection. Cells have operated over 200 cycles with high performance and stable overcharge tolerance. In Fig. 7, the electrode potentials vs. percent of capacity utilization for a U.P. FeS_2 cell (LiAl + 10 mol % $Li_5Al_5Fe_2$/LiCl-LiBr-KBr (MgO)/U.P. FeS_2) are given for a charge-discharge cycle. A bulk charge at 25 mA/cm^2 to 2.03 V is followed by a trickle charge of 3.0 mA/cm^2. As seen, the Li-alloy electrode undergoes about a 200 mV transition near full-charge capacity. As is crucial for the preservation of cell longevity, the U.P. FeS_2 electrode indicates negligible change in potential; that is, it is protected from the deleterious polarization of overcharge. Also, the Li-alloy electrode potential is little changed from -200 mV vs. LiAl during the trickle-charge period. The self-discharge rate undergoes a stepwise increase (a 20-fold increase by the lithium-shuttle mechanism) to become equal and opposite in effect to the trickle-charge rate. In this test, the trickle-charge period (8 h) charged 15% more coulombs than the "rated" capacity, but the extended trickle charge did not contribute to additional capacity in the subsequent discharge. The coulometric and galvanic analysis of the overcharge-tolerant cell design indicated approximately 0% charge acceptance for a trickle charge at 3.0 mA/cm^2 for the U.P. FeS_2 cell at 425°C.

Tests of overcharge-tolerant FeS cells (12-24 Ah capacity) with the two-phase Li-alloy electrode (LiAl + $Li_5Al_5Fe_2$) have demonstrated even higher rates of overcharge tolerance, 3-5 mA/cm^2. Comparable overcharge tolerance has also been measured for an LiAlSi/FeS couple[11] in a 1.0-Ah pellet cell. The FeS cells were operated at higher temperature, 475-500°C, and with an all-lithium cation electrolyte. The higher temperature can be expected to increase the rate of the lithium-shuttle mechanism due to higher lithium solubility in the molten salt. As with the FeS_2 cell tests, electrode potentials during an overcharge tolerance test (LiAl + 10% $Li_5Al_5Fe_2$/LiF-LiCl-LiBr (MgO)/FeS) exhibited the desired bimodal self-discharge rate and protected the FeS electrode from excessive polarization. These overcharge-tolerant FeS cells have been operated for over 200 cycles and demonstrated the stability of the MgO powder separator to the high Li activity occurring during the overcharge state. As a result of a 150-200 mV step in Li-electrode potential into an overcharge capacity state, a 5 mA/cm^2 trickle charge was continued for an extended period (4-8 h) without destructive polarization of the FeS electrode. An additional charge of 10-20% of cell capacity (beyond the overcharge capacity) was tolerated. When the cell was charged to a 1.47 V cutoff, it exhibited 99+% coulombic efficiency and a self-discharge rate of 0.2-0.4 mA/cm^2. When the cell was charged to a 1.57 V cutoff (into the overcharge capacity), its coulombic efficiency for the full cycle was noticeably reduced, to about 93%. As is the overcharge capacity and overcharge tolerance of these advanced FeS cells would allow a battery to be charged/equalized without electronic monitoring.

SUMMARY

Because of the outstanding conductivities for Li-ion-containing molten salt, 1-5 S/cm^2, coupled with the high energy densities of Li-alloy and FeS_x electrodes, ~1.0-2.0 Wh/cm^3, rechargeable lithium cells have attained high specific energy and specific power. Two cell types, FeS and U.P. FeS_2, have been tested with low-cost MgO powder separator. The MgO-powder separator requires electrolyte-starved cell operation to avoid fluidization of the high-surface-area MgO (e.g., Maglite S). Westinghouse Oceanic Division is fabricating and testing Li-AlSi/LiF-LiCl-LiBr (MgO)/FeS cells at 475°C. Specific energy at C/3 is about 100 Wh/kg, and specific power is about 100 W/kg, and lifetime is 350 cycles. At Argonne National Laboratory, U.P. FeS_2 cells with LiCl-LiBr-KBr eutectic, and BN felt separator operated at 400°C have demonstrated long cycle life (1000 cycles) and high performance prospects (175 Wh/kg at C/3 and 200 W/kg at 80% DOD for a monopolar cell design). Recently, electrolyte-starved U.P. FeS_2 cells have also achieved high performance with a LiCl-rich composition of LiCl-LiBr-KBr (34:32.5:33.5 mol %) electrolyte and MgO powder separator. The 25% increase in ionic conductivity of the LiCl-rich electrolyte approximately compensated for the lower electrolyte content with starved-electrolyte operation. Low cell impedance that is virtually flat through 80% of discharge capacity provides outstanding cell power. High utilization of the U.P. FeS_2 electrode theoretical capacity (95%, even at 100-mA/cm^2 discharge current density) results in excellent specific energy.

Recent development of new materials for metal-to-ceramic seals that are molten-salt retentive have heightened prospects for a bipolar battery.[12] Significant reduction in non-active material weights is projected to increase specific energy and power to >200 Wh/kg and >500 W/kg, respectively, for a sealed bipolar Li-alloy/U.P. FeS_2 battery.

An overcharge-tolerant cell design has been developed for both Li-alloy/FeS and Li-alloy/U.P. FeS_2 cells. Based on a "lithium-shuttle" mechanism, the self-discharge rate of the cell rises abruptly to tolerate an extended period to trickle charge at 2-5 mA/cm^2. This mechanism safeguards the cell by eliminating excessive polarization of the positive electrode. This cell feature enables molten-salt lithium batteries to be safely operated without individual cell voltage monitoring. Battery durability is improved along with cost savings for this design.

Lithium-alloy/FeS battery development based on multiplate monopolar cells is expected to resume under DOE sponsorship. The emphasis of this program is to demonstrate new battery hardware, such as high-efficiency thermal enclosures, and to improve cycle life with the overcharge-tolerant cells. Development of the Li-alloy/U.P. FeS_2 cell will be focused on the bipolar battery configuration with the novel hermetic seals. This bipolar battery design reduces cost and fabrication concerns for the disulfide-electrode current collector. The sealed bipolar U.P. FeS_2 battery has prospects of combining excellent performance and cycle life with low cost.

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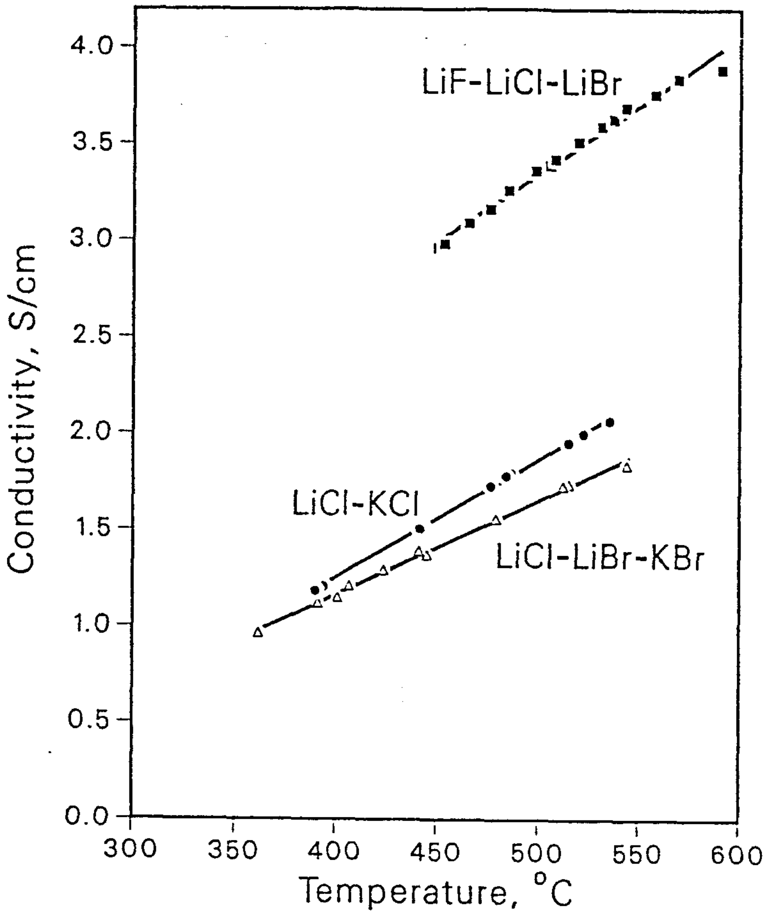

Fig. 1. Conductivities of Molten Salts for Rechargeable Lithium Batteries. The data for LiCl-KCl at 450°C are from Van Artsdalen and Jaffe, J. Phys. Chem. 59, 119 (1955).

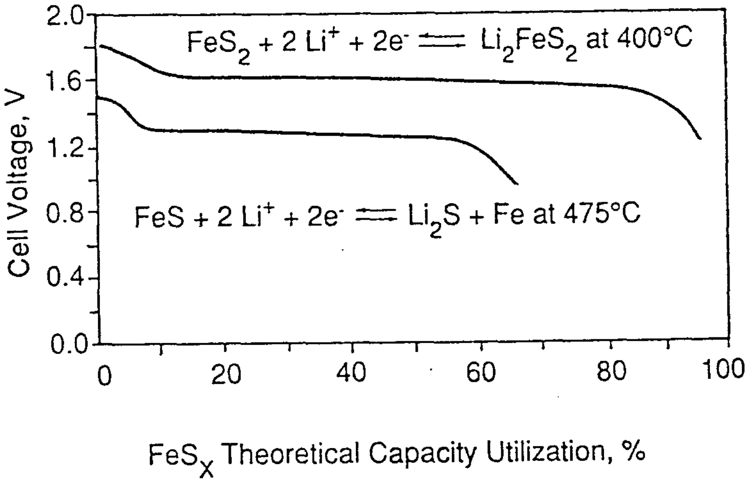

Fig. 2. Voltage/Capacity Utilization of FeS and U.P. FeS_2 Electrodes.

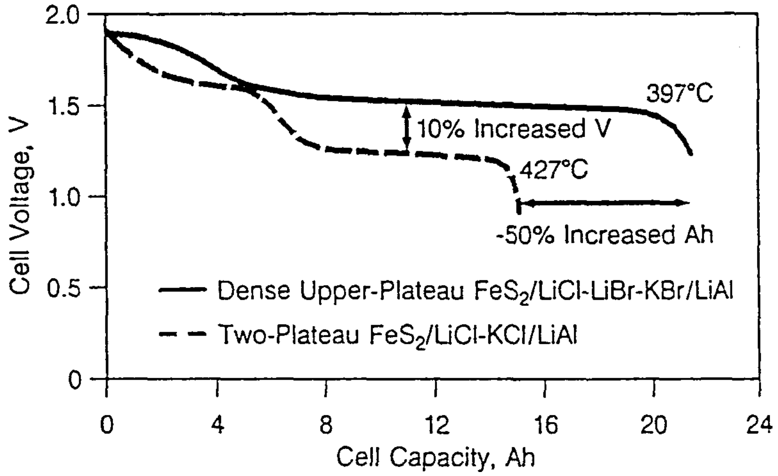

Fig. 3. Voltage/Capacity Utilization of the Upper-Plateau FeS_2 Cell Compared with the Two-Plateau FeS_2 Cell.

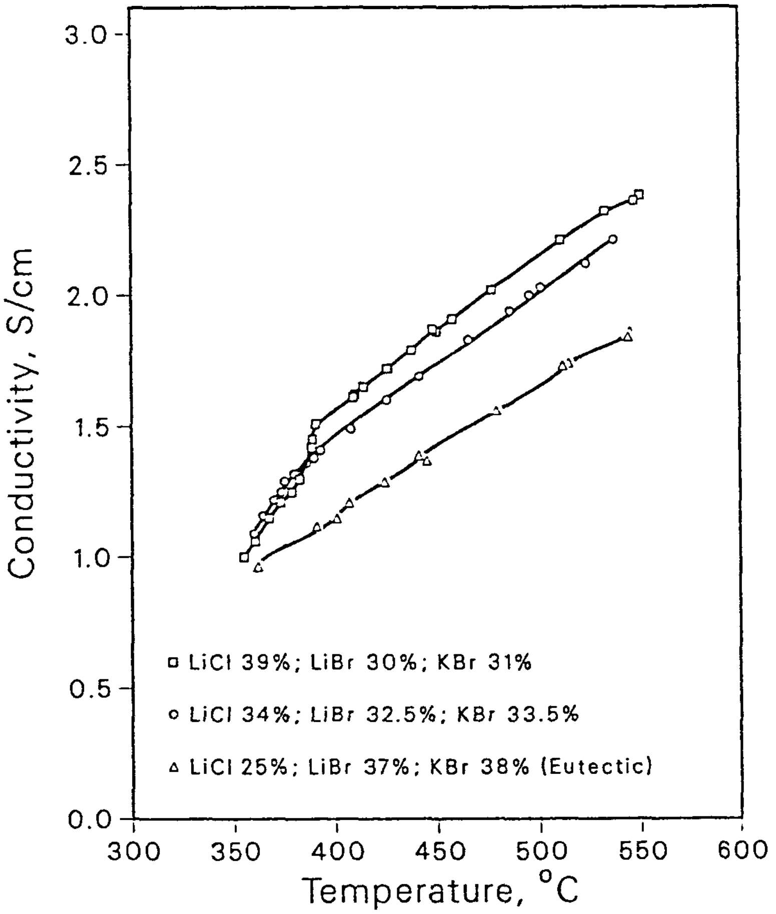

Fig. 4. Conductivities for three Compositions of the LiCl-LiBr-KBr Electrolyte.

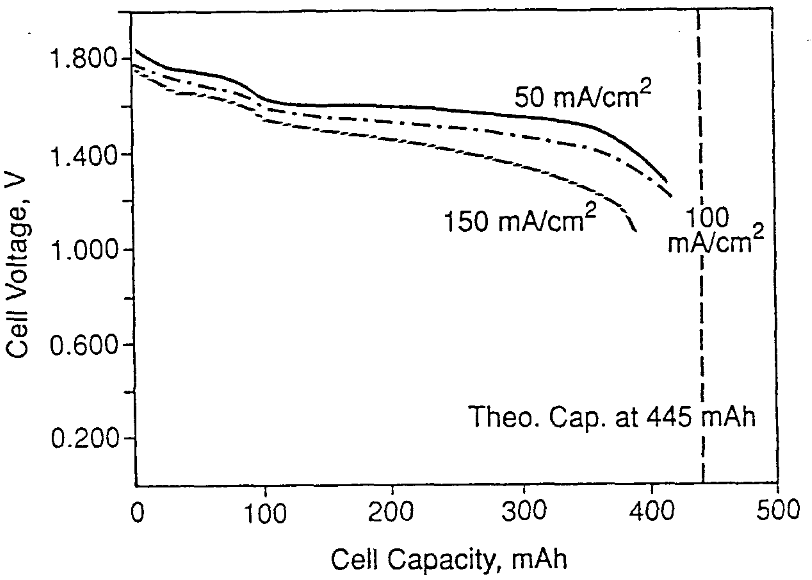

Fig. 5. Utilization of Electrolyte-Starved (LiCl-LiBr-KBr, 34:32.6:33.5 mol%) U.P. FeS_2 Electrode Capacity at 425°C.

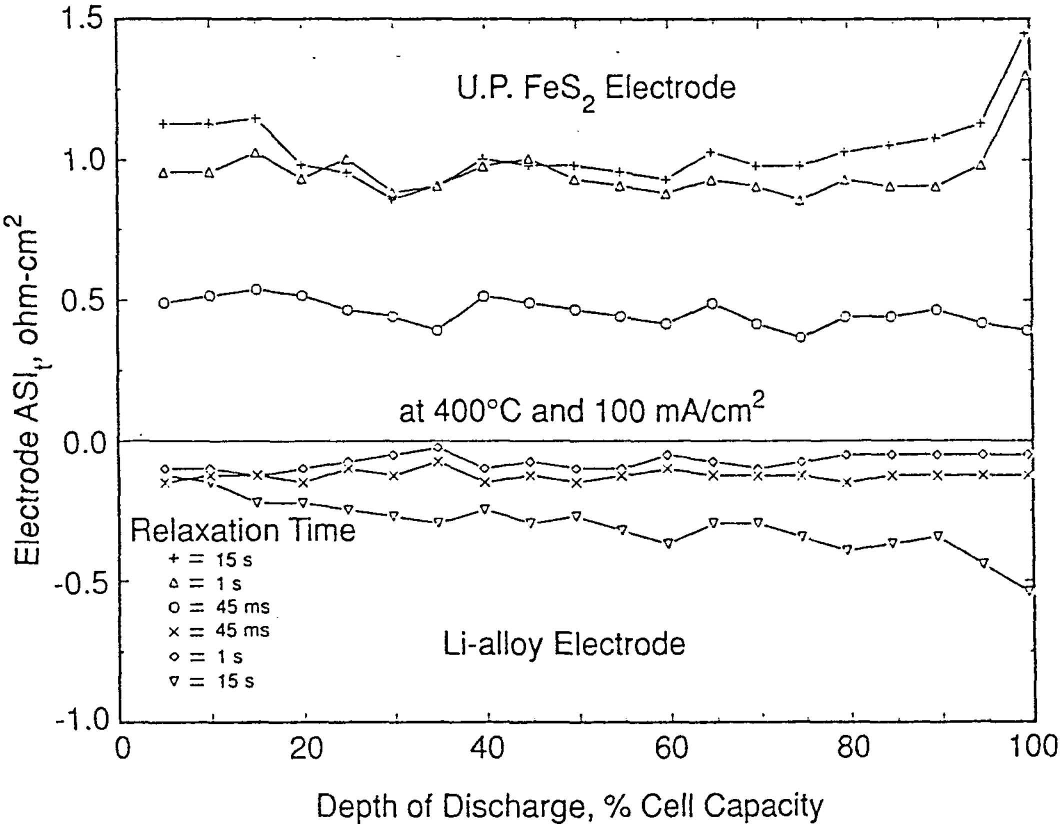

Fig. 6. Half-Cell Impedance Measurements of Electrolyte-Starved U.P. FeS_2 Cell.

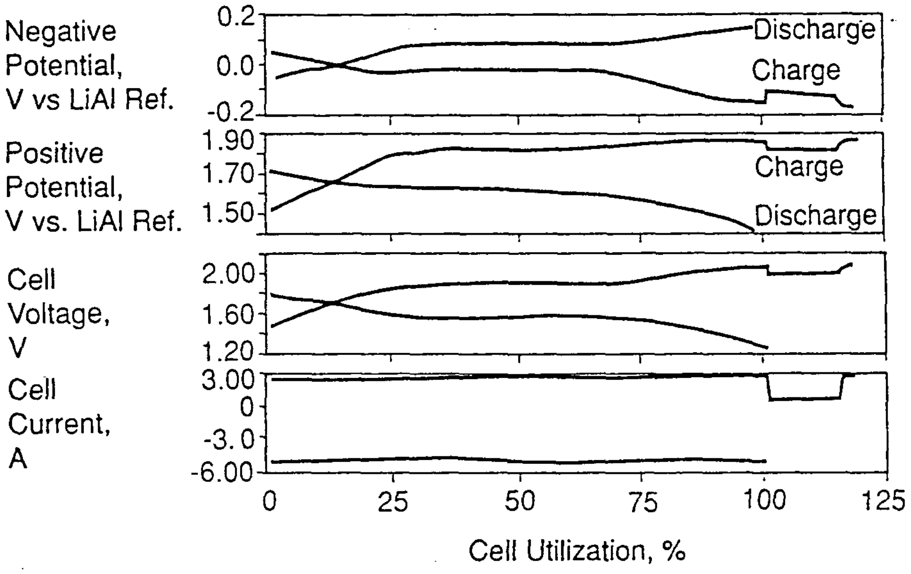

Fig. 7. Overcharge Tolerance of U.P. FeS_2 Cell. Electrolyte-starved cell safely overcharged 15% at 3 mA/cm^2. No polarization of U.P. FeS_2 (positive) electrode indicates overcharge safeguard.