Short communication

Functionalized imidazolium ionic liquids as electrolyte components of lithium batteries

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Abstract

Some basic properties and compatibility toward lithium electrode for electrolytes based on substituted imidazolium ionic liquid have been investigated. The ionic liquids having imidazolium cation substituted by methylcarboxyl or cyano group suffers from low conductivity. However, reversible lithium deposition–dissolution process was observed in electrolytes based on these electrolytes. In particular, lithium salt solution in cyanomethyl-substituted imidazolium ionic liquid provided similar cycle efficiency to conventional organic solvent electrolyte at constant-current condition. The mixed ionic liquid electrolyte containing the cyanomethyl-substituted ionic liquid also provided good cycle performance despite of containing large amount of 1-ethyl-3-methyl imidazolium (EMI)-based ionic liquid. Such mixed electrolyte system serves both the stability of lithium electrode process and valid conductivity for practical use.
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1. Introduction

Ionic liquids have been attracted to the researchers on lithium battery as novel candidates for electrolyte solvent with thermal stability. Many attempts have been made to apply ionic liquids to lithium battery electrolyte [1–12]. While ionic liquids based on 1,3-substituted imidazolium cation have some good fluid properties as versatile solvent, they suffer from their low cathodic stability so that they decompose irreversibly on negative electrode surface [2,13,14]. Therefore, much effort has been attempted to apply ionic liquids based on linear or circular quaternary ammonium cations [4–6,9–11]. Several ionic liquid electrolytes based on alkylpyrrolidinium [5], alkylpiperidinium [6], and methoxyethyl-substituted quaternary ammonium [9] cations have reported to be compatible for lithium battery systems. However, these kinds of ionic liquids have some draw-

backs, such as low conductivity and the limitation of anion selection to obtain liquid at room temperature.

The authors have proposed a series of ionic liquid having cyano-substituted quaternary ammonium cation for the use in lithium battery electrolyte [7,15,16]. The electrolyte based on cyano-substituted ionic liquid provided reversible lithium deposition–dissolution. Moreover, electrolyte based on the mixture of cyano-substituted quaternary ammonium ionic liquid and 1-ethyl-3-methyl imidazolium (EMI)-based ionic liquid also provided both reversible lithium electrode process and charge–discharge of LiCoO$_2$. The cyano-substituted quaternary ammonium ionic liquid is expected to form a surface film which inhibits the cathodic decomposition of EMI cation as observed in conventional organic solvent electrolyte system. It is expected that the substitution of such functional groups to side chain of imidazolium cation may contribute to the surface film formation in similar manner. Recently, Lee et al. exhibited that methylcarboxyl-substituted ionic liquid has a potential electrolyte component for lithium battery in view of the compatibility with lithium electrode [12]. In the present study,

Table 1
Properties of imidazolium ionic liquids and their lithium salt solutions

Abbreviation[a]	Neat		20 mol% LiTFSI solution	
	σ^{b} (mS cm^{-1})	η^{c} (cP)	σ^{b} (mS cm^{-1})	η^{c} (cP)
EMI (–C$_2$H$_5$)	9.2	20	3.6	47
CmMI (–CH$_2$CN)	0.99	195	0.29	664
CpMI (–C$_3$H$_6$CN)	1.2	187	0.35	550
McmMI (–CH$_2$CO$_2$CH$_3$)	0.70	223	0.22	>1000

[a] In all cations 3-positions are substituted by –CH$_3$.
[b] Conductivity at 25 °C.
[c] Viscosity at room temperature (not controlled).

some properties and lithium electrochemistry of various ionic liquid-based electrolytes containing functionalized imidazolium cations. The contribution of such functional group may be clarified by the comparative study.

2. Experimental

Cations for imidazolium-based ionic liquids used in the present study are listed in Table 1. In all cases, a bis(trifluoromethane)sulfone imide (TFSI) anion was combined with cation and liquid was formed at room temperature. All ionic liquids used in the present study was kindly supplied by the Nippon Synthetic Chemical Industry Co., Ltd. (Japan). The water content in these ionic liquids was controlled below 100 ppm by the supplier. Furthermore, these ionic liquids were dried under vacuum at 100 °C before use. LiTFSI (Fluka) was dissolved up to 20 mol% into these ionic liquids, or mixtures of ionic liquids to prepare electrolyte solutions. All these preparation procedures were carried out in an Ar-filled glove box. The viscosity of ionic liquids and lithium salt solutions at ambient temperature was measured in an Ar-filled glove box using an Ostwald viscosity meter.

The conductivity of these liquids was measured using a T-shaped glass cell with platinum electrodes under controlled temperature and an impedance analyzer (Solartron 1260).

A three-electrode Teflon cell was assembled in a glove box with a SS working electrode, lithium (Mitsui Metal Co., Japan) counter electrode, and Ag/Ag$^+$ reference electrode for cyclic voltammetry measurements. The reference electrode was prepared by using a preparation kit (BAS Co., Japan) with ca. 0.1 mol dm^{-3} AgBF$_4$/EMITFSI. Cyclic voltammetry measurement at ambient temperature was carried out using a polarization unit (HZ-3000, Hokuto Denko Co., Japan) under scan rate of 5 mV s^{-1} and potential region between −5.0 to −2.5 V versus Ag/Ag$^+$. For constant-current lithium deposition–dissolution tests, a 2032-type SS coin cell was used. Lithium foil was placed on the base and the cap plate was used as a working electrode. Lithium was deposited on the SS electrode under 0.01 mA constant current during 12,000 s, and then stripped under the same current until the potential of SS electrode reached 2.0 V versus lithium counter electrode. The similar coin cell but lithium foils were plated at both electrodes for ac impedance measurement (Solartron 1260 ± 1287). The measurement frequency range is from 1 MHz to 1 Hz. These cells were assembled in the Ar-
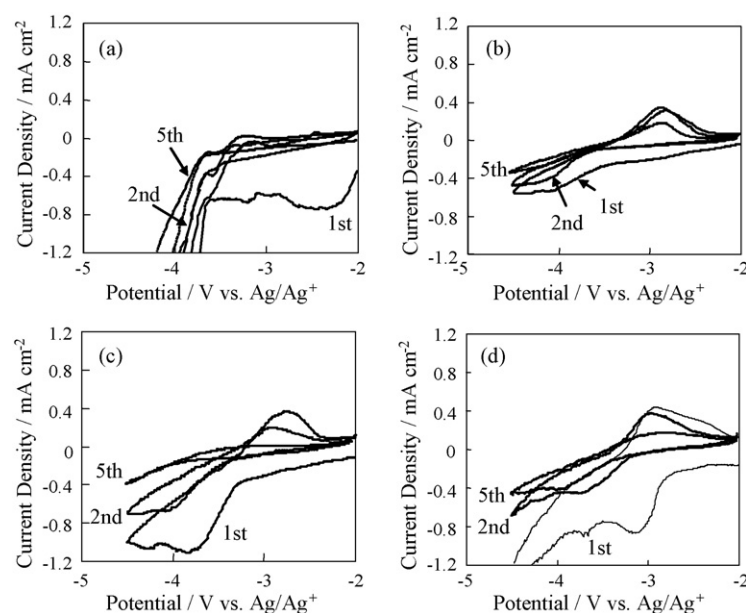

Fig. 1. Cyclic voltammograms of lithium deposition–dissolution processes in various ionic liquid electrolytes. Electrode: stainless steel, scan rate: 5 mV s^{-1}. Electrolyte: 20 mol% LiTFSI solution of (a) EMITFSI; (b) CmMITFSI; (c) CpMITFSI; (d) McmMITFSI.
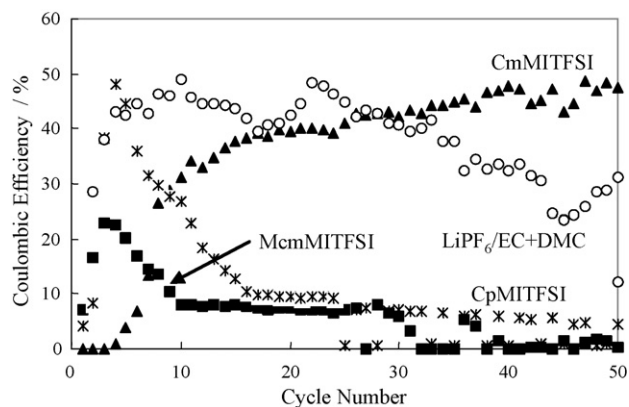
Fig. 2. Cycle efficiencies for lithium deposition–dissolution under constant-current mode in various electrolytes. Current: 0.01 mA, charge amount: 1.20 C; discharge cut-off voltage: 2 V.

filled glove box except for crimp seal of a coin cell. These electrochemical measurements were performed under ambient temperature.

3. Results and discussion

Some properties of ionic liquids used in the present study and their lithium salt solutions are included in Table 1. The ionic liquids having functionalized imidazolium cations shown here are more viscous and have lower conductivity than EMITFSI regardless the kind of functional group. The conductivity of McmMITFSI was similar to that reported by Lee et al. [12]. Comparing the property of CmMITFSI with that of CpMITFSI, it is suggested that a long alkyl chain between functional group and imidazolium ring slightly improves the properties of resulting ionic liquid. The origin of the viscous nature of the functionalized ionic liquids is still not clear. This behavior appears to be related to the reported properties of ionic liquids having an imidazolium cation with double-bonded side chain. A functional group containing a double or triple bond may provide rigidity to ionic liquid. For all ionic liquid systems used in the present study, conductivity markedly decreases and viscosity increases by dissolving 20 mol% of LiTFSI.

Fig. 1 shows the cyclic voltammograms of SS electrode in the lithium salt solutions of ionic liquids. As already reported, only irreversible reduction of electrolyte around -2.0 V versus Ag/Ag$^+$ was observed in EMI-based electrolyte solution. In contrast, other ionic liquid-based electrolytes provided a redox couple around -3.5 V at each cycle. The peak current decreased in all the cases providing the redox couple, suggesting the existence and generation of surface film on electrode followed by the increase of surface resistance. This redox couple is considered to be attributed to the deposition–dissolution process of lithium because the redox potential is close to the known standard one for Li/Li$^+$ from Ag/Ag$^+$. The results in Fig. 1 indicate that lithium salt solutions of ionic liquids based on functionalized imidazolium cation provide reversible lithium deposition–dissolution in contrast to EMI-based ionic liquid electrolyte. The voltammograms for CmMITFSI(b) and CpMITFSI(c) electrolytes exhibit
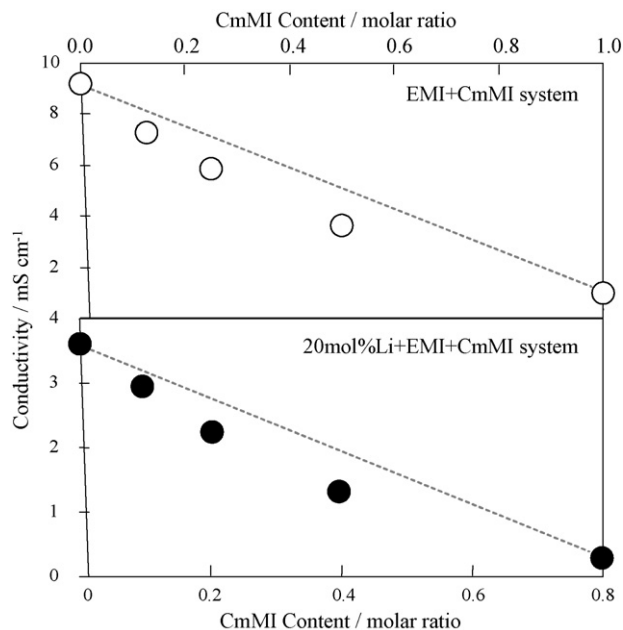

Fig. 3. Conductivity at 25 °C of ionic liquid mixtures at various CmMITFSI content.

a rather large extent of polarization over 1 V, suggesting that the mass transfer of lithium ion is slow in these electrolytes.

The constant-current cycle tests of lithium deposition–dissolution were performed using a two-electrode coin cell system for ionic liquid electrolytes where the lithium deposition–dissolution couple was observed on cyclic voltammogram. The coulombic efficiency for each cell at each cycle is plotted in Fig. 2. The efficiency for a Li/SS coin cell containing 1 mol dm^{-3} LiPF$_6$/EC-DMC electrolyte is also included in Fig. 2. The condition of lithium deposition–dissolution in the present case was so severe that the efficiency reached only 40% when conventional organic solvent electrolyte was applied. The cells containing ionic liquid electrolytes were exhibited different behavior for the kind of ionic liquid. When
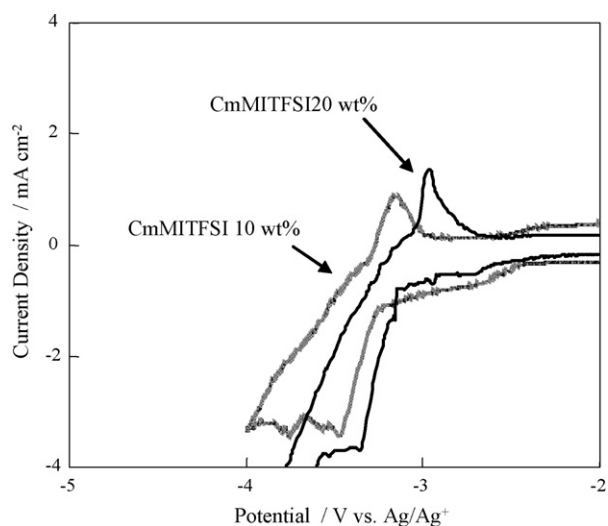

Fig. 4. Cyclic voltammograms of lithium deposition–dissolution processes in LiTFSI/CmMITFSI/EMITFSI mixed ionic liquid electrolytes.
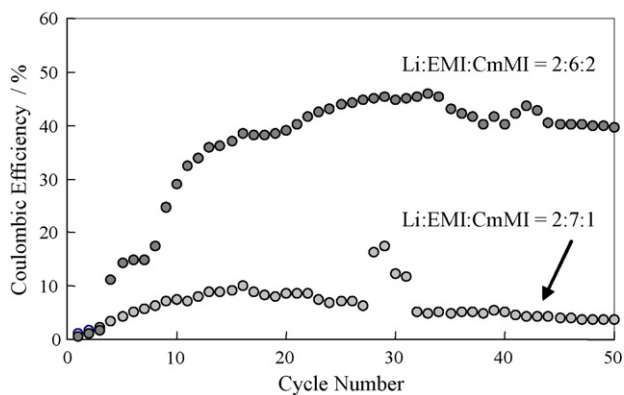
Fig. 5. Cycle efficiencies for lithium deposition–dissolution under constant current in mixed electrolyte of 20 mol% LiTFSI/EMITFSI/CmMITFSI. Current: 0.01 mA; charge amount: 1.20 C; discharge cut-off voltage: 2 V.

CpMI- or McmMI-based ionic liquid was used, at initial several cycles the coulombic efficiency reached ca. 30–40%, and then rapidly decreased to below 10%. In contrast, when CmMI-based ionic liquid electrolyte was applied, coulombic efficiency reached over 40% after several inductive cycles. It is clearly indicated that the functional group in side chain of imidazolium cation in ionic liquid electrolyte affects the lithium deposition–dissolution process, perhaps through the formation of surface film. Among ionic liquids used in the present study, CmMITFSI provided the highest performance.

Nevertheless its compatibility toward lithium metal electrode, LiTFSI/CmMITFSI electrolytes has a large drawback on its low conductivity. If the lithium deposition–dissolution reversibility using this electrolyte is brought by stable surface film on electrode, mixed electrolyte system containing EMITFSI and CmMITFSI is also expected to be compatible with lithium negative electrode. Here such mixed electrolyte systems were examined at different mixing ratio.

The conductivity for EMITFSI/CmMITFSI and LiTFSI/EMITFSI/CmMITFSI mixed electrolyte systems containing 20 mol% LiTFSI is plotted toward the molar ratio of CmMITFSI in Fig. 3. In both mixture systems, the conductivity value is below expected one for an assumption of the combination by independent contribution from both EMITFSI and CmMITFSI. CmMI$^+$ is a negative influence to the conductivity of such mixed system. Therefore, the content of CmMITFSI should be depressed in order to maintain high conductivity of EMI-based system.

Fig. 4 shows the cyclic voltammograms at first cycle of lithium deposition–dissolution in LiTFSI/CmMITFSI/EMITFSI electrolytes with various composition. Even when only 10 mol% of CmMITFSI is added into LiTFSI/EMITFSI system, dissolution peak of lithium is observable around 3 V versus Ag/Ag$^+$. The deviation of the peak from the cases using 10 mol% CmMITFSI to 20 mol% CmMITFSI is included may be due to the difference in lithium junction potential between electrolyte and the solution where a Ag wire immersed. On the view at cathodic scan, small current started at ca. −2.5 V is to be noted. This current is considered to be assigned to the formation of surface film. Furthermore,

the main reduction peak around −3.5 V is well resoluted into two parts: one at higher potential is assigned to the deposition of lithium and the other is assigned to the decomposition of electrolyte. In these cases the lithium deposition and its dissolution peaks less polarized than in LiCmMITFSI system shown in Fig. 2b.

The cycle performances of SS/Li coin cells containing Li/EMI/CmMITFSI mixed ionic liquid electrolytes with various CmMITFSI contents and 20 mol% of LiTFSI are shown in Fig. 5. When the content of CmMITFSI is 10%, the coulombic efficiency of lithium deposition–dissolution process is suppressed below 10% over the whole cycle. In contrast, the mixed electrolyte with 20 mol% of CmMITFSI provided similar cycle behavior and efficiency, ca. 40%, to that for CmMI-based ionic liquid electrolyte. The result that the coexistence of CmMITFSI inhibits the decomposition of EMITFSI clearly indicates the formation of surface film from CmMITFSI. Being different from the result of cyclic voltammetry shown in Fig. 4, the surface film may be sufficiently compact to inhibit the decomposition of EMITFSI above 20 mol% of CmMITFSI content. The mixed electrolyte with 20 mol% of CmMITFSI shows ca. 3.6 mS cm^{-1} of conductivity at 25 °C, highest value among ionic liquid-based electrolyte which provides sufficient reversibility of lithium electrode process ever reported.

To estimate the nature of surface film between lithium electrode and ionic liquid electrolyte, ac impedance measurement was conducted for Li/ionic liquid electrolyte/Li cells. Fig. 6 shows the Cole–Cole plots for such cells containing 20 mol% LiTFSI/CmMITFSI (a) and 20 mol% LiTFSI/20 mol% CmMITFSI/EMITFSI (b) electrolytes. Both diagrams appear to include at least two semi-circles. Perhaps low frequency (∼1 Hz) region of these diagrams includes a contribution of mass transfer limit [17]. However, it is clearly found that the charge-transfer resistance, including the ion-transfer resistance of surface film, is particularly large in LiTFSI/CmMITFSI electrolyte, and rather moderate in LiTFSI/CmMITFSI/EMITFSI. The polariza-
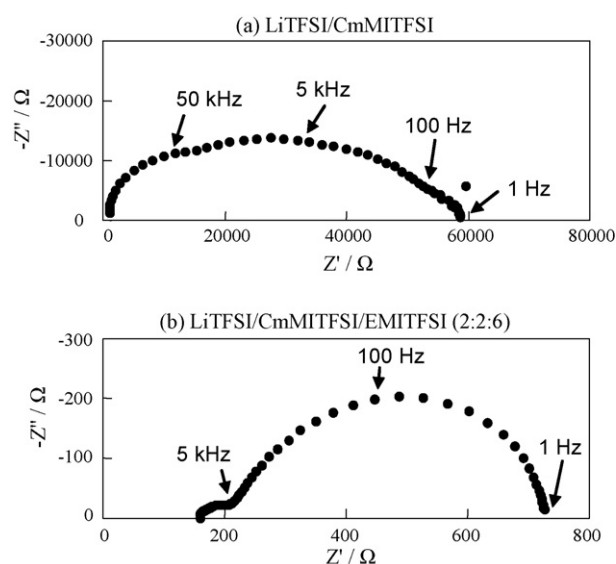

Fig. 6. Cole–Cole plots for Li/ionic liquid electrolyte/Li symmetric cells.

tion observed in cyclic voltammogram for LiTFSI/CmMITFSI (Fig. 2b) appears to be related to these resistance values. Similar impedance features to both ones in Fig. 6 were obtained from approximately 1 day after assembling the cells, suggesting the long-term stability of surface film. Such a film-forming ability of CmMITFSI is considered to be an analog to that of cyano-substituted quaternary ammonium ionic liquid previously reported by the authors [7]. The chemistry of cyano-substituted cations to provide a stable surface film is an attracting matter, which is to be discussed elsewhere [18].

4. Conclusion

Among the applied imidazolium ionic liquids in the present study, cyanomethyl-substituted one (CmMITFSI) provided most stable cycle performance of lithium deposition–dissolution. The cycle efficiency of lithium in CmMITFSI-based electrolyte was even higher than that in conventional organic solvent electrolyte in the condition used here. In addition, the mixed electrolyte containing 20 mol% CmMITFSI also provided similar efficiency of lithium electrode process. CmMITFSI clearly has an ability to form an adequate surface film on electrode which inhibits the decomposition of EMITFSI and exhibits good cycle performance of lithium.

Acknowledgements

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