



Short communication

New iodide-based molten salt systems for high temperature molten salt batteries

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ABSTRACT

Novel multi-component molten salt systems containing iodides, LiF–LiBr–LiI, LiF–NaBr–LiI, and LiF–LiCl–LiBr–LiI, were investigated for use as electrolytes in high temperature molten salt batteries to improve the discharge rate-capability. The iodide-based molten salts showed higher ionic conductivity ($\sim 3 \text{ S cm}^{-1}$ at 500°C) than conventional LiCl–KCl, and had low enough melting points (below 400°C) that can be used in practical high temperature molten salt batteries. The iodide-based salts showed instability at temperatures higher than 280°C in dried air. The decomposition mechanism of iodide-based molten salts was discussed, and it was found that elimination of oxygen from the environment is effective to stabilize the iodide-based molten salts at high temperatures.

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1. Introduction

For several decades, molten salts have been studied for use as electrolytes in batteries because of their unique features, such as high ionic conductivity, low vapor pressure, and so on. There are two types of molten salt systems: conventional high temperature molten salts and room-temperature molten salts (often called ionic liquids). The high temperature molten salts are one of the candidates for high-power batteries, because of their incomparably higher electrical conductivity, $>1 \text{ S cm}^{-1}$, than any other electrolyte systems. High power batteries using Li–Al alloy anode, FeS_2 cathode and high temperature molten salts, such as a binary LiCl–KCl system and a ternary LiCl–LiBr–KBr system, have been developed for electric vehicle applications vigorously at a research group of Argonne National Laboratory [1,2]. This combination has also been adopted into the so-called thermally activated batteries, or thermal batteries [3], because of their high output power, superior stability in long-term storage, and so on.

The high temperature molten salts show high ionic conductivity only in the liquid state, and thereby should be used at high temperatures above their melting points. Hence the thermally activated batteries consist of two functional parts. One is the “heat generation system” that generates heat and maintains the molten salt in the liquid state, and the other part is the “electrochemical cell system” that generates electric power. The thermally activated batteries can

be stored over 10 years, because the electrolytes are kept in an inactive solid state at ambient temperature. Once the salt is melted and activated at elevated temperatures with an adequate heat source, the battery can produce enormously high output power due to the high electronic conductivity of the molten salt.

The conventional LiCl–KCl molten salt used in thermally activated batteries has an ionic conductivity of 1.85 S cm^{-1} at 500°C and a melting point of 350°C . In the present study, novel molten salt systems with improved ionic conductivity were developed to further increase the output power of the thermally activated batteries. The target of the ionic conductivity was set at 2.0 S cm^{-1} at 500°C . In terms of the working temperature range, the target for the melting point was set in the range of $350\text{--}430^\circ\text{C}$ to be fitted to the conventional design of the heat generation system used for the conventional LiCl–KCl salt.

Several new multi-component salt systems containing bromides and iodides have been investigated to improve the ionic conductivity and to reduce the melting point [4–7]. The ionic conductivities and melting points of some molten salt systems containing bromides have been reported as LiCl–LiBr–KBr (1.23 S cm^{-1} at 500°C , m.p. 310°C), LiF–LiBr–KBr (1.66 S cm^{-1} at 500°C , m.p. 312°C), and LiF–LiCl–LiBr (3.39 S cm^{-1} at 500°C , m.p. 443°C) [4,5], which do not meet our targets described above. In contrast, iodide-containing salt systems seem to be suitable for controlling the balance between the conductivity and the melting point [6,7]. For example, the ionic conductivities and the melting points of some molten salt systems containing iodides have been reported in the literature as: LiF–LiCl–LiI (2.88 S cm^{-1} at 500°C , m.p. 341°C), LiBr–LiCl–LiI (3.83 S cm^{-1} at 500°C , m.p. 368°C), LiCl–LiCl–LiI–KI (1.97 S cm^{-1} at 500°C , m.p. 265°C) [4,5].

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In the present study, we focused on molten salt systems containing iodides, and investigated the ionic conductivities and melting points of new ternary salt systems, LiF–LiBr–LiI and LiF–NaBr–LiI and a quaternary salt system, LiF–LiCl–LiBr–LiI, the ionic conductivity of which has not been reported yet to the best of our knowledge. Their conductivities and melting points were compared with those of other salt systems, LiF–LiBr–KBr, LiF–LiCl–LiBr, and LiCl–KCl, which did not contain iodides. We also investigated the stability of the iodide-based molten salt systems [8], which has not been reported in detail in the literature, and discussed the mechanism for the decomposition of the iodide-based molten salts to improve their stability.

2. Experimental

2.1. Materials

LiF, LiBr and KBr from Kanto Chemicals, LiCl and NaBr from Kojyundo Kagaku, and LiI from Cerac were used as raw materials. All these materials were of reagent grade with purity over 99.9%. After these salts were dried separately at 200 °C under vacuum for 48 h, they were mixed to obtain six kinds of molten salt systems, LiF–LiBr–LiI, LiF–NaBr–LiI, LiF–LiCl–LiBr–LiI, LiF–LiBr–KBr, LiF–LiCl–LiBr, and LiCl–KCl at eutectic compositions as listed in Table 1.

2.2. Ionic conductivity

The cell for ionic conductivity measurements was made of a quartz body and Pt wire electrodes. Prior to measurements, the cell constant K was determined with a 1 mol l⁻¹ KCl solution (111.34 mS cm⁻¹ at 20 °C) and molten salts with well-accepted ionic conductivities, e.g. LiCl–KCl (1.85 S cm⁻¹ at 500 °C) [9]. The ionic conductivity measurements were conducted by the alternating current (AC) impedance method. The ionic conductivity κ was obtained from the resistance R of the sample using the following equation:

$$\kappa = KR^{-1} \quad (1)$$

The preparation of the molten salts and conductivity measurements were conducted in a glove box filled with dried air unless otherwise noted. The dew point in the glove box was maintained below -45 °C. In some experiments, a glove box filled with high purity argon gas (>99.999%, oxygen content: less than 1 ppm) was used to eliminate the effect of oxygen.

2.3. Melting point and thermal stability

The melting points of the molten salts were determined by differential thermal analysis (DTA) and thermal stability was evaluated by thermogravimetry (TG) using a TG–DTA system (Bruker Axs, TG-DTA2000SA). The compositions of the multi-salt systems after measurements were analyzed by ion chromatography (IC, DIONEX, ICS-1500) and inductively coupled plasma analysis (ICP, Thermo Fisher Scientific, icap6300).

Table 1
Eutectic compositions of molten salt systems.

Molten salt system	Composition (mol%)
LiF–LiBr–LiI	13–34–53
LiF–NaBr–LiI	42–7–51
LiF–LiCl–LiBr–LiI	13–18–38–30
LiF–LiBr–KBr	0.7–53.5–45.8
LiF–LiCl–LiBr	21–23–56
LiCl–KCl	59–41

3. Results and discussions

To improve the discharge rate-capability of batteries, the electrolyte should have a high electronic conductivity. In addition, the melting point is another important factor for use in thermally activated batteries. The high temperature molten salt batteries are activated by a proper heat generation system to keep the molten salt being in liquid state. After activated, they work until reaching either the capacity limit of active materials or the solidification temperature of the molten salt electrolyte. The lower limit of this working temperature is the melting point of molten salt electrolyte, and the upper limit is the decomposition temperature of the FeS₂ cathode at around 600 °C [10]. The batteries are thus expected to work within a proper temperature range between the melting point of the salt around 400 °C or lower and the decomposition temperature of the positive electrode material about 600 °C.

The ionic conductivities and the melting points for various salt systems are plotted in Fig. 1. New ternary and quaternary molten salt systems, LiF–LiBr–LiI, LiF–NaBr–LiI and LiF–LiCl–LiBr–LiI, which contained iodides, gave high ionic conductivities of 3.18, 2.90, and 3.32 S cm⁻¹, respectively, at 500 °C, and rather low melting points below 400 °C. These iodide-containing systems meet our targets in ionic conductivity (>2.0 S cm⁻¹ at 500 °C) and melting point (350–430 °C). Their ionic conductivities were much higher than the conventional LiCl–KCl system (1.85 S cm⁻¹ at 500 °C) or a ternary system LiF–LiBr–KBr (1.66 S cm⁻¹ at 500 °C), both of which did not contain iodides. Though a ternary system LiF–LiCl–LiBr did not contain iodides, it showed one of the highest ionic conductivity values (3.29 S cm⁻¹ at 500 °C). However, its melting point was higher than 400 °C [11]. The measured ionic conductivities and melting points of the other systems, LiCl–KCl (1.85 S cm⁻¹ at 500 °C, m.p. 350 °C), LiF–LiBr–KBr (1.66 S cm⁻¹ at 500 °C, m.p. 325 °C), and LiF–LiCl–LiBr (3.29 S cm⁻¹ at 500 °C, m.p. 438 °C), well agreed to those reported in the literature, LiCl–KCl (1.83 S cm⁻¹ at 500 °C, m.p. 354 °C), LiF–LiBr–KBr (1.66 S cm⁻¹ at 500 °C, m.p. 312 °C), and LiF–LiCl–LiBr (3.39 S cm⁻¹ at 500 °C, m.p. 443 °C) [4,5].

From these results, the addition of iodide anions is effective for both increasing the ionic conductivity and lowering the melting point, as reported in the literature [4,5]. These effects are probably brought about by the large ionic radius of iodide anions. Large iodide anions reduce the total stability of the crystal structures of the iodide-based systems in the solid states, and this resulted in lowering their melting points. They also reduce the cation–anion interactions and decrease the number of ion-pairing in the liquid states, which effectively raises the ionic conductivity. These effects are one of our major subjects to be discussed in the future.

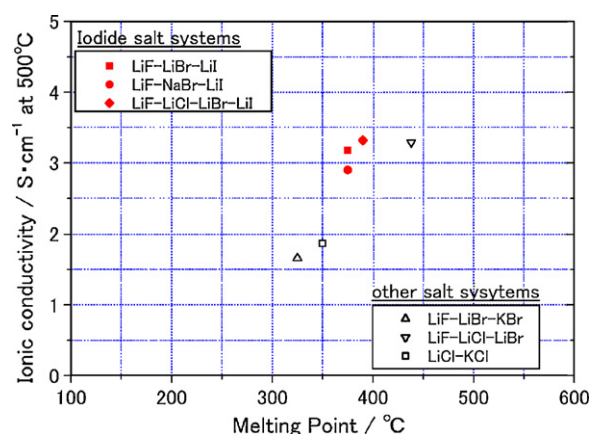


Fig. 1. Relationship between melting point and ionic conductivity at 500 °C.

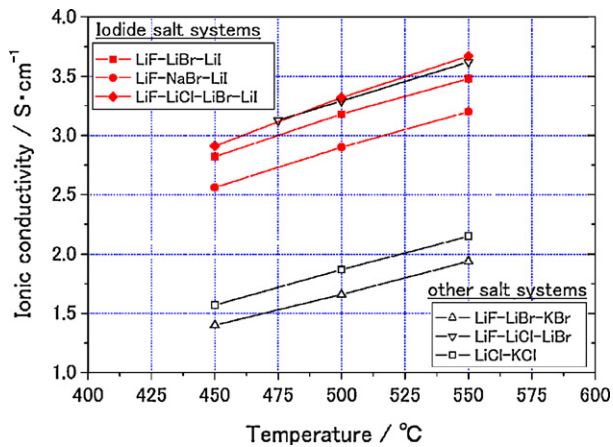


Fig. 2. Temperature dependencies of ionic conductivity of molten salt systems.

The temperature dependencies of the ionic conductivity of various molten salts in the range 450–550 °C are shown in Fig. 2. In the case of the LiF–LiCl–LiBr system, the lower temperature limit was set at 475 °C to avoid solidification. The temperature dependencies of the iodide-based systems are almost the same as that of the conventional LiCl–KCl system. The discharge rate-capability, therefore, can be improved by the use of the iodide systems because of their high ionic conductivity, and a similar temperature-dependence of discharge characteristics would be expected in practical battery applications.

Thermal stability in the range from room temperature to 600 °C was investigated by TG. Fig. 3 shows TG curves for LiF–LiBr–LiI, LiF–NaBr–LiI, and LiF–LiCl–LiBr in air. The LiCl–KCl system showed good stability up to 600 °C; however, a significant weight loss in the range of 280–600 °C was observed for all the iodide-based systems. Fig. 4 shows TG curves for pure LiF, LiCl, LiBr, and LiI samples. No appreciable weight loss was observed for LiF and LiCl up to 600 °C, and for LiBr up to 550 °C. In contrast, a significant weight loss was observed at temperatures above 280 °C for LiI, which clearly indicates that the observed weight loss for the iodide-based molten salts in Fig. 3 originated from the instability of iodides.

The instability of the iodide-based molten salts at high temperatures can be explained as follows:

- (i) The iodide anions in the molten salt are oxidized by oxygen in air to form triiodide ion (I_3^-).

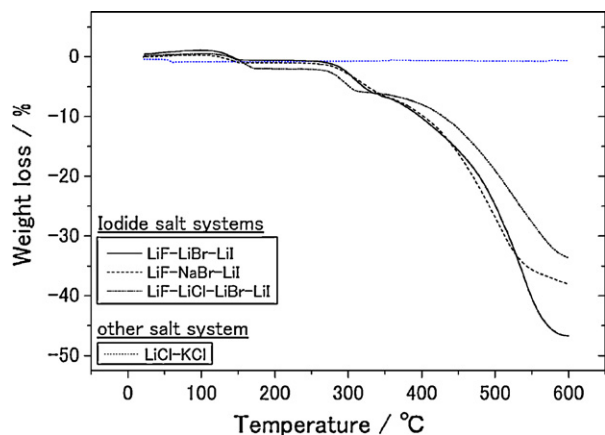


Fig. 3. TG curves of iodide-based salt systems and LiCl–KCl under dried air atmosphere.

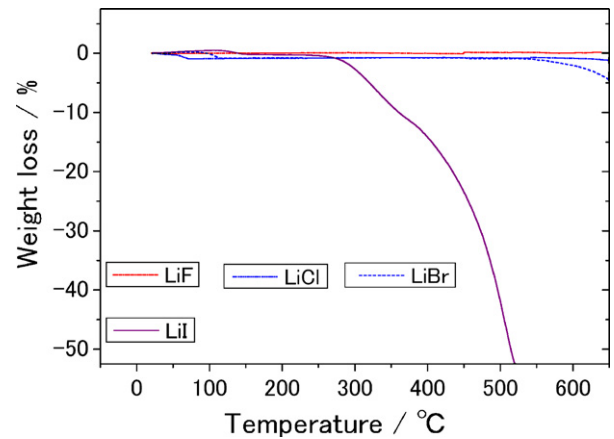


Fig. 4. TG curves of pure LiF, LiCl, LiBr, and LiI under dried air atmosphere.

- (ii) Iodine molecules are formed from the triiodide ions (I_3^-) by the following equilibrium.



Though I^- ions do not have an appreciable vapor pressure, I_2 molecules evaporate at high temperatures (boiling point of I_2 : 184.25 °C). In addition, high temperature accelerates the oxidation rate in Eq. (2), by which the equilibrium in Eq. (3) is shifted to the right-hand side. Hence both the formation and evaporation of I_2 reaction are accelerated at high temperatures.

Based on this mechanism, it is clear that elimination of oxygen from the environment is effective for an improvement of the thermal stability of the iodide-based molten salt systems. To confirm this, TG analysis of the iodide-based systems was conducted under highly pure Ar atmosphere (less than 1 ppm in oxygen content). TG curves obtained for LiF–LiBr–LiI, LiF–NaBr–LiI, and LiF–LiCl–LiBr are shown in Fig. 5. Though a weight loss of several percents at 600 °C was still observed for each iodide-based system, the stability at higher temperatures above 280 °C was greatly improved in the absence of oxygen.

So far molten salt electrolytes had been prepared in a glove box under dried air. To confirm the effect of oxygen more clearly, all processes (weighing, mixing, melting, and crushing) in the preparation of the LiF–LiCl–LiBr–LiI molten salts were conducted under highly pure Ar atmosphere (less than 1 ppm in oxygen content), and the salt compositions were checked by IC and ICP after weighing/mixing and melting/crushing processes. The results are

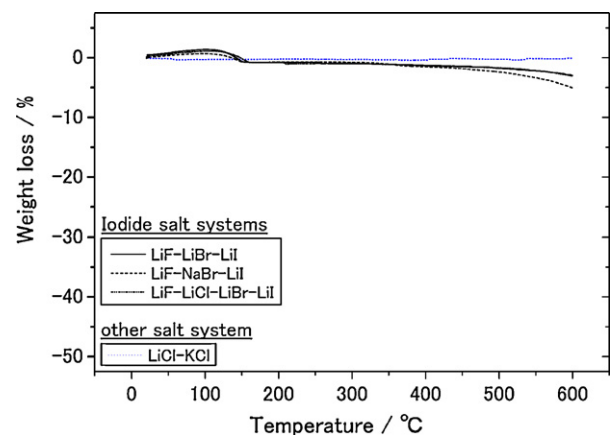


Fig. 5. TG curves of iodide-based salt systems and LiCl–KCl under high purity Ar atmosphere.

Table 2

Compositions after the weighing/mixing and melting/crushing processes for LiF–LiCl–LiBr–LiI under high-purity Ar atmosphere.

Material	Nominal composition (mol%)	Weighing/mixing (IC) (mol%)	Weighing/mixing (ICP) (mol%)	Melting/crushing (IC) (mol%)
LiF	13.5	14.3	14.4	13.4
LiCl	17.9	16.1	17.0	17.5
LiBr	38.6	39.6	38.4	37.6
LiI	30.0	30.1	30.3	31.6

summarized in Table 2. The composition of the LiF–LiCl–LiBr–LiI salt system did not change without any weight loss even after melted at high temperatures under pure Ar atmosphere. It is therefore concluded that the stability of the new iodide-based molten salts can be improved by elimination of oxygen from the atmosphere.

4. Conclusions

To improve discharge rate-capability of high temperature molten salt batteries, new multi-component salt systems containing iodides were investigated as electrolytes. The iodide-based molten salts gave higher ionic conductivities ($\sim 3 \text{ S cm}^{-1}$ at 500°C) than conventional LiCl–KCl system with low enough melting point (below 400°C). However, the iodide-based salts showed instability at high temperatures in dried air. They decomposed at temperatures higher than 280°C owing to the oxidation of iodides by oxygen in dried air. It was found that elimination of oxygen greatly relieves the instability of the iodide-based molten salts. It is therefore concluded that the newly developed iodide-based molten salt systems are promising for use as electrolytes in thermally activated batteries. However, considering practical severe usage of the high temperature molten salt batteries, further investigation on other critical

subjects such as stability during long-term storage and the cost of the salts is needed before used in practical batteries.

References

- [1] T.D. Kaun, M.C. Hash, G.L. Henriksen, A.N. Jansen, D.R. Vissers, Conference: 2. Chilean Lithium Symposium, Santiago (Chile), 1994, pp. 171–192.
- [2] T.D. Kaun, P.A. Nelson, L. Redey, D.R. Vissers, G.L. Henriksen, *Electrochimica Acta* 38 (9) (1993) 1269–1287.
- [3] R.A. Guidotti, The 27th International Technical Conference of the Society for the Advancement of Material and Process Engineering (SAMPE): Diversity into the Next Century, Albuquerque, NM, 1995, pp. 807–818.
- [4] P. Masset, K. Winnacker, *Journal of Power Sources* 160 (1) (2006) 688–697.
- [5] P. Masset, A. Henry, J.Y. Poinso, J.C. Poignet, *Journal of Power Sources* 160 (1) (2006) 752–757.
- [6] P. Masset, J.-Y. Poinso, J.-C. Poignet, The 41st Power Sources Conference, Philadelphia, Pennsylvania, 2004, pp. 137–140.
- [7] P. Masset, S. Schoeffert, J.Y. Poinso, J.C. Poignet, *Journal of the Electrochemical Society* 152 (2) (2005) A405–A410.
- [8] S. Fujiwara, The 43rd Power Sources Conference, Philadelphia, Pennsylvania, 2008, pp. 121–124.
- [9] G.J. Janz, R.P.T. Tomkins, C.B. Allen, J.R. Downey Jr., G.L. Gardner, U. Krebs, S.K. Singer, *Journal of Physical and Chemical Reference Data (JPCRD)* (1975) 871–1178.
- [10] A.G. Ritchie, P. Carter, The 38th Power Sources Conference, Cherry Hill, New Jersey, 1998, pp. 215–218.
- [11] R.A. Guidotti, G.L. Scharrer, F.W. Reinhardt, The 39th Power Sources Conference, Fort Monmouth, New Jersey, 2000, pp. 547–551.