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Re-evaluation of the Eutectic Region of the LiBr-KBr-LiF System

Laszlo Redey
Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439

Ronald A. Guidotti
Sandia National Laboratories, P.O. Box 5800, Albuquerque, NM 87185-0614

Abstract

Using a custom-designed high-temperature conductivity cell, we were able to readily determine the liquidus region for the various compositions studied around the original "eutectic" for the LiBr-KBr-LiF system. The actual eutectic composition was found to be 60.0 m/o LiBr-37.5 m/o KBr-2.5 m/o LiF with a melting point of 324° ± 0.5°C.

Introduction

The separator pellet in a thermal battery consists of electrolyte immobilized by a binder (typically, MgO powder). The melting point of the electrolyte determines the effective operating window for its use in a thermal battery. The development of a two-hour thermal battery required the use of a molten salt that had a lower melting point and larger liquidus range than the LiCl-KCl eutectic which melts at 352°C.[1] Several candidate eutectic electrolyte systems were evaluated for their suitability for this application. One was the LiCl-LiBr-KBr eutectic used at Argonne National Laboratories for high-temperature rechargeable batteries for electric-vehicle applications. This material melts at 321°C and has a reasonable liquidus range. The second electrolyte was the LiBr-KBr-LiF eutectic that was reported to have a melting point of 280°C at a composition of 63.5 m/o LiBr-34.0 m/o KBr-2.5 m/o LiF.[2]

The resistivity of the electrolyte-binder (EB) or separator has a profound impact upon performance as does the deformation properties at operating temperature. In earlier work, the EB compositions were optimized for a number of electrolytes, including the two low-melting ones discussed here.[3] We subsequently measured the resistivities of pellets of a number of EB mixes based on these low-melting electrolytes as a function of MgO content.[4] The deformation properties were also measured for these same materials.[5] Base on the results of these studies, a separator based on the LiBr-KBr-LiF eutectic and containing 25% MgO was selected for used in the two-hour thermal battery.

The thermal properties of this material were subsequently determined, to obtain data for use in Sandia's thermal model for thermal batteries. During the initial determination of the heat capacity of this EB by differential scanning calorimetry (DSC), it was observed that the onset temperature for melting of 313°C was much higher than the literature value of 280°C.[2] The DSC trace showed a major shoulder or a second peak on the primary peak which occurred upon melting. This indicated it was not a eutectic composition.

The present work describes the results of the re-evaluation of the eutectic region of the LiBr-KBr-LiF system using the electrical conductivity of the electrolyte to monitor electrolyte freezing.

Experimental Procedures

Materials - The electrolyte mixes were fused in quartz crucibles from reagent-grade constituents in either a glovebox (<1 ppm each water and oxygen) or in a dry room (<100 ppm water). High-purity LiCl-KCl (Anderson Physics Laboratory, Urbana, IL) was used for reference and calibration purposes.

Conductivity Cell - A schematic diagram of the high-temperature conductivity cell is shown in Figure 1. The type K thermocouples were 1.59-mm in diameter and were stainless-steel sheathed. They were high-accuracy types and were obtained from Omega. The sheathed thermocouples served as the electrodes in the cell. The distance that the sheathed thermocouple was inserted in the alumina tube could be adjusted to change the effective length of the current path and, consequently, the cell constant. The cell constant was determined over a temperature range of 400° to 550°C, with the

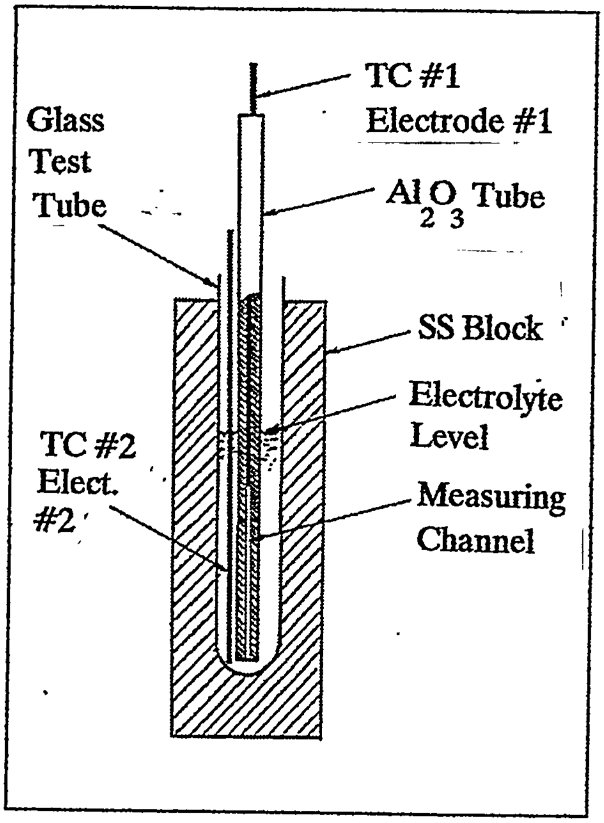

Figure 1. High-Temperature Electrical Conductivity Cell.

median cell constant being 64.5×10^{-4}.

Test Procedure - The cell was maintained in a glovebox during measurement tests and was interfaced to a current source and a digital voltage-measuring oscilloscope. A current-interruption technique, similar to the one reported earlier,[6] was used to measure the resistance of the salt mixture in the alumina tube. The current was periodically interrupted with a special, very-fast switching relay to generate a train of pulses (~130 µs wide) which was applied to the cell. The voltage response of the cell was then monitored with the digital oscilloscope.

The resistivity was measured during both heating and cooling, to ensure that thermal-equilibrium data were obtained. The cell was calibrated using high-purity LiCl-KCl eutectic. Then, the reported values of the LiCl-KCl eutecitic[7] were used to calculate the cell constant.

Results

The compositions of the various melts were adjusted around the reported eutectic values and the freezing points were determined using the conductivity cell. The 33 compositions tested and the observed freezing points are summarized in Table 1. The lightly shaded row is for the Russian "eutectic" and the darker shaded row is for the true eutectic.

Table 1. Composition and Freezing Points of Electrolyte Mixtures Examined in This Study.

Mole %			
LiF	LiBr	KBr	Freezing Pt., °C
0.0	65.1	34.9	331.5
1.0	64.5	34.5	328.8
2.5	63.5	34.0	326.0
3.7	62.7	33.6	325.0
5.5	61.6	33.0	324.5
6.6	60.8	32.6	324.5
8.3	60.7	32.0	324.6
10.4	58.3	31.2	324.6
1.9	63.9	34.2	325.0
12.8	56.8	30.4	325.0
15.1	29.6	55.3	325.0
17.9	28.6	53.5	325.0
20.7	51.6	27.6	325.0
30.2	45.5	24.4	325.2
30.5	45.3	24.2	325.4
33.9	13.0	23.1	325.4
43.4	36.9	19.7	325.4
2.5	63.5	34.0	323.8
6.3	61.0	32.7	324.0
11.3	57.8	30.9	324.0
20.4	51.8	27.8	325.0
2.5	63.5	34.0	324.0
61.0	25.4	13.6	323.5
6.9	60.7	32.5	324.8
6.5	62.6	32.5	324.8
5.2	70.0	24.8	325.0
3.5	80.0	16.5	324.8
14.3	18.2	67.6	323.5
2.5	63.5	34.0	325.8
3.5	80.0	16.5	325.0
2.5	60.0	37.5	324.0
2.5	56.5	41.0	325.0
2.5	50.0	47.5	325.0

Typical traces of resistivity versus temperature are shown in Figure 2 for four electrolyte compositions, including the purported "eutectic" composition (dotted line) and the true

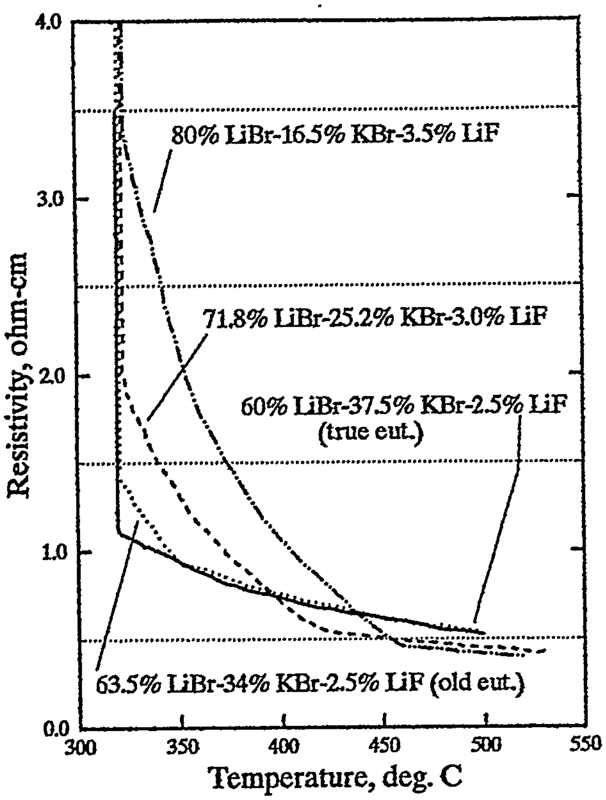

Figure 2. Typical Resistivities of Select Electrolyte Composition as a Function of Temperature.

eutectic (solid line). The first inflection that is observed at the higher temperature in the curves indicates the onset of freezing; that is, the first formation of solid material from the melt. The electrical resistivity rises dramatically upon the completion of freezing of the electrolyte. At the true eutectic composition, there will be only one inflection in the resistivity-temperature trace at the eutectic temperature as the electrolyte freezes. This is readily seen for the solid line in Figure 2.

From the inflection points of the resistivity-temperature curves, one is able to construct a partial phase diagram. This is illustrated in Figure 3 for a mole ratio of F^-/Br^- of 0.0256. Based on the analysis of the resistivity-temperature data for the electrolyte compositions examined in this study, we find that the true eutectic composition is 60.0 m/o LiBr-37.5 m/o KBr-2.5 m/o LiF and that the corresponding melting point is 324.0° ± 0.5°C.

The error in the eutectic reported in reference 2 is most likely a result of impure halides or contamination of the electrolyte during measurements. LiBr is a very hygroscopic material and readily picks up moisture if care is not taken during handling.

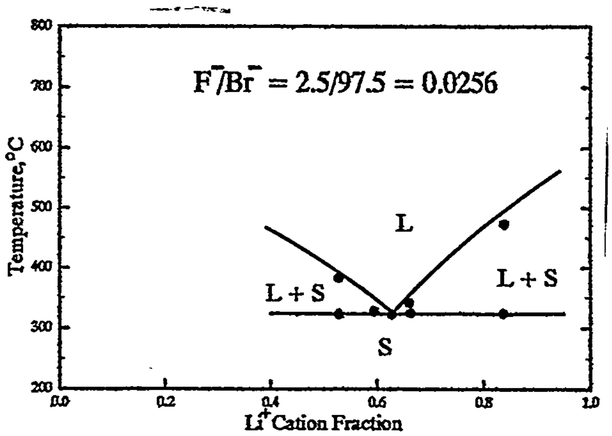

Figure 3. Partial Phase Diagram for LiBr-KBr-LiF System for a Mole Ratio of F^-/Br^- = 0.0256.

We have found that the so-called "eutectic" picked up water almost eight times as fast as did LiCl-KCl eutectic at a dew point of -39°C to -44°C (110 ppm H_2O, avg.). The rate of water absorption increased an order of magnitude when the dew point was increased to about -32°C (~305 ppm H_2O).[8]

We studied the effect of moisture on the observed melting point of the eutectic by deliberate contamination with water by exposure to ambient conditions. At the maximum water level of 3.54 w/o examined, the observed depression in the freezing point was only 5.5°C. This is much lower than the observed difference of 44.5°C that we observed between the freezing points of the actual and purported eutectics. This suggests that there was significant contamination of the electrolyte used in reference 2, either during preparation or during measurement of data, and that moisture contamination was not the dominant factor in the observed lower eutectic temperature.

Discussion

That the true composition of the electrolyte differs from that of the original purported "eutectic" raises a question as to the ramifications for its use in thermal batteries. The data of Figure 2 indicate that the effect upon the electrical resistivity will be beneficial overall. The resistivity for the true eutectic (solid line) is almost identical to that of the old "eutectic" (dotted line) from 500°C down to ~350°C. Below this temperature, the resistivity is lower for the new eutectic, as the liquidus range is now greater. The overall effect will be to enhance the performance of thermal batteries that use the true eutectic composition. This will result in longer activated lives; that is, the batteries will run longer (all other parameters being identical) before electrolyte freezing terminates the discharge.

Conclusions

The melting point of 280°C reported earlier by Russian researchers for the LiBr-KBr-LiF eutectics[2] is grossly in error. They reported a eutectic composition at 63.5 m/o LiBr-34 m/o KBr-2.5 m/o LiF. Using a high-temperature conductivity cell, we measured the electrical resistivity during freezing for 33 electrolyte compositions around the so-called eutectic composition. The sharp inflection in the resistivity-temperature trace allowed us to accurately measure the onset and termination of freezing. We find the true eutectic composition to be 60.0 m/o LiBr-37.5 m/o KBr-2.50 m/o LiF or 53.51 w/o LiBr-45.82 w/o KBr-0.67 w/o LiF; the corresponding melting point is 324.0° ± 0.5°C. Use of the true eutectic composition should enhance the performance of thermal batteries that use it in place of the earlier purported eutectic.

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Acknowledgments

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