MODIFICATION OF LiCl-LiBr-KBr ELECTROLYTE FOR LiAl/FeS$_2$ BATTERIES

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MODIFICATION OF LiCl-LiBr-KBr ELECTROLYTE FOR LiAl/FeS\textsubscript{2} BATTERIES

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ABSTRACT

The bipolar LiAl/FeS\textsubscript{2} battery is being developed to achieve the high performance and long cycle life needed for electric vehicle application. The molten-salt (400 to 440°C operation) electrolyte composition for this battery has evolved to support these objectives. An earlier change to LiCl-LiBr-KBr electrolyte is responsible for significantly increased cycle life (up to 1000 cycles). Recent electrolyte modification has significantly improved cell performance; approximately 50% increased power, with increased high rate capacity utilization. Results are based on power-demanding EV driving profile test at 600 W/kg. The effects of adding small amounts (1-5 mol%) of LiF and LiI to LiCl-LiBr-KBr electrolyte are discussed. By cyclic voltammetry, the modified electrolytes exhibit improved FeS\textsubscript{2} electrochemistry. Electrolyte conductivity is little changed, but high current density (200 mA/cm\textsuperscript{2}) performance improved by approximately 50%. A specific feature of the LiI addition is an enhanced cell overcharge tolerance rate from 2.5 to 5 mA/cm\textsuperscript{2}. The rate of overcharge tolerance is related to electrolyte properties and negative electrode lithium activity. As a result, the charge balancing of a bipolar battery configuration with molten-salt electrolyte is improved to accept greater cell-to-cell deviations.

INTRODUCTION

The LiAl/FeS\textsubscript{2} bipolar battery is being developed to achieve the high performance and long cycle life needed for electric vehicle batteries. The electrolyte used in this molten-salt battery has a major impact on cell performance and cycle life. The initial development of the LiAl/FeS\textsubscript{2} cell, with LiCl-LiBr-KBr electrolyte (25-37-38 mol%), enhanced cycle life dramatically (from 100 to about 1000 cycles) without severely compromising performance. The lower temperature cell operation (400-425°C) increased cycle life [1]. The phase diagram of the LiCl-LiBr-KBr (Fig. 1) has a broad liquidus range of composition related to ion content. Its liquidus range of 1.25 to 2.6 Li\textsuperscript{+}/K\textsuperscript{+} ratio at 400°C is of particular interest to the dynamic conditions of electrode operation at high current density. Melting point and
cooling curve determinations at APL [6] indicated a melting point of 312 ± 1°C, but once liquid, this molten salt exhibits a lower freezing point of 296 ± 4°C. For LiCl-KCl, the liquidus range at 400°C is only 1.2 to 1.81 Li+/K+ ratio. The melting point of the LiCl-KCl electrode is 354°C. Thus, the local lithium content of the LiCl-LiBr-KBr electrolyte can deviate from that in the bulk electrolyte without experiencing localized salt freezing.

A number of electrolyte characteristics must be juggled to achieve an overall improvement in cell performance: lithium conductivity, liquidus range, and cell operating temperature. In the past, the LiCl content of the LiCl-LiKBr-KBr electrolyte has been increased with concomitant increase in cell performance. Electrolyte-starved cells with 34 mol% LiCl salt gave cell impedances comparable to flooded cells. The off-eutectic composition, with its increased lithium conductivity, compensated for the reduced electrolyte volume in the electrolyte-starved, MgO powder separator used in the FeS₂ cell. Historically, increased lithium content produces increased cell performance, but usually at the expense of cycle life, as with LiF-LiCl-LiBr at 465°C. Analyses with cyclic voltammetry has showed improved kinetics in FeS₂ electrodes using the electrolytes with higher lithium-ion content. The charge/discharge reversibility also improves with higher lithium-ion content, as had been observed earlier with LiCl-LiBr-KBr at a given temperature when compared to the 58 mol% LiCl-KCl electrolyte [2]. FeS₂ cells have 34 mol% LiCl-32.5 mol% LiBr-33.5 mol% KBr electrolyte, which has a liquidus transition at 360°C. Adding LiF to LiCl-LiBr-KBr has also been examined, but smaller increases in ionic conductivity were obtained. Based on the LiF-LiBr-KBr phase diagram [3], the eutectic composition contains only a few mole percent LiF.

We set general guidelines for modifying the LiCl-LiBr-KBr (34-33-33 mol%) electrolyte with other lithium halides: (1) The lithium-ion content should be raised without raising the electrolyte liquidus temperature. (2) The liquidus range of the lithium-ion content at 425°C should not be diminished. (3) The relatively lower ionic conductivity of some lithium halides (e.g., LiI compared to LiF) should be minimized.

BACKGROUND

Three lithium-ion-containing molten salts have been employed in lithium/sulfide battery development: LiCl-KCl, LiCl-LiBr-KBr, and LiF-LiCl-LiBr [4]. We have determined conductivities as a function of temperature for their eutectic compositions using the AC impedance technique. The results are plotted in Fig. 2. Each of these molten salts has unique properties that affect cell development. The LiCl-KCl eutectic has a 354°C melting point, while cells are operated at 450°C where the conductivity is 1.4 S cm⁻¹ [5]. Although the LiCl-KCl electrolyte was the baseline electrolyte for primary thermal batteries and secondary batteries, it is being replaced by the three-component salts. The LiF-LiCl-LiBr (all lithium electrolyte) has the highest conductivity, about 3.0 S cm⁻¹ at 450°C [6]. On the other hand, the LiCl-LiBr-KBr electrolyte, with its low melting point of 320°C and broad liquidus region, allowing large Li/K ion ratio deviations from that of the eutectic, provides
a stable operating environment at 400°C for the FeS₂ electrode [2,7]. It has a conductivity of 1.3 S cm⁻¹ at 450°C. The Li⁺ and K⁺ ion activities of these molten salts regulate solubilities of charge/electrode discharge products and electrode kinetics. As will be discussed later, self-discharge rates, cell performance, and cycle-life stability strongly depend upon the electrolyte properties.

Use of LiCl-LiBr-KBr electrolyte allows Li/FeS₂ cell operation at considerably lower temperatures (400-425°C) than do the other electrolytes (LiCl-KCl or LiF-LiCl-LiBr). In general, Li/FeS₂ cells with LiF-LiCl-LiBr are operated at 475°C, where corrosion reactions are more likely to limit cycle life. Also, thermal management of the Li/FeS₂ battery operated at 475°C requires an active heating and cooling system, whereas at 425°C greater temperature fluctuations can be tolerated to ease requirements of the thermal management system.

A variation of this electrolyte, an LiCl-rich composition, was identified as the electrolyte of choice for use in "electrolyte-starved" cells (i.e., cells that contain only a limited quantity of electrolyte in the pores of the MgO powder separator). The LiCl-rich composition of LiCl-LiBr-KBr (34-33-33.5 mol %) possesses a 25% higher ionic conductivity (1.7 S cm⁻¹) than the LiCl-LiBr-KBr eutectic at 425°C (Fig. 2). This higher conductivity allows these electrolyte-starved cells to operate with a cell impedance, AS₁, comparable to that of flooded cells that employ the eutectic electrolyte [11].

The addition of LiI (5 mol%) to LiCl-LiBr-KBr was found to lower the eutectic electrolyte melting point 10°C. The increased lithium content of the modified electrolyte due to the LiI addition does not anticipate higher conductivity because the Li⁺ conductivity of LiI is lower than that of the other lithium halides. Therefore, the two effects counterbalance. Any addition of LiI should also be minimized due to its high density and high affinity for water. A small addition is sufficient to improve cell kinetics. As discussed earlier, the liquidus range of the electrolyte has proven to be an important property to support high performance. The effect of LiI addition to the LiCl-LiBr-KBr electrolyte is suggestive of an extended range of liquidus composition of the cell operating temperature.

**Electrochemistry of the FeS₂ Electrode**

The electrochemistry of FeS₂ in LiCl-LiBr-KBr was examined previously using cyclic voltammetry and compared to LiCl-KCl [2]. The LiCl-LiBr-KBr electrolyte exhibits improved reversibility. The cyclic voltamograms are generated at a low sweep rate of 0.02 mV/s on a 75-mg sample of FeS₂. Under these conditions, summed areas of either anodic or cathodic peaks exceed 80% of theoretical capacity. LiAl/FeS₂ are only operated in the upper voltage plateau of the FeS₂ electrode. As such, the potential sweep is approximately 1.6 to 1.9 volts vs. LiAl reference electrode.
The dominant features of these voltammograms, Fig. 3a, are consistent with those of FeS\textsubscript{2} in LiCl-KCl eutectic, which were reported by Preto et al. [8]. Roman numerals label the peaks, with "a" for anodic and "c" for cathodic. The corresponding sequence of phases at the various states of charge are assigned according to the work of Tomczuk et al. [9] as follows:

\[
\begin{align*}
\text{FeS}_2 & \quad \text{IV}_a \quad \text{Li}_3 \text{Fe}_2\text{S}_4 \quad \text{III}_a \quad \text{Li}_{2.2} \text{Fe}_{0.8} \text{S}_2 \quad \text{and} \\
\text{Fe}_{1+x} \text{S} & \quad \text{II}_a \quad \text{Li}_2 \text{FeS}_2 \quad \text{I}_a \quad \text{Fe and Li}_2 \text{S}
\end{align*}
\]

These are equilibrium phases and do not imply reaction mechanisms. Of particular interest for this study is the separation of the anodic and cathodic high-voltage peaks (IV\textsubscript{a} and IV\textsubscript{c}), which indicates the reversibility of this reaction. A notable difference between the cyclic voltammograms of FeS\textsubscript{2} in LiCl-LiBr-KBr and those of FeS\textsubscript{2} in LiCl-KCl is that this peak separation (difference in leading edge potentials, LEP) is less: 95 mV vs. 120 mV, respectively. (The lower plateau capacity of reaction peak I is not shown). Also, the leading edge of peak IV\textsubscript{a} does not exhibit the shoulder found for FeS\textsubscript{2} in LiCl-KCl [2]. These differences indicate improved reversibility from a molten salt with a higher Li\textsuperscript{+} ion activity.

The emf for the FeS\textsubscript{2} \rightarrow Li\textsubscript{3}Fe\textsubscript{2}S\textsubscript{4} phase transition has been reported by Tomczuk et al. [10], as

\[
\text{emf} = 1.542 + 0.0005231 \times T (^\circ \text{C})
\]

The differences between the equilibrium potentials of the reaction peaks with their leading-edge potentials (LEPs) for peaks IV\textsubscript{a} and IV\textsubscript{c} indicate the over potentials for these reactions. The cathodic over potentials are quite small (4-14 mV), while the anodic overpotential of peak IV\textsubscript{a} is about 85 mV at 400\(^\circ\)C. Most significantly, the overpotential of charging the high voltage reaction of FeS\textsubscript{2} (IV\textsubscript{a}) in LiCl-LiBr-KBr at 450\(^\circ\)C is 20 mV less than it is in LiCl-KCl eutectic.

The cyclic voltammograms indicate good stability of FeS\textsubscript{2} in LiCl-LiBr-KBr. At 425\(^\circ\)C, soluble polysulfides are not generated, as evidenced by the lack of activity in the voltage region 1.95 to 2.10 V vs. LiAl. Generation of soluble polysulfides would lead to electrode capacity loss. Unlike FeS\textsubscript{2}, CoS\textsubscript{2} and NiS\textsubscript{2} generate Li\textsubscript{2}S in charging their high voltage reaction, which can be further oxidized to soluble Li\textsubscript{2}S\textsubscript{2} [2].
Electrolyte modifications are also assessed by cyclic voltammetry, Fig. 3. Adding LiF is a unique approach to improving FeS₂ electrochemistry. For the most part, the LiF remains as a separate solid phase in molten LiCl-LiBr-KBr (as indicated by differential thermal analysis). The liquidus point and the liquidus range of lithium-ion content are largely unaffected. Only about 1 mol% LiF solubilizes, as shown by the LiF-LiBr-KBr phase diagram. [3] As shown in the cyclic voltammograms, Fig. 3b, a dispersion of LiF within the positive electrode can have a significant effect upon FeS₂ electrode reversibility. Reversibility of the positive electrode is assessed by examining the difference in leading-edge potentials (ALEP) of the oxidation and reduction reaction peaks (FeS₂=Li₃Fe₂S₄). As indicated by the cyclic voltammograms in Fig. 3, the ALEP of the FeS₂ electrode with the LiF-containing salt is 40 mV, compared to 85 mV for the standard electrolyte LiCl-LiBr-KBr. A local increase in Li⁺ concentration would explain the improved FeS₂ electrode reversibility. The improved reversibility in 2.5-cm-dia cells using the dispersed LiF was indicated by a 20% reduced cell impedance.

The Li-alloy Electrode and Overcharge Tolerance

A "lithium shuttle" mechanism (LSM) was developed to provide lithium/sulfide cells with an overcharge tolerance capability [11-13] by forming a second lithium alloy phase in the negative electrode, as the cell reaches the overcharged state. This second phase possesses a higher lithium activity than the standard α + β Li-Al alloy, thereby significantly increasing the concentration of lithium metal dissolved in the electrolyte. Dissolved lithium is free to diffuse across the electrolyte/separator and react chemically at the positive electrode in a self-charge reaction. The higher dissolved lithium concentration produces a higher self-discharge rate and allows electrochemical charging of the cell to proceed at a rate equivalent to the self-discharge rate without causing any net change in the state-of-charge of the cell. The ultimate LSM rate is controlled by the lithium activity of the overcharge alloy, the electrolyte composition, the operating temperature, and the structure and thickness of the separator. Figure 4 illustrates the effects of electrolyte composition and temperature on the LSM rate for a given alloy and separator design. The rates are fit to Arrhenius expressions for the three electrolyte compositions shown. These rate expressions agree well with available physical data for lithium solubility, including dimerization of lithium for the respective molten-salt compositions. That is, Li⁺ would form in all lithium (LiF-LiCl-LiBr) electrolyte, whereas LiK⁺ would form in the K⁺-containing molten salts (LiCl-KCl and LiCl-LiBr-KBr). In general, the electrolyte composition establishes a level of lithium solubility to enable the LSM to operate [11].

Modifying the LiCl-LiBr-KBr has directly influenced the LSM rate at a given temperature. Typically, an end-of-charge trickle-charge rate of 2.5 mA/cm² was available to charge/equalize the bipolar Li/FeS₂ battery. This rate was sufficient for extremely well-matched cells having only low-level defects and similar separator characteristics, but it meant that cells with greater than 1 to 2 mA/cm² self-discharge rate would eventually be lost from the battery. The addition of LiF diminished the LMS rate to 1.5 mA/cm², while adding
LiI increased the LSM rate to 5 mA/cm² at 425°C. The extent of lithium solubility in the modified molten-salt explains the changed LSM rates. The lithium content is little changed by the modifications. The LiI addition provides a much-sought-after 50% enhancement of the LSM rate. With the increased LSM rate of 5 mA/cm², a battery developer can accept a greater cell-to-cell deviation and still maintain bipolar battery charge/equalization capability.

A combination of LiF and LiI electrolyte additives is of interest because it increased cell capacity utilization by 23% for 13% increased specific energy. Subsequent tests established that the enhanced overcharge tolerance of LiI addition is retained and overcomes the reduced LSM rate that occurred from the singular LiF addition. The LSM rate for overcharge tolerance with both additives, LiF and LiI, was also determined to be 5 mA/cm² at 440°C. Two consecutive cycles are compared: one charge to a voltage cutoff, a subsequent cycle of charge, followed by a 1.0 A trickle charge. A 2.5 Ah overcharge capacity (without increased discharge capacity) over a 4-h period translates into a 5 mA/cm² trickle charge tolerance rate. An underlying self-discharge rate of 0.3 mA/cm² is taken into account. Another examination of LSM rate submits the cell to 4-h periods of trickle charge at 0.4 to 0.8 A, Fig. 5. Again, 0.6 A (or 5 mA/cm²) produces a steady cell voltage during the extended trickle-charge period as it equals the LSM rate for the cell. This rate closely approximates the LSM rates for LiCl-LiBr-KBr with only LiI added.

**Cell Performance with Modified Electrolyte**

Tests with full-sized bipolar cells were conducted to evaluate performance improvement related to electrolyte modifications. The electrolyte additives indicated a progressive improvement in achieved specific energy. Three cells were operated with the same FeS₂-15 mol% CoS₂ positive electrode of 40 Ah theoretical capacity but different electrolyte (Fig. 6). A 5 mol% LiI addition increased FeS₂ capacity utilization by 13.7% to 78.6% of theoretical capacity. The further addition of a LiF dispersion (4 wt%) further increased FeS₂ capacity utilization by 22.7% to 85% of theoretical capacity. The cell capacity was increased from approximately 28 Ah to approximately 34 Ah at 75 mA/cm² discharge current density. With two additives, cell specific energy at the C/3 rate was increased by 13%, to 189 Wh/kg.

The ultimate evaluation of the electrolyte modification is the cell power capability. Simulated electric-vehicle driving profiles of repetitive power pulsing (DST) as seen in Fig. 7 are generally used for performance assessment. By testing a cell under a series of driving profiles having increased power demand (70 to 150 W/cell), a Ragone-type plot can be generated. This new method of testing provides specific energy/specific power tradeoffs to aid battery design. As shown in Fig. 8, the electrolyte modification provided nearly 50% increased power performance at test profiles that achieved similar net specific energy. For example, at 140 Wh/kg, the modified-electrolyte cell supported 600 W/kg power pulses (8-s duration), in comparison to only 400 W/kg for the standard-electrolyte cell.
A further objective of the electrolyte modification studies is to improve battery-level performance. Specifically, for bipolar battery operation, a LSM has been developed to enable equalization of cell capacities in a bipolar stack without hard-wired equalization equipment. The chemistry of each cell is capable of tolerating a trickle charge (5 mA/cm²). A strong cell can tolerate the trickle charge without destructive overcharging, while a weaker cell would gain in discharge capacity. [11] A 4-cell stack Li/FeS₂ is shown to equalize in state of charge by undergoing a period of trickle charge after a normal charge to a battery voltage cutoff, Fig.9. During two trickle-charge periods shown (125 to 127 h and 135.5 to 137.5 h) the voltage of the weaker cell (02) increases in voltage and subsequent discharge capacity, while the remaining three cells safely tolerate a 0.6A trickle-charge period of 2 h. The weak cell (02) picks up charge as the trickle charge exceeds its self-discharge rate, while the other cells, closer to full-charge state, have an LSM rate of 5 mA/cm² to equal the trickle-charge rate. The electrolyte modification has improved the rate of cell capacity equalization at the battery level through an increased rate of the trickle-charge tolerance. Greater cell-to-cell deviations are tolerated, such that battery cycle life and performance is improved.

SUMMARY

Small additions of LiF and LiI to LiCl-LiBr-KBr electrolyte has produced some significant improvements in bipolar Li/FeS₂ battery performance and bipolar battery operation. Physical property changes, such as lithium content, lithium-ion conductivity, and liquidus range, promote FeS₂ electrode reversibility. The influence of the LiF additive was examined by cyclic voltametry; if increased reversibility and reduced electrode polarization. A phase diagram for LiF-LiBr-KBr provides insight into the effect of LiF addition, but no comparable diagram is available to gain understanding of the LiI addition. The significant influence of LiI on Li/FeS₂ cell chemistry implies a broadening of the liquidus range for lithium-ion content at 440°C. Likewise, lithium solubility is apparently increased by adding LiI to LiCl-LiBr-KBr to bring about an increase of overcharge tolerance rate at 5 mA/cm². LiF has limited solubility and remains in the FeS₂ electrode as a dispersion of a solid (4 wt% of the positive electrode), whereas the 5 mol% LiI added permeates the cell. These electrolyte modifications increased the FeS₂ electrode capacity utilization by 28%, under a 3 h-rate discharge, 75 mA/cm², rate. Of even greater significance, high power pulse capability is improved by 50% under the power-demanding EV driving profile testing (DST). With the modified electrolyte, specific energy under DST increased by 50%. Specifically, a 155 Wh/kg specific energy is achieved under DST having a repeating demand of over 500 W/kg pulse power (8-s duration). The same cell chemistry can operate at continuous high power of 170 W/kg and deliver 165 Wh/kg specific energy. Finally, the battery operation is improved with the modified electrolyte. Greater cell-to-cell deviation is accepted by an enhanced overcharge tolerance, 5 mA/cm². Bipolar Li/FeS₂ battery can be charge/equalized with a faster rate of battery-level trickle charging.
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REFERENCES

Fig. 1. Phase Diagram of LiCl-BiCl-LiBr-KBr Molten-Salt.

LiCl-LiBr-KBr, 310°C m.p., has a broad liquidus range.

Fig. 2. Conductivities of Molten Salts for Rechargeable Lithium Batteries. The data for the three eutectic compositions are compared to a LiCl rich composition of LiCl-LiBr-KBr.
(a) LiCl-LiBr-KBr

\[ \Delta \text{LEP} = 85 \text{ mV} \]

(b) LiCl-LiBr-KBr with LiF solid dispersion

\[ \Delta \text{LEP} = 40 \text{ mV} \]

Fig. 3. Cyclic voltammograms of FeS$_2$ electrode in LiCl-LiBr-KBr exhibiting improved kinetics with a LiF dispersion.
Fig. 4. Effect of Temperature Upon Lithium Shuttle Rates at about -250 mV vs. Li-Al Reference Electrode in Three Molten-Salt Electrolytes.

Fig. 5. Rate of overcharge tolerance determined at 5.0 mA/cm² under varied trickle-charge rates.
Fig. 6. Improved cell capacity as a result of LiCl-LiBr-KBr electrolyte modification.

Fig. 7. Driving profile voltage and current for improved Li/FeS₂ cell, 0.275 kg.
Fig. 8. The Lil modified electrolyte increases power capability for simulated driving profile tests (DST Ragone).

Fig. 9. Voltage of 4 cells in a bipolar Li/FeS₂ stack exhibiting charge/equalization during trickle charge.
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