

New inorganic ionic liquids possessing low melting temperatures and wide electrochemical windows: Ternary mixtures of alkali bis(fluorosulfonyl)amides

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Four kinds of ternary phase diagrams of alkali bis(fluorosulfonyl)amides, LiFSA-NaFSA-KFSA, LiFSA-NaFSA-CsFSA, LiFSA-KFSA-CsFSA and NaFSA-KFSA-CsFSA, have been constructed. All the ternary systems possess the only one eutectic point around equimolar composition with the temperature of 309-318 K. The electrochemical window of the eutectic LiFSA-KFSA-CsFSA ($(x_{\text{Li}}, x_{\text{K}}, x_{\text{Cs}})=(0.30, 0.35, 0.35)$) is as wide as 5.4 V at 323 K with the cathode limit being lithium metal deposition. The electrochemical window of the eutectic NaFSA-KFSA-CsFSA ($(x_{\text{Na}}, x_{\text{K}}, x_{\text{Cs}})=(0.40, 0.25, 0.35)$) is 4.9 V at 323 K with sodium metal

deposition as the cathode limit reaction.

Keywords: Bis(fluorosulfonyl)amide; Molten salt; Ionic liquid; Phase diagram; Electrochemical window

1. Introduction

We have been investigating new class of ionic liquids or molten salts which possess high thermal and electrochemical stability and are capable of electrodepositing alkali metals reversibly. Firstly, we focused on binary [1,2] and ternary [3] mixtures of alkali bis(trifluoromethylsulfonyl)amides, MTFSA (M = Li, Na, K, Rb, Cs). We found that some selected binary and ternary mixtures of MTFSAs give reasonably lower melting temperatures (typically 390-423 K) than constituent single salts (typically over 473 K). In addition, it was revealed that some selected mixed melts possess more desirable properties as electrolytes than the single salts [2]. As one of the promising fields of application, the LiTFSA-KTFSA-CsTFSA ternary melt ($(x_{\text{LiTFSA}}, x_{\text{KTFSA}}, x_{\text{CsTFSA}}) = (0.20, 0.10, 0.70$ in mole fraction)) was tested as an electrolyte for a rechargeable lithium metal battery, in which a Li/LiFePO₄ cell exhibited a good cycle performance at 423 K [4].

Secondly, in order to lower melting temperatures, we aimed at alkali bis(fluorosulfonyl)amides, MFSAs. For some MFSAs, the route of synthesis and the crystal structures have been studied [5-8]. Especially, LiFSA is expected to be used as electrolyte salts for lithium batteries and has been useful as an electrolyte salt for lithium batteries with PEO-based gel [9,10], EC/DMC [11] and ionic liquid [12] electrolytes for lithium ion batteries with LiFePO₄ cathodes. Table 1 summarizes the melting and decomposition temperatures of MFSAs single salts [13]. The melting temperatures are around 373 K, much lower than those for MTFSA single salts. However, the decomposition temperatures are also low (typically, 413-443 K). We investigated ten

kinds of MFSA binary mixtures as shown in Table 2 [14]. All the binary systems exhibit a simple eutectic type. Their eutectic temperatures range from 325 K to 360 K, which is lower than the melting temperatures of constituent single salts. According to the electrochemical measurements, it was revealed that the eutectic LiFSA-KFSA and NaFSA-KFSA melts possess wide electrochemical windows of over 5 V with the cathode limits of lithium metal deposition and sodium metal deposition, respectively [14]. These ionic liquids are unique in the point that they contain only inorganic compounds. Since they contain only alkali metal cations, they are essentially free from electrochemical instability originating from organic cations. Moreover, the absence of organic solvent/ions offers very interesting opportunities in investigating the effects of a solid-electrolyte interface and/or stability of the eutectic electrolyte in contact with active electrodes in battery applications.

Since the eutectic temperatures of ternary systems are expected to be lower than those of binary systems, thermal properties of four kinds of MFSA ternary systems, LiFSA-NaFSA-KFSA, LiFSA-NaFSA-CsFSA, LiFSA-KFSA-CsFSA and NaFSA-KFSA-CsFSA, were investigated in this study. Furthermore, the electrochemical windows and ionic conductivities were measured for selected eutectic melts, LiFSA-KFSA-CsFSA and NaFSA-KFSA-CsFSA.

2. Experimental

MFSA salts were prepared in the same manner as given in the previous report [6]. Several

important points and new procedures are described here. KFSA (Dai-ichi Kogyo Seiyaku Co., Ltd., purity > 99 %, Li < 0.01 ppm, Na < 6 ppm) was used after drying in a vacuum line at 353 K. LiFSA and NaFSA were synthesized by the reactions of KFSA with LiClO₄ (Wako Pure Chemical Industries, purity > 0.99 in weight) and NaClO₄ (Aldrich, purity > 0.98 in weight) in acetonitrile (Wako Pure Chemical Industries, purity > 99.5 %), respectively. CsFSA was synthesized by the reaction of HFSA with CsCl (Wako Pure Chemical Industries, purity > 0.99 in weight) in nitromethane (Wako Pure Chemical Industries, purity > 99 %), where HFSA was prepared by the reaction of KFSA and HClO₄ beforehand. In order to remove water, LiFSA and NaFSA were added thionyl chloride (Wako Pure Chemical Industries, purity > 99 %) and stirred for 1 hour under N₂ atmosphere. The samples were filtered off under vacuum and washed by dichloromethane (Wako Pure Chemical Industries, purity > 99 %) three times. After that, the residual dichloromethane were dried under vacuum at 323 K. CsFSA was recrystallized twice in tetrahydrofuran (Wako Pure Chemical Industries, purity > 99 %). The products, LiFSA, NaFSA and CsFSA were identified by Raman spectroscopic analysis and elemental analysis. Ternary mixtures of (Li,Na,K), (Li,Na,Cs), (Li,K,Cs) and (Na,K,Cs) were prepared by thoroughly mixing the constituent single salts using a mortar and a pestle.

Melting and thermal decomposition temperatures of the ternary mixtures were measured by means of a differential scanning calorimeter (DSC-60 (Shimadzu Co., Ltd.)) and a thermogravimeter (DTG-60/60H (Shimadzu Co., Ltd.)), respectively. Observations of the phase transitions were conducted for mixtures at intervals of 0.10 in the mole fraction range of 0.10-0.90.

Samples were placed in aluminum sealed pans. The DSC measurements were performed at rate of 2 K min⁻¹ under N₂ atmosphere. The transition temperatures were determined in the heating process in order to avoid uncertainty by supercooling. The phase diagrams of the ternary MFSA systems were constructed by plotting the temperatures of endothermic peaks found in the DSC curves against the compositions of the salts.

Electrochemical windows of the eutectic LiFSA-KFSA-CsFSA and NaFSA-KFSA-CsFSA melts were measured by means of cyclic voltammetry. The limiting potentials are defined as the potentials at a current density of 0.1 mA cm⁻². The electrochemical measurements were performed by the three-electrode method in an argon-filled glove box. A copper disk (6 mm in diameter, 0.1 mm in thickness) or a glassy carbon rod (3 mm in diameter) was used for the working electrode according to the scanning potential range. Lithium foil was used for the counter and reference electrodes in LiFSA-KFSA-CsFSA melts. In the cases of NaFSA-KFSA-CsFSA, sodium metal lump was pressed to make a foil for the counter and reference electrodes. The scan rate for the cyclic voltammetry was 10 mV s⁻¹.

Ionic conductivities of the eutectic LiFSA-KFSA-CsFSA melts were measured with an AC impedance method using an electrochemical interface and impedance analyzer (IVIUMSTAT, Ivium technologies). The measurement device was composed of Pyrex glass container, platinum disk electrodes connected with copper bar and a thermocouple covered with a Pyrex glass tube. The cell constant was determined by the measurement of a KCl standard solution at 291 K and LiNO₃-KNO₃ eutectic molten salt at 413-573 K.

3. Results and Discussion

3.1 Phase diagrams of MFSA ternary systems

The ternary phase diagrams constructed for LiFSA-NaFSA-KFSA, LiFSA-NaFSA-CsFSA, LiFSA-KFSA-CsFSA and NaFSA-KFSA-CsFSA systems are shown in Figures 1-4. In the diagrams, liquidus surfaces are shown as a contour map. Temperatures are given in K and the following abbreviations are used: E_B , binary eutectic point; E_T , ternary eutectic point.

Figure 1 shows the ternary phase diagram of LiFSA-NaFSA-KFSA system. This system is classified into a simple eutectic type as expected by the results of the binary mixtures. The ternary eutectic point is found at $(x_{Li}, x_{Na}, x_K) = (0.30, 0.40, 0.30)$ with the temperature of 318 K. The eutectic composition was not determined more accurately because similar DSC traces were observed at the compositions around $(x_{Li}, x_{Na}, x_K) = (0.30, 0.40, 0.30)$. Figures 2-4 show the ternary phase diagrams of LiFSA-NaFSA-CsFSA, LiFSA-KFSA-CsFSA and NaFSA-KFSA-CsFSA systems, respectively. These three systems are also classified into a simple eutectic type as expected. Table 3 summarizes the compositions and temperatures for eutectic points of these systems. It is found that the ternary MFSA systems possess the only one eutectic point at around equimolar composition with the temperatures of 309-318 K, which are lower than those of constituent binary subsystems. In this study, we constructed the basic phase diagrams in order to investigate

physicochemical properties of these alkali metal salts at the lowest possible melting temperatures.

Construction of detailed phase diagrams is interesting future task.

The thermal decomposition temperatures of all the eutectic mixtures were measured by thermogravimetric analysis. It was confirmed that the decomposition temperature of each ternary system is determined by the lowest decomposition temperature of the constituent single salt. Thus, there is no effect of the mixing of MFSA salts on the decomposition temperatures.

According to our previous study [13], the thermal decomposition temperature of LiFSA is as low as 343 K. Concerning the four binary eutectic mixtures containing LiFSA, the eutectic temperatures range from 335 to 349 K, as shown in Table 2. Thus, the binary systems have no or very narrow temperature ranges in which the melts are stable as liquid. For the ternary systems, however, they possess the eutectic temperatures of 311-318 K, indicating that the temperature ranges of stable liquid are extended. Moreover, all the ternary MFSA eutectic melts are unique in the point that they consist of entirely inorganic ions. To the best of our knowledge, the eutectic temperatures for ternary MFSA melts are lower than melting temperatures for any other inorganic ionic liquids or molten salts containing alkali metal cations.

3.2 Electrochemical windows of selected eutectic melts

In our previous study, the order of deposition potential was determined to be $\text{Na} > \text{Li} > (\text{K}, \text{Rb}, \text{Cs})$ for binary MTFSA melts [2]. Concerning the binary MFSA melts, it was assumed that the

deposition potential of sodium was also more positive than that of lithium. Thus, in order to deposit lithium from the ternary MFSA melts, NaFSA should not be included as a constituent salt based on this assumption. Therefore, the LiFSA-KFSA-CsFSA eutectic melt was selected for electrochemical measurement. On the other hand, it is expected that the deposition of sodium always occurs at the most positive potential in the melts containing sodium ion. Considering the relatively poor thermal stability of LiFSA, the NaFSA-KFSA-CsFSA eutectic melt was selected as the electrolyte for sodium deposition avoiding lithium salt in the system.

Figure 5 shows cyclic voltammograms in the LiFSA-KFSA-CsFSA eutectic melt at 323 K. A pair of cathodic and anodic currents is observed at 0 V vs. Li^+/Li on a copper electrode. These cathodic and anodic currents are interpreted as the deposition of lithium metal and its dissolution, respectively. On the other hand, an anodic current is observed at 5.4 V vs. Li^+/Li on a glassy carbon electrode. This anodic current is considered to correspond to the irreversible oxidation of FSA anion, though more studies are required to elucidate the detail of this reaction. The electrochemical window is determined as 5.4 V at 323 K, when the limiting potentials are defined as the potential at a current density of 0.1 mA cm^{-2} . This new inorganic ionic liquid is highly promising as an electrolyte for lithium secondary batteries due to its high content of lithium ion, reversible electrodeposition of lithium metal and wide electrochemical window.

Figure 6 shows cyclic voltammograms in the NaFSA-KFSA-CsFSA eutectic melt at 323 K. A pair of cathodic and anodic currents is observed at 0 V vs. Na^+/Na on a copper electrode. These cathodic and anodic currents are interpreted as the deposition of sodium metal and its dissolution,

respectively. An anodic current is observed at 4.9 V vs. Na^+/Na on a glassy carbon electrode. This anodic current is considered to correspond to the oxidation of FSA anion as in the case of LiFSA-KFSA-CsFSA eutectic melt. The electrochemical window in the same definition as above is determined as 4.9 V at 323 K. The NaFSA-KFSA-CsFSA eutectic melt is full of promise as an electrolyte for sodium secondary batteries for its high content of sodium ion, reversible electrodeposition of sodium metal and wide electrochemical window. This melt has another advantage of higher thermal stability compared with the LiFSA-KFSA-CsFSA eutectic melt.

Figure 7 shows ionic conductivity of LiFSA-KFSA-CsFSA eutectic melt at 313-338 K. At 323 K, the conductivity of this melt is $0.41 \text{ mS} \cdot \text{cm}^{-1}$, which is much lower than that of the salt mixture containing an organic cation-based ionic liquids such as $\text{PY}_{14}\text{FSA-LiFSA}$ [12]. However, the absence of organic solvent/ions will offer very interesting opportunities in investigating the effects of a solid-electrolyte interface and/or stability of the eutectic electrolyte in contact with active electrodes in battery applications.

4. Conclusions

The ternary phase diagrams were constructed for LiFSA-NaFSA-KFSA, LiFSA-NaFSA-CsFSA, LiFSA-KFSA-CsFSA and NaFSA-KFSA-CsFSA systems and the ternary eutectic temperatures and compositions were determined. All the ternary systems possess the only one eutectic point around equimolar composition with the temperatures of 309-318 K. These

temperatures are lower than melting temperatures for any other inorganic ionic liquids or molten salts containing alkali metal cations. The electrochemical window of the eutectic LiFSA-KFSA-CsFSA ($(x_{\text{Li}}, x_{\text{K}}, x_{\text{Cs}})=(0.30, 0.35, 0.35)$) was determined to be 5.4 V at 323 K with the cathode limit identified as lithium metal deposition. The electrochemical window of the eutectic NaFSA-KFSA-CsFSA ($(x_{\text{Na}}, x_{\text{K}}, x_{\text{Cs}})=(0.40, 0.25, 0.35)$) was 4.9 V at 323 K with sodium metal deposition as the cathode limit reaction. The results of this study evidenced the possibility to prepare new ionic liquids starting from alkali salts that exhibit much higher melting points. The new inorganic ionic liquids of ternary MTFSA are expected to be used for electrochemical applications such as lithium and sodium secondary batteries.

Acknowledgement

This work was financially supported by a Grant in Aid for Scientific Research for Priority Area “Science of Ionic Liquids” from Japanese Ministry of Education, Culture, Sports, Science and Technology.

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Table 1. The melting and decomposition temperatures of MFSA single salts [13].

	T_m / K	T_d / K
LiFSA	403*	343
NaFSA	379	413
KFSA	375	423
RbFSA	368	435
CsFSA	386	443

* The decomposition rate of LiFSA was slow enough to measure its melting point by DSC at 10 K·min⁻¹[13].

Table 2. The eutectic temperatures and compositions of MFSA binary systems [13].

System	Composition	T / K
LiFSA-NaFSA	$x_{\text{Li}} = 0.40, x_{\text{Na}} = 0.60$	349
LiFSA-KFSA	$x_{\text{Li}} = 0.41, x_{\text{K}} = 0.59$	341
LiFSA-RbFSA	$x_{\text{Li}} = 0.38, x_{\text{Rb}} = 0.62$	337
LiFSA-CsFSA	$x_{\text{Li}} = 0.47, x_{\text{Cs}} = 0.53$	335
NaFSA-KFSA	$x_{\text{Na}} = 0.56, x_{\text{K}} = 0.44$	334
NaFSA-RbFSA	$x_{\text{Na}} = 0.50, x_{\text{Rb}} = 0.50$	328
NaFSA-CsFSA	$x_{\text{Na}} = 0.47, x_{\text{Cs}} = 0.53$	325
KFSA-RbFSA	$x_{\text{K}} = 0.31, x_{\text{Rb}} = 0.69$	354
KFSA-CsFSA	$x_{\text{K}} = 0.54, x_{\text{Cs}} = 0.46$	336
RbFSA-CsFSA	$x_{\text{Rb}} = 0.65, x_{\text{Cs}} = 0.35$	360

Table 3. The eutectic temperatures and compositions of MFSA ternary systems.

System	Composition	T / K
LiFSA-NaFSA-KFSA	$E: x_{\text{Li}} = 0.30, x_{\text{Na}} = 0.40, x_{\text{K}} = 0.30$	318
LiFSA-NaFSA-CsFSA	$E: x_{\text{Li}} = 0.30, x_{\text{Na}} = 0.40, x_{\text{Cs}} = 0.30$	311
LiFSA-KFSA-CsFSA	$E: x_{\text{Li}} = 0.30, x_{\text{K}} = 0.35, x_{\text{Cs}} = 0.35$	312
NaFSA-KFSA-CsFSA	$E: x_{\text{Na}} = 0.40, x_{\text{K}} = 0.25, x_{\text{Cs}} = 0.35$	309

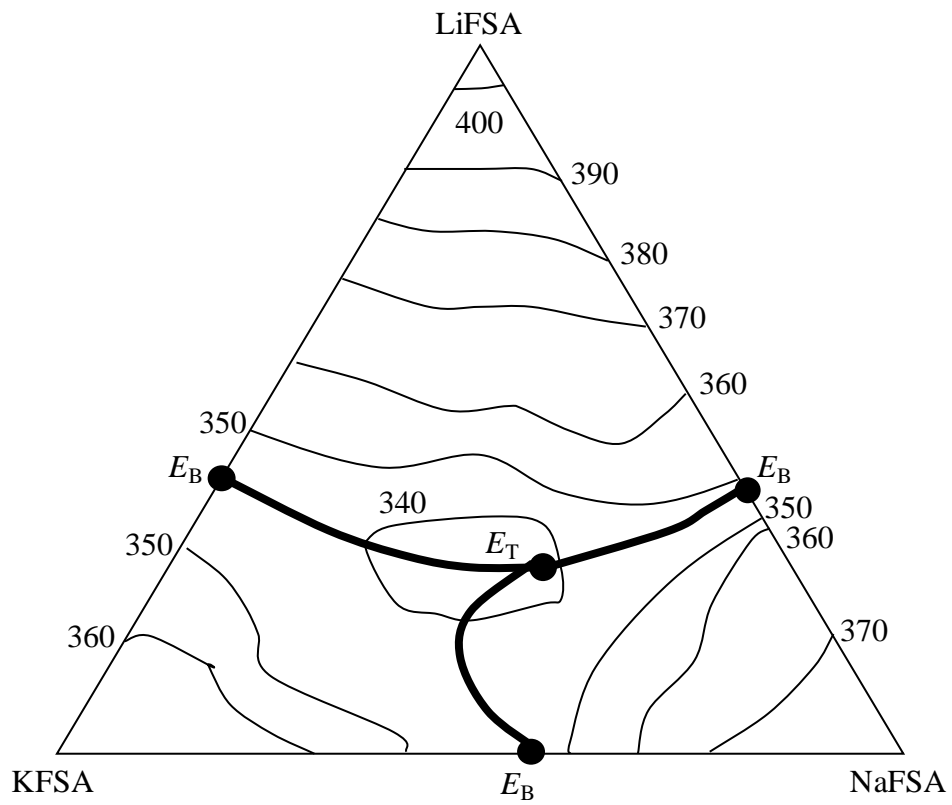


Figure 1. Phase diagram of LiFSA-NaFSA-KFSA system.

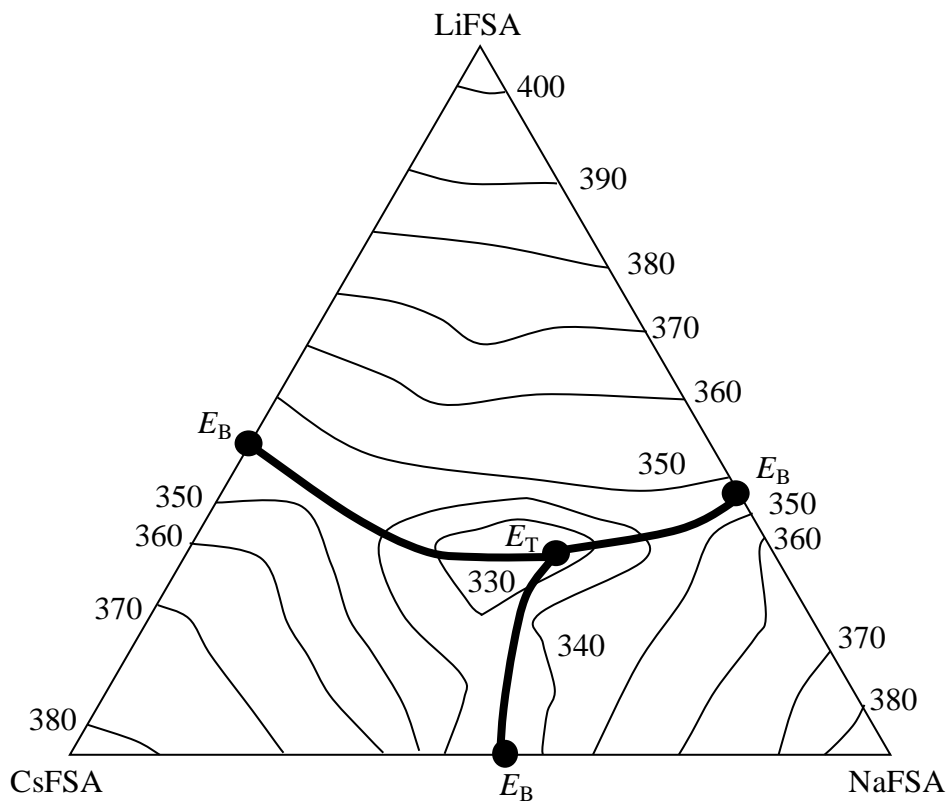


Figure 2. Phase diagram of LiFSA-NaFSA-CsFSA system.

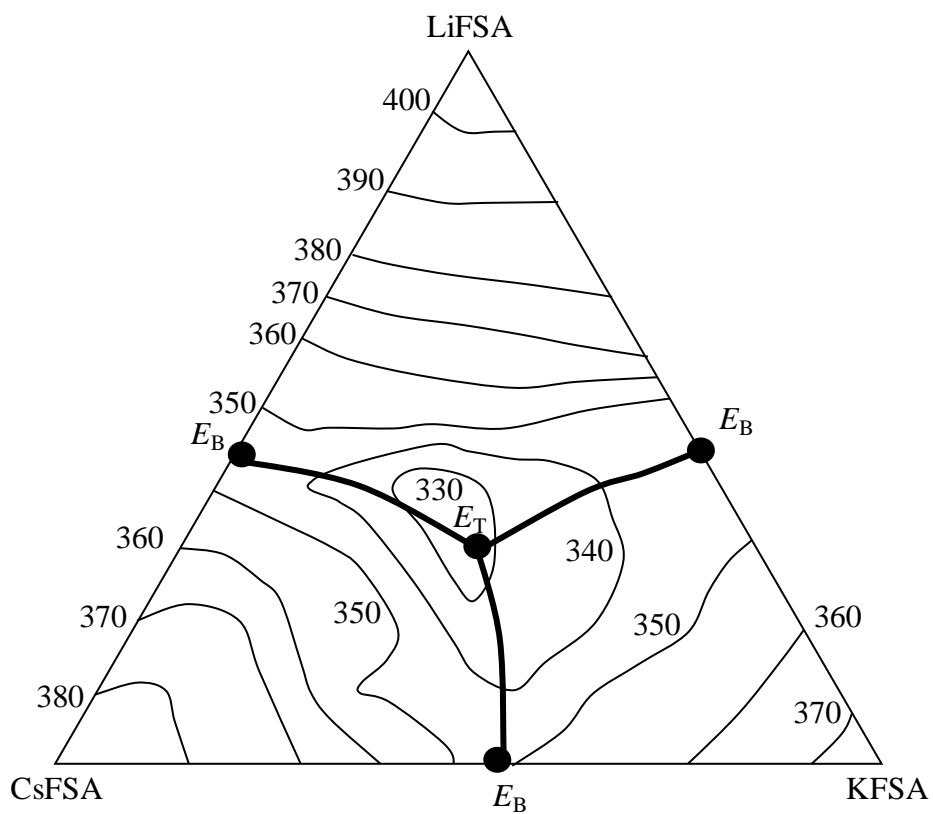


Figure 3. Phase diagram of LiFSA-KFSA-CsFSA system.

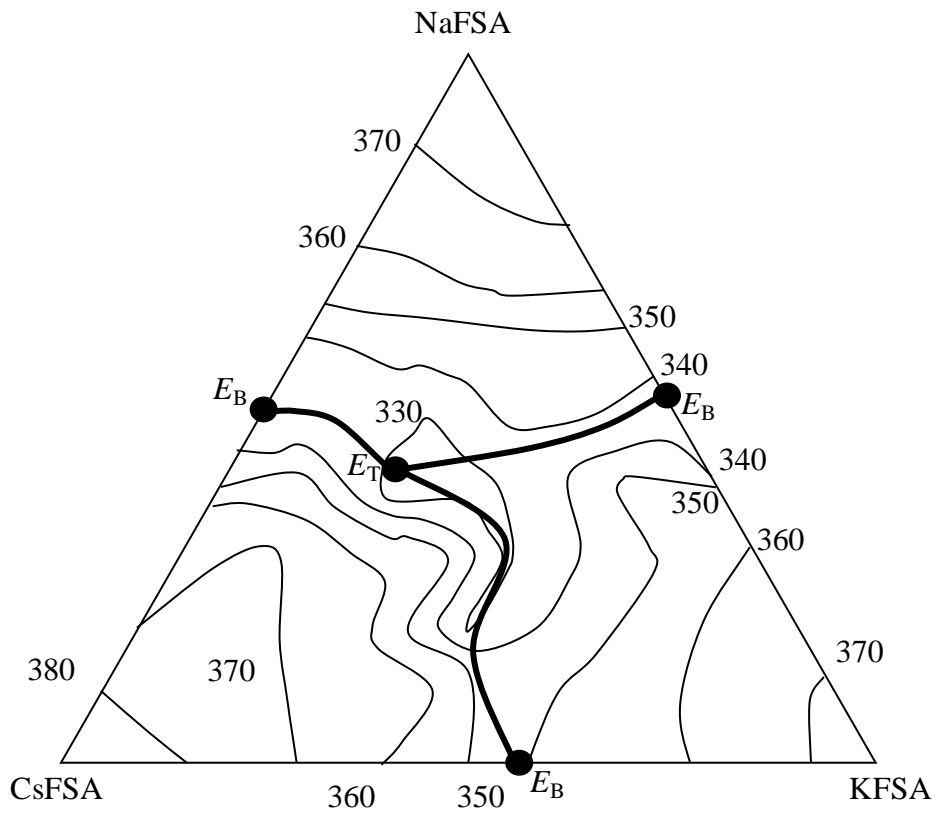


Figure 4. Phase diagram of NaFSA-KFSA-CsFSA system.

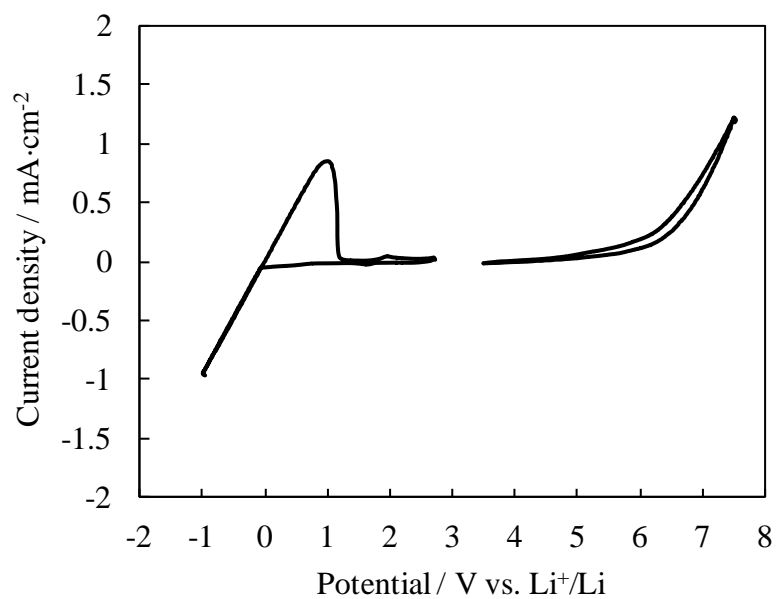


Figure 5. A combined cyclic voltammogram at a Cu electrode (negative potential region, -1.0 – 2.7 V) and a glassy carbon electrode (positive potential region, 2.8 – 7.5 V) in LiFSA-KFSA-CsFSA eutectic melt at 323 K (Scan rate: 10 m V s⁻¹).

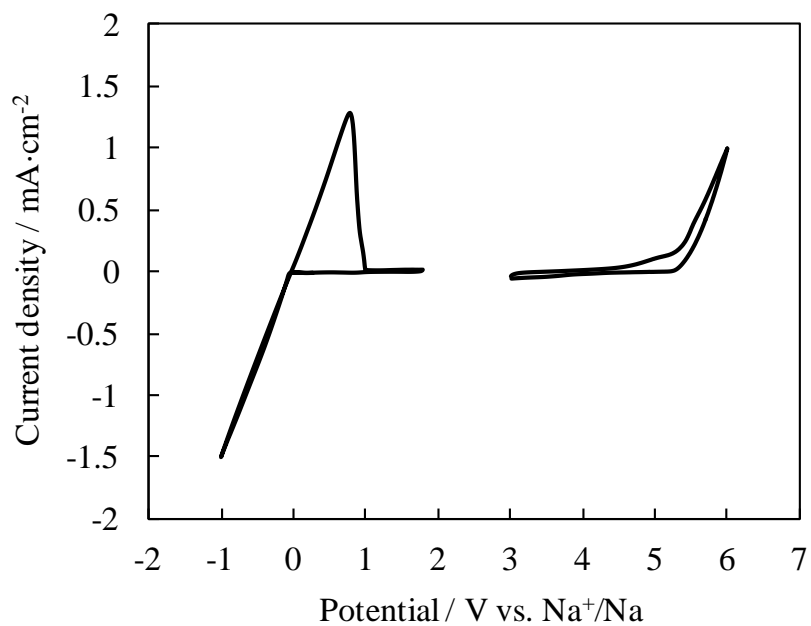


Figure 6. A combined cyclic voltammogram at a Cu electrode (negative potential region, -1.0 – 1.8 V) and a glassy carbon electrode (positive potential region, 3.0 – 6.0 V) in NaFSA-KFSA-CsFSA melt at 323 K (Scan rate: 10 m V s⁻¹).

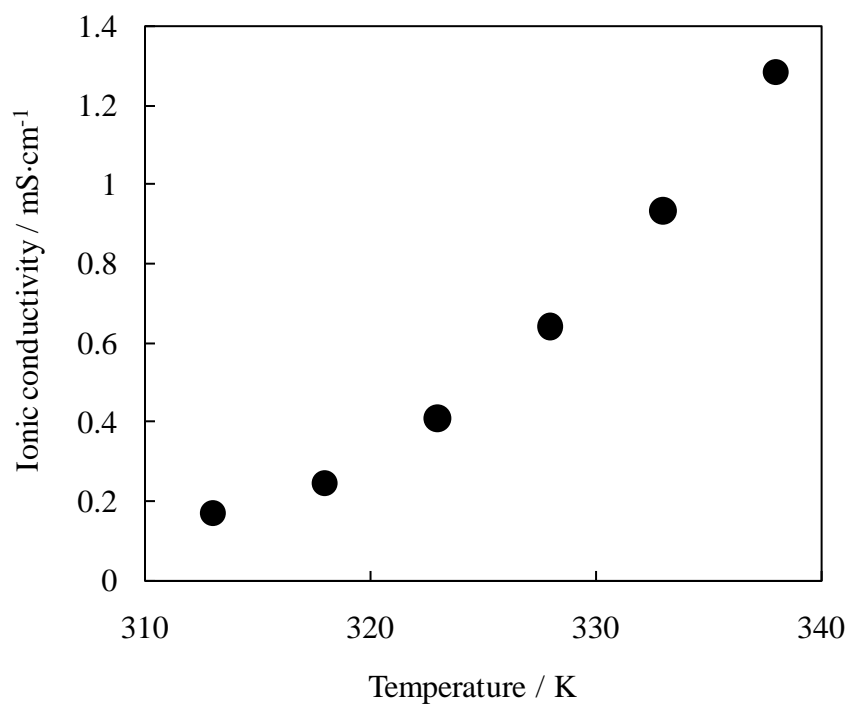


Figure 7. Temperature dependence of ionic conductivity in LiFSA-KFSA-CsFSA eutectic melt at 313-338 K.

Highlights

- Four ternary phase diagrams of alkali bis(fluorosulfonyl)amides were constructed.
- These ternary systems possess eutectic temperature at as low as 309-318 K.
- Electrochemical window of LiFSA-KFSA-CsFSA is as wide as 5.4 V at 323 K.
- Electrochemical window of NaFSA-KFSA-CsFSA is 4.9 V at 323 K.
- These inorganic ILs are promising as electrolytes for Li and Na batteries.