Characterization of High-Voltage Cathodes in CsBr-LiBr-KBr Eutectic Electrolyte

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Abstract

The transition-metal oxides LiMn$_2$O$_4$, MnO$_2$, CrO$_2$, and LiCoO$_2$ were evaluated for possible use as high-voltage cathodes for potential geothermal power applications. These were coupled with Li(Si) anodes and a low-melting CsBr-LiBr-KBr eutectic electrolyte that melts at 228.5°C. Single-cell tests at 250°C and 300°C at 15.8 and 31.6 mA/cm$^2$ showed that MnO$_2$ performed the best overall and had the lowest polarization. A 5-cell battery test using LiMn$_2$O$_4$ cathodes was only modestly successful due to possible parasitic chemical reactions between the cathode and electrolyte at the much higher temperature (500°C) during discharge. The overall energy densities for these cathode were still less than for FeS$_2$.

Introduction

The Li(Si)/LiCl-KCl/FeS$_2$ couple is the main system used in thermally activated ("thermal") batteries. This is a nominal 2-V couple at 500°C. The need for increasing energy densities for many applications has given impetus for the development of replacement cathodes with higher emfs. In an earlier extensive screening study of transition-metal oxides in LiCl-KCl eutectic, mixed results were obtained. A number of couples that were found to have emfs of over 3 V did not function well when tested at 500°C. There is the possibility of electrolyte reaction if the emf exceeds the thermodynamic decomposition potential of electrolyte components.

More recently, we have been evaluating the CsBr-LiBr-KBr eutectic as an electrolyte for medium-temperature batteries for geothermal borehole power applications. This electrolyte melts at 228.5°C and shows promise for use at temperatures of 250°C and greater. Some transition-metal oxides that are not stable in molten-halide salt mixtures at 500°C are stable at lower temperatures. We undertook a screening and characterization study of a number of candidate transition-metal oxides with the goal of developing an alternative cathode to FeS$_2$ for geothermal borehole power use. We examined the performance of CrO$_2$, LiCoO$_2$, MnO$_2$ and LiMn$_2$O$_4$ cathodes in the CsBr-LiBr-KBr eutectic with Li(Si) anodes. Tests with reference electrodes were carried out in a number of cases, to identify the relative contribution of each half cell to the overall polarization. In this paper, we present the results of single-cell tests with these materials at temperatures of 250°C and 300°C, along with preliminary data for limited 5-cell battery tests with LiMn$_2$O$_4$ cathodes.

Experimental

Materials – Flooded anodes of 25% electrolyte and 75% active anode (44% Li/56% Si) were used for all tests. The final anode pellet weight was 0.99 g. The presence of electrolyte aids in pelletizing and improves the electrochemical performance. The separator was formulated with 35% Maglite 'S' MgO and weighed 1.0 g. A sulfidized Ni wire (Ni/NiS$_2$ couple) was used for the reference electrode in limited tests. Catholytes were formulated with 70% cathode material, 20% electrolyte, and 10% KS-6 graphite as a conductive additive, or 60% cathode material, 20% electrolyte, and 20% KS-6. Cathode pellets of these materials weighed 1.10 g and 2.29 g, respectively, to maintain the same active mass of cathode per pellet. All processing of powders and materials for battery construction was conducted in a dry room maintained at <3% relative humidity.

Apparatus and Testing – The single cells were 1.25" (3.18 cm) in diameter and were tested in a glovebox under high-purity argon that contained <10 ppm each water and oxygen. A reusable test fixture was used for the 5-cell battery that also used a 1.25"-dia. stack. The single cells and battery were tested using an HP6060B programmable electronic load under computer control. Constant-current loads of 0.125 A (15.8 mA/cm$^2$) or 0.250 A (31.6 mA/cm$^2$) were applied as a background. Every 30 s or 60 s, the current was doubled for 0.5 s to 1 s, to obtain polarization information. Steady-state voltage readings were taken with an HP3456A digital voltmeter (DVM) interfaced to an HP3497A data acquisition unit that multiplexed several channels.
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Pulse readings were taken with an HP3458A high-speed DVM at a 1.2 kHz rate. The cells and battery were typically discharged to a cutoff voltage of 1.00 V/cell.

**Results and Discussion**

**Single-Cell Tests** - A test temperature of 250°C was the lowest that could be practically used with the CsBr-LiBr-KBr eutectic. The voltage responses of the various cathodes are compared in Figure 1 at 250°C for a current density of 15.8 mA/cm². The cell with the LiCoO₂ cathode immediately dropped to a voltage plateau of 1.1 V from an open-circuit value of 2.8 V. It may be possible to charge the cell prior to discharge, however, to attain a higher-voltage plateau.

The cell with the LiMn₂O₄ cathode showed a short plateau near 2.6 V, with a gradual sloping decline with discharge, after an open-circuit voltage of 2.9 V. The cell with the CrO₂ cathode had an open-circuit voltage of 3.1 V but showed a gradual decline with discharge. The cell with the MnO₂ cathode showed a high-voltage plateau that was the largest of all the cells, after an open-circuit voltage of 3.1 V. Tests with reference electrodes showed that the voltage transitions were associated with the cathode.

The corresponding cell polarizations are shown in Figure 2. The polarization (predominantly ohmic) for the cells with the CrO₂ and LiMn₂O₄ cathodes showed a continual increase with depth of discharge (DOD), which explains their voltage responses (Figure 1). In contrast, the polarization for the MnO₂ cell was relatively flat with a maximum near 120 C/g, corresponding to a voltage (phase) transition during discharge. The polarization of the LiCoO₂ cell was relatively low.

The voltage responses of the various cathodes are compared in Figure 3 at 300°C for a current density of 15.8 mA/cm².

The response of the LiCoO₂ cell was similar to that at 250°C, with a low-voltage plateau near 1.3 V. However, the performance of the cells with LiMn₂O₄ and CrO₂ showed a dramatic improvement relative to 250°C, now being comparable to that for MnO₂. The length of the high-voltage plateau for the MnO₂ cell increased from ~100 C/g to 320 C/g with the 50°C increase in temperature.
The corresponding total polarizations for these tests are shown in Figure 4. The polarization for the LiMn$_2$O$_4$ cell was now fairly flat during discharge, showing two weak maxima corresponding to voltage transitions (Figure 3). The polarization for the MnO$_2$ and LiCoO$_2$ cells remained flat, as for the 250°C discharge.

The polarization continued to ramp up with DOD for the CrO$_2$ cell. However, when a thicker separator was used (as in reference-electrode tests), the discharge plateau voltage remained flatter longer. The discharge capacity increased from about 400 C/g to almost 740 C/g and the rapid increase in polarization was delayed until 450 C/g from a value of 100 C/g. This is attributed to an electrolyte-reservoir effect, which provides a large volume of electrolyte for dissipation of Li$^+$ concentration gradients at the anode-separator interface. This effect has previously been observed with the Li(Si)/FeS$_2$ couple with this same electrolyte.$^2$

Increasing the graphite content of the CrO$_2$ cathode from 10% to 20% did not increase the discharge capacity but did serve to flatten the discharge and delay the onset of rapid polarization increase from 90 C/g to almost 300 C/g.

The tests at 300°C were repeated but at twice the current density, to see if the cells could sustain the higher load with acceptable polarization. The results of those tests are summarized in Figure 5. Only the LiMn$_2$O$_4$ and MnO$_2$ cells were able to function well under the higher load. The CrO$_2$ cell showed a gradual roll-off with DOD as noted earlier (Figure 1).

The corresponding total polarizations are summarized in Figure 6. Both the LiMn$_2$O$_4$ and MnO$_2$ cells showed similar maxima, reflecting voltage transitions (Figure 5), except that the LiMn$_2$O$_4$ cell exhibited a rapid increase in resistance afterwards. The polarization for the CrO$_2$ cell showed a gradual increase with DOD, as observed at the lower current density (Figure 4).

Battery Test – The performance of the Li(Si)/CsBr-LiBr-KBr/LiMn$_2$O$_4$ couple was examined in a 5-cell battery that was activated at room temperature. The heat balance for this battery was 85.5 cal/g of total cell mass. The voltage response of the battery is compared on a per-cell basis with data for single-cell tests at 250°C and 300°C in Figure 7. Data for FeS$_2$ cells under the same conditions are included for comparison. The battery response on a per-cell basis was intermediate between those of the two single-cell tests. The observed loss in capacity for the battery may be due to parasitic chemical reactions between the electrolyte and the LiMn$_2$O$_4$ cathode. Such effects were observed previously with a Ag$_2$CrO$_4$ cathode.$^3$ Differential scanning calorimetry examination of the cathode showed a weak exotherm near 370°C. The battery temperature peaked at 500°C at 25 s and was 276°C at the end of the test. However, the instantaneous peak temperature can exceed 1,000°C during burning of the Fe/KClO$_4$ heat pellet.
The performance of MnO₂, LiMn₂O₄, LiCoO₂, and CrO₂ cathodes with Li(Si) anodes in CsBr-LiBr-KBr electrolyte is strongly influenced by the current density and temperature. At 250°C and 15.8 mA/cm², only MnO₂ exhibits adequate performance. LiMn₂O₄ and CrO₂ show a gradual roll-off in voltage because of a dramatic increase in polarization (resistance) during discharge. The polarization for MnO₂ is flat throughout discharge. LiCoO₂ shows an unacceptable low-voltage plateau during discharge at 250°C as well as 300°C. The remaining cathodes, in contrast, show a dramatic improvement in capacity at 300°C, with similar capacities and reduced polarization for LiMn₂O₄ and CrO₂. At 300°C and 31.6 mA/cm², MnO₂ is the best performer, followed by LiMn₂O₄ and CrO₂. This cathode has the biggest potential for use in geothermal borehole power supplies because of its robust performance. A cathode pellet based on MnO₂ still has a lower specific energy and energy density than FeS₂ because of its lower capacity and the need for the use of diluent conductive additives.

An initial 5-cell battery test with LiMn₂O₄ indicates some loss of capacity due to parasitic chemical reactions involving the electrolyte and cathode. More battery tests are planned, especially with MnO₂ cathodes.

### Conclusions

The specific energies of the oxide cathodes were less than that of FeS₂. For LiMn₂O₄ at 250°C and 15.8 mA/cm², the energy density was 28.5 mWh/g of active cathode, compared to 61.0 mWh/g for FeS₂. At 300°C, these numbers were 201 mWh/g and 231 mWh/g, respectively. The best oxide cathodes had higher voltages than FeS₂ but exhibited shorter discharge capacities. The oxide cathodes also require the use of a conductive additive, which FeS₂ does not. This results in a lower volumetric energy density for these materials.

### References

2. Ronald A. Guidotti and Frederick W. Reinhardt, "Characterization of the LiSi/CsBr-LiBr-KBr/FeS₂ System for Potential Use as a Geothermal Borehole Battery Source," 199th Meeting of The Electrochemical Society, Honolulu, HI, October 17-22, 1999.
3. Ronald A. Guidotti and Frederick W. Reinhardt, "Performance of Li-Alloy/CsBr-LiBr-KBr/Ag₂CrO₄ Couples in Molten CsBr-LiBr-KBr Eutectic," 198th Meeting of The Electrochemical Society, Honolulu, HI, October 17-22, 1999.

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