Room Temperature Molten Salts Based on Trialkylsulfonium Cations and Bis(trifluoromethylsulfonyl)imide

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Symmetric and aliphatic trialkylsulfonium cation form room temperature molten salts (RTMS) with bis(trifluoromethylsulfonyl)imide (TFSI). In particular RTMS based on triethylsulfonium shows low melting point (–35 °C) and the lowest viscosity (30 mPs at 25 °C) of all the TFSI based RTMS as reported so far. The conductivity of 7.1 mS cm^{-1} at 25 °C is the highest of all the non-chloroaluminate RTMS based on aliphatic onium cations.

Room temperature molten salts (RTMS) have unique properties such as involatility, incombustibility, and relatively high conductivity. From this, RTMS have been studied as an attractive candidate for novel and safe electrolytes. Especially 1-ethyl-3-methylimidazolium (EMI) systems have attracted much attention due to their high conductivity.[1–5] Recently, other type of RTMS based on aliphatic quaternary ammonium (QA) has been reported.[6–8] We demonstrated the preparation of the highest conductive QA-based RTMS (trimethylmethoxymethyl-ammonium-TFSI) as reported so far.[8] The cathodic limit of QA-based melt was 1.0 V more negative than that of EMI-based RTMS.[8]

However the conductivity of QA-based melt is still about half of EMI-based melt when the same anion (TFSI) was used. The reasons why the conductivity of EMI-based melts is higher than that of the QA-based melts have not been clearly understood. Considering the fact that cyclic planar QA such as pyrrolidinium exhibited relatively higher conductivity than the other chain like QA of the same molecular weight, the planarity of cation might be an important factor to exhibit higher conductivity and low viscosity.[7] Trialkylsulfonium is one of the candidates for the planar cation comparing with QA. To the best of our knowledge, such symmetric sulfonium-based RTMS have not been reported except for the trialkylsulfonium-polyiodide system.[9] However, such melt containing redox active species can not be used as a conventional electrolyte.

In this study, we tried to prepare RTMS consisted of planar and symmetric trialkylsulfonium and TFSI anion to improve the conductivity of aliphatic onium systems. As a result, symmetric trialkylsulfonium cation could form RTMS with TFSI. In particular, triethylsulfonium (TES) and TFSI anion, shown in Scheme 1 (TES–TFSI), exhibited low melting point (–35 °C)
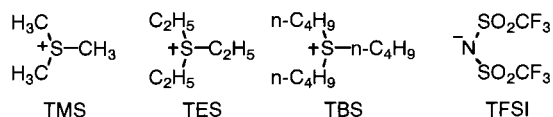
Scheme 1. Structures of newly developed sulfonium based salts. TMS: Trimethylsulfonium. TES: Triethylsulfonium. TBS: Tributylsulfonium. TFSI: bis(trifluoromethylsulfonyl)imide.
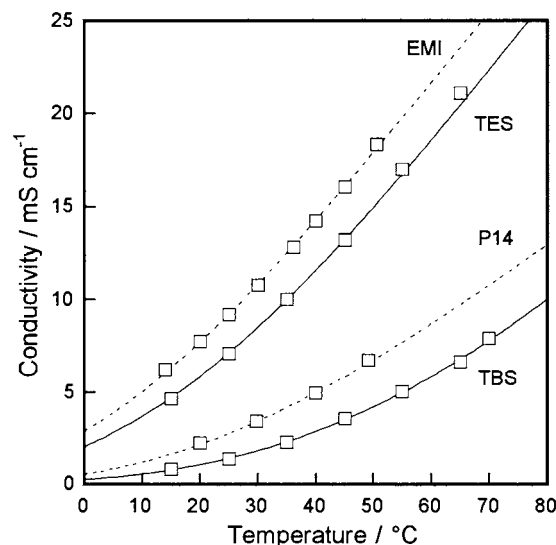
Figure 1. Conductivity of RTMS based on TFSI anion. TES:Triethylsulfonium, TBS:Tributylsulfonium EMI: 1-Ethyl-3-methylimidazolium. P14: N-methylbutylpyrrolidinium.

and the highest conductivity of all the aliphatic onium based RTMS reported so far.

The preparation of sulfonium-based RTMS was basically followed by the preparation of QA–TFSI melts.[8] Three sulfonium iodide, TMS–I (Tokyo Kasei), TES–I (Lancaster), TBS–I (Tokyo Kasei) were recrystallized from ethanol–ethylacetate solutions. Sulfonium-based RTMS was easily obtained by the mixing of two aqueous solutions which contain the same concentration of Li–TFSI and trialkylsulfonium iodide. The resulting RTMS was washed with H_2O several times until no residual byproduct (LiI) was detected with the use of $AgNO_3$. Then the RTMS was extracted with CH_2Cl_2 and dried under vacuum (100 °C) for 24 h. The yield of the sulfonium–TFSI systems were shown in Table 1. The measurements of conductivity (TOA, CV-40M), viscosity (Yamco, VM-100) and the electrochemical measurement (ALS, model 600A) were performed in a globe box ($[O_2] < 1$ ppm, $[H_2O] < 1$ ppm). The calculated composition of the synthesized salt was almost agreed with the result of the elemental analysis.[10] The melting point of RTMS was measured by DSC (Perkin/Elmer, Pyris 1).

As shown in Table 1, the yields of sulfonium–TFSI salts were decreased with decreasing the number of carbon in the alkyl chain of sulfonium cations. This suggests that the solubility to water of the sulfonium–TFSI salts increased with decreasing the number of carbon in the alkyl chain of cations. The increase of solubility to water might lower the efficiency of the extraction with CH_2Cl_2.

Table 1. Properties of room temperature molten salts based on TFSI anion at 25 °C

cation	yield /%	m.p. /°C	Density /g cm^{-3}	C^a /mol dm^{-3}	η^b /mPa s	σ^c /mS cm^{-1}	Λ^d /S cm^{2}mol^{-1}
TMS	30	44.5	1.58^e	4.43^e	44^e	8.2^e	1.84^e
TES	70	-35.5	1.46	3.66	30	7.1	1.94
TBS	86	-7.5	1.29	2.66	75	1.4	0.53
EMI^f	78	-12.0	1.51	3.88	34	9.2	2.40
TMPA^f	76	17.0	1.44	3.75	72	3.3	0.88

^{a}Concentration. ^{b}Viscosity. ^{c}Conductivity. ^{d}Molar conductivity. ^{e}At 45°C. ^{f}From Ref. 8.

The physical properties of TFSI-based RTMS in this study are also summarized in Table 1. The melting point of TES–TFSI (–35 °C) was much lower than QA-based RTMS such as trimethylpropylammonium (TMPA)–TFSI and the value was close to the cyclic aliphatic ammonium cation of *N*-methyl-*n*-butylpyrrolidinium (P14)–TFSI (–18 °C)[6] and a cyclic aromatic EMI–TFSI. This fact suggests that the melting points of TFSI salts might be lowered with the use of planar cations in the case of TFSI system.

The conductivities of TES–TFSI and TBS–TFSI are shown in Figure 1. This figure also shows the other cyclic planar system such as EMI–TFSI, P14–TFSI for the comparison. The conductivity of TES–TFSI is much higher than that of P14–TFSI, which was previously reported as the highest conductivity of all the QA-based RTMS.[7] However not only the conductivity but also the molar conductivity of TES–TFSI was a little lower than that of EMI–TFSI though the viscosity of TES–TFSI was almost the same as that of EMI–TFSI (Table 1). The ionic conductivity varies in proportion to the number of carrier ion and ionic mobility. If ionic mobility would be simply proportional to the viscosity in the case of such ionic liquids, the difference of the number of an ionic carrier caused the difference of molar conductivity between TES–TFSI and EMI–TFSI at almost the same viscosity. Considering that the number of ionic carrier contributed to the ionic conductivity might decrease with increasing the number of associated ion pair, such difference of the conductivity between TES–TFSI and EMI–TFSI might attribute to the degree of association between cation and anion. It means that the degree of association of TES and TFSI might be a little stronger than that of EMI and TFSI. However, further investigation will be necessary to clear the relationships between the ionic structure and the physical properties of RTMS.

As previously reported, QA-based RTMS exhibited high electrochemical stability comparing with aromatic cations such as EMI.[8] However, in the case of trialkylsulfonium-based RTMS, the cathodic limits were about 1.0 V positively shifted from the cathodic limit of QA-based RTMS as shown in Figure 2. The cathodic limit of trialkylsulfonium-based RTMS were almost the same as that of EMI-based RTMS. This must be due to the poor cathodic stability of sulfonium cations comparing with QA.
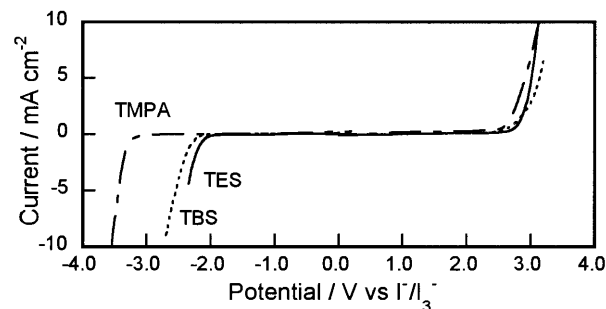

Figure 2. Linear sweep voltammogram of RTMS based on TFSI. Scan rate: 50 mV sec^{-1}. Temperature: 25 °C. Working electrode: Glassy carbon (0.00785 cm^2). Counter electrode: Pt (1.0 cm^2). Reference electrode: Pt wire immersed in EMI-TFSI contained 60 mM N(*n*-C$_3$H$_7$)$_4$I, 15 mM I$_2$.

In conclusion, we have succeeded in the synthesis of RTMS based on symmetric sulfonium cation with the use of TFSI. As we expected, the conductivity of the planar sulfonium based RTMS was much higher than that of QA–TFSI melts. Though the cathodic limit of trialkylsulfonium-based melt were not so much negative comparing with QA-based RTMS, it should be noted that the symmetric cation could also form RTMS. Currently, the preparation and investigation of asymmetric or cyclic sulfonium-based melts are in progress to elucidate the relationship between the ionic strucuture and the physical properties such as viscosity, conductivity, and melting point.

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10 Results of elemental analysis. Found: C, 16.5 ; H, 2.4 ; N, 3.8 ; F, 31.8 ; S,27.8%. Calcd for TMS–TFSI: C, 16.8; H, 2.5; N, 3.9; F, 31.9; S, 26.9%. Found: C, 23.9; H, 3.8; N, 3.5; F, 28.7; S, 24.6%. Calcd for TES–TFSI: C, 24.1; H, 3.8; N, 3.5; F, 28.5; S, 24.1%. Found: C, 34.6; H, 5.6; N, 2.9; F, 23.6; S, 20.3%. Calcd for TBS–TFSI: C, 34.8; H, 5.6; N, 2.9; F, 23.6; S, 19.9%.