

## Low Melting and Electrochemically Stable Ionic Liquids Based on Asymmetric Fluorosulfonyl(trifluoromethylsulfonyl)amide

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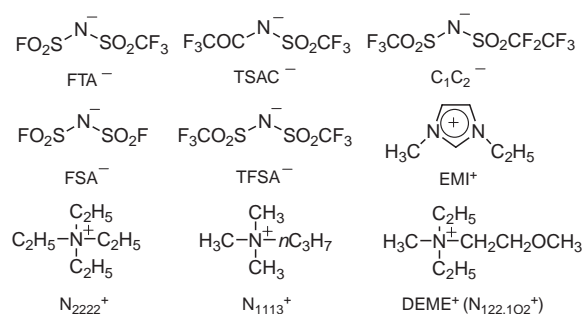
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An asymmetric amide anion, FTA<sup>-</sup> {[F(SO<sub>2</sub>)(CF<sub>3</sub>SO<sub>2</sub>)-N]<sup>-</sup>}, has a significant ability to reduce the melting points of an aliphatic quaternary ammonium salts even for a symmetric tetraethylammonium. Much more interestingly, the electrochemical stability of this anion was comparable to a typical amide anion, such as bis(trifluoromethylsulfonyl)amide.

Ionic liquids (ILs) composed of the aliphatic quaternary onium cation and perfluoroanion have various unique properties, such as a less flammability, less volatility, and good electrochemical stability both in the cathodic and anodic regions.<sup>1</sup> However, these aliphatic systems have a disadvantage when used in energy storage devices such as lithium secondary batteries and electric double layer capacitors due to their relatively high viscosity and melting point compared to that of 1-ethyl-3-methylimidazolium (EMI<sup>+</sup>) ILs, even which have a one order of magnitude higher viscosity than that of molecular liquids. Besides the viscosity of the ILs, decreasing the melting point of ILs is another important challenge for the actual application such as in a battery for next-generation automobiles such as the electric vehicle and hybrid car. Therefore, it is important to investigate low viscosity ILs with a low melting point as a less flammable electrolyte. There are a few reports on the preparation of low viscosity and low melting ionic liquids by modifying the structure of the perfluoroanion. Zhou et al. reported that a series of perfluoroalkyltrifluoroborate anions have an superior ability to reduce both the melting point and viscosity of the resulting ILs compared to the tetrafluoroborate ILs.<sup>2</sup> We also reported that asymmetric amide anions such as [(CF<sub>3</sub>SO<sub>2</sub>)(CF<sub>3</sub>CO)N]<sup>-</sup> (TSAC<sup>-</sup>)<sup>3</sup> and [(CF<sub>3</sub>SO<sub>2</sub>)(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)N]<sup>-</sup> (C<sub>1</sub>C<sub>2</sub><sup>-</sup>)<sup>4</sup> reduce the melting point of ILs when combined with aliphatic ammonium cations. As far as we know, TSAC<sup>-</sup> is the only anion to form ILs with the symmetric tetraethylammonium, however, the electrochemical window of the TSAC-ILs is narrow owing to the poor electrochemical stability of the TSAC<sup>-</sup>.<sup>4</sup>

In this paper, we report the preparation and physical properties of ILs composed of various aliphatic quaternary ammonium and another asymmetric perfluoroanion, such as fluorosulfonyl-(trifluoromethylsulfonyl)amide for the first time (Figure 1). This anion also form ILs with not only asymmetric, but also with symmetric cations, such as tetraethylammonium (N<sub>2222</sub><sup>+</sup>) as in the case of TSAC<sup>-</sup>. However, the FTA<sup>-</sup> system possesses a much more suitable nature for electrochemical devices when compared to the TSAC<sup>-</sup> system as stated below.



**Figure 1.** Structure of anions and cations reported in this paper.

ILs composed of FTA<sup>-</sup> could be easily prepared by a methathesis reaction between onium bromide or iodide and K[FTA] in an aqueous solution owing to their hydrophobicity. Almost all the typically studied cations, such as EMI<sup>+</sup>,<sup>5</sup> *N*-methyl-*N*-propylpyrrolidinium (Py<sub>13</sub><sup>+</sup>),<sup>6</sup> *N*-methyl-*N*-propylpiperidinium (PP<sub>13</sub><sup>+</sup>),<sup>7</sup> trimethylpropylammonium (N<sub>1113</sub><sup>+</sup>),<sup>8</sup> and *N,N*-dimethyl-*N*-ethyl-*N*-(2-methoxymethyl)ammonium (DEME<sup>+</sup>),<sup>9</sup> have a lower viscosity, melting point, and glass-transition temperature than the corresponding TFSA<sup>-</sup> salts as we expected. Their thermal decomposition temperatures measured by TGA were higher than that of FSA<sup>-</sup> and lower than that of TFSA<sup>-</sup>. Details of the physical, thermal, and electrochemical properties of the FTA system compared to the TFSA and FSA systems and also the preparation of K[FTA] will be published elsewhere.

Table 1 shows melting point and glass-transition temperature (*T<sub>g</sub>*) of various amide salts. It is quite interesting that not only the typical ammonium cations in ionic liquids such as EMI<sup>+</sup> and DEME<sup>+</sup>, as stated above, but also a symmetric tetraethylammonium (N<sub>2222</sub><sup>+</sup>) also forms low melting ILs with

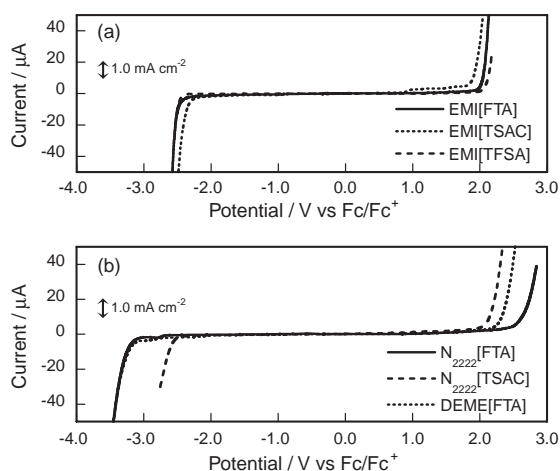
**Table 1.** Melting point of various amides salts (°C) by DSC upon heating (10 °C min<sup>-1</sup>). The data in parentheses are the glass-transition temperatures of the ILs (*T<sub>g</sub>*)

Anion/Cation	EMI <sup>+</sup>	DEME <sup>+</sup>	N <sub>1113</sub> <sup>+</sup>	N <sub>2222</sub> <sup>+</sup>
TFSA <sup>-</sup>	-16 <sup>a</sup>	(-95) <sup>b,d</sup>	19 <sup>c</sup>	114 <sup>c</sup>
FSA <sup>-</sup>	-13 <sup>a</sup>	-21.6 (-112) <sup>e</sup>	42 <sup>c</sup>	40 <sup>e</sup>
TSAC <sup>-</sup>	-1.5 <sup>c</sup>	(-98) <sup>d,f</sup>	10 <sup>c</sup>	21 <sup>c</sup>
C <sub>1</sub> C <sub>2</sub> <sup>-</sup>	(-93) <sup>c,d</sup>	(-96) <sup>d,f</sup>	19 <sup>c</sup>	69 <sup>c</sup>
FTA <sup>-</sup>	-28 (-107) <sup>e</sup>	(-107) <sup>d,e</sup>	-28 (-103) <sup>e</sup>	8.5 <sup>e</sup>

<sup>a</sup>Ref. 10. <sup>b</sup>Ref. 11. <sup>c</sup>Ref. 4. <sup>d</sup>*T<sub>g</sub>* only. <sup>e</sup>These data were taken during this study. The chemical analysis data of these salts are indicated in Ref. 12.

FTA<sup>-</sup>. Previously, we reported that another asymmetric amide, TSAC<sup>-</sup>, also formed ILs with N<sub>2222</sub><sup>+</sup>, however, the melting point of N<sub>2222</sub>[FTA] (8.5 °C) might be the lowest of all the N<sub>2222</sub><sup>+</sup> salts composed of not only fluorine-containing anions, but also conventional anions without containing the fluorine atom, except for the corresponding hydrate salts. We have proposed that introducing asymmetry into an amide anion is a key strategy to reduce the melting point of aliphatic quaternary ammonium salts through the preparation of ILs based on TSAC<sup>-</sup>,<sup>3,4</sup> however, this seems not to be valid for EMI<sup>+</sup>. The exact reason has not been totally determined, however, the existence of a carbonyl group in TSAC<sup>-</sup> could be responsible for this result since the melting point of EMI[FTA] without containing a carbonyl group was the lowest of all the EMI<sup>+</sup> salts with amide anions. Furthermore, asymmetric anions are not always decrease melting point of ammonium salts as observed in C<sub>1</sub>C<sub>2</sub><sup>-</sup>. This indicates that size of anion is another important factor to decrease quaternary ammonium salts based on amide anions.

As previously reported,<sup>4</sup> the electrochemical windows (EWs) of TSAC salts were much narrower than the other amides, such as the TFSA<sup>-</sup> system, owing to the poor electrochemical stability of TSAC<sup>-</sup>. This might be caused by the poor electrochemical stability of the carbonyl group in the amide anions. For a series of EMI<sup>+</sup> salts, the difference in the electrochemical stability among the amide anions was masked by the both oxidation and reduction of EMI<sup>+</sup> as shown in Figure 2a. However, a much wider EW of the FTA<sup>-</sup> salt occurred by changing the cation from EMI<sup>+</sup> to the more electrochemically stable N<sub>2222</sub><sup>+</sup> (Figure 2b). Judging from the EW of N<sub>2222</sub>[FTA], which was almost the same as PP13[TFSA],<sup>4</sup> the oxidation stability of FTA<sup>-</sup> might be almost electrochemically the same as TFSA<sup>-</sup>. On the other hand, the EWs of N<sub>2222</sub>[TSAC] and DEME[FTA] were much narrower than that of the N<sub>2222</sub>[FTA]. These results indicate that the electrochemical oxidation of DEME<sup>+</sup> and TSAC<sup>-</sup> occurred at much more negative potentials than that of FTA<sup>-</sup> and the reduction of TSAC<sup>-</sup>.



**Figure 2.** Linear sweep voltammogram of ionic liquids composed of asymmetric anions; (a) imidazolium ILs, (b) aliphatic quaternary ammonium.  $T = 25\text{ }^{\circ}\text{C}$ , scan rate:  $50\text{ mV s}^{-1}$ . Working electrode: Glassy carbon disk (diameter: 1 mm), Counter electrode: Pt wire, potential referenced to ferrocene (Fc)/ferrocenium (Fc<sup>+</sup>) redox couple.

In conclusion, a series of new hydrophobic ionic liquids consisting of [(FSO<sub>2</sub>)(CF<sub>3</sub>SO)N]<sup>-</sup> (FTA<sup>-</sup>) were prepared. As far as we know, the melting point of N<sub>2222</sub>[FTA] (8.5 °C) is the lowest value among the tetraethylammonium salts. The low melting FTA salts will improve a low-temperature performance of electrolytes for various electrochemical devices.

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- Chemical shift values are referenced to internal TMS for <sup>1</sup>H (500.2 MHz) and internal CCl<sub>3</sub>F for <sup>19</sup>F (470.6 MHz), and methanol-*d*<sub>4</sub> was used as solvent. **EMI[FTA]**: Anal. Calcd (Found): C, 24.6 (24.7); H, 3.3 (3.2); N, 12.3 (12.5)%. <sup>1</sup>H NMR: δ 1.53 (t, 3H), 3.92 (s, 3H), 4.25 (q, 2H), 7.54 (s, 1H), 7.62 (s, 1H), 8.88 (s, 1H); <sup>19</sup>F NMR: δ 56.5 (s, F), -78.3 (s, 3F); MS *m/z* (%) 111 (100) [EMI]<sup>+</sup>, 230 (100) [FTA]<sup>-</sup>. **DEME[FTA]**: Anal. Calcd (Found): C, 24.6 (24.7); H, 3.3 (3.2); N, 12.3 (12.5); F, 20.2 (20.2)%. <sup>1</sup>H NMR: δ 1.33 (m, 6H), 3.04 (s, 3H), 3.38 (s, 3H), 3.43 (q, 4H), 3.51 (t, 2H), 3.78 (m, 2H); <sup>19</sup>F NMR: δ 56.6 (s, F), -78.2 (s, 3F); MS *m/z* (%) 146 (100) [DEME]<sup>+</sup>, 230 (100) [FTA]<sup>-</sup>. **N<sub>2222</sub>[FTA]**: Anal. Calcd (Found): C, 30.0 (29.8); H, 5.6 (5.5); N, 7.8 (7.8); F, 21.1 (21.1)%. <sup>1</sup>H NMR: δ 1.29 (t, 12H), 3.29 (q, 8H); <sup>19</sup>F NMR: δ 56.7 (s, F), -78.1 (s, 3F); MS *m/z* (%) 130 (100) [N<sub>2222</sub>]<sup>+</sup>, 230 (100) [FTA]<sup>-</sup>. **N<sub>1113</sub>[FTA]**: Anal. Calcd (Found): 25.3 (25.5); H, 4.9 (4.8); N, 8.4 (8.5); F, 22.9 (22.7)%. <sup>1</sup>H NMR: δ 1.02 (t, 3H), 1.78–1.86 (m, 2H), 3.12 (s, 9H), 3.26–3.32 (m, 2H); <sup>19</sup>F NMR: δ 56.8 (s, F), -78.1 (s, 3F); MS *m/z* (%) 102 (100) [N<sub>1113</sub>]<sup>+</sup>, 230 (100) [FTA]<sup>-</sup>. **DEME[FSA]**: Anal. Calcd (Found): C, 29.4 (29.4); H, 6.2 (6.2); N, 8.6 (8.5); F, 11.6 (11.6)%. <sup>1</sup>H NMR: δ 1.33 (m, 6H), 3.04 (s, 3H), 3.38 (s, 3H), 3.43 (q, 4H), 3.51 (t, 2H), 3.78 (m, 2H); <sup>19</sup>F NMR: δ 52.0 (s, F); MS *m/z* (%) 146 (100) [DEME]<sup>+</sup>, 180 (100) [FSA]<sup>-</sup>. **N<sub>1113</sub>[FSA]**: <sup>1</sup>H NMR: δ 1.02 (t, 3H), 1.78–1.89 (m, 2H), 3.12 (s, 9H), 3.26–3.32 (m, 2H); <sup>19</sup>F NMR: δ 52.2 (s, F); MS *m/z* (%) 102 (100) [N<sub>1113</sub>]<sup>+</sup>, 180 (100) [FSA]<sup>-</sup>. **N<sub>2222</sub>[FSA]**: <sup>1</sup>H NMR: δ 1.29 (t, 12H), 3.29 (q, 8H); <sup>19</sup>F NMR: δ 52.2 (s, F); MS *m/z* (%) 130 (100) [N<sub>2222</sub>]<sup>+</sup>, 180 (100) [FSA]<sup>-</sup>. **DEME[TSAC]**: <sup>1</sup>H NMR: δ 1.33 (m, 6H), 3.04 (s, 3H), 3.38 (s, 3H), 3.43 (q, 4H), 3.51 (t, 2H), 3.78 (m, 2H); <sup>19</sup>F NMR: δ -75.8 (s, 3F), -78.5 (s, 3F). **DEME[C<sub>1</sub>C<sub>2</sub>]**: <sup>1</sup>H NMR: δ 1.33 (m, 6H), 3.03 (s, 3H), 3.38 (s, 3H), 3.43 (q, 4H), 3.51 (t, 2H), 3.78 (m, 2H); <sup>19</sup>F NMR: δ -78.96 (s, 3F), -79.03 (s, 3F), -117.0 (s, 2F).