Thermal Properties of Alkali (Fluorosulfonyl)(trifluoromethylsulfonyl)amides

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An asymmetric perfluorosulfonylamide anion, $[(FSO_2)(CF_3SO_2)N]^-$ (C0C1$^-$), has a significant ability to lower the melting temperatures of alkali salts down to around 373 K. Among alkali salts which have melting temperatures around 373 K, they have comparatively high decomposition temperature. The melting point of LiC0C1 is the lowest among the lithium salts of perfluoroalkyl- or fluorosulfonylamide anions of this kind.

Molten salts consisting of alkali metal cations and halide anions have high chemical stability compared with room-temperature ionic liquids (RTILs) consisting of onium cations such as 1-ethyl-3-methylimidazolium (EMI$^+$) because alkali metal cations are monatomic ions. However, molten alkali halides have a difficulty in handling because of their high melting points. On the other hand, RTILs can be used easily due to their low melting points below room temperature. Thus, the development of molten alkali salts simultaneously possessing low melting points and excellent chemical and electrochemical properties similar to alkali halides has a great significance for practical applications and its widespread use. Particularly, lithium salts are studied as supporting electrolytes for secondary lithium batteries as well as molten salts. The lowering melting point of supporting electrolytes is important for better performance in secondary lithium batteries at low temperature.

Kubota et al. have reported that salts consisting of alkali metal cations and perfluorosulfonylamide anions such as $[(FSO_2)_2N]^-$ (FSA$^-$, abbreviated to C0C0$^-$ in this paper),[1] $[(CF_3SO_2)_2N]^-$ (TFSA$^-$, C1C1$^-$),[2–4] and $[(C_2F_5SO_2)_2N]^-$ (BETA$^-$, C2C2$^-$)[5] (Figure 1a) possess much lower melting points than conventional alkali halides. Among them, alkali C0C0 salts have melting points around 373 K.[1]

Recently, RTILs composed of onium cations such as EMI$^+$ and asymmetric anions such as $[(CF_3SO_2)(C_2F_5SO_2)N]^-$ (C1C2$^-$)[6,7] and $[(FSO_2)(CF_3SO_2)N]^-$ (FTA$^-$, C0C1$^-$)[8] (Figure 1b) were reported to have lower melting temperatures than those composed of the corresponding cations and symmetric anions such as C0C0$^-$ and C1C1$^-$. For alkali salts, $[(FSO_2)(C_2F_5SO_2)N]^-$ (FPFSA$^-$, C0C2$^-$) compounds have been reported very recently.[9] Compounds consisting of alkali metal cations and asymmetric perfluorosulfonylamide anions are expected to have lower melting temperatures than those composed of symmetric anions as is the case in those consisting of onium cations. In this study, five salts composed of alkali metal cations and C0C1 anion, MC0C1s (M: Li, Na, K, Rb, and Cs) were prepared, and their thermal properties were investigated.

As shown in Scheme 1, MC0C1s were synthesized by a cation exchange[10] and neutralization. KC0C1 was synthesized according to the literature.[11] HC0C1 was prepared by passing
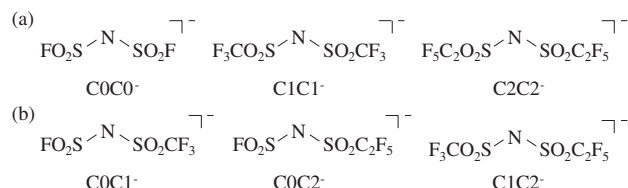
Figure 1. Structures of (a) symmetric and (b) asymmetric perfluorosulfonylamide anions.
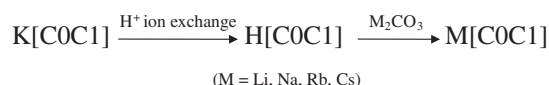

Scheme 1.

Table 1. Glass-transition (T_g), melting (T_m), and decomposition (T_d) temperatures of MC0C1 salts

	T_g/K	T_m/K	T_d/K
LiC0C1	265	373	423
NaC0C1		431	503
KC0C1		374	493
RbC0C1	266	385	500
CsC0C1	256	381	536

aqueous KC0C1 solution through acid ion-exchange resin (Mitsubishi Chemical, SK1BH). Then, the HC0C1 was neutralized by alkali carbonates (Wako Pure Chemical Industries). The products except for LiC0C1 are easily dried in vacuum at 1.0 Pa. For LiC0C1, removal of absorbed water was performed by reaction with thionyl chloride due to its hygroscopic nature. After drying, all products were characterized by mass spectrometry and elemental analysis. For MC0C1s and LiC1C2 (provided from CENTRAL GLASS Co., Ltd.), the melting and decomposition temperatures were measured by DSC (Perkin-Elmer, Pyris 1) and TG-DTA (SII NanoTechnology Inc., Exstar TG/DTA6000), respectively.

According to the synthetic methods in Scheme 1, MC0C1 salts were prepared in the forms of white powder after drying the reaction products. The chemical analysis data are indicated bellow.[12] Table 1 shows glass-transition (T_g), melting (T_m), and decomposition (T_d) temperatures of MC0C1 salts. The melting behaviors at each T_m were confirmed by visual observation.

Figure 2 shows the plots of T_m and T_d against the reciprocal radii of the cations on the assumption that their coordination numbers are uniformly eight.[13] For the salts composed of common anions, T_m generally decreases with increase in radius of cation. Except for MC2C2s, the differences of T_m become
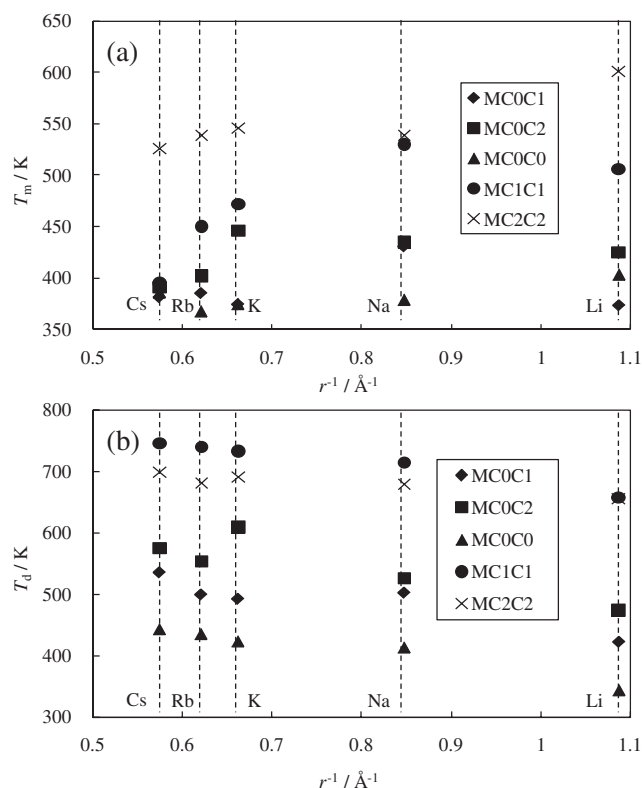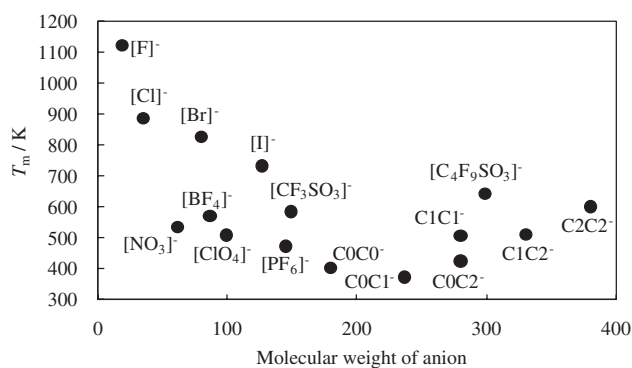
Figure 2. Plots of (a) T_m and (b) T_d against the reciprocal radius of the cations for MC0C1s (this study), MC0C2s,[9] MC0C0s,[1] MC1C1s,[2] and MC2C2s.[5]

Figure 3. Plots of T_m of anhydrous lithium salts against molecular weight of constituent anions.

smaller with increase in radius of cation. The dependence of cation on T_m is consistent with the relationship between T_m and lattice energy. Concerning T_d, the value is always the lowest for the lithium salt when comparing the salts composed of a common anion due to the strong electric field of lithium cation. The dependence of cation on T_d indicates that the effect of alkali cation size on decomposition of anion become stronger with decrease in radius of cation. For MC0C1s, T_d's are higher than those for MC0C0s, falling in the middle values between MC0C0s and MC1C1s. As molten salt electrolytes, MC0C1 salts are capable of being used at around 373 K, that is, the same temperature range as for MC0C0 salts. In addition, MC0C1 salts possess higher thermal stability than that of the corresponding MC0C0 salts.

Concerning the lithium salts, it is found from Figure 2 that LiC0C1 has better thermal properties, lower T_m and higher T_d, than LiC0C0. Figure 3 shows the T_m of lithium salts in which molecular weight of anion are below 400, they are supporting electrolyte candidates for secondary lithium batteries. LiC0C1 has the lowest T_m among them. Electrolytes composed of supporting electrolytes possessing low melting temperature are expected to remain in liquid phase at low temperature range. Thus, LiC0C1 is promising as a component of electrolytes for secondary lithium batteries.

In conclusion, thermal properties of MC0C1s have been revealed. Their melting points are around 373 K, which is lower than those of most alkali salts. The decomposition temperatures of MC0C1s are higher than those of MC0C0s which have melting temperature as high as MC0C1s. Particularly, LiC0C1 is expected to be a supporting electrolyte for secondary lithium batteries because of lower melting temperature than most lithium salts. In addition, applying the same idea of our previous studies,[1–5] binary or ternary mixtures of MC0C1s are expected to have lower melting temperature than single salts. Examination of thermal properties and other physicochemical properties of MC0C1 mixtures are now underway.

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12 LiC0C1: Anal. Calcd (Found): C, 5.07 (4.83); N, 5.91 (5.50)%. MS *m/z* (%) 230 (100) [C0C1]⁻, 467 (15.9) Li[C0C1]$_2$⁻. NaC0C1: Anal. Calcd (Found): C, 4.74 (4.61); N, 5.53 (5.72)%. MS *m/z* (%) 230 (100) [C0C1]⁻, 483 (19.6) Na[C0C1]$_2$⁻. KC0C1: Anal. Calcd (Found): C, 4.46 (4.45); N, 5.20 (5.12)%. MS *m/z* (%) 230 (100) [C0C1]⁻, 499 (12.4) K[C0C1]$_2$⁻. RbC0C1: Anal. Calcd (Found): C, 3.81 (3.81); N, 4.44 (4.47)%. MS *m/z* (%) 230 (100) [C0C1]⁻, 545 (36.1) Rb[C0C1]$_2$⁻. CsC0C1: Anal. Calcd (Found): C, 3.31 (3.27); N, 3.86 (3.92)%. MS *m/z* (%) 230 (100) [C0C1]⁻.
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