Highly Conductive Room Temperature Molten Salts Based on Small Trimethylalkylammonium Cations and Bis(trifluoromethylsulfonyl)imide

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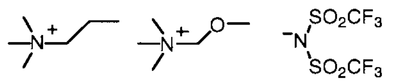
The electrochemically stable and relatively high conductive room temperature molten salts (RTMS) have been obtained with the use of small ammonium cations such as methoxymethyltrimethylammonium and bis(trifluoromethylsulfonyl)imide. The RTMS showed high conductivity (4.7 mS cm^{-1} at 25 °C) which is the highest value of all the ammonium based RTMS reported so far.

Room temperature molten salts (RTMS) have unique properties such as unvolatility, imcombastibility, 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] However, cathodic decomposition of EMI occurs a few hundred mV positive to the redox potential of Li/Li^+.[4] Therefore, EMI-based RTMS could not be used as electrolytes for lithium metal battery. On the other hand, an aliphatic quaternary ammonium (QA) cation seems to be an attractive candidate for a battery electrolyte because of its cathodic stability compared with that of EMI system. However, the conductivity of QA-based RTMS has been very low until the recent report by MacFarlane et al.[6–8] They reported that various asymmetric and cyclic QA's formed RTMS with bis(trifluoromethylsulfonyl)imide anion (TFSI). However, the conductivity of those RTMS was still a few times lower than that of EMI–TFSI.[7,8]

In this study, we tried to prepare high conductive and electrochemically stable RTMS based on QA. As a result, newly developed RTMS based on small trimethylalkylammonium cation and TFSI anion, shown in Scheme 1 (**1**–TFSI, **2**–TFSI), exhibited the highest conductivity of all the QA-based RTMS reported so far.



1 2 TFSI

Scheme 1. Structures of newly developed quaternary ammonium salts. 1: trimethylpropylammonium. 2: methoxymethyltrimethylammonium. TFSI: bis(trifluoromethylsulfonyl)imide.

The preparation of QA-based RTMS was basically followed by the reference[7] except that the starting material was recrystallized and the resulting RTMS was washed until no residual halogen was detected as stated below. QA-based RTMS was easily obtained by the mixing two aqueous solutions which contains equimolar of Li–TFSI and trimethylalkylammonium bromide. The resulting RTMS was washed with H_2O several times until no residual byproduct such as LiBr was detected with the use of $AgNO_3$. Then the RTMS was extracted with CH_2Cl_2 and dried under vacuum (130 °C) for 24 h. The yield of the QA–TFSI systems were at least over 70%. For the comparison, *N*-methylbutylpyrrolidinium (P14)–TFSI and EMI–TFSI were also prepared following the references 2 and 7, respectively. The measurement of conductivity (TOA, CV-40M), viscosity (Yamco, VM-100) and the electrochemical measurement (ALS, model 600A) were performed in a glove 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.[9] The melting point of RTMS was measured by DSC (Perkin/Elmer, Pyris 1).

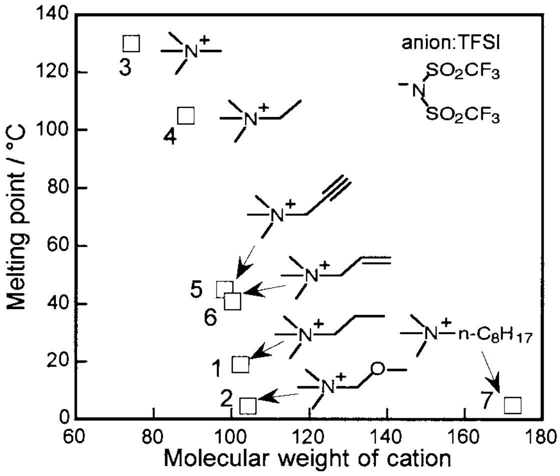


Figure 1 Melting point of QA-TFSI salt. 1: trimethylpropylammonium; 2: methoxymethyltrimethylammonium; 3: tetramethylammonium; 4: trimethylethylammonium; 5: trimethylpropargylammonium; 6: trimethylallylammonium; 7:trimethyl-n-octylammonium.

Figure 1 shows the melting points of various trimethylalkylammonium salts prepared in this study. The melting point of trimethylalkylammonium salt was decreased with increasing the length of the alkyl chain of the cation. In order to form RTMS consisted of QA cation and TFSI anion, at least the length of propyl group was necessary in the side chain of the cation.

The conductivity of **1**–TFSI and **2**–TFSI is shown in Figure 2. This figure also shows the data of EMI–TFSI and P14–TFSI for the comparison. The conductivity of **2**–TFSI is higher than that of P14–TFSI, which was previously reported as the highest conductivity of all the QA-based RTMS.[8] MacFarlane et al. reported that cyclic cations such as P14 were desirable for exhibiting high conductivity than the other trimethyl and triethylammonium systems.[8] However, the high conductivity of **1**–TFSI and **2**–TFSI show that such a cyclic system seems to be not always needed. However, the conductivity was not as high as that of EMI–TFSI.

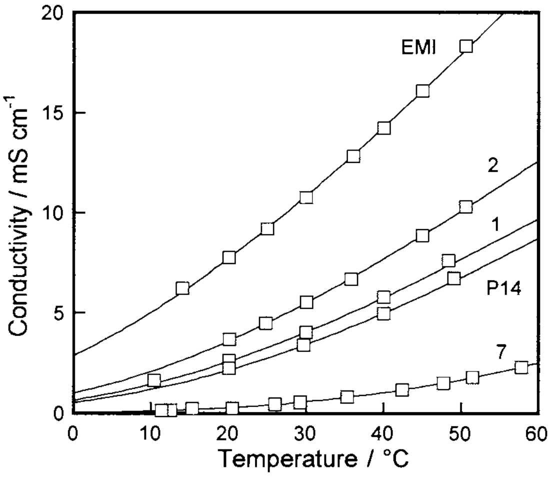


Figure 2. Conductivity of RTMS based on TFSI anion. EMI: 1-Ethyl-3-methylimidazolium. P14: N-methylbutylpyrrolidinium.

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

cation	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}
1	17	1.44	3.75	72	3.3	0.88
2	4.5	1.51	3.93	50	4.7	1.2
EMI	-12	1.51	3.88	34	9.2	2.4
P14	-18^{e}	1.41	3.34	70	2.9	0.87

[a]Concentration. [b]Viscosity. [c]Conductivity. [d]Molar conductivity. [e]From Ref. 8.

The physical properties of TFSI-based RTMS in this study are summarized in Table 1. The molar conductivity of TFSI-based RTMS is increased with decreasing the viscosity. It is interesting that the product of the viscosity and the molar conductivity was an almost constant, which means that Walden's rule might be approved between TFSI-based RTMS shown in Table 1. This suggests that the viscosity of TFSI-based RTMS is mainly governed by simple physical interactions such as electrostatic interactions between cation and anion. In the case of EMI-TFSI, such interactions between EMI and TFSI might be smaller than that of QA and TFSI since the charge density of aromatic EMI cation seems much smaller than that of aliphatic QA. Therefore the viscosity of EMI–TFSI is smaller than that of QA–TFSI and the conductivity of EMI–TFSI is higher than that QA–TFSI.

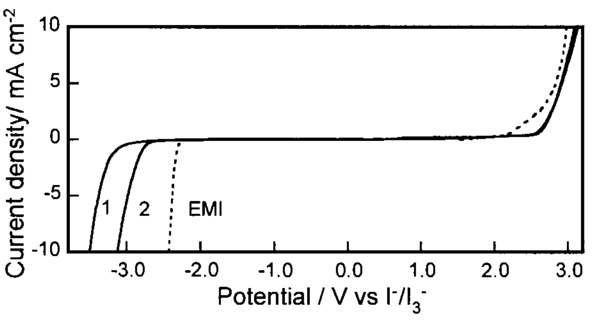


Figure 3. Linear sweep voltammogram of RTMS based on TFSI. Scan rate: 50 mV sec^{-1}. Temperature: 25 °C. Working electrode: Glassy carbon (0.00785 cm^{2}). Counter electrode: Pt (1.0 cm^{2}). Reference electrode: Pt electrode immersed in EMI-TFSI contained 60 mM N(n-C_3H_7)$_4$I, 15 mM I_2.

One of the reasons to investigate QA-based RTMS is to form highly electrochemically stable RTMS for a battery electrolyte. Figure 3 shows the electrochemical windows of RTMS containing TFSI. The potential window of QA-based RTMS was wider than that of EMI–TFSI as we expected. Especially, the potential window of **1**–TFSI was over 5.5 V. This was due to the improvement of cathodic stability of cations (1>2>>EMI). Furthermore, the redox behavior of lithium was observed in **1**–TFSI since the redox potential of Li^{+}/Li is –2.95 V vs I^{-}/I$_3^{-}$, which was a few hundred mV negative to the cathodic limit of EMI. The detail of the lithium electrochemistry in **1**–TFSI will be published elsewhere.

In conclusion, we have succeeded in the synthesis of RTMS based on small quaternary ammonium with the use of TFSI. As we expected, the electrochemical stability of the QA based RTMS was much higher than that of EMI. Since the melting point of QA-based melt was steeply raised at **1**–TFSI, **1** was the smallest ammonium cation to form RTMS with TFSI. Considering the difference of cathodic limit between **1**–TFSI and **2**–TFSI, QA cation, which does not contain heteroatoms such as oxygen, might be essential for RTMS with high electrochemical stability. Therefore, further improvement of the conductivity of QA-based melt, which keeps the high electrochemical stability, need to investigate an appropriate anion other than TFSI.

References and Notes

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9 Results of elemental analysis. Found: C, 25.1 ; H, 4.20 ; N, 7.40; F, 29.9%. Calcd for **1**–TFSI: C, 25.1; H, 4.22; N, 7.33; F, 29.8%. Found: C, 21.8 ; H, 3.60; N, 7.30; F, 29.5%. Calcd for **2**–TFSI**:** C, 21.9; H, 3.67; N, 7.29; F, 29.7%. Found: C, 20.4; H, 3.50; N, 7.80; F, 31.8%. Calcd for **3**–TFSI: C, 20.3; H, 3.41; N, 7.91; F, 32.2%. Found: C, 22.2; H, 3.80; N, 7.40; F, 30.5%. Calcd for **4**–TFSI**:** C, 22.8; H, 3.83; N, 7.61; F, 30.9%. Found: C, 25.6; H, 3.30; N, 7.40; F, 30.8%. Calcd for **5**–TFSI: C, 25.4; H, 3.20; N, 7.40; F, 30.1%. Found: C, 25.3; H, 3.80; N, 7.30; F, 31.1%. Calcd for **6**–TFSI**:** C, 25.3; H, 3.71; N, 7.37; F, 30.0%. Found: C, 34.4; H, 5.70; N, 6.10; F, 25.2%. Calcd for **7**–TFSI: C, 34.5; H, 5.79; N, 6.19; F, 25.2%.