

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 alkylopyrrolidinium [5], alkyloperidinium [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<sub>2</sub>. 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,

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

Abbreviation <sup>a</sup>	Neat		20 mol% LiTFSI solution	
	$\sigma^b$ (mS cm <sup>-1</sup> )	$\eta^c$ (cP)	$\sigma^b$ (mS cm <sup>-1</sup> )	$\eta^c$ (cP)
EMI (-C <sub>2</sub> H <sub>5</sub> )	9.2	20	3.6	47
CmMI (-CH <sub>2</sub> CN)	0.99	195	0.29	664
CpMI (-C <sub>3</sub> H <sub>6</sub> CN)	1.2	187	0.35	550
McmMI (-CH <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub> )	0.70	223	0.22	>1000

<sup>a</sup> In all cations 3-positions are substituted by -CH<sub>3</sub>.

<sup>b</sup> Conductivity at 25 °C.

<sup>c</sup> 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<sup>+</sup> 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<sup>-3</sup> AgBF<sub>4</sub>/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<sup>-1</sup> and potential region between -5.0 to -2.5 V versus Ag/Ag<sup>+</sup>. 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-

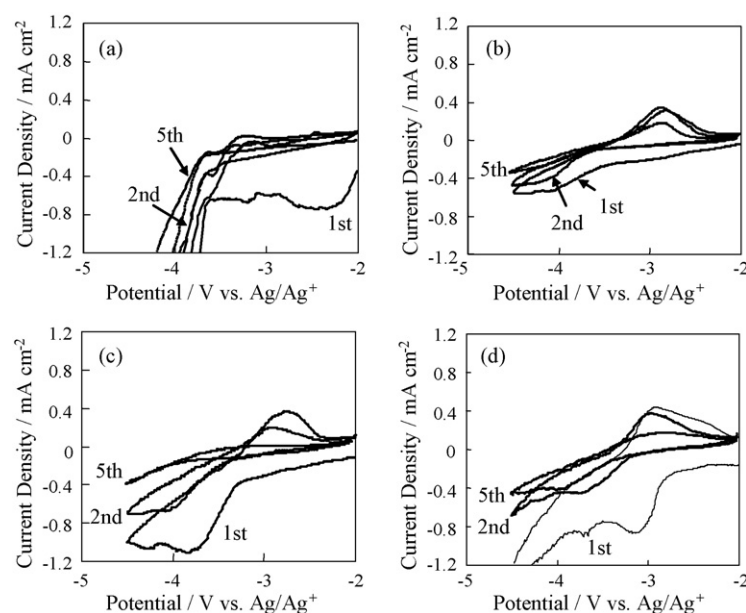


Fig. 1. Cyclic voltammograms of lithium deposition–dissolution processes in various ionic liquid electrolytes. Electrode: stainless steel, scan rate: 5 mV s<sup>-1</sup>. Electrolyte: 20 mol% LiTFSI solution of (a) EMITFSI; (b) CmMITFSI; (c) CpMITFSI; (d) McmMITFSI.

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