

# The preparation of quaternary ammonium-based ionic liquid containing a cyano group and its properties in a lithium battery electrolyte

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Received 19 January 2004; received in revised form 16 June 2004; accepted 16 June 2004

Available online 12 August 2004

## Abstract

A room temperature ionic liquid consisting of *N,N,N,N*-cyanomethyl trimethyl ammonium (CTMA) cation and bis(trifluoromethane sulfonyl)imide (TFSI) anion was newly synthesized, and its electrochemical properties were investigated. This ionic liquid has a melting point of 35 °C and an order of conductivity of  $10^{-4}$  S cm<sup>-1</sup>. Lithium deposition/dissolution tests in 0.2 mol dm<sup>-3</sup> LiTFSI/CTMATFSI electrolytes showed an improved cycle behavior compared with that of a Li electrolyte based on a tetraalkylammonium ionic liquid without a cyano group. It is suggested that such an improvement may be associated with the formation of a protective film on the lithium surface. Introducing a proper functional group is suggested to be effective to improve the interfacial properties of ionic liquid.

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**Keywords:** Ionic liquid; Lithium battery; Cyano group

## 1. Introduction

Room temperature ionic liquids have been recently attracted considerable interest in the field of battery research for their use as advanced nonaqueous, non flammable and non volatile electrolytes [1–5]. Almost all ionic liquids consist of a large organic cation whose charge is delocalized. Specifically, through its combination with various kinds of anions, the 1-ethyl-3-methyl imidazolium (EMI) cation provides ionic liquid at room temperature with a conductivity as high as  $10^{-2}$  S cm<sup>-1</sup> [6]. The greatest difficulty in applying this kind of ionic liquid as lithium battery electrolytes is its low cathodic stability; EMI-based ionic liquids are usually unstable toward lithium [7,8]. Lithium battery electrolytes, even conventional organic solvent electrolytes, are reactive with lithium; however, in this case, the formation of a passivation film on the lithium surface inhibits further decompo-

sition of the electrolyte. Indeed, this film, known as a solid electrolyte interphase (SEI), is assumed to be a key factor in controlling the performance of lithium batteries [9–11]. EMI-based ionic liquids do not seem to provide an equally stable SEI when they are decomposed on the lithium surface. The relatively low cathodic stability of these ionic liquids is assumed to be caused by the nature of the EMI cation.

Two general approaches have been proposed to improve the cathodic stability of ionic liquids and to utilize them as lithium battery electrolytes. One approach is to use more stable cations such as 2-substituted imidazolium [7], tetraalkyl ammonium [12,13], pyrrolidinium [14], or piperidinium [15] cations. Ionic liquids consisting of such cations have been found to exhibit improved cathodic stability, or stability toward lithium; however, they suffer from low ionic conductivity. The other approach is to add film-forming materials to the ionic liquids: proton sources such as HCl [16], SOCl<sub>2</sub> [3], and H<sub>2</sub>O [8] have been reported to be effective additives for forming a protective film on the lithium surface. Organic solvents, commonly used as lithium battery electrolytes, are

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also effective to improve lithium deposition/dissolution behavior [17]. However, proton sources may inhibit cell reactions at both the positive and negative electrodes. Organic solvent additives may not have such an inhibitory effect, but their addition eliminates the advantage of using ionic liquid electrolytes.

Taking the above into consideration, an ionic liquid capable of providing a protective film on the lithium surface would be highly welcome as an ideal lithium battery electrolyte or at least as an ideal electrolyte additive. In the present study, a tetraalkylammonium cation containing a cyano group was prepared. The salt which consists of this cation and a bis(trifluoromethane sulfone)imide (TFSI) anion behaves like an ionic liquid at room temperature when used as an electrolyte in a lithium cell. This ionic liquid also demonstrates an improved lithium deposition/dissolution behavior.

## 2. Experimental

We have prepared two kinds of tetraalkylammonium ionic liquids, the first of which consisted of three methyl groups and a cyanomethyl group (hereafter referred to as CTMA), and the second of which consisted of three methyl groups and a butyl group (hereafter referred to as BTMA). In both cases, the anion was TFSI. Fig. 1 illustrates the structure of the cations and the anion used here. The syntheses of these ionic liquids were carried out in two steps. First the tetraalkylammonium iodides were synthesized by the addition of methyl iodide to the corresponding dimethyl amines in ether at room temperature, according to the procedure described by Bhattacharjee et al. [18]. Ionic liquids were obtained by the ion-exchange of these iodides and equimolar LiTFSI in water. The hydrophobic phase in this ion-exchange reaction was washed with distilled water several times to remove ionic impurities, collected and purified with a column of neutral alumina (Aldrich, as received). The neutral alumina for the column content was selected according to the report by Fuller et al. [8]. Acetonitrile was used as a mobile phase in this column. After drying in a vacuum, transparent liquids were obtained, and the products were identified by elemental analysis. The C, H, and N ratios of the produced CTMATFSI and BTMATFSI were 22.10, 2.95, and 11.42% (CTMATFSI), and 24.30, 3.59,

and 7.07% (BTMATFSI), respectively, while their calculated ratio of them were 22.10, 2.92, and 11.08% (CTMATFSI) and 24.24, 3.56, and 7.07% (BTMATFSI), respectively. In addition, the purity of these ionic liquids was monitored by  $^1\text{H-NMR}$  (JEOL Co., JNM-LA400). Here in both cases no peaks were observed more than expected ones from their structures. The melting points of ionic liquids were measured using a differential scanning calorimeter (DSC; ThermoPlus 8230L by Rigaku Co., Japan).

Each ionic liquid exhibited a low solubility of LiTFSI, with the maximum concentration limited to  $0.5 \text{ mol dm}^{-3}$  at room temperature. Therefore, in each case,  $0.2 \text{ mol dm}^{-3}$  of LiTFSI was dissolved in an ionic liquid to produce the electrolyte. The preparation of these Li/ionic liquid electrolytes was carried out in a dry box filled with argon, and their water contents was confirmed to be below 30 ppm by Karl–Fischer titration using a Hiranuma AQ-7 aquacounter.

The conductivity of ionic liquids and electrolytes was measured by the alternative current method using a Hewlett-Packard 4284A LCR meter. Cell temperature during the measurement of the conductivity was controlled by a temperature chamber (Tabai Espec SU241, Japan). The electrochemical stability of ionic liquids was estimated by linear sweep voltammetry using a highly sensitive potentiostat (Huso Electronic Co., HECS318C, Japan). In this measurement a Ag wire dipped in AgTFSI/BTMATFSI was used as a reference electrode. The lithium deposition/dissolution behavior of Li/ionic liquid electrolytes was examined both by cyclic voltammetry and by the constant current method. In all electrochemical measurements, a 3-electrode sealed cell in a T-shaped Teflon tube with a 6-mm diameter stainless-steel working electrode. For lithium deposition/dissolution test, a lithium foil as the reference and the counter electrode was used. The cyclic voltammetry tests were performed at potential ranges from 1.5 to 0.2 or 0.5 V versus lithium, and at  $0.5 \text{ mV s}^{-1}$  scan rate. The constant current measurement was performed by lithium deposition for 2 h followed by lithium dissolution up to a cut-off voltage of 2.0 V, using a charge–discharge cell cycler (Nagano Co., BTS2004, Japan). In both steps, current densities were set at  $0.01 \text{ mA cm}^{-2}$  and the estimated charge in the charging step was approximately  $0.17 \text{ C cm}^{-2}$ . Alternative current impedance was measured on Li/electrolyte/Li symmetrical cell under open-circuit situation using Hioki 3522 LCR meter. The cell temperature was maintained at  $25^\circ\text{C}$  during storage.

## 3. Results and discussion

The melting point of CTMATFSI was estimated to be at  $35.2^\circ\text{C}$ , which is slightly higher than room temperature. Therefore, this ionic liquid, like other types of ionic liquids, has a strong supercooling property and it can be treated as a liquid electrolyte even under room temperature conditions.

Fig. 2 shows the linear sweep voltammograms of CTMATFSI with the comparison of those of BTMATFSI and

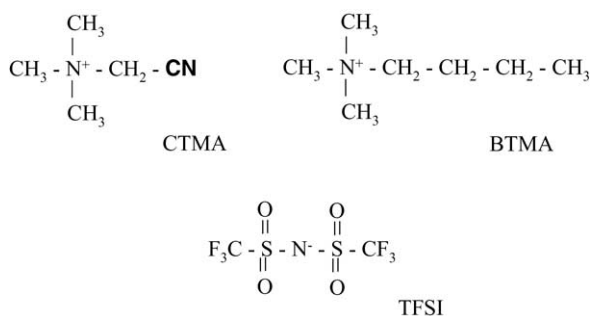


Fig. 1. Cations and an anion for ionic liquids prepared in the present study.

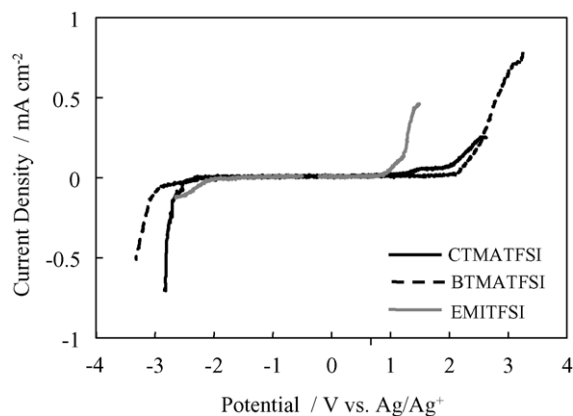


Fig. 2. Linear sweep voltammograms of a SS electrode in various ionic liquids. Sweep rate:  $0.5 \text{ mV s}^{-1}$ .

EMITFSI. CTMATFSI has an electrochemical window between 1.3 and  $-2.5 \text{ V}$  versus  $\text{Ag}/\text{Ag}^+$ . Such an electrochemical window is wider than that of EMITFSI both to anodic and cathodic directions. However, compared with BTMATFSI, CTMATFSI is unstable both anodically and anodically. Such instability may originate from the cyano group in cation.

Fig. 3 shows the Arrhenius plots of the conductivity of BTMATFSI, CTMATFSI, and the lithium salt solutions of these ionic liquids. CTMATFSI showed a conductivity one order lower than that of BTMATFSI, i.e.,  $10^{-4} \text{ S cm}^{-1}$  versus  $10^{-3} \text{ S cm}^{-1}$  at room temperature. The conductivity of CTMATFSI may not be sufficiently high for a lithium battery electrolyte. However, this ionic liquid presents a unique feature in that the LiTFSI/CTMATFSI alone. This is explained by assuming that the cyano group interacts weakly with lithium ion, thus causing a decrease in the interaction between lithium ion and the anion, followed by a decrease in viscosity and an increase in lithium ion mobility. In contrast, almost all of the most commonly investigated ionic liquids show a tendency to decrease in conductivity after the addi-

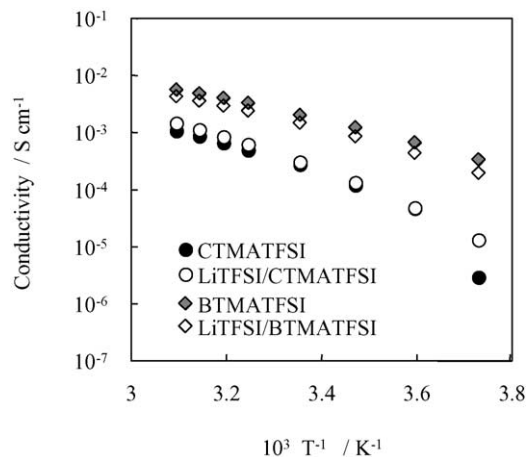


Fig. 3. Arrhenius plots for the conductivities of various ionic liquids and their lithium electrolytes.

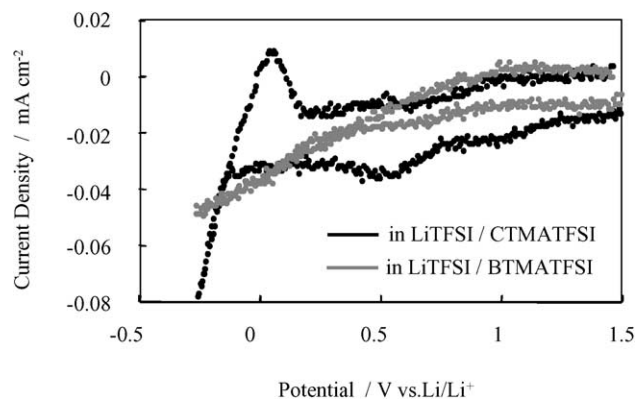


Fig. 4. Cyclic voltammograms of a stain-less electrode in various Li/ionic liquid electrolytes. Sweep rate:  $0.5 \text{ mV s}^{-1}$ ; sweep range:  $-0.3$  to  $1.5 \text{ V}$  vs.  $\text{Li}/\text{Li}^+$ .

tion of lithium salts as a result of the concomitant increase in viscosity [19]. The LiTFSI/BTMATFSI electrolyte follows this trend since it shows a conductivity lower than that of BTMATFSI itself. In contrast, the LiTFSI/CTMATFSI electrolyte exhibits a conductivity similar to or slightly higher than that of CTMATFSI alone.

Fig. 4 shows the cyclic voltammograms of the stainless-steel electrode in LiTFSI/CTMATFSI and LiTFSI/BTMATFSI electrolyte cells with the lower potential limit set at  $-0.2 \text{ V}$  versus  $\text{Li}/\text{Li}^+$ . A reversible lithium deposition/dissolution behavior was observed only in the CTMATFSI electrolyte cell, while only an irreversible anodic current was observed in the BTMATFSI electrolyte cell. It is clear that in this potential region the cathodic current was consumed for lithium deposition in the former case. One may then assume that the CTMATFSI electrolyte is capable of providing a protective surface film which prevents the reaction of deposited lithium with the electrolyte, while this is not the case for the BTMATFSI electrolyte.

When the potential limit was set at  $-0.5 \text{ V}$ , a lithium deposition/dissolution electrochemical couple was observable in both electrodes, suggesting that under these conditions, some kind of surface film was produced on the deposited lithium in the case of the BTMATFSI electrolyte as well. It appears that CTMATFSI is reduced at a higher potential and thus provides a more stable surface film.

Fig. 5 shows the plot of the coulombic cycling efficiency of lithium dissolution to lithium deposition in the two ionic liquid electrolytes under constant current conditions. The CTMATFSI electrolyte provided 30–50% efficiency in the whole region except during the initial two cycles, while the efficiency of the BTMATFSI electrolyte remained below 20%. We assumed that the improved efficiency in the case of CTMATFSI is associated with the formation of the protective film on the deposited lithium surface as discussed above. The irreversible charge observed in the initial three cycles is thought to be due to the formation of this film.

We would like to point out that the charge–discharge conditions that were applied here were not optimized.

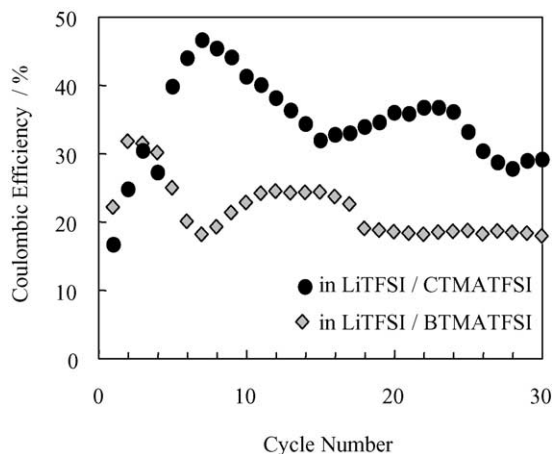


Fig. 5. Plots in coulombic efficiencies for constant-current lithium deposition-dissolution on stain-less electrode. Cut-off potential:  $-2.0$  to  $2.0$  V; current density:  $0.1 \text{ mA cm}^{-2}$ .

For example, similar constant current cycle tests using  $0.2 \text{ mol dm}^{-3}$   $\text{LiClO}_4$ /ethylene carbonate (EC) + diethyl carbonate (DEC) (1:1, v/v) electrolyte provided an efficiency level of about 60% or less. It is possible that the factors for such a low efficiency are supposed as follows. In this case the surface film on lithium may renews itself by consuming electricity at each cycle. The applied current seemed to be small, partially due to low conductivity and/or lithium ion mobility of the Li/ionic liquid electrolyte.

A Cole-Cole plot of Li/ionic liquid electrolyte/Li cells always provides a single semicircle with some intercept on the real axis, as in the case of conventional organic solvent electrolytes. Here the intercept of the real axis and the diameter of the semicircle are assumed to indicate the bulk resistance ( $R_B$ ) and interfacial resistance ( $R_I$ ), respectively. The  $R_B$  (a) and  $R_I$  (b) values are plotted versus cell storage time in Fig. 6. The  $R_B$  in CTMATFSI electrolyte was at the order of  $10^3 \Omega$  under the storage terms, while  $R_B$  in BTMATFSI electrolyte increased from  $10^2$  to  $10^3 \Omega$ ; the  $R_B$  value in CTMATFSI was larger than that in BTMATFSI, reflecting the order of conductivity. The increase in  $R_B$  in BTMATFSI electrolyte may be caused by the chemical decomposition of the electrolyte toward lithium. In contrast, CTMATFSI electrolyte was stable during the measurement time scale. In the development of  $R_I$ , CTMATFSI promoted more rapid change than BTMATFSI, and in both cases the resulting  $R_I$  values were at the order of  $10^4 \Omega$ . In an organic solvent electrolyte system,  $R_I$  between lithium and electrolyte contains resistance from the surface protective film. In the present case, the time region for the increase of  $R_I$  may be attributed to the formation process of the protective film. The increase of  $R_B$  in BTMATFSI until around 70 h and its later relative stability may reflect the increase of also  $R_I$  within the same time period. In other words, BTMATFSI electrolyte might decompose until the formation of a protective film is completed. In the case of CTMATFSI electrolyte,  $R_I$  increased faster than in BTMATFSI, and the stable  $R_I$  value was similar to that found in BTMATFSI. How-

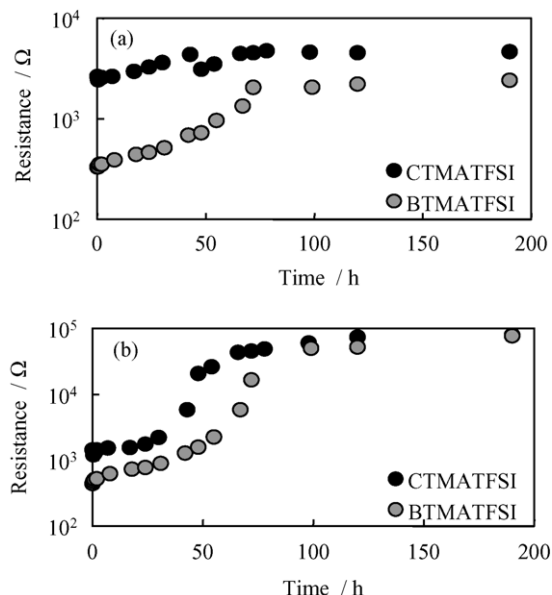


Fig. 6. Time courses of components of alternative current impedance in Li/ionic liquid/Li cells: (a) bulk resistance,  $R_B$ ; (b) interfacial resistance,  $R_I$ .

ever, it is still unclear whether such a protective film is formed at the interface between ionic liquid and lithium despite the surface analyses reported by Howlett et al. [20]. Also in our cases, further studies are necessary to clarify the interface structure between ionic liquid electrolyte and lithium and its effect on deposition/dissolution properties.

Howlett et al. recently reported good lithium deposition/dissolution efficiency in pyrrolidinium ionic liquid electrolytes, even at a temperature of  $50^\circ\text{C}$  [20]. For CTMATFSI, on the other hand, it is not reasonable to expect such a good cycle. In addition, the conductivity of this ionic liquid is not in sufficient level. However, the introduction of cyano group improves the cycle performance in such non-cyclic quaternary ammonium ionic liquids, and it may be possible to design ionic liquids with a sufficient conductivity and cycle stability toward lithium deposition/dissolution by introducing appropriate functional groups.

## Acknowledgement

Part of this work has been carried out with the financial support of MIUR-COFIN 2002 under the project “Nanostructured electrode and electrolyte materials for advanced lithium batteries”. Another part of this study has been financially supported by CREST of Japan Science and Technology Agency (JST).

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