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Novel inorganic ionic liquids possessing low melting temperatures and wide

electrochemical windows:

Binary mixtures of alkali bis(fluorosulfonyl)amides

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Thermal properties of alkali bis(fluorosulfonyl)amides, MFSI (M = Li, Na, K, Rb, Cs), have been investigated. Binary phase diagrams of LiFSI-KFSI and NaFSI-KFSI systems have been constructed. Eutectic point for LiFSI-KFSI is 338 K at $(x_{\text{Li}}, x_{\text{K}}) = (0.45, 0.55)$ and, that for NaFSI-KFSI is 330 K at $(x_{\text{Na}}, x_{\text{K}}) = (0.45, 0.55)$. The electrochemical window of the eutectic LiFSI-KFSI is as wide as 6.0 V at 348 K with the cathode limit being lithium metal deposition. The electrochemical window of the eutectic NaFSI-KFSI is 5.0 V at 340 K with sodium metal deposition at the cathode limit. These new inorganic ionic liquids are highly promising for various electrochemical applications.

Introduction

The authors have been exploring new class of molten salts or ionic liquids which possess wide electrochemical windows and are capable of electrodepositing alkali metals reversibly. We have focused on the salt systems consisting of alkali metal cations and bis(fluoroalkylsulfonyl) amide anions [1-3]. In our previous study, thermal properties of single salts, binary and ternary mixtures of alkali metal bis(trifluoromethylsulfonyl)amides, MTFSI ($M = \text{Li, Na, K, Rb, Cs}$) were investigated [1,2]. Although single MTFSI salts have relatively high melting points (typically over 473 K), it has been found that binary [1] and ternary [2] systems give reasonably low melting points (typically 390-423 K). Among the ternary systems, we have already demonstrated that the $(x_{\text{Li}}, x_{\text{K}}, x_{\text{Cs}}) = (0.20, 0.10, 0.70)$ system is highly promising as an electrolyte for rechargeable lithium metal battery. The conductivity is as high as 14.2 mS cm⁻¹ at 423 K. The electrochemical window is as wide as 5.0 V with cathode limit of lithium metal deposition. A Li/LiTFSI-KTFSI-CsTFSI/LiFePO₄ test cell has been demonstrated to exhibit a good cycle performance [3].

Recently, room temperature ionic liquids consisting of organic cations and bis(fluorosulfonyl)amide, FSI, anions have been attracting much attention. For example,

1-ethyl-3-methylimidazolium bis(fluorosulfonyl)amide, EMImFSI, was reported to have lower viscosity and higher ionic conductivity than those found for EMImTFSI [4]. The EMImFSI and *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)amide, Py13FSI containing LiFSI showed good performance for the application to Li-ion batteries [5]. In addition, gel electrolytes containing LiFSI-organic solvents have been reported to possess excellent properties as gel polymer electrolytes for Li-ion batteries at room temperature [6,7].

In the present study, applying the same idea of our previous study on MTFSI, we focused on the ionic liquids consisting of only alkali metal cations and FSI anions, MFSI ($M = \text{Li, Na, K, Rb, Cs}$). These ionic liquids are unique in the point that they are inorganic compounds. So far, the melting points and the crystal structures of LiFSI, KFSI, CsFSI, and the melting points of NaFSI and RbFSI have been reported [8-10]. However, there is no report concerning binary systems and electrochemical properties of MFSI melts. In this study, the melting and decomposition temperatures of MFSI single salts ($M = \text{Li, Na, K, Rb, Cs}$) were investigated and the phase diagrams of LiFSI-KFSI and NaFSI-KFSI systems were constructed. For the eutectic melts of these two systems, cyclic voltammetry was performed to determine the electrochemical windows.

Experimental Section

KFSI (Dai-ichi Kogyo Seiyaku Co., Ltd.) was used as received. LiFSI and NaFSI were synthesized reacting of KFSI with LiClO_4 (Wako Pure Chemical Industries, purity > 99 %) and NaClO_4 (Aldrich, purity > 98 %), respectively [7]. RbFSI and CsFSI were synthesized by neutralization of HFSI with Rb_2CO_3 and CsCl (Wako Pure Chemical Industries, purity > 99 %), where HFSI was prepared by the reaction of KFSI and HClO_4 beforehand [8].

Melting points and thermal decomposition temperatures of single and mixed salts were measured by means of differential scanning calorimetry (DSC) and thermogravimetry (TG), respectively. For all the samples, scanning rate was 10 K min^{-1} . The transition temperatures were determined in the heating process in order to avoid uncertainty by supercooling. The first measurements were performed for the rate 10 mol% and secondly, further measurements were performed at every 5 mol% for the regions where the low liquidus temperatures were observed in the first measurements.

Electrochemical measurements were performed in a three-electrode system by means of a potentio/galvenostat. Electrochemical windows of the eutectic LiFSI-KFSI

and NaFSI-KFSI melts were measured by cyclic voltammetry. As a working electrode material, a glassy carbon rod (3 mm ϕ) was used to investigate the anode limit and a nickel plate (6 mm ϕ , $t = 0.1$ mm) was used for measuring the cathode limit. As counter and reference electrode materials, lithium metals were used for the LiFSI-KFSI melt and sodium metals were used for the NaFSI-KFSI melt.

Results and discussion

Melting and thermal decomposition temperatures of single MFSI salts

The melting and thermal decomposition temperatures of single MFSI salts summarized in Table 1 were determined by DSC and TG, respectively. The melting temperatures determined in this study are in good agreement with the previously reported data also listed in Table 1 for comparison [8]. The melting temperatures of MFSIs are 373 K or above. The thermal decomposition temperatures are above 413 K except for LiFSI. Nevertheless the melting temperature of LiFSI was able to be determined owing to its slow decomposition rate.

Phase diagrams of LiFSI-KFSI and NaFSI-KFSI systems

Binary phase diagrams of LiFSI-KFSI and NaFSI-KFSI systems were constructed from the DSC data for various binary mixtures. Figure 1 shows the phase diagram of LiFSI-KFSI system. The phase diagram is a simple eutectic type. The eutectic point is found at $(x_{\text{Li}}, x_{\text{K}}) = (0.45, 0.55)$ with the temperature of 338 K. Figure 2 shows the phase diagram of NaFSI-KFSI system, again a simple eutectic type. The eutectic point is found at $(x_{\text{Na}}, x_{\text{K}}) = (0.45, 0.55)$, being the same composition of KFSI in the above, with the temperature of 330 K. For both the systems, eutectic temperatures are much lower than the melting temperatures of constituent single salts.

Electrochemical windows of LiFSI-KFSI and NaFSI-KFSI eutectic melts

Electrochemical windows were measured for the eutectic LiFSI-KFSI and NaFSI-KFSI systems at temperatures 10 K higher than the melting points. As for the LiFSI-KFSI eutectic melt, the experimental temperature, 348 K, was higher than the decomposition temperature of solid LiFSI salt, 340 K. The weight loss was observed for solid LiFSI at 340 K after several hours in the long-term TG measurement. However,

we found that the eutectic melt was stable enough for conducting electrochemical measurements for more than several hours. To confirm this, a TG measurement was performed for the eutectic melt at 348 K. The weight loss was hardly observed for 8 hours. Figure 3 shows a cyclic voltammogram in the LiFSI-KFSI eutectic melt at 348 K. A pair of cathodic and anodic currents is observed at 0 V vs. Li^+/Li on a nickel electrode, which is interpreted as the deposition/dissolution of lithium metal. An anodic current is observed at 6.0 V vs. Li^+/Li on a glassy carbon electrode, which is attributed to oxidation of FSI anion. The electrochemical window is determined as 6.0 V, when the limiting potentials are defined as the potential at a current density of 0.1 mA cm^{-2} . Although this melt may be used as electrolytes for lithium rechargeable batteries and electrodepositions of reactive metals, the temperature range existing as a stable liquid is limited. If the melting point can be lowered by introducing the third component such as CsFSI, the melt is promising for practical applications.

Figure 4 show a cyclic voltammogram in the NaFSI-KFSI eutectic melt at 340 K. In the same manner as above, a pair of cathodic and anodic currents is observed at 0 V vs. Na^+/Na on a nickel electrode. This current corresponds to the deposition/dissolution of sodium metal. An anodic current, which is explained by the oxidation of FSI anion, is observed at 5.0 V vs. Na^+/Na at a glassy carbon electrode.

Thus, the electrochemical window in the same definition as above is determined as 5.0

V. This melt is expected to be used in practical applications, for examples, sodium rechargeable batteries like Na/S and Na/NiCl₂ batteries owing to its low melting point, high sodium ion content and capability of sodium metal deposition/dissolution.

Conclusions

Thermal properties of MFSI (M = Li, Na, K, Rb, Cs) have been investigated. The binary phase diagrams have been constructed for the LiFSI-KFSI and NaFSI-KFSI systems. The eutectic point for LiFSI-KFSI is 338 K at (x_{Li} , x_{K}) = (0.45, 0.55) and that for NaFSI-KFSI is 330 K at (x_{Na} , x_{K}) = (0.45, 0.55). The electrochemical window of LiFSI-KFSI eutectic melt is 6.0 V at 348 K and that of NaFSI-KFSI eutectic melt is 5.0 V at 340 K. These new inorganic ionic liquids are promising electrolytes for various electrochemical applications.

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Figure Captions

Figure 1. The phase diagram of LiFSI-KFSI system.

Figure 2. The phase diagram of NaFSI-KFSI system.

Figure 3. A combined cyclic voltammogram at a Ni electrode (negative potential region, $-0.8 \text{ V} < E < 3.0 \text{ V}$) and a glassy carbon electrode (positive potential region, $3.0 \text{ V} < E < 7.0 \text{ V}$) in LiFSI-KFSI eutectic melt ($x_{\text{LiFSI}} = 0.45$) at 348 K.

Figure 4. A combined cyclic voltammogram at a Ni electrode (negative potential region, $-0.5 \text{ V} < E < 3.0 \text{ V}$) and a glassy carbon electrode (positive potential region, $3.0 \text{ V} < E < 6.7 \text{ V}$) in NaFSI-KFSI eutectic melt ($x_{\text{NaFSI}} = 0.45$) at 340 K.

Table 1. Melting temperature, T_m , reported melting temperature T_m^R [8], and decomposition temperatures, T_d , of MFSI single salts.

	T_m/K	T_m^R/K	T_d/K
LiFSI	403	397-401	340
NaFSI	379	385-390	413
KFSI	369	-	453
RbFSI	368	365-369	435
CsFSI	386	385-389	443

Figure 1. The phase diagram of LiFSI-KFSI system.

Figure 2. The phase diagram of NaFSI-KFSI system.

Figure 3. A combined cyclic voltammogram at a Ni electrode (negative potential region, $-0.8 \text{ V} < E < 3.0 \text{ V}$) and a glassy carbon electrode (positive potential region, $3.0 \text{ V} < E < 7.0 \text{ V}$) in LiFSI-KFSI eutectic melt ($x_{\text{LiFSI}} = 0.45$) at 348 K.

Figure 4. A combined cyclic voltammogram at a Ni electrode (negative potential region, $-0.5 \text{ V} < E < 3.0 \text{ V}$) and a glassy carbon electrode (positive potential region, $3.0 \text{ V} < E < 6.7 \text{ V}$) in NaFSI-KFSI eutectic melt ($x_{\text{NaFSI}} = 0.45$) at 340 K.