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# Design of organic–inorganic hybrid ion-gel electrolytes composed of borosilicate and allylimidazolium type ionic liquids

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## ABSTRACT

Research towards the design of novel electrolytes for the development of safer and efficient Li-ion batteries has gained widespread momentum in recent years. Design of novel borosilicate glass/ionic liquid hybrid type electrolyte was undertaken. Organic–inorganic hybrids have the dual advantages of high ionic conductivity due to the organic component and high thermal stability due to the inorganic components. In the present work, an in-situ sol–gel method using alkoxysilanes and alkoxyboranes was carried out, in the presence of low viscous ionic liquids. This resulted in the formation of highly homogenous organic–inorganic hybrids. A low viscous diallylimidazolium type ionic liquid was employed as the organic component. Arrhenius plots evinced constant temperature dependence of ionic conductivity. A maximum ionic conductivity of  $2.0 \text{ mS cm}^{-1}$  at  $51^\circ\text{C}$ , was observed among the prepared hybrids.  $\text{LiPF}_6$  based hybrids showed higher ionic conductivity due to larger phase separation order of organic and inorganic components which enables better connection of ion-conductive organic components. On the other hand,  $\text{LiTFSI}$  based hybrids were highly homogenous and exhibited much improved thermal stability. Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

With increasing dependence on portable electronic gadgets in our daily lives, there is an increasing demand for safe and time-durable energy storage devices. Lithium ion secondary batteries (LiBs) are widely employed in various electronic appliances like laptops, mobiles and even in the automobile hybrids. LiBs have greater energy density compared with the conventional batteries such as Ni–Cd and Ni–hydrogen batteries. However, safety issue with the presently used electrolytes in the LiBs is a tentative grey area which needs to be addressed. Ethylene carbonate and propylene carbonate are

commonly used electrolytes in the LiBs, and both of them are highly flammable. Thus, extensive researches have been conducted to explore novel non-flammable electrolyte materials [1,2].

LiBs using non-liquid electrolytes are deemed safer and reliable than the conventional liquid electrolytes. Much attention has been focussed on the use of dry solid polymer or polymer gel electrolytes or composite polymer electrolytes. On the other hand, ionic liquids (ILs) have gained considerable popularity in research field on account of their properties such as low viscosity, non-volatility, thermal stability, etc. [3–5]. Use of ionic liquids in the design of novel electrolytes in the

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lithium rechargeable batteries has been a significant area of research [6–8].

Ionic liquids have been valuable component in the design of these electrolytes on account of their stability at high temperatures and considerable ionic conductivity [9]. To further improve the ion-conductive characteristics of IL based electrolytes, incorporation of boron into the matrices was found to be an effective approach [10]. Boron atom facilitates the dissociation of the lithium salt and further traps the anion enhancing the cationic conduction. Various types of organo-boron polymers with enhanced ionic conductance profiles have been reported [11]. Keeping in view the enhancement of ionic conductivity or lithium ion transference number via organoboron incorporation, the concept of organic–inorganic composite hybrids including borosilicate glass should be an attractive approach. Borosilicates are relatively softer material compared with silicates, and are also more stable than organoboron compounds.

Previously, borosilicate based ion-gel electrolytes prepared via in-situ polymerization of the ionic liquid component were reported by Ohno et al. [12]. In those systems, significant enhancement of ionic conductivity was observed in the presence of appropriate amount of boron in borosilicate glass. In the present work, preparation of a series of novel borosilicate based ion-gels was undertaken in the presence of low viscous allylimidazolium type ionic liquids without the polymerization of ionic liquid component. Use of low viscous allylimidazolium type ionic liquid should lead to improved ion-conductive properties of the resulting hybrids. Effect of morphological factor on ion-conductive properties of the hybrids was also studied.

## 2. Experiment

### 2.1. Materials and instruments

The ionic liquid, 1,3-diallylimidazolium TFSA was synthesized by the reaction between 1-allylimidazole and allylchloride, followed by an ion-exchange reaction using LiTFSA (lithium bis(trifluoromethylsulfonyl)amide) [13]. Commercially available trimethoxyborane, LiTFSA and LiPF<sub>6</sub> (Wako chemicals), tetramethylorthosilicate (Shin-Etsu Chemical Co. Ltd.) were purchased and were used without further purification. Similarly, lithium sheets were purchased from Honjo Chemical Co. Ltd. Mesityldimethoxyborane was synthesized according to the literature [14].

The IR spectra of the hybrids were measured on a JASCO FT-IR420 (JASCO). The ionic conductivity for the organic–inorganic hybrids was evaluated by complex impedance method on a Solartron 1260 impedance analyser using an amplitude of 100 mV and in the frequency range of 0.1 Hz–1 MHz. The sample was sandwiched between two blocks of stainless steel electrodes. All samples were thoroughly dried in *vacuo* at 100 °C before use.

The apparent lithium ion transference number ( $t_{Li^+}$ ) was estimated according to the method of Evans et al. The polarization current obtained from chronoamperometry and the charge transfer resistance between the electrolyte/lithium metal electrodes observed from the impedance

spectra were substituted to Evans–Vincent–Bruce equation [16], where  $I_o$  and  $I_s$  respectively denote the initial state and steady state current. Here,  $R_o$  and  $R_s$  denote the charge transfer resistance for the initial and steady state, respectively.

$$t_{Li^+} = \frac{I_{(s)}[\Delta V - I_o R_o]}{I_{(o)}[\Delta V - I_s R_s]} \quad (1)$$

All the operations were carried out under an argon atmosphere using identical Li electrodes using potentiostat coupled with Frequency Response Analyser (Versastat-3; Princeton Applied Research Co. Ltd.). Scanning Electron Microscopy (SEM) analysis was carried out on a Hitachi H-7100. Thermogravimetric analyzer (Perkin Elmer 7) was used to determine the decomposition temperature of the sample. Thermogravimetry was conducted under nitrogen atmosphere at a heating rate of 10 °C per minute.

### 2.2. Preparation of organic–inorganic hybrid ion-gels

A typical procedure for the preparation of the organic–inorganic hybrid ion-gel is as follows. To 0.43 g (1.0 mmol) of 1,3-diallylimidazolium TFSA, 0.38 g (2.5 mmol) of tetramethylorthosilicate (TMOS) was added. Further, requisite amount of alkoxyboranes [B(OCH<sub>3</sub>)<sub>3</sub> or MesB(OCH<sub>3</sub>)<sub>2</sub>] was added along with unimolar quantity of lithium salt (LiTFSA or LiPF<sub>6</sub>). Then, 0.16 g (5.0 mmol) of methanol was added in the presence of 0.06 g of 1.0 N HCl aq. as the catalyst. Finally, 2.5 ml of acetonitrile was added and the mixture was stirred at room temperature for 3 h. The resulting mixture was further dried at 60 °C for a week. The mixture was gradually converted into a film.

## 3. Results and discussion

A series of organic–inorganic hybrids were synthesized by the sol–gel condensation reaction of alkoxy silanes/alkoxyboranes in the presence of ionic liquid and a lithium salt additive (Scheme 1). The composition chart of the parent matrix of the ion-gel electrolyte matrix is shown in Table 1. The concentration of boron source was chosen to be the variable component in the compositional matrix in every set of hybrids. Thus, the temperature dependence of ionic conductivity was analysed for various hybrid ion-gels under different boron concentrations. A comparative account of ionic conductivity in each set of synthesized hybrids can be an effective way to bottleneck the anion-trapping effect under doping carriers of hybrid type electrolytes. This approach would help us to determine the optimum concentration of alkoxyborane required for the enhancement of ionic conductivity without excessive anion-trapping effect. LiTFSA and LiPF<sub>6</sub> were used as doping carriers in this study. The molar concentration of the lithium salt was optimized to be equimolar to that of the ionic liquid. The LiTFSA based hybrids consistently showed a transparent structural fabric while the LiPF<sub>6</sub> based hybrids were almost turbid in all the cases. The different appearances of hybrids under various boron concentrations are shown in Fig. 1.

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