

Ionic liquids containing an ester group as potential electrolytes

Hoon Sik Kim¹, Je Seung Lee², Nguyen Dinh Quan², Hyunjoo Lee², Sang Deuk Lee² and Honggon Kim²

¹Department of Chemistry, Kyung Hee University, 1 Hoegi-dong, Dondaemoon-gu, Seoul 130-701, Korea. Fax: 02 966 3701; Tel: 02 961 0432; E-mail: khs2004@khu.ac.kr.

²Reaction Media Research Center, Korea Institute of Science and Technology, Sungbuk-gu, Seoul 136-791, Korea.

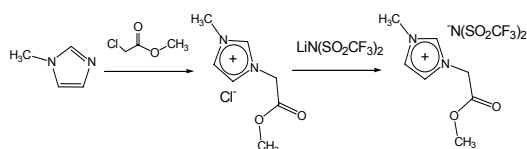
Lithium-based battery, a key component of various electronic devices including cellular phones, laptop computers, and digital cameras, is now expanding its applications to vehicles and other large-scale power systems due to the high energy density and energy efficiency. However, the current lithium battery system has an inherent safety problem arising from the use of volatile and flammable organic carbonate compounds as electrolyte solvents. Besides the safety problem, the organic carbonate-based electrolyte systems for lithium ion batteries have many other drawbacks in terms of charge/discharge capacity, operating temperature limit, and ionic conductivity, and thus there is a room for possible improvement. Recently, imidazolium-based room temperature ionic liquids (RTILs) have received considerable interest as potential electrolytes for lithium batteries, due to their favourable properties such as wide electrochemical window, high ionic conductivity, non-flammability, and wide operating temperature range.¹⁻⁵

However, the application of imidazolium-based ionic liquids as electrolytes of lithium ion battery has been restricted due to their low cathodic stability toward lithium.^{6,7} For this reason, many attempts were made to develop alternative ionic liquids with high cathodic stability. Ionic liquids based on 2-substituted imidazolium,⁸ tetraalkylammonium,^{9,10} pyrrolidinium,¹¹ and piperidinium¹² cations were found to exhibit better cathodic stability toward lithium.

Recently, M. Egashira et al. showed that the introduction of cyano group onto the quaternary ammonium cation significantly improved the cycle performance and the conductivity of the corresponding quaternary ammonium-based ionic liquids.¹³ Even though this result clearly demonstrates that the electrochemical properties of an ionic liquid can be tuned by the substitution of an appropriate functional group on the cation, detailed investigation on the interaction between a functional group and a lithium salt has rarely been attempted.

In this regard, we have prepared several ionic liquids containing a methyl ester group on the cations with a hope that the favourable interaction between the ester group and a lithium salt could improve various electrochemical properties of the resulting electrolytes such as lithium ion conduction.

Imidazolium, pyrrolidinium, morpholinium, and piperidinium-based ionic liquids were prepared in two steps by reacting methyl chloroacetate with 1-methylimidazole, *N*-methylpyrrolidine, *N*-methylmorpholine, or *N*-methylpiperidine followed by anion exchange with LiN(SO₂CF₃)₂ (LiTFSI). A typical example is depicted in Scheme 1.



< Scheme 1 >

The thermal stabilities of these ionic liquids were tested in a nitrogen atmosphere between 50 and 900 °C at a heating rate of 10 °C/min. As shown in Table 1, all the ionic liquids tested exhibited high thermal stabilities and similar TGA tendencies, showing two distinct decomposition temperatures between 290 and 440 °C. The decompositions at lower temperatures are likely to be attributed to the decomposition of the ester group.

The melting temperatures of these ionic liquids were also determined using a TA Instruments Q10 differential scanning calorimeter (DSC) in the range from -90 to 100 °C at a scan rate of 10 °C/min under a nitrogen atmosphere. As listed in Table 1, the ionic liquids containing an ester group melt at around -42 °C, demonstrating wide liquid temperature ranges for these ionic liquids.

Table 1. Thermal Properties of Ionic Liquids

	$T_m/^\circ\text{C}^a$	$T_{\text{decomp}1}/^\circ\text{C}^b$	$T_{\text{decomp}2}/^\circ\text{C}^b$
[MMEIm][TFSI]	-42.5	340	440
[MMEPyr][TFSI]	-42.1	290	400
[MMEMor][TFSI]	-42.0	310	400
[EMEPip][TFSI]	-42.2	335	410

^a T_m = melting temperature, ^b $T_{\text{decomp}1}$, $T_{\text{decomp}2}$ = decomposing temperatures. MMEIm = methyl 1-methylimidazolium-3-acetate, MMEPyr = methyl *N*-methylpyrrolidinium-*N*-acetate, MMEMor = methyl *N*-methylmorpholinium-*N*-acetate, EMEPip = methyl *N*-ethylpiperidinium-*N*-acetate, TFSI = bis(trifluoromethanesulfonyl)imide.

The ionic conductivities measured by a solartron 1260A frequency response analyzer (FRA) are presented in Fig. 1 and 2 as a function of temperature. The conductivities of these ionic liquids increased with increasing temperature, possibly due to the decrease in viscosity at higher temperatures. It is well known that the addition of a lithium salt drastically decreases the conductivities of ionic liquids, however, as shown in Fig. 2, the conductivities decreased to a much smaller extent around 30% when LiTFSI was added to an ionic liquid containing a methyl ester group. This result suggests that the ester group on the ionic liquid is playing a favorable role in the conductivity of ionic liquids through an interaction with a lithium salt.

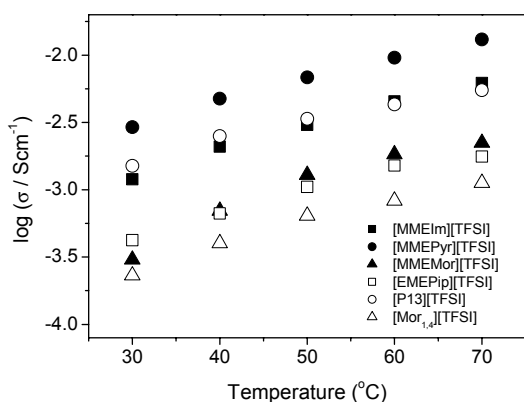


Fig. 1 The ionic conductivities of ionic liquids as a function of temperature.

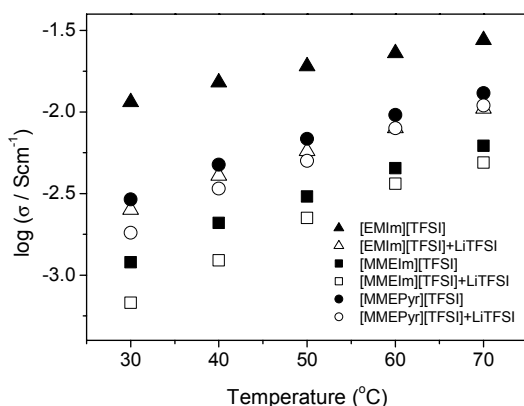


Fig. 2 The ionic conductivities of ionic liquids with 1m LiTFSI as a function of temperature.

The interaction of the ester group with a lithium salt is clearly demonstrated by a FT-IR experiment. The peak associated with the carbonyl group of methyl 1-methylimidazolium-3-

acetate bis(trifluoromethylsulfonyl) imide ([MMEIm][TFSI]) shifted to a lower frequency from 1759 to 1747 cm^{-1} upon mixed with 2 equivalents of LiPF_6 . On the contrary, the stretching frequency assigned to the C-O single bond moved to a higher frequency to 1209 from 1184 cm^{-1} , possibly due to a resonance between the carbonyl group and the C-O single bond.

The electrochemical stabilities of the ionic liquids were also analyzed by using a cyclic voltammetry (CH Instruments Electrochemical Work Station) at an ambient temperature. A glassy carbon working electrode of 3 mm diameter was used with a platinum wire as the counter electrode and a silver wire as the reference electrode. Fig. 3 displays the cyclic voltammograms for four different types of ionic liquids containing a methyl ester group. All the ionic liquids exhibited surprisingly wide electrochemical windows of at least 5.0 V, indicating the contribution of the ester group to the electrochemical stability of these salts.

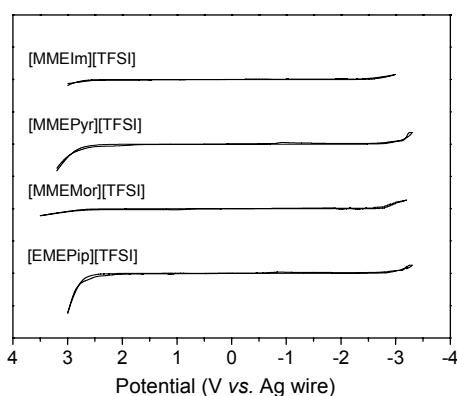


Fig. 3 Cyclic voltammograms of ionic liquids at 25 °C.

In conclusion, the presence of an ester group on the cations was found to improve thermal and electrochemical properties of room temperature ionic liquids. Due to their excellent thermal and electrochemical stability of the ionic liquids containing an ester group, it is expected that these ionic liquids may find some application as promising alternatives to the conventional carbonate-based electrolytes used in the secondary batteries.

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