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EVALUATION OF FIBER SEPARATORS FOR USE IN THERMAL BATTERIES

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ABSTRACT

Fiberglass tape and borosilicate filter discs impregnated with molten LiCl-KCl eutectic were examined for potential use as separators for high-temperature LiSi/LiCl-KCl/FeS_2 thermal batteries. Test discs were punched from these materials and evaluated at 400°C in single cells at a steady-state current of 63 mA/cm^2. The performance generally improved with electrolyte loading for most of the materials. Better results were obtained with the filter discs than with the tape. The best overall results were obtained with Whatman GF/A discs. Active lives for cells with these separators were about 85% of the standard cells with pressed-powder separators. More work with other materials and electrolytes over a wider temperature range is underway, along with 5-cell-battery tests..

INTRODUCTION

Thermally activated ("thermal") batteries employ a Li-alloy anode (either Li-Si or Li-Al) and, most commonly, a cathode based on FeS_2 (pyrite). The separator is composed of a halide mixture, such as LiCl-KCl eutectic (melting point of 352°C), blended with MgO to immobilize the salt when it becomes molten upon activation by an internal pyrotechnic source. All the active components are prepared by cold pressing of powder mixtures into pellets that are stacked as required to obtain the desired voltage.

There is an increasingly higher demand for raising the power and energy density of thermal batteries today, especially for Dept. of Defense applications. This requires reducing the thickness of piece parts as much as possible. The limit for thinner anodes and cathodes is dictated by the mass of electroactive material necessary to meet the intended application. The separator, on the other hand, could be reduced, since a thicker separator results in a higher IR drop in the battery. Pressing separator pellets to a thickness of 0.015" is generally not a problem. However, pressing pellets that are less than 0.010" thick becomes increasingly more difficult as the diameter of the pellet is increased. Fabricating separator that are 3"–5" in diameter and <0.020" thick is extremely difficult—if not impossible—as they are extremely fragile and break easily during handling. Also, it is not easy to spread a thin layer of powder into the pressing die cavity. Consequently, there is a tendency for soft (low-density) spots or holes to form in such separator pellets. This results in a reduced pellet yield.

One way of mitigating this problem is to use a ceramic (e.g., AlN or MgO) monolith that can be impregnated with electrolyte. This approach has been explored by workers at Northrop-Grumman (1) and Argonne National Laboratory. This type of separator is prepared by conventional ceramic processing but suffers from certain physical constraints. A high porosity is necessary to minimize IR losses in the separator, but under such

conditions, the separator tends to lack strength and crushes under the applied force needed during thermal-battery construction.

A number of workers have examined the use of tapecasting to prepare separator discs. Various organic binders are blended with the separator powder to form a plastic material that can be calendared or rolled into sheets. Varta reported on the use of this technique for separator preparation for secondary high-temperature LiAl/FeS_2 batteries (2,3). The key factor for success with this approach is to use a binder that can be cleanly removed by heat treatment without melting the electrolyte. For the LiCl-KCl-based separators, that means a binder that will volatilize at much less than 352°C. Polyisobutlyene (PIB) meets this criterion, as it decomposes cleanly at 320°C. Pyrolysis to form elemental carbon would be unacceptable, as this would impart electronic conductivity to the separator. One disadvantage of tapecast separators is that it can be difficult to accurately control shrinkage and warpage during heat treatment. Thermal batteries require close dimensional control on the battery-stack components. There are also issues with strength and electrolyte retention with this method that need to be addressed further.

An alternate approach involves the use of glass- or ceramic-fiber separators that are impregnated with the molten electrolyte. In many cases, these are readily available commercially in thickness under 0.010". An attractive feature of this approach is that the separator would provide additional insurance against intercell shorting because of the mechanical barrier that it would provide. With pressed-powder separators, there can be a tendency for material movement in very thin cells over prolonged (>2 h) discharge times. This could lead to bridging of the anode and cathode, initiating a potential thermal runaway. Use of such separators would obviate the need for expensive dies for large-diameter separator—the desired sizes could simply be punched from the impregnated materials—which could significantly reduce production costs for thermal batteries. This concept is also attractive in that, in theory, it would allow the use of a prismatic design for thermal batteries. The standard right circular cylinder has certain volume constraints in terms of packaging for some applications.

While there have been some indications of their previous use, little has been reported in the literature in terms of the properties of such material. We undertook to conduct a systematic and comprehensive evaluation of this concept for our internal needs. A number of commercial fiberglass and quartz filter media and tapes were evaluated in the course of this work. The electrolyte is held in place in these materials in the same manner as with the powdered MgO separators, i.e., by capillary action. Consequently, the porosity and pore-size distribution will determine the electrolyte loading and the consequent separator resistance.

The bulk of the work was conducted with the LiCl-KCl eutectic, with a smaller effort directed toward the LiCl-LiBr-LiF all-Li electrolyte, which melts at 436°C. The loaded separator materials were incorporated into LiSi/FeS_2 single cells and tested galvanostatically at temperatures of 400° to 550°C under a range of current densities. These data were then compared to those for standard cells made with conventional pressed-powder separators. The results of initial screening tests at 400°C will be presented in this report, as this is where the most impact on performance would be expected. The promise and problem areas associated with the commercialization of this technology will be addressed.

EXPERIMENTAL

Materials

Single cells 1.25" in diameter were fabricated using with flooded anodes consisting of 75% of 44% Li/56%[a] Si alloy and 25% LiCl-KCl eutectic electrolyte (0.93-g, 0.042" thick). The Li-Si alloy was obtained from Eagle-Picher Industries and the eutectic electrolyte was made in house by fusion of reagent grade LiCl and KCl in the appropriate amounts at 600°C for three hours in a quartz crucible in a dry room maintained at <3% relative humidity. The electrolyte was pulverized and blended with 35% MgO (Merck Maglite 'S') and fused overnight at 400°C in the dry room to prepare the control separator material, which was then pelletized (1.03 g, 0.027" thick). The catholyte composition was 73.5% FeS_2/35% separator/1.5% Li_2O (1.03 g, 0.018" thick).

The materials that were evaluated in this work are listed in Table I, along with the loading of electrolyte per 1.25"-dia. disc. All of these filter materials are borosilicate glasses rated to 500°C. The fiberglass tape was obtained from Mutual Industried (P/N 950801-P). The filter discs and tape were impregnated with electrolyte by dipping into molten LiCl-KCl eutectic at 450°C. Some materials wetted readily (GF/F), while the others required contact times up to 20 minutes, to ensure complete wetting. After impregnation, the materials were placed on a quartz plate and heated at 400°C for 15 minutes in an oven, followed by removal and cooling. This was done to ensure flat samples for the subsequent punching of the 1.25"-dia. test discs.

Electrochemical Characterization

Single cells were tested between heated platens at 400°C using an applied pressure of 8.0 psig. They were discharged galvanostatically under computer control in a glovebox under an atmosphere of high-purity argon (<1 ppm each of O_2 and H_2O). The cells were discharged to a cutoff voltage of 1.25 V at a steady-state current of 0.5 A (~63 mA/cm^2). The current was doubled for 1 s every 60 s (126 mA/cm^2), to allow overall cell polarization to be monitored as a function of depth of discharge. Each test was repeated at least once.

RESULTS AND DISCUSSION

Physical Characterization

The electrolyte loadings for the various samples were measured prior to the assembly of the separator discs into single cells. As seen in the data of Table I, the filter discs with the smallest nominal pore size had the highest electrolyte loading. If the electrolyte loading is insufficient, the separator will be starved which will result in a greater tortuosity, with a corresponding higher internal cell impedance during discharge. Similarly, excessive loading of electrolyte can lead to electrolyte leakage during discharge which can cause parasitic losses between cells in a battery stack. Also, when the sample is

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[a] Unless noted otherwise, all compositions are reported in weight percent.

removed from the over after impregnation with electrolyte, greater stress can result during electrolyte freezing if there is excess electrolyte present.

A number of representative impregnated samples were taken for examination by scanning electron microscopy. Figure 1 shows a surface profile for a sample of GF/C impregnated with electrolyte. The wetting was fairly uniform and complete, as seen in Figure 2 for a photomicrograph of this sample after cross-sectioning.

The mechanical properties of the impregnated materials are as important. If the impregnated material is too brittle, it can break during punching. This was not commonly observed with the tape materials, as the fibers are much longer and act as reinforcing material to increase strength. Preliminary tests with the LiCl-LiBr-LiF electrolyte were not very encouraging in this respect. The higher impregnation temperature needed (500°C) is close to the softening point of these materials. Heating them at this temperature in the electrolyte tended to embrittle them. Many of the test samples—both borosilicate glass discs and fiberglass tapes—cracked badly or even shattered on cooling after impregnation with the all-Li electrolyte. More work in this area with more-thermally-stable quartz discs and tapes is underway.

Electrochemical Characterization

Typical performance at 400°C for $LiSi/LiCl-KCl/FeS_2$ single cells made with the various impregnated filter discs are shown in Figure 3. Data for a cell built with a standard pressed-powder separator are also shown for comparison. A temperature of 400°C was chosen for the initial characterization tests, as any concentration gradients originating at the LiSi anode will be accentuated. At this temperature, the cell is only ~50°C above the melting point of the electrolyte. Any strong concentration gradients will quickly move the electrolyte composition in the separator quickly off the eutecitc at the anode-separator interface, giving rise to LiCl precipitation, with an attendant increase in the cell impedance.

The standard cell and the cells with the GF/C and GF/F separators showed a voltage transition near 8 minutes. This was not readily evident, however, for the cell with the GF/A separator. The corresponding cell-polarization data show maxima occurring during these same voltage transitions. Complementary tests with a reference electrode show that these transitions are associated with the cathode, during formation of the first discharge phase, $Li_3Fe_2S_4$. The overall cell polarization was the lowest for the cell with the GF/A separator, which had the lowest loading of electrolyte. The cells with the GF/C and GF/F separators showed polarization similar to that for the standard cell with a pressed-powder separator. The pulse response of the cell with the GF/A separator showed essentially all of the polarization to be ohmic, whereas some concentration polarization was evident for the standard cell under the same conditions.

The performance at 400°C of $LiSi/LiCl-KCl/FeS_2$ single cells made with the glass-tape separator and the standard pressed-powder separator is shown in Figure 4. The initial voltages for the cell with the glass-tape separator was equal to or greater than that of the standard cell for the first ten minutes, after which the voltage rapidly fell. Also, the polarization response was quite different for the cell with the glass-tape separator, showing a rapid increase corresponding to the rapid drop in voltage. The initial polarization was also slightly higher for this cell. The performance of the glass-tape separator was inferior to that of the filter discs under the same conditions, with the appearance of concentration polarization during the pulse at 10 min. This was not observed for the cells with the filter discs and is most likely the result of the low electrolyte loading of this material—the lowest of all the samples tested.

As mentioned earlier, the degree of electrolyte loading is important for thermal-cell performance. There is some minimum loading that is necessary for proper functioning of the cell. As the electrolyte loading was increased, there is a corresponding improvement in cell performance. After a certain level, however, the relative performance did not increase further. This loading will depend on the pore-size distribution of the particular separator material. This is seen in Table II, where the active lives of the cells are listed to a 1.25-V cutoff for the various cells tested. The improvement was dramatic for the GF/A vs. the glass-tape cell, due to doubling of the electrolyte present in the separator. However, there wasn't a corresponding improvement for the other separators when the electrolyte loading reached 0.6 g/disc. The best performance was still obtained with the standard cell using the MgO separator. *In the end, the final overall performance will depend on how much of the original electrolyte remains in the separator during discharge.* This, in turn, will depend on the pore-size distribution and electrolyte wettability of the separator—whether glass tape or discs, or MgO powder. During discharge, migration of the electrolyte in the separator can occur to the adjacent anode and cathode pellets, thus resulting in some degree of electrolyte starvation in the separator. There will be competition for the electrolyte to remain in the separator or to wick into the adjoining electrode. The outcome of this process will determine the ultimate cell performance.

The processing steps taken in the preparation of samples for laboratory evaluation need to be scalable to be viable in a commercial thermal-battery environment. Once a suitable material has been identified, it should be possible to develop the necessary processes and procedures with appropriate equipment (e.g., moving-belt furnace) to make this approach feasible for large-scale production.

Future Work

The filter discs are made using a paper-type process, in which the final pore-size distribution will depend on fiber diameter and processing conditions. In the case of the glass-tape separator, the effective porosity will depend on the size of the fibers used in its construction and the spacing (warp and weave) for the final fabric. The material of construction can also be important, as this can affect the contact angle of the electrolyte and, therefore, the wetting properties. Parallel tests are underway with other fiberglass and borosilicate-glass materials as well as with quartz filters and tape, in an attempt to develop thin, suitable fabric separators for use in thermal cells.

CONCLUSIONS

The use of borosilicate filter discs and woven fiberglass tapes as potential separators in thermal batteries was evaluated. The impregnation of these materials with molten LiCl-KCl at 450°C occurs readily in most cases (e.g., Whatman GF/F) but requires 15-20 minutes of contact time for others to ensure complete wetting and loading of electrolyte.

In LiSi/LiCl-KCl/FeS_2 single-cell tests at at 400°C and 64 mA/cm^2, the initial performance of the GF/F and GF/C cells is comparable to that of the standard cells with pressed-powder separators. The initial performance of the GF/A cells is better, as well, with a higher voltage and lower polarization. After extensive discharge, however, the voltage drops below that of the standard cell, with an accompanied increase in polarization. This may be due to electrolyte wicking from the fabric separators into the adjoining anode and cathode pellets in the cell. The woven-cloth separators are somewhat stronger than the filter discs made by a paper process but have a lower electrolyte loading. Cells with these separators don't run as long as the standard cells or the cells with the borosilicate glass filters. The ultimate performance will depend strongly on the degree of electrolyte loading and how well the electrolyte is retained in the separator.

More work is underway to extend this initial work to higher temperatures with additional filter discs and woven tapes, and will include the LiCl-LiBr-LiF electrolyte. Complementary 5-cell battery tests are also in progress. If a suitable material can be found that can deliver performance equal to, or close to, that of the standard pressed-powder separators, the likelihood of attaining a large-diameter separator that can be fabricated under 0.010" thick will be greatly enhanced. This will ultimately result in a substantial increase in the energy and, possibly, power density of thermal batteries.

ACKNOWLEDGMENTS

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REFERENCES

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Table I. Materials Screening in Separator Study.

Material	**Nominal Thickness, in**	**Nominal Pore Size, µm**	**Electrolyte Loading Per 1.25" Disc, g**
Whatman GF/A filter	0.010	1.6	0.273-0.395
Whatman GF/C filter	0.010	1.2	0.430-0.517
Whatman GF/F filter	0.017	0.7	0.592-0.610
Fiberglass tape	0.005	Not available	0.183

Table II. Relative Performance of LiSi/LiCl-KCl/FeS_2 Cells at 400°C Under a Steady-State Load of 63 mA/cm^2.

Separator Material	**Average Active Life to 1.25 V, s**	**Electrolyte Loading Per 1.25" Disc, g**
Fiberglass tape	782	0.183
Whatman GF/A filter	1618	0.395
Whatman GF/C filter	1735	0.474
Whatman GF/F filter	1495	0.601
MgO powder	2045	0.650

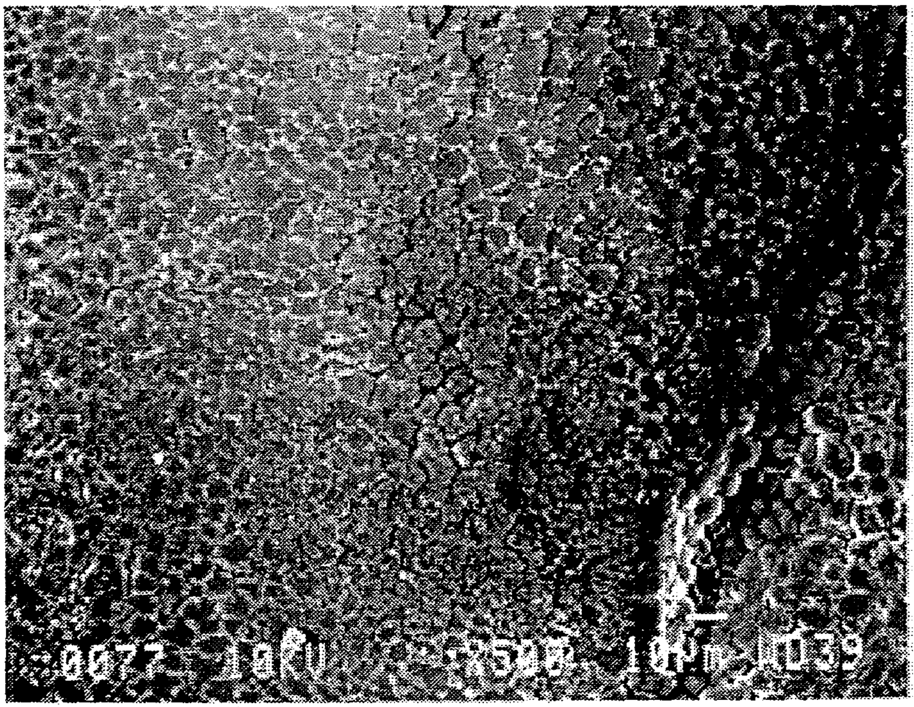

Figure 1. Surface of GF/C Filter Impregnated with Molten LiCl-KCl Eutectic.

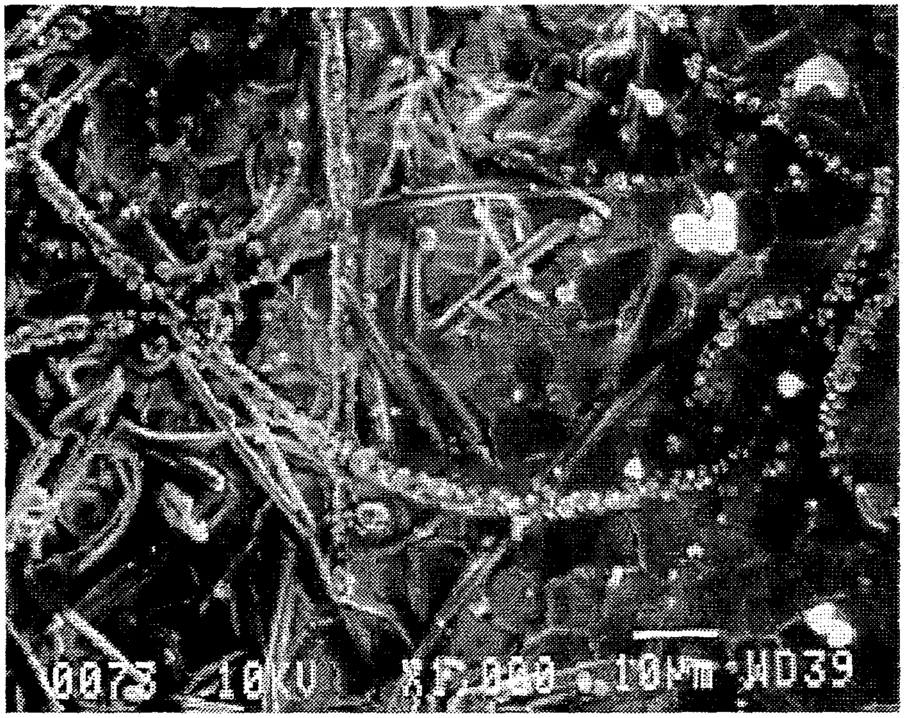

Figure 2. Cross-Section of Sample from Figure 1.

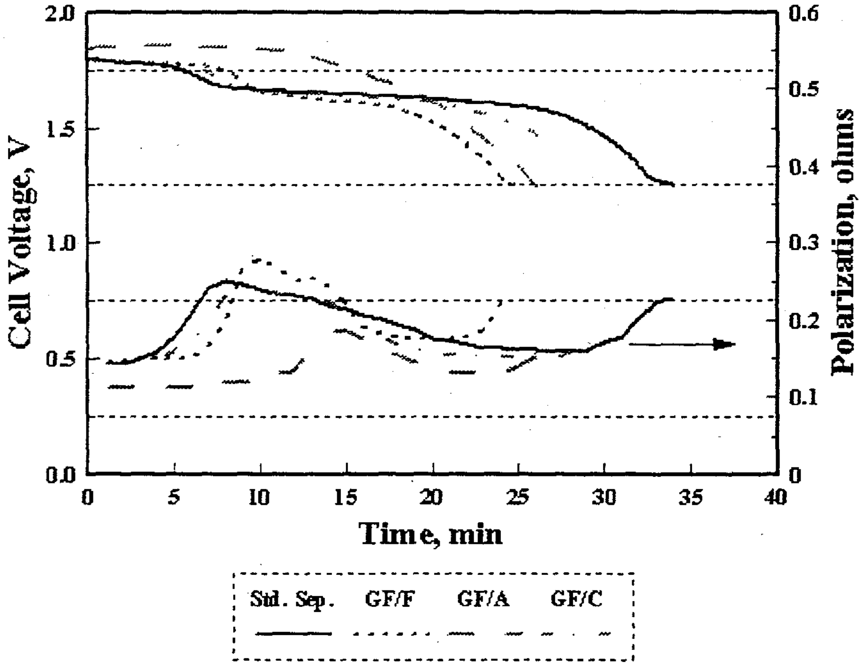

Figure 3. Relative Performance at 400°C of LiSi/LiCl-KCl/Fe_2 Single Cells Made with GF/x Filter Separators and Pressed-Powder Separator.

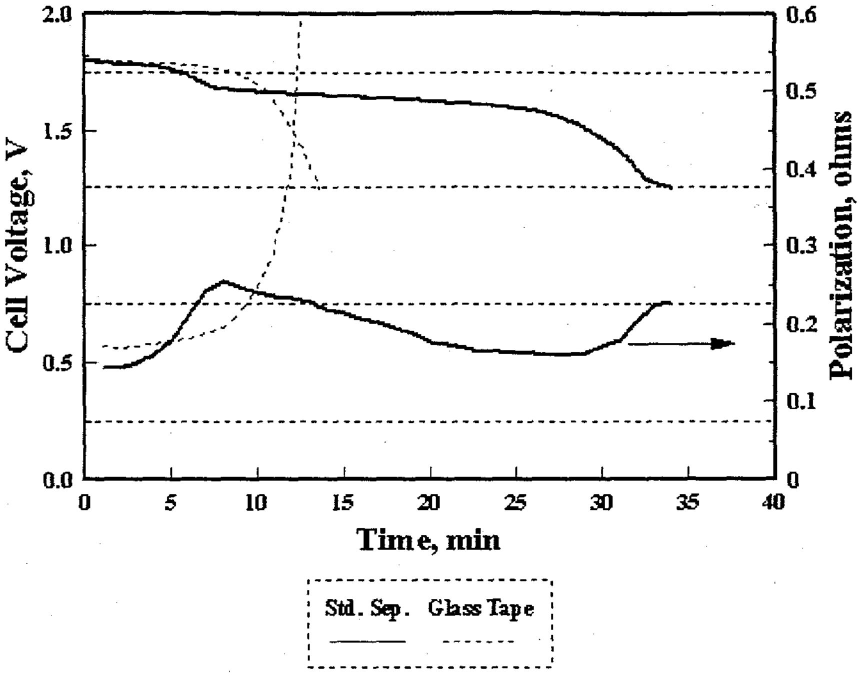

Figure 4. Relative Performance at 400°C of LiSi/LiCl-KCl/Fe_2 Single Cells Made with Glass-Tape Separator and Pressed-Powder Separator