Thermal Properties of Alkali Bis(fluorosulfonyl)amides and Their Binary Mixtures

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Thermal properties of alkali bis(fluorosulfonyl)amides, Mf_2N (M = Li, Na, K, Rb, Cs), have been examined as well as their binary mixtures. The eutectic compositions were determined by Tammann's rule, and the phase diagrams have been constructed for all of the binary systems. It has been revealed that the binary mixtures have melting points in the temperature range of (325 to 360) K which are much lower than that found for the corresponding perfluoroalkylsulfonylamide salts such as alkali bis(trifluoromethylsulfonyl)-amides, MTf_2N, and alkali bis(pentafluoroethylsulfonyl)amides, MPf_2N. The thermal properties of the single salts and binary mixtures are discussed for Mf_2N, MTf_2N, and MPf_2N.

Introduction

The authors have been exploring a new class of molten salts or ionic liquids which possess high thermal and electrochemical stability and are capable of electrodepositing alkali metals reversibly. In our previous study, thermal and physicochemical properties of single salts, binary and ternary mixtures of alkali metal bis(trifluoromethylsulfonyl)amides, MTf_2N, and bis(pentafluoroethylsulfonyl)amides, MPf_2N (M = Li, Na, K, Rb, Cs), were investigated.[1−5] Although the single MTf_2N salts have relatively high melting temperatures of about 500 K, it has been found that MTf_2N binary mixtures give reasonably low melting points (typically (390 to 460) K),[1] and they possess more desirable properties as electrolytes than the single salts.[3] Among the ternary systems, we have already demonstrated that the x_{Li}, x_K, x_{Cs} = (0.20, 0.10, 0.70) mole fraction system is highly promising as an electrolyte for a rechargeable lithium metal battery.[2,4]

Applying the same idea of our previous studies on MTf_2N, we focused on the ionic liquids consisting of only alkali metal cations and bis(fluorosulfonyl)amide anions, Mf_2N (M = Li, Na, K, Rb, Cs). Recently, we have reported thermal properties of Mf_2N single salts and phase diagrams of $Lif_2N + Kf_2N$ and $Naf_2N + Kf_2N$ systems.[8] Although Mf_2N single salts have melting temperatures at around 373 K, the binary mixtures of $Lif_2N + Kf_2N$ and $Naf_2N + Kf_2N$ exhibit the eutectic temperatures at (338 and 330) K, respectively, considerably lower than the melting temperatures of the single salts. In addition, we revealed that the eutectic $Lif_2N + Kf_2N$ and $Naf_2N + Kf_2N$ melts possess wide electrochemical windows of over 5 V with the cathode limits of lithium metal deposition and sodium metal deposition, respectively. Thus, the Mf_2N binary melts are promising as electrolytes for various electrochemical applications such as lithium or sodium rechargeable batteries.

In this study, thermal properties of Mf_2N single salts and their binary systems have been systematically investigated. First, several minor revisions were made for thermal properties of single salts. Then, 10 binary phase diagrams, including eight new diagrams, were constructed. The eutectic compositions for the two reported systems, $Lif_2N + Kf_2N$ and $Naf_2N + Kf_2N$, were refined according to the Tammann's rule.[6] Finally, the thermal properties are compared with our previously reported data on MTf_2N and MPf_2N.

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Experimental Section

Mf_2N salts were prepared in the same manner as reported by Beran et al.[7] Several important points and new procedures are described here. Kf_2N (Dai-ichi Kogyo Seiyaku Co., Ltd.) was used after drying in a vacuum line at 353 K. Lif_2N and Naf_2N were synthesized by the reaction of Kf_2N with $LiClO_4$ (Wako Pure Chemical Industries, purity > 0.99 in mass) and $NaClO_4$ (Aldrich, purity > 0.98 in mass), respectively. Rbf_2N and Csf_2N were synthesized by the reaction of Hf_2N with Rb_2CO_3 and CsCl (Wako Pure Chemical Industries, purity > 0.99 in mass), where Hf_2N was prepared by the reaction of Kf_2N and $HClO_4$ beforehand. Rbf_2N and Csf_2N were recrystallized twice. All of the chemicals were handled in an argon glovebox whose dew point is below 197 K to prevent the absorption of moisture. The samples of mixtures were prepared by grinding in a mortar.

Transition and thermal decomposition temperatures of single Mf_2N salts and their mixtures were measured by differential scanning calorimeter DSC-60 (Shimadzu Co., Ltd.) and thermogravimeter DTG-60/60H (Shimadzu Co., Ltd.), respectively. Observations of the phase transitions were conducted for mixtures at every 0.1 mole fraction in the range (0.1 to 0.9). The amount of each sample was small enough (around 10 mg) to avoid uneven heating. Samples were placed in aluminum sealed pans. A continuous heating with the scanning rates of (2 and 10) $K \cdot min^{-1}$ and a stepwise heating with the interval of 2 K were performed for DSC measurements. The stepwise heating was not conducted for Lif_2N single salt and binary mixtures containing Lif_2N due to the low decomposition temperature of Lif_2N.[8] For each sample, thermal behavior was preliminarily observed by a continuous heating with 10 $K \cdot min^{-1}$. Then, detailed transition temperatures were determined by a stepwise heating method as well as a continuous heating method with 2 $K \cdot min^{-1}$. The transition temperatures were determined in the heating process to avoid uncertainty by supercooling. The analyses were performed for the first scan because the complete solidification was difficult for Mf_2N melts. The phase diagrams of the binary Mf_2N mixtures were constructed by plotting the

10.1021/je9010932
Published on Web 05/25/2010

Table 1. Melting Temperature, T_m, and Decomposition Temperatures, T_d, of Mf_2N Single Salts (M = Li, Na, K, Rb, Cs)[a]

Mf_2N	T_m(this study)/K	T_m(previous study[7])/K	T_d/K
Li	403	377−401	*343*
Na	379	385−390	413
K	*375*		*423*
Rb	368	365−369	435
Cs	386	385−389	443

[a] Italic numbers indicate the revised data compared with our previous report.[8]

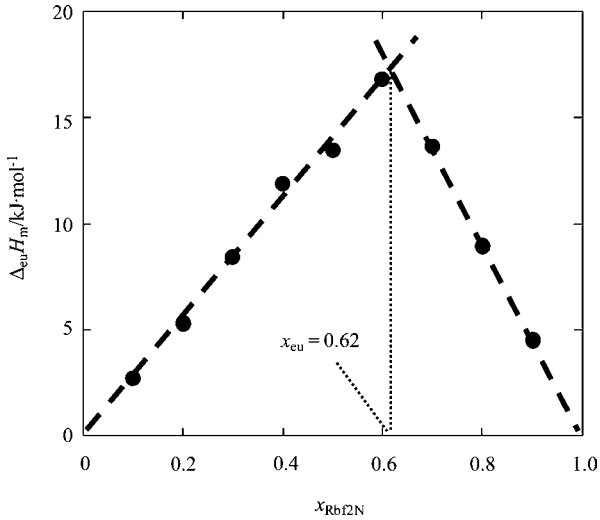

Figure 1. Composition dependence of eutectic fusion enthalpy in the Lif_2N + Rbf_2N system.

temperatures of endothermic peaks found in the DSC curves against the compositions of the salts. In this study, inaccuracies of composition and temperature measurements were within ± 0.01 in mole fraction and ± 2 K, respectively. For the calorimetry of fusion enthalpy, calibration was conducted by a DSC curve of indium metal (Aldrich, purity 0.99999 in weight).

Results and Discussion

Thermal Properties of Mf_2N Single Salts. Table 1 lists the melting and decomposition temperatures of Mf_2N single salts. Italic numbers indicate the revised data compared with our previous data.[8] The thermal decomposition temperatures are above melting temperatures except for Lif_2N. Nevertheless, the melting temperature of Lif_2N was able to be determined owing to a higher scan rate compared with its decomposition rate. Thus, the melting temperature of Lif_2N determined in this study is in good agreement with the other reported data.[7] The melting temperatures for Mf_2N single salts are found in the range (368 to 403) K, which is lower than those for MTf_2N, (400 to 530) K,[1] and MPf_2N, (520 to 600) K.[5] The decomposition temperatures are also lower for Mf_2N, (343 to 443) K, than those for MTf_2N, (600 to 650) K,[1] and MPf_2N, (650 to 700) K.[5] These tendencies are discussed in terms of ionic radius later.

Application of Tammann's Rule to the Determination of Eutectic Composition. For an eutectic binary system, an eutectic composition is determined by Tammann's rule in which the heat of isothermal transition has a linear relationship with the composition of the mixtures.[6]

As an example, we show the process of determining the eutectic composition in the Lif_2N + Rbf_2N system in accordance with Tammann's rule. Figure 1 shows the composition dependence of eutectic fusion enthalpy per one mole of each mixture, $\Delta_{eu}H_m$ (kJ·mol^{-1}), measured by DSC. The data were fitted to

Table 2. Eutectic Temperature, T_{eu}, and Composition, x_{eu}, for Mf_2N Binary Systems, M_Af_2N + M_Bf_2N (M_A, M_B = Li, Na, K, Rb, Cs)[a]

M_A + M_B	T_{eu}/K	$x_{eu}(xM_B)$
Li + Na	349	0.60
Li + K	*341*	*0.59*
Li + Rb	337	0.62
Li + Cs	335	0.53
Na + K	*334*	*0.44*
Na + Rb	328	0.50
Na + Cs	325	0.53
K + Rb	354	0.69
K + Cs	336	0.46
Rb + Cs	360	0.35

[a] Italic numbers indicate the revised data compared with our previous report.[8]

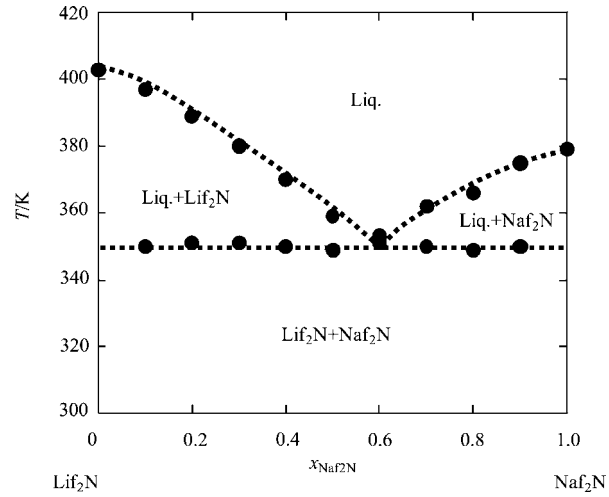

Figure 2. Phase diagram of the Lif_2N + Naf_2N system.

straight lines by the least-squares method. For x_{Rb} of smaller than eutectic composition, the obtained relation is:

$$\Delta_{eu}H_m/\text{kJ}\cdot\text{mol}^{-1} = 28.0x_{Rb} - 0.0408 \quad (1)$$

On the other hand, the obtained relation in which x_{Rb} is larger than eutectic composition is as follows:

$$\Delta_{eu}H_m/\text{kJ}\cdot\text{mol}^{-1} = -45.6x_{Rb} + 45.5 \quad (2)$$

From the intersection of these two lines, the eutectic composition and the maximum fusion enthalpy were determined to be x_{Rb} = 0.62 and 17 kJ·mol^{-1}, respectively. It should be also noted that the extrapolation of enthalpy line 1 to $\Delta_{eu}H_m$ = 0 kJ·mol^{-1} gives x_{Rb} = 0.00146 and that the enthalpy line 2 also gives x_{Rb} = 0.998 at $\Delta_{eu}H_m$ = 0 kJ·mol^{-1}. Those values of compositions are within the margin of measurement error (± 0.01 in mole fraction). Thus, the solid solutions of Lif_2N and Rbf_2N are not identified at the corresponding eutectic temperature.

Tammann's rule was also applied to the other binary systems. Table 2 summarizes the eutectic temperatures and compositions for all binary systems. Solid solutions of Mf_2Ns are not found at the corresponding eutectic temperatures as in the case of Lif_2N + Rbf_2N.

Phase Diagrams of the Mf_2N Binary Mixtures. Figures 2 to 11 show the phase diagrams of the Lif_2N + Naf_2N, Lif_2N + Kf_2N, Lif_2N + Rbf_2N, Lif_2N + Csf_2N, Naf_2N + Kf_2N, Naf_2N + Rbf_2N, Naf_2N + Csf_2N, Kf_2N + Rbf_2N, Kf_2N + Csf_2N, and Rbf_2N + Csf_2N systems. All of the liquidus lines are drawn by hand, connecting experimental plots and the calculated eutectic point. In the diagrams of the systems containing Lif_2N, the broken lines are used for the data over the decomposition

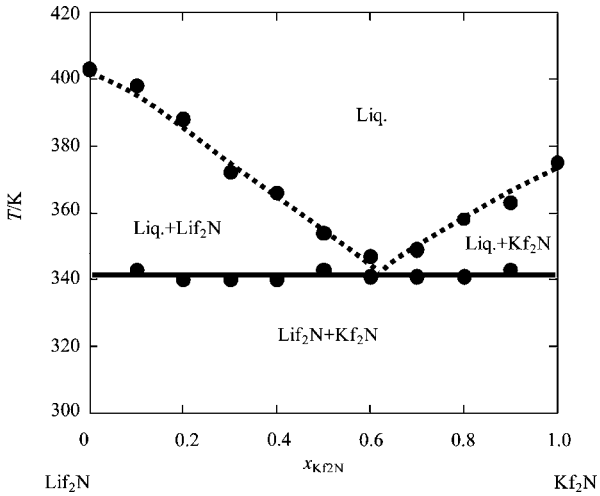

Figure 3. Phase diagram of the $Lif_2N + Kf_2N$ system.

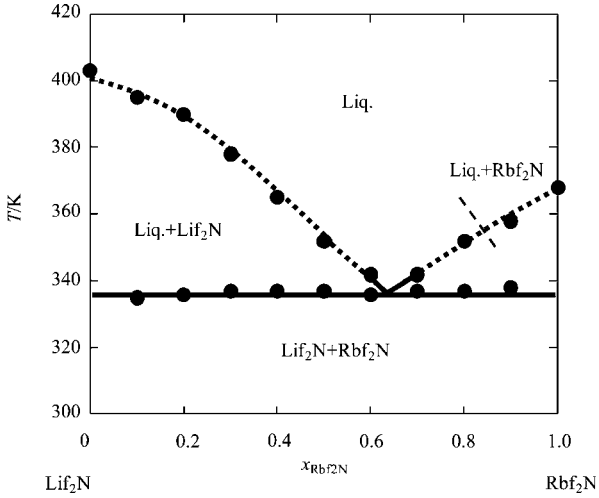

Figure 4. Phase diagram of the $Lif_2N + Rbf_2N$ system.

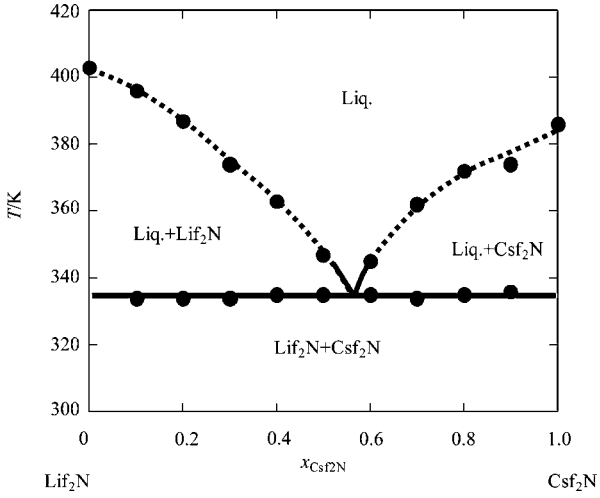

Figure 5. Phase diagram of the $Lif_2N + Csf_2N$ system.

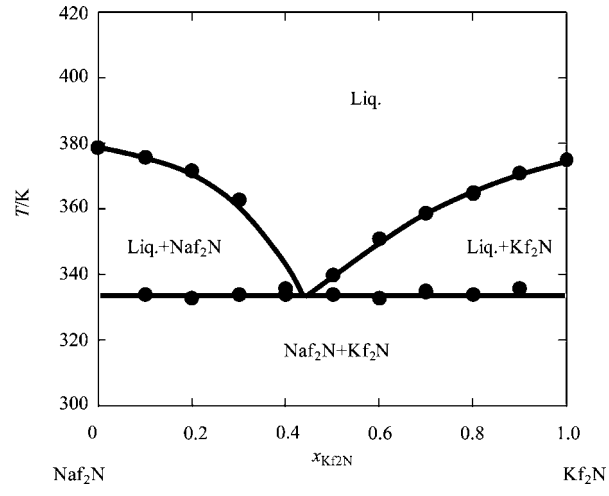

Figure 6. Phase diagram of the $Naf_2N + Kf_2N$ system.

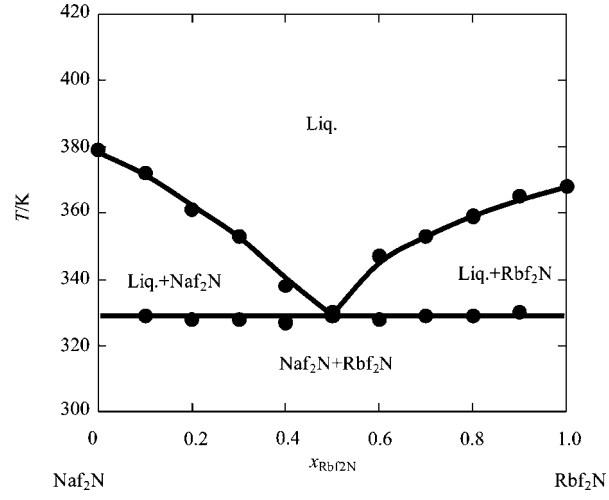

Figure 7. Phase diagram of the $Naf_2N + Rbf_2N$ system.

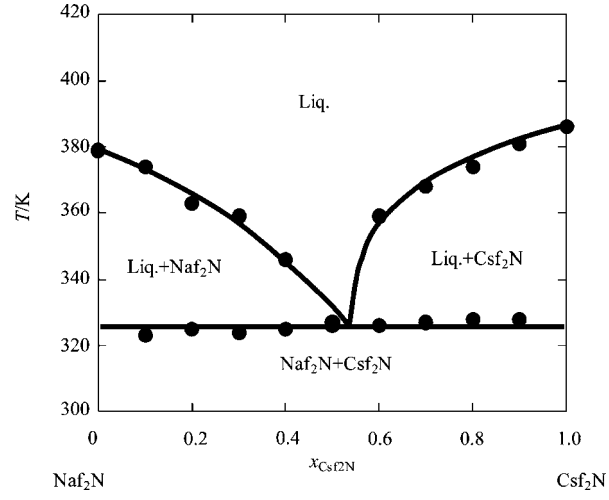

Figure 8. Phase diagram of the $Naf_2N + Csf_2N$ system.

temperature of Lif_2N, 343 K. These data were collected by continuous heating with 10 $K \cdot min^{-1}$ in the DSC measurement so that the scan rate is high enough to detect the transition temperature without the interference by the decomposition of Lif_2N. For $Lif_2N + Kf_2N$ and $Naf_2N + Kf_2N$ systems, several points have been revised from our previous paper.[8] In our previous study, the scan rate of DSC was 10 $K \cdot min^{-1}$. In this study, the scan rate was slowed to 2 $K \cdot min^{-1}$. The stepwise heating was also performed for a more precise measurement. Moreover, the eutectic compositions have been determined by Tammann's rule. Thus, the revised two diagrams in this study are more accurate. For the systems containing Lif_2N, liquidus lines above 343 K, the decomposition temperature of Lif_2N, were drawn by broken lines because Lif_2N in mixture is unstable above the decomposition temperature. These liquidus temperatures were able to be determined owing to a higher scan rate

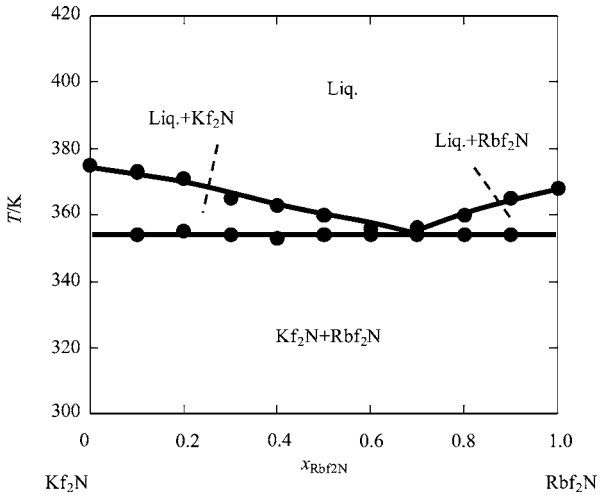

Figure 9. Phase diagram of the Kf_2N + Rbf_2N system.

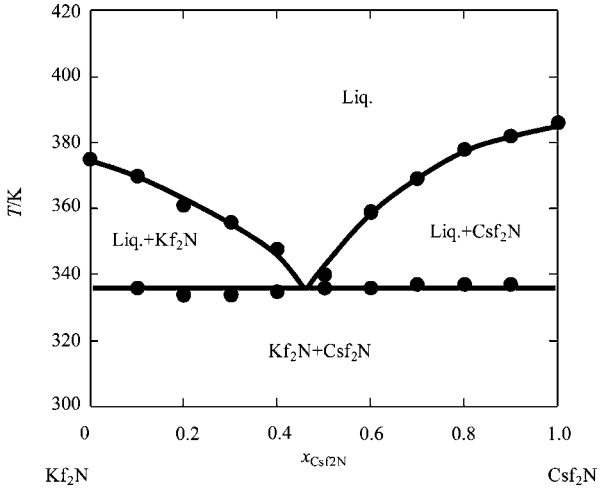

Figure 10. Phase diagram of the Kf_2N + Csf_2N system.

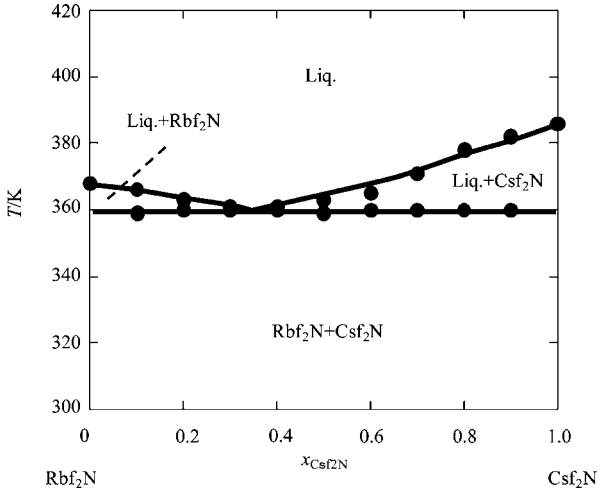

Figure 11. Phase diagram of the Rbf_2N + Csf_2N system.

compared with the decomposition rate of Lif_2N as in the case of Lif_2N single salt. All binary systems are a simple eutectic type with small solid solubility limits.

Advantages of Mf_2N Binary Melts as Electrolytes. The thermal decomposition temperatures of all of the eutectic mixtures were measured. It was confirmed by TG measurements that the lower decomposition temperature of the constituent single salt determines the decomposition temperature of each

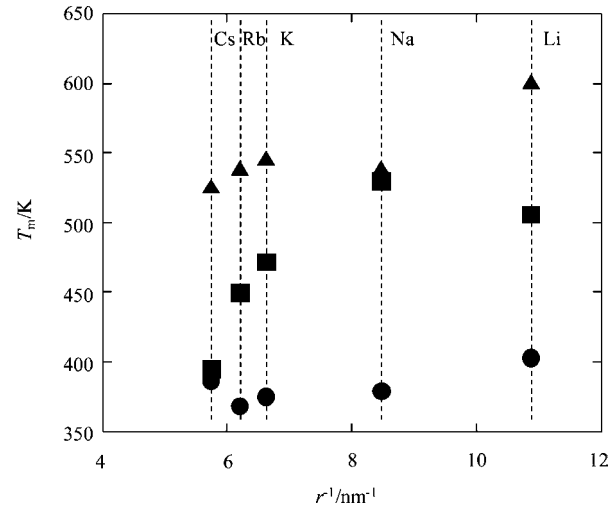

Figure 12. Plots of the melting temperature, T_m, against the reciprocal radius of the cations of the salts, r, for Mf_2Ns (●, this study), MTf_2Ns (■, ref 1), and MPf_2Ns (▲, ref 5).

binary system. Thus, there is no effect of the mixing of Mf_2N salts on the decomposition temperatures.

Mf_2N binary eutectic mixtures have considerably lower melting temperatures, (325 to 349) K, than Mf_2N single salts, except for Kf_2N + Rbf_2N and Rbf_2N + Csf_2N systems. Particularly, binary eutectic melts consisting of Lif_2N have melting temperatures lower than the decomposition temperature of Lif_2N (343 K). Thus, they can be used as stable electrolytes below 343 K. In conclusion, binary eutectic Mf_2N mixtures are expected to be used as a new type of electrolyte possessing unique features: they are ionic liquids consisting of entirely inorganic compounds, and they have wide electrochemical windows with alkali metal deposition as a reaction at the cathode limit.

Comparison of Thermal Properties among Mf_2N, MTf_2N, and MPf_2N. Figure 12 shows the melting temperatures of Mf_2N, MTf_2N,[1] and MPf_2N[5] (M = Li, Na, K, Rb, Cs) against the reciprocal radii of the cations on the assumption that their coordination number is uniformly eight.[9] For the salts composed of common anions, the melting temperatures generally decrease with an increase in the radius of the cation except for some salts such as $NaTf_2N$, $NaPf_2N$, and Rbf_2N. The melting temperatures of the salts possessing the same cation are increased with the increase in the radius of the anion, $Mf_2N < MTf_2N < MPf_2N$. Figure 13 shows the decomposition temperatures of Mf_2N, MTf_2N,[1] and MPf_2N[5] against the reciprocal radii of the cation. On the contrary to the melting temperatures, the decomposition temperatures become higher with the increase in the radius of the cation. The decomposition temperatures of the salts possessing the same cation are increased in the order of $Mf_2N < MPf_2N < MTf_2N$.

Table 3 lists the type of phase diagram for binary systems of Mf_2N, MTf_2N, and MPf_2N. The ratio of reciprocal radii of the corresponding two cations is also listed. There are three types of binary phase diagrams, a simple eutectic type, a eutectic type possessing intermediate compound, and an isomorphous type with complete solid solubility for all compositions. For all Mf_2N binary systems, they are classified as a simple eutectic type. However, this type decreases to be found for the system with a larger anion; here, the radius is in the order of $f_2N < Tf_2N < Pf_2N$. For MTf_2N and MPf_2N, the binary systems tend to become an isomorphous type when the ratio of reciprocal radii of their cations is small. These tendencies are summarized as follows:

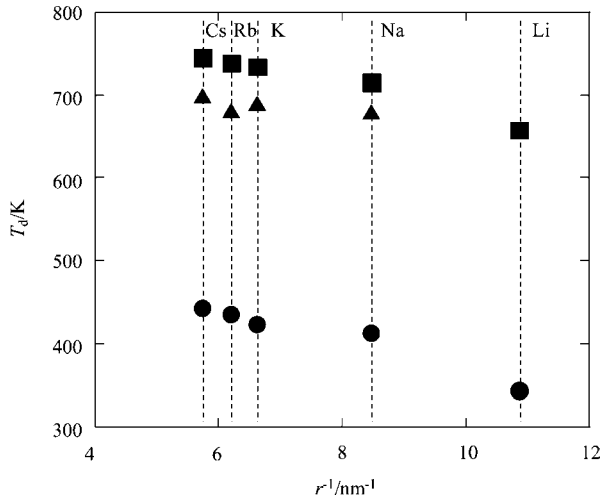

Figure 13. Plots of the decomposition temperature, T_d, against the reciprocal radius of the cations of the salts, r, for Mf_2Ns (●, this study), MTf_2Ns (■, ref 1), and MPf_2Ns (▲, ref 5).

Table 3. Type of Binary Phase Diagram and the Ratio of Cation Radii, r_B/r_A, for $M_AX + M_BX$ (M_A, M_B = Li, Na, K, Rb, Cs; X = f_2N, Tf_2N, Pf_2N)[a]

$M_A + M_B$	r_B/r_A	Mf_2N	MTf_2N	MPf_2N
Li + Cs	1.89	A	B	A
Li + Rb	1.75	A	B	A
Li + K	1.64	A	B	A
Na + Cs	1.47	A	B	A
Na + Rb	1.36	A	A	C
Li + Na	1.28	A	A	B
Na + K	1.28	A	B	C
K + Cs	1.15	A	A	C
Rb + Cs	1.08	A	C	C
K + Rb	1.07	A	C	C

[a] A, simple eutectic; B, eutectic with intermediate compound; and C, isomorphous.

the smaller size of anions or larger difference in the size of cations gives phase diagrams of eutectic types.

Conclusions

Melting and decomposition temperatures have been measured for Mf_2N (M = Li, Na, K, Rb, Cs) single salts. For 10 binary Mf_2N systems, the eutectic temperatures and the eutectic compositions have been determined, and all binary phase diagrams have been constructed. Mf_2N binary eutectic mixtures are expected to be used as novel ionic liquid electrolytes due to their low melting temperatures, (325 to 360) K, and wide electrochemical windows.

Supporting Information Available:

Tables of data for figures are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Hagiwara, R.; Tamaki, K.; Kubota, K.; Goto, T.; Nohira, T. Thermal properties of mixed alkali bis(trifluoromethylsulfonyl)amides. *J. Chem. Eng. Data* **2008**, *53*, 355–358.
(2) Kubota, K.; Nohira, T.; Goto, T.; Hagiwara, R. Ternary phase diagrams of alkali bis(trifluoromethylsulfonyl)amides. *J. Chem. Eng. Data* **2008**, *53*, 2144–2147.
(3) Kubota, K.; Tamaki, K.; Nohira, T.; Goto, T.; Hagiwara, R. Electrochemical properties of alkali bis(trifluoromethylsulfonyl)amides and their eutectic mixtures. *Electrochim. Acta* **2010**, *55*, 1113–1119.
(4) Watarai, A.; Kubota, K.; Yamagata, M.; Goto, T.; Nohira, T.; Hagiwara, R.; Ui, K.; Kumagai, N. A rechargeable lithium metal battery operating at intermediate temperatures using molten alkali bis(trifluoromethylsulfonyl)amide mixture as an electrolyte. *J. Power Sources* **2008**, *183*, 724–729.
(5) Kubota, K.; Nohira, T.; Hagiwara, R. Thermal properties of alkali bis(pentafluoromethylsulfonyl)amides and their binary mixtures. *J. Chem. Eng. Data* **2010**; DOI: 10.1021/je900902z.
(6) Mills, E. R.; Coyle, R. T. Differential analysis of phase equilibria in mixtures of anhydrous carbonates. *Thermochim. Acta* **1988**, *124*, 65–77.
(7) Beran, M.; Příhoda, J.; Žák, Z.; Černík, M. A new route to the syntheses of alkali metal bis(fluoroslfuryl)imides; Crystal structure of $LiN(SO_2F)_2$. *Polyhedron* **2006**, *25*, 1292–1298.
(8) Kubota, K.; Nohira, T.; Goto, T.; Hagiwara, R. Novel inorganic ionic liquids possessing low melting temperatures and wide electrochemical windows: Binary mixtures of alkali bis(fluorosulfonyl)amides. *Electrochem. Commun.* **2008**, *10*, 1886–1888.
(9) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr., Sect. A* **1976**, *32*, 751–767.

Received for review January 7, 2010. Accepted May 13, 2010. 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.

JE9010932