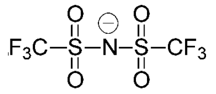
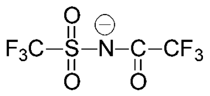
Physical and Electrochemical Properties of Room Temperature Molten Salt Based on Aliphatic Onium Cations and Asymmetric Amide Anion

Hajime Matsumoto*, Hiroyuki Kageyama, and
Yoshinori Miyazaki
Special Division of Green Life Technology,
National Institute of Advanced Industrial Science and
Technology (AIST)
1-8-31 Midorigaoka Ikeda, Osaka 563-8577, Japan.
*e-mail h-matsumoto@aist.go.jp

Room temperature molten salts (RTMS) have attracted attention as a novel safe electrolyte for electrochemical energy devices, such as lithium battery, because of various unique properties such as nonvolatility, incombustibility.[1,2] We have studied the physical and electrochemical properties of RTMS based on aliphatic quaternary ammonium (AQA) and bis(trifluoromethylsulfonyl)imide (TFSI) systems because of their high cathodic stability comparing with imidazolium systems and high chemical stability in air.[3] In AQA-TFSI melts, lithium deposition/stripping peak could be observed, however, AQA systems have several defects in view of battery electrolyte, such as. For example, they have higher viscosity, lower conductivity and higher melting point than imidazolium systems at the same molecular weight.

Though TFSI anion has ability to lowering melting point of even in the symmetric aliphatic onium salts such as trialkylsulfonium salts[4], tetraalkylammonium salts[5], the melting point of small onium cation such as trimethylsulfonium, tetramethylsulfonium, which was expected to show low viscosity due to their small molecular weight, were no longer below room temperature. In this study, we proposed new anionic species with asymmetric structure (2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide, TSAC) to improve the melting point and the viscosity of small aliphatic onium cations. The physical and electrochemical properties of those new RTMS were reported comparing with corresponding TFSI salts.


TFSI (*symmetric*)


TSAC(*asymmetric*)

The preparation of RTMS based on TSAC was followed by that of AQA-TFSI melts in an aqueous solution. Since the solubility to water of TSAC salts were slightly higher than that of TFSI salts, the yields of TSAC salts were decreased comparing with corresponding TFSI salts. Table 1 shows the melting point and the viscosity of TSAC salts and that of TFSI. TSAC anion makes RTMS with various cations even in low molecular weight (MW<100) except that tetramethylammonium salt. The melting points of TSAC salts were 70~100°C decreased comparing with corresponding TFSI salts. These fact indicated that asymmetry of anionic species was effective to decrease the melting point of the salts containing poor charge dispersible cations such as aliphatic onium cations. It was interesting that the melting point of EMI-TSAC was increased comparing with corresponding TFSI melt.

Though the viscosity of RTMS was decreasing with decreasing the molecular weight of the component ions as showing in various reports[3,6-7], the viscosity of TSAC melts was no longer decreased dramatically with decreasing the MW of small aliphatic onium cations. However, the viscosity of TSAC melts was decreased comparing corresponding TFSI melts.

Figure 1 shows the potential windows of RTMS based on TSAC and TFSI melts. Unexpected results were obtained. The cathodic limit of TEA-TSAC was almost the same as that of EMI-TFSI. This indicates that the cathodic limit of RTMS is not simply decided with the reduction potential of cationic species. On the other hand, anodic limit might not be simply reflecting the oxidation of anion too. Further study will be necessary to clear what decide the cathodic and anodic limit of RTMS.

1. Y.S. Fung *et al., J.Appl.Electrochem.*,**23**,346(1993).
2. J. Caja *et al.,Proc.-Electrochem.Soc.*,99-*41 (Molten Salts XII)*, p. 150.(2000).
3. H. Matsumoto *et al.,Proc.-Electrochem.Soc.*,99-*41 (Molten Salts XII)*, p. 186(2000).
4. H. Matsumoto *et al, Chem. Lett.*,1430 (2000).
5. H. Matsumoto *et al, Chem. Lett.*,182 (2001).
6. P. Bonhôte *et al, Inorg. Chem.*, **35,**1168 (1996).
7. J. Sun *et al, J. Phys. Chem.*, **103,**4164 (1999).

Acknowledgement

We are indebted to TOKUYAMA,Corp. for providing K-TSAC salt.

Table 1 Melting point (m.p./°C) and viscosity (η/mPas, T=25°C) of RTMS based on aliphatic onium cations.

Cation	MW[a]	TFSI anion m.p.	TFSI anion η	TSAC anion m.p.	TSAC anion η
$(CH_3)_3N^+$-R					
R=CH_3	74	130	-	64	-
C_2H_5	88	105	-	-10	51
propargyl	98	45	-	b	65
allyl	100	41	-	-2.9	42
iC_3H_8	102	129	-	29	108
nC_3H_8	102	19	72	10	45
nC_6H_{13}	144	27	132	b	119
$(C_2H_5)_3N^+$-R					
R=CH_3	116	129	-	20	61
C_2H_5	130	110	-	23	80
$(C_2H_5)_2N(CH_3)_2{}^+$	102	>60	-	<4	42
P_{11}[c]	100	105	-	14	80
TMS[d]	77	44.5	-	<4	n.d.
EMI	111	-12	34	2.6	25

[a]Molecular weight of cation, [b]tg only, [c]N,N-dimethyl-pyrroridinium.[d]trimethylsulfonium. n.d.: no data.

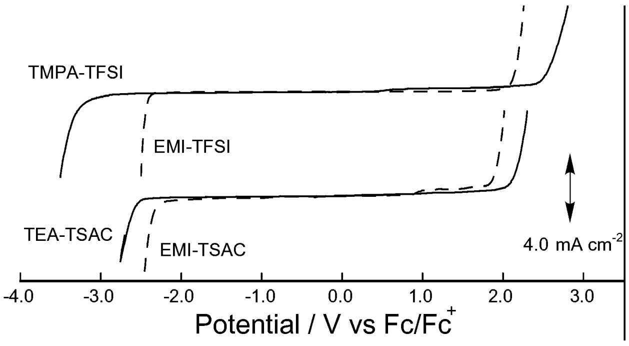


Figure 1 Linear sweep voltammogram of glassy carbon electrode in dried RTMS ([H_2O]<30ppm). TMPA:trimethylpropylammonium, TEA:tetraethylammonium, Temperature: 25°C, Scan rate: 50 mV sec^{-1}, Reference electrode: Pt immersed in EMI-TFSI containing 15 mM I_2 and 60 mM tetrapropylammonium-iodide.[6] Potential was corrected with the redox potential of ferrocene in each melts.