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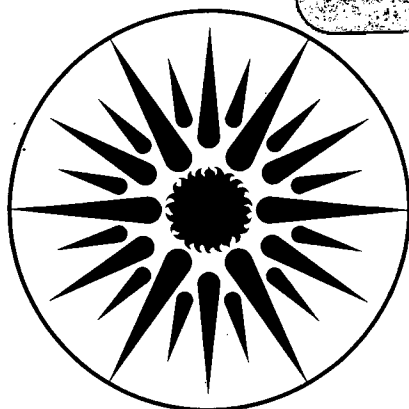
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April 1986

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by

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STABILITY OF A VITREOUS ELECTROLYTE FOR POSSIBLE USE IN HIGH-TEMPERATURE LITHIUM/SULFUR CELLS

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ABSTRACT

A family of lithium-borate glasses has been identified by H. Tuller and co-workers at the Massachusetts Institute of Technology¹ as candidate electrolytes for use in high-temperature Li/S cells. Based upon screening tests, a glass composition (mol%) of 26% Li_2O -7% Li_2Cl_2 -67% B_2O_3 was selected to exhibit an acceptable ionic conductivity of $3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 400°C , $T_g = 475^\circ\text{C}$, resistance to attack by S at 400°C , and minimal attack by Li at 350°C . A procedure was developed to form and seal glass tubes, and LiSn/glass/S cells were operated at various temperatures. It was possible to charge and discharge cells at current densities up to 70 mA/cm^2 (for 1-3 min) or 20 mA/cm^2 (for several hours) into the two-phase $\text{S-Li}_2\text{S}_x$ region, but the electrolyte tended to fail when the cell was recharged from near the two-phase/single-phase boundary at $\sim 73 \text{ mol}\%$ S. The charge-discharge curves also exhibited hysteresis effects, and a crystalline reaction layer was observed on the S side of the electrolyte tubes. X-ray diffraction analyses suggested that the reaction layer contained crystalline lithium-borate compounds, and static immersion tests showed that the glass was slowly attacked by polysulfides at the 400°C cell operating temperature.

INTRODUCTION

The search for a reliable and efficient electrochemical energy storage system which could be used as an electric utility load-leveling device or as a power source for an electric vehicle has led to the investigation of several high-specific-energy systems which operate at temperatures where the electrolyte and/or the electrodes are liquids. One of these is the Li/S system on which research began as early as 1960 at Argonne National Laboratory.² The theoretical specific energy of the Li/S cell is 2700 Wh/Kg , and its potential at 400°C is 2.18 volts. These values are sufficiently high to make the Li/S system an attractive candidate for meeting goals of high specific energy (200 Wh/Kg) and specific power (200 W/Kg) in practical cell hardware.

The earliest work on the Li/S system followed the approach of having molten electrodes in contact with molten-salt electrolytes. These efforts encountered difficult problems: (1) molten Li from the negative electrode was not retained by the current collector, and (2) the lithium polysulfides from the positive electrode were soluble in the electrolyte. The most typical solution to this problem has been to alloy the Li and to react the S with some non-participating materials; these approaches reduce the mobility and solubility of the electrode materials, but they also degrade the values of specific energy and power that can be realized. However, another solution

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to these problems is to use a solid electrolyte in conjunction with molten electrodes. The solid electrolyte would act as a rigid barrier to contain both the metallic Li and the lithium polysulfides in their respective compartments. This solution has not been pursued extensively because of the lack of a suitably stable and conductive electrolyte. Recently there have been discoveries of fast-Li-ion conducting materials which show promising characteristics. The electrolyte used in this work is one of a family of vitreous lithium-borate materials, which exhibit Li-ion conductivity as high as $10^{-2}(\text{ohm-cm})^{-1}$ at 300°C , with an activation energy of 0.46 eV .¹

Among these fast-Li-ion conducting materials is the family of lithium-chloroborate glasses. The work reported here concentrated on one particular composition of lithium-chloroborate glass, which showed high ionic conductivity and was somewhat stable to Li attack.³

EXPERIMENTAL

The chemicals used to prepare the glass electrolyte were: 99.9% pure LiCl (Mallinckrodt), 99.9% pure Li_2O (Cerac), and 99% pure anhydrous B_2O_3 (Spectrum Chemicals Mfg. Corp.). The procedure to prepare the glass was as follows: first, ~ 40 grams of B_2O_3 was poured into a 100-ml Pt crucible and heated above 500°C for several minutes to ensure that only anhydrous B_2O_3 remained. An accurate weight of B_2O_3 was then determined by subtracting the weight of the empty crucible. Next, the appropriate amounts of anhydrous Li_2O and LiCl were added to the crucible, which was then placed in a 950°C furnace for 15-20 minutes. The crucible was removed from the furnace, and the molten glass was stirred with a Pt rod. The glass was then reheated for another 15-20 minute period, stirred, and then returned to the furnace for a final 20-30 minute heating period. After this sequence, the glass was either poured into a mold and made into discs or was blown into tubes. The glass was analyzed for Li, B and Cl content by atomic absorption spectroscopy. It was found to be lower in LiCl than expected, probably as a result of vapor being released from the melt at $800\text{--}1000^{\circ}\text{C}$. The glass composition determined by atomic absorption was 7.3 mol% Li_2Cl_2 , 25.7 mol% Li_2O and 67.0 mol% B_2O_3 .

The mold for making the discs consisted of two $0.64\text{ cm} \times 10\text{ cm} \times 10\text{ cm}$ pieces of stainless steel stacked on top of one another. The bottom plate served as the base while the top plate, which had four 2.5-cm diameter holes drilled through it, served as the mold. After being allowed to cool, the discs were placed in a helium-atmosphere glove box. Care was taken never to handle the discs directly nor leave them in a moist environment longer than necessary. The formation of thin-walled tubes required that a glass-blowing technique be developed, which was complicated by the tendency of the glass to crystallize when reheated. The procedure for making these tubes was to place the Pt crucible full of molten glass ($\sim 1000^{\circ}\text{C}$) in a pre-heated (700°C) stainless-steel block, where it was allowed to cool until the viscosity of the glass was that of a heavy syrup. At this point, a flame-heated pyrex tube (10-mm OD) was dipped into the molten glass and gently stirred to ensure wetting of the pyrex by the molten glass. Once wetted, the tube was pulled up while blowing a steady pressure of air into the other end of the pyrex tube. This method resulted in thin-walled constant-diameter tubes which could be drawn to lengths of $10\text{--}60\text{ cm}$. After cooling, the tubes were cut into lengths of $\sim 10\text{ cm}$, and one end was sealed over the flame of a bunsen burner. The final wall thickness of these tubes varied from 0.02 cm to 0.05 cm . Before being used as an electrolyte in an electrochemical cell, tubes were screened for structural weaknesses and flaws. Only the tubes which had uniform wall thicknesses and were free of air bubbles and crystals were used.

The S used for the positive electrode was obtained from AESAR and was reported to be 99.999% pure. The current collector was a 0.08-mm thick piece of cleaned Mo ribbon, around which 95% porosity graphite felt was packed tightly. The current collector filled the inside of the glass tube to a depth of $\sim 3\text{ cm}$. Enough S was loaded in the tubes so that when melted it would fill the voids in the porous graphite felt. The Mo ribbon was spot welded to a 0.25-mm diameter

Pt wire, and the glass was pinch-sealed around the Pt. The glass tubes were sealed inside a helium-atmosphere glove box by rapidly heating the glass to its softening point in an electrically-heated Mo coil and then gently pinching it closed with a pre-heated pair of needle-nose pliers. The temperature of the coil had to be sufficiently high to soften the glass in less than 5 seconds or the glass would crystallize. No attempt was made to evacuate the tubes during sealing, and tests showed that the tubes were able to withstand the excess internal pressure caused by heating to the normal operating temperature.

The negative electrode was a two-phase Li-Sn alloy. The Li and Sn were obtained from AESAR, and each was reported to be 99.9% pure. Because the negative electrode was a two-phase two-composition alloy, for a given temperature the cell potential was constant with respect to minor compositional changes. The LiSn electrode could, therefore, be used as a reference as well.

There were two types of experiments employed: the first type was to measure the change-in-voltage caused by a change in current, which was done at various states-of-charge. From these experiments, the pseudo-steady-state polarization could be determined as a function of current and state of charge. The second type of data resulted from measuring the cell voltage, while passing a constant current, as a function of time (or percent Li in the S electrode). This produced charge/discharge (capacity) curves.

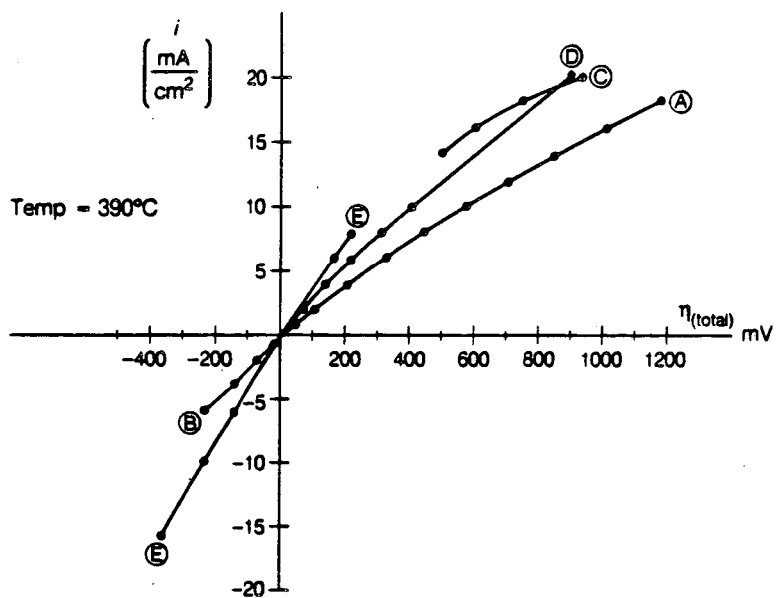
RESULTS

Figure 1 is a plot of the pseudo-steady-state polarization η versus current density i for a typical cell. The curves represent data recorded at different states-of-charge and different rest conditions. The data for curve A were obtained when the cell was discharged for the first time, i.e. between 0.12 and 1.6 mol% Li. The data for curve B were taken when the cell was being recharged from curve A back to 0.9 mol% Li. Higher currents than those shown on the graph were passed but these caused the cell potential to climb very rapidly; this phenomenon was attributed to the formation of a S layer of the glass walls. Curve C represents data obtained by discharging the cell immediately following curve B, or between 0.9 and 3.9 mol% Li. The data for curve D were taken after discharging the cell at a rate of 28 mA (5.5 mA/cm^2) for 8 hours, which produced 17 mol% Li in the S electrode. Finally the set of points for curve D were taken by alternating every few minutes between charging and discharging, at $\sim 18 \text{ mol\% Li}$. At the conclusion of these experiments, the ohmic resistance was measured with an A.C. bridge and found to be $0.0025 (\text{ohm-cm})^{-1}$.

These tests revealed two significant characteristics of these Li/S cells. First, a comparison of curves A and D shows that the pseudo-steady-state polarization was higher when the cell was nearly fully charged than it was partially discharged. This is attributed to the low conductivity of nearly-pure S. Second, for a given state-of-charge, the pseudo-steady-state polarization was higher following a long discharge period than it was following either a significant relaxation period or period of charging. Comparison of A to C or D to E illustrates this trend. This phenomenon might be attributed to the formation of a reaction layer, which either blocks some of the active transfer area or reduces the glass ionic conductivity. The relaxation period and charging could have helped rid the glass of some of the reaction layer, and therefore decrease the polarization caused by the blocking film.

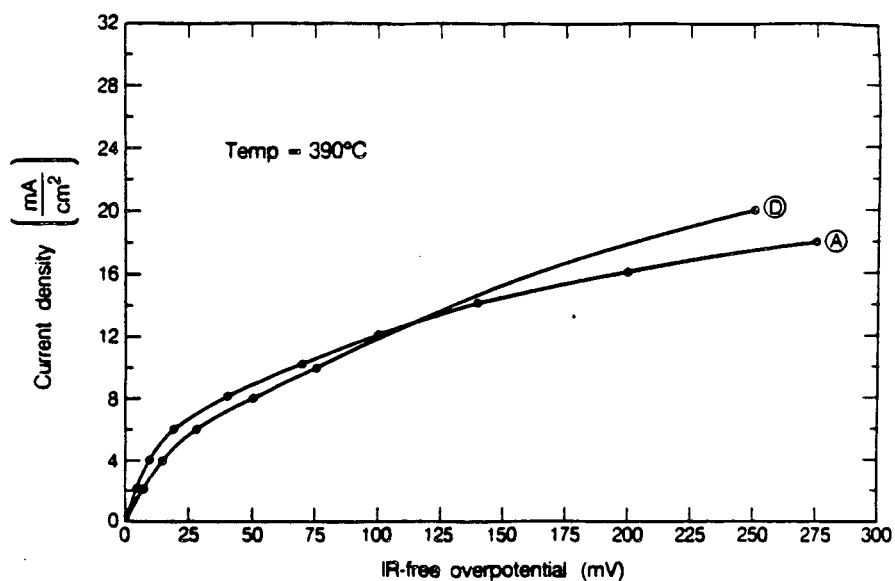
The contribution of ohmic resistance can be eliminated from the total polarization by subtracting the product of the total current and cell resistance from the total pseudo-steady-state polarization. Figure 2 is a plot of the IR-free overpotential versus current density for curves A and D in Figure 1. The shapes of these curves qualitatively resemble the shape expected for a cell which has a mass-transfer-limited current density $i_{\text{lim}} \sim 23 \text{ mA/cm}^2$. However, the curves do not

quantitatively follow the expected shape. Therefore, the limiting current can not be solely attributed to mass-transfer phenomena, but rather, a combination of mass-transfer and other effects.



XBL 859-12111

Figure 1. Pseudo-steady-state overpotential versus current density.



XBL 859-12110

Figure 2. IR-free overpotential versus current density.

Charge-discharge cycle experiments were attempted with cells in both the fully-charged state and in a partially-discharged state. Figure 3 shows data from three cells for which galvanostatic discharges were initiated in the fully-charged state. Unfortunately, all three cells shorted before a complete cycle was obtained, and similar behavior was observed for every cell which was loaded with pure S. Some shorts were catastrophic and others were gradual, and they were the result of discharging the cells either too fast or too far. A cell which was discharged incrementally, with periods of rest separating the discharge periods, could be discharged farther than if it were discharged continuously. Also, the cells which were discharged at lower current densities could be discharged farther than those discharged at higher rates.

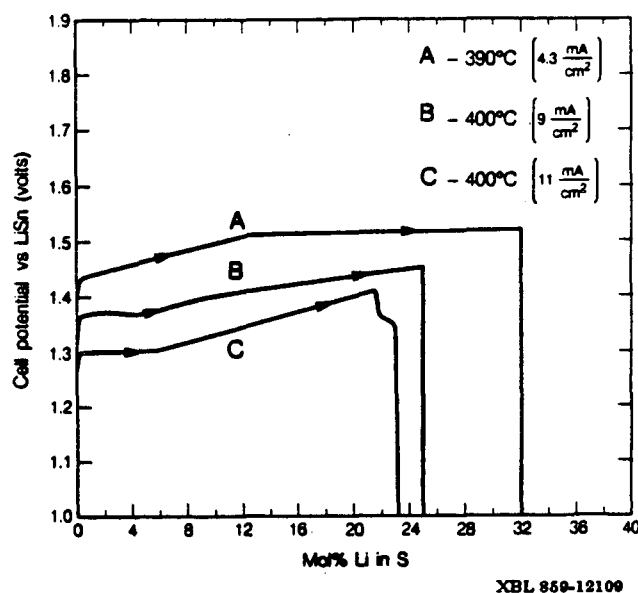


Figure 3. Galvanostatic discharge of three fully-charged cells.

The cells were also used to measure the solubility of Li (as a polysulfide) in S by monitoring the open-circuit cell potential as a function of quantity of Li titrated into the S compartment. The solubility limit was found to occur at $0.04 \pm 0.03/-0.01$ mol% Li at 400°C , in agreement with the value reported by Sharma.⁴

Figure 4 shows two plots: the first is current versus mol% Li, for a potentiostatic charge, and the second is voltage versus mol% Li, for a galvanostatic discharge. This cell was loaded in a partially discharged state, 23.8 mol% Li, and the open-circuit cell potential was 1.65 volts versus LiSn at 400°C . The cell was first charged potentiostatically until the S electrode contained ~6 mol% Li, at which point the cell resistance rose to nearly 800 ohms. The high resistance is attributed to the formation of a layer of low-conductivity S. The cell was then discharged at a constant-current of 2 mA to 14 mol% Li, where it shorted.

After the failure of a cell, the glass tubes were examined and most were found to be coated with a yellowish-white reaction layer. Some of the reaction layer from a few of the tubes was removed, cleaned in CS_2 and methanol, and analyzed using an X-ray diffractometer. Figure 5 is an X-ray pattern from a powdered sample of the reaction layer of a typical cell, and Table 1 summarizes the compounds which could be identified. This X-ray pattern is very similar to those obtained from static immersion tests. There is strong evidence in the pattern for crystalline lithium chloroborate and lithium hydroxide, but when the glass was analyzed after being contacted with molten S, there was no evidence of any crystalline material. A significant finding was that there was a major peak at 35 degrees, which could not be confidently assigned to any known

compound. There are at least two lithium-borosulfide compounds known to exist, $\text{Li}_2\text{B}_2\text{S}_5$ and LiBS_2 ,⁵ but for which the X-ray diffraction patterns are not available.^{6,7} Table 2 is a partial list of potential reactions between lithium polysulfides and the lithium-chloroborate glass. Estimation of the X-ray patterns for these compounds, using data for analogous Na compounds, is likely to be rather unreliable because of the significant size difference of the Li and Na ions.

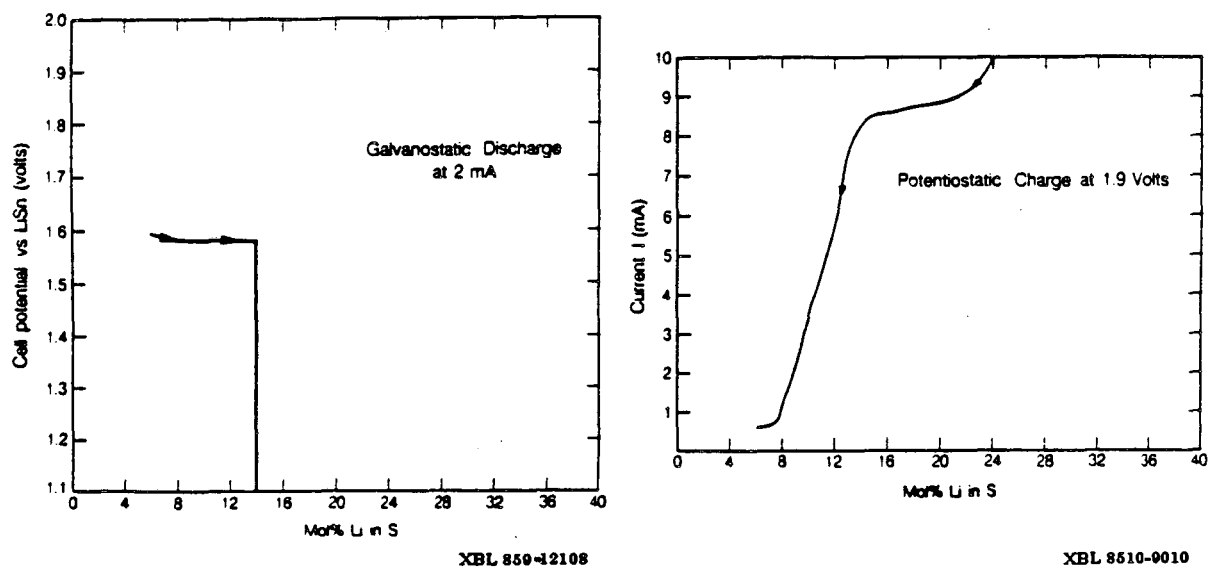


Figure 4. Potentiostatic charge and galvanostatic discharge versus mol% Li at 400 °C.

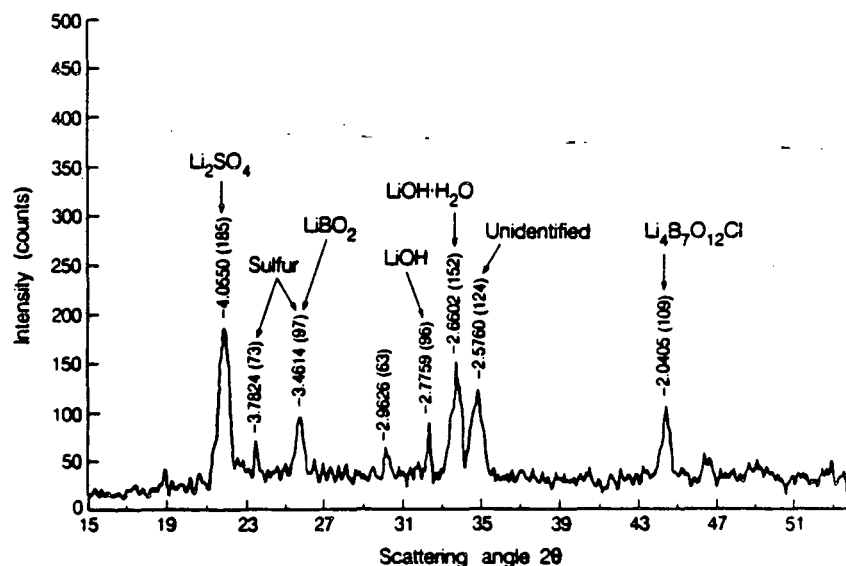
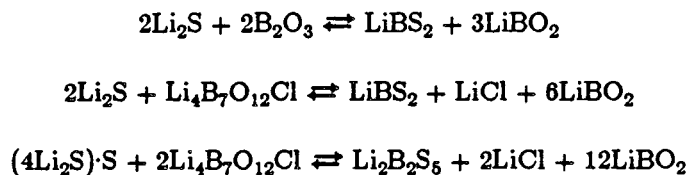


Figure 5. X-ray diffraction pattern for corrosion products in S-22 mol% Li_2S at 400 °C.

Table 1. Summary of Possible Compounds in the Reaction Layer based on X-ray Diffraction Patterns.

Compound	d values	2 θ values	Confidence	Comments
$\text{Li}_4\text{B}_7\text{O}_{12}\text{Cl}$	2.05 _x 2.70 ₃ 3.48 ₂	44.1 33.2 25.6	High	9.1 mol% $(\text{LiCl})_2$ 27.3 mol% Li_2O 63.6 mol% B_2O_3
LiOH	2.75 _x 4.35 ₄ 2.51 ₂	32.5 20.4 35.8	Medium/High	Hydrated Li_2O
$\text{LiOH} \cdot \text{H}_2\text{O}$	2.67 _x 2.70 ₆ 2.44 ₅	33.5 33.2 36.8	Medium/High	Hydrated Li_2O
Li_2S	3.30 _x 2.02 ₄ 1.72 ₃	27.0 44.8 53.2	Medium/Low	Hygroscopic
Li_2SO_4	4.04 _x 4.00 _x 3.92 ₅	22.0 22.2 23.7	High	Caused by Contaminations
HBO_2	4.20 _x 3.07 _x 6.75 ₃	21.1 29.1 13.1	Low	Hydrated B_2O_3
LiBO_2	3.53 _x 2.19 _x 1.80 ₈	25.2 41.2 50.7	Medium	50% Li_2O 50% B_2O_3
Li_3BO_3	3.02 _x 2.63 ₆ 2.67 ₅	29.5 34.1 33.5	Medium	75% Li_2O 25% B_2O_3
Sulfur -#	3.89 _x 2.73 ₇ 3.12 ₃	22.8 32.8 28.6	Medium/High	Hexagonal
Sulfur -#	3.29 _x 6.65 ₃ 3.74 ₂	27.1 13.3 23.8	Low	Monoclinic
Sulfur -#	3.85 _x 3.21 ₆ 3.44 ₄	22.8 27.8 25.8	Medium/High	α -phase

Table 2. Partial List of Reactions Between Lithium Polysulfides and Lithium Chloroborate Glass.



DISCUSSION AND CONCLUSION

The attractiveness of using lithium-chloroborate glass as the electrolyte in a Li/S cell was supported by the observation that the glass was able to support current densities of 5-15 mA/cm² for 15-20 hours, or as high as 70 mA/cm² for 3-5 minutes. There appeared to be a limiting current at ~23 mA/cm². However, while the cells were being discharged, the glass apparently reacted with the lithium polysulfides, causing the cells to fail. These failures have been attributed to fractures in the glass, caused by one of two effects: volume mismatches between the glass and the reaction layer, and the reaction layer growing and blocking most of the cell's active area (which causes the remaining area to support a very high current density). Local current densities in excess of some critical value have been found to be responsible for failures of other solid electrolytes, e.g., the ceramic β'' -alumina used in Na/S cells.⁸

The exact composition of the reaction layer could not be identified; however, it was clear that there were present some crystalline lithium-chloroborate compounds and possibly some lithium borosulfides. It is believed that discharging the cells does not cause formation of a reaction layer, but rather that discharging the cells accelerates such reactions. This is consistent with the idea that the lithium polysulfides were the attacking species. The reaction between the glass and the polysulfides would be accelerated during discharge, because the concentration of polysulfides near the glass wall would be greater than when the cells were being charged or at open-circuit. This conclusion is similar to some results reported for the Na/S system.⁹

RECOMMENDATIONS

The high ionic conductivity and workability of lithium-chloroborate glasses make them attractive candidates for use as electrolytes in Li/S cells. The conductivity is sufficiently high that during discharge in a Li/S cell, the ohmic potential drop would be only a small fraction of the open-circuit cell potential. However, there are significant problems which must be overcome: first, the glass needs to be made more resistant to Li attack; this problem is actively being worked by Tuller et al.¹⁰⁻¹⁵ Recent findings show that some glasses may be stable to melts with Li activity as high as 0.08 at 380°C. Second, the glass needs to be more resistant to attack by polysulfides. The first step to solving this problem should be to identify the compounds in the reaction layers. This would help to understand the attack mechanism and possibly indicate a method to stabilize the glass.

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