

# Cyano-containing quaternary ammonium-based ionic liquid as a ‘co-solvent’ for lithium battery electrolyte

Minato Egashira<sup>a,\*</sup>, Maika Nakagawa<sup>b</sup>, Izumi Watanabe<sup>b</sup>,  
Shigeto Okada<sup>b</sup>, Jun-ichi Yamaki<sup>b</sup>

<sup>a</sup> Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University,  
2-16-1 Tokiwadai, Ube, 755-8611 Yamaguchi, Japan

<sup>b</sup> Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga Koen 6-1, Kasuga 816-8580, Japan

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## Abstract

Imidazolium-based ionic liquid is one of attractive candidates for advanced lithium battery electrolyte. However, its cathodic stability is not sufficient for the reversible charge–discharge of negative electrodes. The authors previously proposed a quaternary ammonium-based ionic liquid containing a cyano group (cyano-QA) as a film-forming electrolyte on the negative electrode surface. In the present study, several cyano-QA ionic liquids have been prepared and their electrolyte properties have been estimated. Some ionic liquids based on cyano-containing quaternary ammonium cation provided reversible lithium deposition/dissolution couple when they were used as ‘co-solvent’ of electrolyte with the co-existence of EMITFSI.

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## 1. Introduction

At room temperature ionic liquids are known to be non-volatile and thermally stable; therefore, they are expected to improve the cell safety when they are applied in lithium battery electrolyte. Recently, the study on such ionic liquids has been expanded and many ionic liquids continue to be synthesized [1–10]. Among them, the family of salts based on 1-ethyl-3-methyl imidazolium (EMI) cation appears to be most promising, because they have  $10^{-2}$  S cm<sup>-1</sup> order of conductivity comparable with organic solvent electrolyte systems, low viscosity compared with every ionic liquid systems and rather wide electrochemical window. However, EMI-based ionic liquids themselves are not available for lithium battery electrolyte mainly due to their poor stability toward reduction. The reduction potential of EMI-based ionic liquids are around 1 V versus Li/Li<sup>+</sup> [11,12], and they provide no surface film as seen in conventional organic sol-

vent systems, which is known as “solid electrolyte interphase (SEI)”. Thus, EMI-based ionic liquids decompose on lithium or lithiated carbon surface, and never proceed for charge–discharge process of such negative electrode. Many efforts have been made to achieve charge–discharge process of lithium in ionic liquid electrolytes. One direction is to apply more stable cation than EMI such as quaternary ammonium, piperidinium or pyrrolidinium cations [9,13]. Howlett et al. reported that *N*-methyl-*N*-propyl pyrrolidinium bis(trifluoromethane sulfone)imide (TFSI)-based electrolyte was sufficiently stable toward lithium and provided rather stable lithium deposition/dissolution [13]. However, most of ionic liquids applying non-EMI cations suffer from their low conductivity, especially when lithium salt is dissolved into them. Another direction is to apply additives in EMI-based ionic liquids. Several additives, such as H<sub>2</sub>O [11], SOCl<sub>2</sub> [14], C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>Cl [15] and organic solvents used in conventional lithium battery electrolyte [12,16,17], have been reported to improve the lithium deposition/dissolution behavior in EMI-based ionic liquid electrolytes. These additives surely succeeded to provide a reversible lithium

\* Corresponding author. Tel.: +81 836859212; fax: +81 836859201.  
E-mail address: [minato@yamaguchi-u.ac.jp](mailto:minato@yamaguchi-u.ac.jp) (M. Egashira).

deposition/dissolution process. However, some of these additives are poisoned the charge–discharge process of high-voltage positive electrode.

The authors previously reported [18] that an ionic liquid based on a cyano-substituted quaternary ammonium cation provided reversible lithium deposition/dissolution. On that study, there are some signs that cyano-containing quaternary ammonium cation may provide a surface protective film on lithium. In the present study, some cyano-containing quaternary ammonium ionic liquids have been synthesized, and have applied for the electrolyte ‘co-solvent’ with EMITFSI to be used in electrochemical lithium deposition/dissolution. Through this study, we expect to design novel hybrid ionic liquid system having high conductivity and cathodic stability.

## 2. Experimental

In the present study, the authors prepared three kinds of cyano group containing ionic liquids. The cation structures of prepared ionic liquids are shown in Fig. 1. In all cases, anion was trifluoromethane sulfone imide (TFSI). The preparation route of these ionic liquids were similar to the one reported previously [18,19]. EMITFSI was prepared by the ion-exchange of EMICI (Aldrich) with LiTFSI (Fluka) in an aqueous phase. The obtained lower-phase liquid was washed by water, purified by alumina column and dried in vacuum. The purity of all ionic liquids used in the present study was checked by  $^1\text{H}$  NMR and elemental analyses. The water content in ionic liquids was confirmed to be below 30 ppm by Karl-Fischer aquacounter (Hiranuma Co., Japan, AQ-7). In Ar-filled glove box, the cyano-containing ionic liquid and EMITFSI were mixed in prescribed gravimetric ratio, and then  $0.2 \text{ mol dm}^{-3}$  of LiTFSI (Fluka) was dissolved into those ionic liquid mixtures to prepare an electrolyte containing lithium ion.

The conductivity of ionic liquids and lithium containing electrolytes was measured using LCR meter (Hewlett Packard, 4284A) and a glass-made T-shape cell with platinum electrodes. A lithium deposition/dissolution test was performed using a three-electrode T-shape cell with Teflon body, SS working electrode and lithium foil counter electrode pressed on a SS lead. For reference electrode, lithium foil was dipped in  $1 \text{ mol dm}^{-3}$   $\text{LiClO}_4/\text{EC-PC}$  (Tomiya Pure Chemical Co.) in a glass tube with a vycor glass tip. Cyclic voltammetry measurements were done using highly sensitive potentiostat (Huso Electronics Co., Japan) under the scanning rate of  $0.5 \text{ mV min}^{-1}$  and the potential range of 1.5

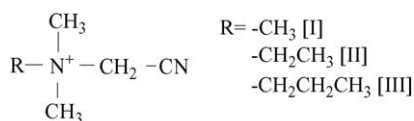


Fig. 1. Structural formula of quaternary ammonium cation prepared at the present study.

to  $-0.5 \text{ V}$  versus  $\text{Li/Li}^+$ . All electrochemical measurements were carried out in temperature chamber (Espec Co., Japan, SU-241).

## 3. Results and discussion

The Arrhenius plots of the conductivity of ionic liquid electrolytes, where the mixing ratio of EMITFSI and cyano-containing liquid was 0:1, 1:0 or 1:1, are shown in Fig. 2. All cyano-containing ionic liquids have conductivity as low as  $10^{-4} \text{ S cm}^{-1}$  around room temperature. These conductivity values are insufficient for the use in lithium battery electrolyte. When these ionic liquids were mixed with EMITFSI, their conductivity values were improved to  $10^{-3} \text{ S cm}^{-1}$  order at room temperature. Such values are still lower than LiTFSI/EMITFSI solution, however, thought to be sufficient for lithium battery use. Especially,  $0.2 \text{ mol dm}^{-3}$  LiTFSI/II-TFSI-EMITFSI solution exhibited  $2.2 \times 10^{-3} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ . The order of conductivity at  $25^\circ\text{C}$  was  $\text{II} > \text{I} > \text{III}$ -TFSI, even in case of co-existing EMITFSI. In this case, the conductivity order may be mainly influenced by cation size. It is generally assumed that a larger sized cation may provide a weaker interaction with surrounded anions. In contrast, it is also assumed that a larger cation has a lower mobility. Therefore, a moderate sized cation may be favorable to obtain the highest conductivity. LiTFSI solutions based on I- or II-TFSI/EMITFSI mixture showed a conductivity drop around  $0^\circ\text{C}$ , while the mixture based on III-TFSI shows a typical VTF relationship at wider temperature region.

It is expected that the conductivity of mixed electrolyte may be improved by increasing the ratio of EMITFSI. The

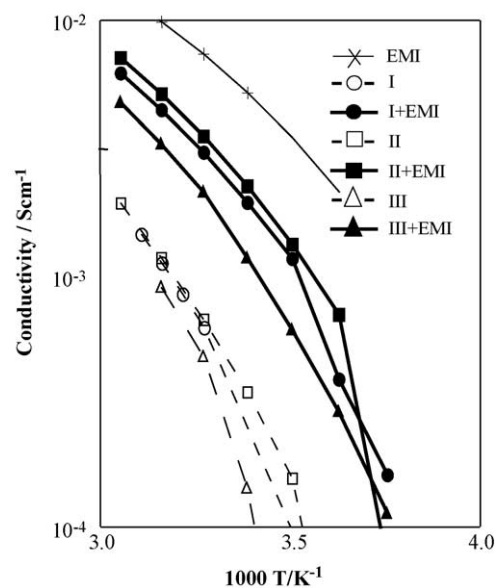


Fig. 2. Arrhenius plots for conductivity of ionic liquids and their lithium salt solutions.

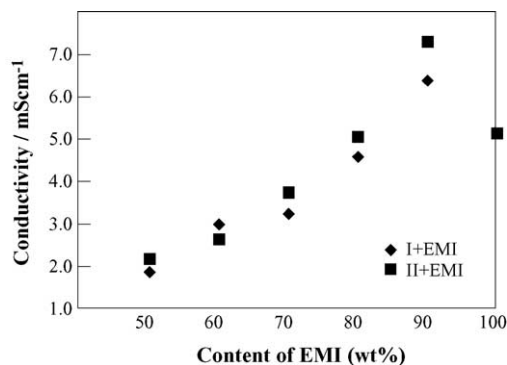


Fig. 3. Conductivity of the ionic liquid mixtures of I- or II-TFSI with EMITFSI vs. the content of I- or II-TFSI at 25 °C.

conductivities of the mixed electrolytes at 25 °C are plotted toward the gravimetric ratio of I- or II-TFSI in EMITFSI in Fig. 3. As it is expected, the conductivity increased as the increase of the ratio of EMITFSI. In addition, the conductivity of electrolyte containing 10 wt% of I- or II-TFSI is higher than LiTFSI/EMITFSI electrolyte. This result, together with the former finding of the conductivity increase of LiTFSI/I-TFSSI solution from I-TFSI itself, suggests that I or II cation contributes to increase the mobility of Li<sup>+</sup> in ionic liquid electrolyte. Such an effect of I- and II-TFSI appears to be very interesting for the use of these salts as an additive to enhance the conductivity of lithium salt solution of various ionic liquids. For example, Sakaebe et al. suffered from the conductivity drop when dissolving lithium salt in a piperidinium-based ionic liquid, even though the electrolyte provided a good cell performance. It is expected that the addition of small amount of I- or II-TFSI may improve the conductivity of such an ionic liquid electrolyte. Also in Fig. 3, the mixed electrolyte containing II-TFSI exhibited a better conductivity than that containing I-TFSI. This conductivity difference was rather clear at lower content of I- or II-TFSI, and when its content reached 40 wt%, the conductivities in both cases were similar. Fig. 4 shows the cyclic voltammograms of SS/Li cells with EMITFSI and its 1:1 mixture with I-, II- and III-TFSI electrolytes at 25 °C. Being similar to well-known results, EMITFSI was decomposed at higher potential than lithium deposition/dissolution equilibrium potential, and only showed an irreversible cathodic current around 0.3 V versus Li/Li<sup>+</sup>. When II-TFSI was mixed with EMITFSI, similar irreversible current was obtained. In contrast, when I- or II-TFSI was mixed with EMITFSI, a reversible couple, which can be attributed to lithium deposition/dissolution, was clearly observed. Indeed, it is very interesting that ionic liquid electrolyte containing EMITFSI provides reversible lithium deposition/dissolution couple. In the previous study, the authors reported that I-TFSI itself similarly exhibited lithium deposition/dissolution electrochemical couple. We also suggested that such cyano-containing ionic liquid provides a surface protective film similar to the SEI in the case of conventional organic solvent electrolyte. From the present results, the existence of I- or

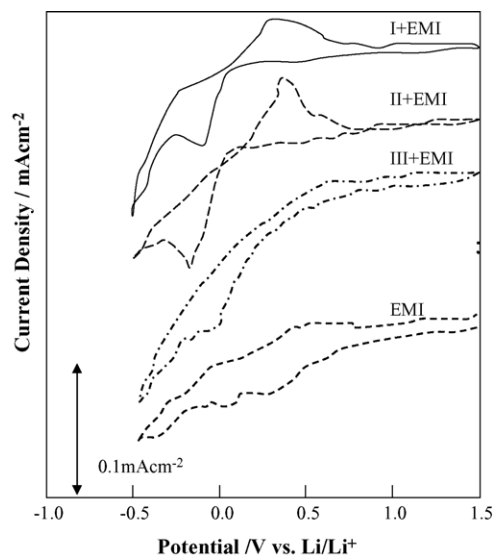


Fig. 4. Cyclic voltammograms for lithium deposition/dissolution on SS electrode in various ionic liquid electrolytes at 25 °C.

II-TFSI surely prevented the decomposition of EMITFSI and provided the reversible lithium deposition/dissolution. This result confirms the formation of protective film from I- and II-TFSI. Cyano group is considered to be less stable than alkyl group toward reduction. Thus, the cyano-containing cation may decompose a higher potential than the one where EMITFSI decompose. It is clear that the surface film formation ability is influenced by cation structure of cyano-containing ionic liquid, in other words, the length of alkyl chain connected with nitrogen. However, it is still unclear whether the chemical structure directly affects to the decomposition behavior of cation or other chemical or

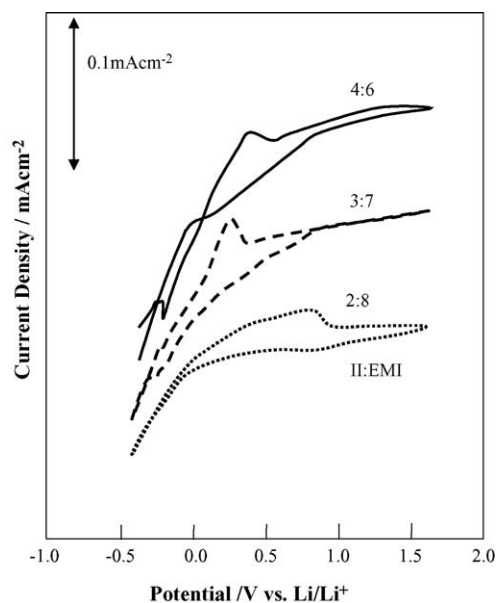


Fig. 5. Cyclic voltammograms for lithium deposition/dissolution on SS electrode in LiTFSI/the mixture of II-TFSI and EMITFSI vs. the content of II-TFSI at 25 °C.

physical properties, such as viscosity of ionic liquid, which should be related to the cation structure affect to lithium decomposition/dissolution behavior. From the viewpoint of chemical stability of cation, if an alkyl chain connected to nitrogen become longer, nitrogen should become more reactive toward reduction. This tendency appears to be reasonable with the experimental results. Fig. 5 shows the cyclic voltammograms of  $0.2 \text{ mol dm}^{-3}$  LiTFSI/II-TFSI/EMITFSI with various ratio of II-TFSI and EMITFSI. When the content of II-TFSI in II-TFSI/EMITFSI system was above 20 wt%, lithium dissolution peak, a sign of reversible lithium deposition/dissolution couple, was observed.

#### 4. Conclusion

Some ionic liquids based on cyano-containing quaternary ammonium cation provided reversible lithium deposition/dissolution couple when they were used as ‘co-solvent’ of electrolyte with the co-existence of EMITFSI. These ionic liquids also enhanced the conductivity of LiTFSI/ionic liquid solution probably due to the contribution to generate dissociated lithium ions in such a solution.

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