



Ionic liquid/boric ester binary electrolytes with unusually high lithium transference number



Raman Vedarajan^a, Kento Matsui^a, Emari Tamaru^a, Jyoti Dhankhar^{a,b}, Toshihiro Takekawa^c, Noriyoshi Matsumi^{a,*}

^a School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, 923-1292, Ishikawa, Japan

^b Department of Chemistry, University of Delhi, Delhi, India

^c Advanced Materials Laboratory, Nissan Motor Co., Ltd., 1 Natsushima-Cho, Yokosuka-shi, Kanagawa 237-8523, Japan

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ABSTRACT

Binary electrolytes composed of ionic liquids and boric esters were prepared by studying compatibility between various combinations of such systems. The study showed that out of various combinations of ionic liquids/boric esters, only TFSI anion (or FSI anion) based ionic liquids/mesityldimethoxyborane (MDMB) systems were found to be miscible. After equimolar amount of lithium salts was added to ionic liquids, the resulting solution showed high ionic conductivity that was comparable to those for ionic liquids. The lithium transference number (t_{Li+}) of these systems at room temperature was found to be very high. A maximum t_{Li+} of 0.93 was observed for a binary mixture of AMImFSI [1-allyl-3-methylimidazolium bis(fluorosulfonyl)imide]/MDMB. Further, this binary mixture as electrolyte in Li/electrolyte/Si cell showed good reversible lithiation-delithiation with > 2500 mAh/g of delithiation specific capacity.

1. Introduction

Research pertaining to lithium ion batteries (LiBs) has reached its epitome owing to various economic and environmental global scenario [1]. In the field of lithium ion secondary batteries, boron compounds have been utilized in a variety of ways. Boron compounds have been employed as additives with electrolytes, to reduce interfacial resistance between electrode and electrolyte. Moreover, a variety of highly dissociable lithium salts based on lithium borate have been developed. As most well-known example, lithium bis(oxalato)borate (LiBOB) has been widely employed among researchers of this field today [2–8]. When boron-anion interaction is very strong, marked increase in t_{Li+} is observed instead of decrease in ionic conductivity. A moderate boron-anion interaction does not strongly enhance the t_{Li+} , however, leads to increase of ionic conductivity [9–15].

As far as we know, boron incorporation to electrolytes was first reported by McBreen et al. [16]. In the early study, addition of boron compounds in 1,2-dimethoxyethane (DME) solution was found to enhance ionic conductivity. On the other hand, boron incorporation to polymer electrolyte was first reported by Fujinami et al. in 1997 [17]. The boroxine ring based network type electrolytes showed significant selectivity for lithium cation transport [17]. This was followed by further molecular design of defined organoboron electrolytes developed by

several research groups. For instance, hydroboration polymerization and dehydrocoupling polymerization via hydroborane reagents were found to be useful method for design of defined organoboron polymer electrolytes [10,13–15].

On the other hand, boron incorporation to molten salt was first reported by Ohno and Matsumi et al., in 2004 [11]. The obtained alkylborane type molten salts showed maximum lithium transference number of around 0.7 due to high Lewis acidity of alkylborane unit. However, this molecular design afforded only solid molten salts showing moderate ionic conductivity of 10^{-5} Scm^{-1} order at 51 °C.

Hence, in the present work, in order to prepare boron incorporated ionic liquid matrices that are liquid at ambient temperature, miscibility of ionic liquids with various boric ester compounds was studied in detail. Some binary electrolytes were found to show high ionic conductivity exceeding 10^{-3} Scm^{-1} due to their lower viscosity than ionic liquid. These electrolytes exhibited unusually high lithium transference number of over 0.9 with electrochemical window of around 5.0 V (Unprecedented properties of the present binary electrolytes are indicated in the graphical abstract). After fabricating a Li/electrolyte/Si half-cell using such a binary electrolyte (AMImFSI/3), reversible charge-discharge with > 2500 mAh/g of delithiation specific capacity was observed under a moderate coulombic efficiency.

* Corresponding author.

E-mail address: matsumi@jaist.ac.jp (N. Matsumi).

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


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Table 1

Aspect of miscibility under various combinations of ionic liquid/boric esters; (–): not miscible and (+) completely miscible.

IL/Boron			
BMIImTFSI	–	–	+
AMImTFSI	–	–	+
AAImTFSI	–	–	+
AMImFSI	–	–	+
EMImFSI	–	–	–
BMIImCl	–	–	–
AMImCl	–	–	–
AMImCH ₃ COO [–]	–	–	–
AMImBr	–	–	–

Where, the abbreviations of the cationic part BMIIm = 1-butyl-3-methylimidazolium; AMIm = 1-allyl-3-methylimidazolium; AAIm = 1,3-allylimidazolium; EMIm = 1-ethyl-3-methylimidazolium and the anionic part Cl = chloride TFSI = bis(trifluoromethanesulfonyl)imide; FSI = bis(fluorosulfonyl)imide; CH₃COO[–] = acetyl; Br = bromide.

2. Methods

2.1. Synthesis of 1-allyl-3-methylimidazolium FSI (AMImFSI)

To 10.8 g (0.030 mol) of 1-allyl-3-methylimidazolium chloride (AMImCl), aqueous solution of 1.1 eq. of potassium bis(fluorosulfonyl) imide (KFSI) (7.23 g, 0.033 mol) was added, and the mixture was stirred for 12 h. After the mixture was stirred for another 30 min, the aqueous supernatant solution was removed. Then organic phase was washed with distilled water four times, and reprecipitated into diethylether. To the aqueous supernatant solution, silver nitrate test was carried out to confirm the completion of ion-exchange. AMImCl is soluble in water. Hence, unreacted AMImCl in water yields white precipitate with AgNO₃ test. Lack of white precipitation due to AgCl formation evinced completion of the reaction. After removal of supernatant solution, 11.8 g of AMImFSI (yield: 100%) was obtained after the liquid precipitate was dried under a reduced pressure.

¹H NMR(CDCl₃): δ(ppm) 4.14 (3H, –NCH₃), 5.03–5.05 (2H, –N–CH₂–CH=CH₂), 5.43–5.50 (2H, –CH=CH₂), 5.99–6.09 (1H, –CH₂CH=CH₂), 7.60–7.85 (2H, –NCH=CH–N), 10.7 (1H, –NCHN–).

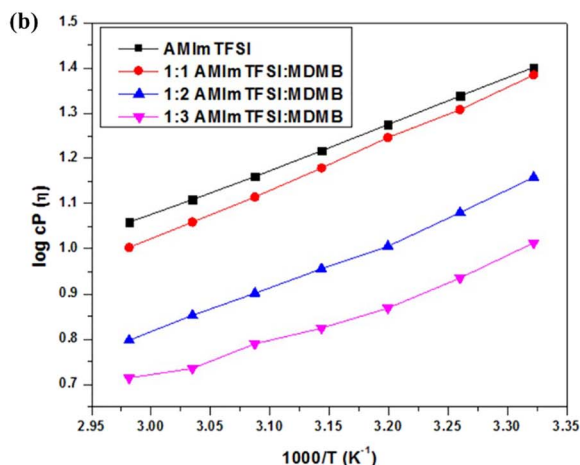
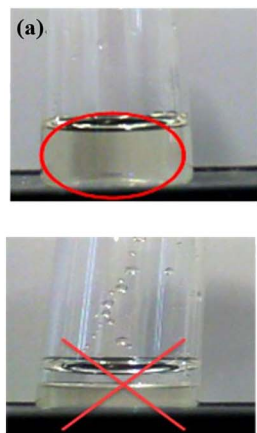


Fig. 1. (a): Images showing miscibility of representative IL/boric ester (top): completely miscible; (bottom): immiscible. (b): Viscosity profiles showing effect of concentration of boric ester in IL (IL = AMImTFSI; boric ester = mesityldimethoxyborane; V/V).

2.2. Electrochemical measurements

Ionic conductivity was measured using a custom designed cell purchased from EC Frontier Co. Ltd. The impedance spectra were recorded on a Solartron 1260 model under frequency range of 1 MHz–1 Hz. Viscosity of binary solution was evaluated using a corn-plate type viscometer (Bruckfield Co. Ltd.). Lithium transference number of binary electrolytes was measured by the method described by Evans et al. [18]. The operations were carried out under an argon atmosphere using identical Li electrodes using potentiostat (Versastat-3; Princeton Applied Research Co. Ltd.). Impedance measurements were carried out under the frequency range of 100 kHz–10 mHz. A DC potential of 0.03 V (vs Li/Li⁺) was applied during the polarization studies. The linear sweep voltammetry measurements were carried out in a sandwich type cell of the configuration Li/binary mixture electrolyte/Pt. The measurements were performed at the scan rate of 10 mV/s under the potential range of 0–5 V vs Li/Li⁺.

For charge-discharge studies, silicon based anodic half-cells were prepared using CR2025 type coin cells with silicon as the working electrode (diameter = 15Φ, NISSAN), lithium metal as the counter electrode (15 mm, Honjo metals, Japan) and a polypropylene based membrane (Celgard®) as separator (outer diameter = 16 mm, inner diameter = 12 mm). The prepared silicon based anodic half-cells were first discharged and then charged in a galvanostatic mode at 0.3 C-rate with potential cut-offs set between 2.1 (OCP)–0.01 mV (vs Li/Li⁺) using compact charge and discharge system of EC Frontier; ECAD-1000.

3. Results and discussion

Firstly, miscibility of various ionic liquids with boric ester compounds was studied (Table 1 and Fig. 1(a)). Under most combinations of ionic liquid/boric ester mixtures, a clear phase separation was observed visually, immediately after mixing. However, only under specific combination of imidazolium TFSI type (or FSI type) ionic liquid and mesityldimethoxyborane, homogeneous solution was readily obtained (Table 1). Moreover, these liquids were miscible under a wide range of volume ratios of ionic liquid and mesityldimethoxyborane. The viscosity of various binary electrolytes under different IL/boric ester volume was measured by corn plate type viscometer, and the results are shown in Fig. 1(b). All the binary mixtures of IL/mesityldimethoxyborane showed significantly lower viscosity in comparison with ionic liquid itself. The viscosity decreased with increase in the volume ratio of mesitylborane. Temperature dependence of viscosity followed Arrhenius behaviour.

These binary mixtures were then subjected to ac-impedance

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