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## IONIC LIQUID [BMIM][BF<sub>4</sub>] - GLASS COMPOSITES FOR SOLID STATE BATTERY APPLICATIONS

Munesh Rathore<sup>1</sup>, \*Anshuman Dalvi<sup>1</sup> and Anil Kumar<sup>2</sup>

<sup>1</sup>Department of Physics, Birla Institute of Technology and Science, Pilani (RJ)-333031

<sup>2</sup>Department of Chemistry, Birla Institute of Technology and Science, Pilani (RJ)-333031

\*Author for Correspondence

### ABSTRACT

The electrical transport and thermal stability of the ionic liquid (IL) - Li<sup>+</sup> oxide glass composites reveals interesting results. These IL-glass composites were prepared from a novel ionic liquid [BMIM][BF<sub>4</sub>] and Li<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> glassy system by mixing and thorough manual grinding. For 5-10 wt% of [BMIM][BF<sub>4</sub>] in the glass matrix the room temperature conductivity found to be enhanced by ~ 4 orders of magnitude. The electrical conductivity of the composites is predominantly ionic and exhibits Arrhenius behavior with low activation energy. The electrical conductivity- temperature cycles, studied as a function of time, also reveal that the composites exhibit stability at least upto 100 °C.

**Key Words:** Ionic Liquid, ionic conductivity, electrical conductivity –temperature cycle.

### INTRODUCTION

Lithium ion glasses are the promising candidates as electrolytes for solid state battery applications. The poor ionic conductivity at room temperature is a major hurdle in their possible applications in solid state ionic devices. Recently it was demonstrated by many workers that the addition of ionic liquids (ILs) into the glassy matrix very significantly enhances the conductivity. However, the reason for such a significant enhancement is not yet clear and thermal stability and ionic transport of the composites has not been studied so far (Button *et al.*, 1980; Souquet, 1981; Hayashi *et al.*, 2010).

To increase the conductivity of Li<sup>+</sup> oxide glasses various methods have been adopted such as using two (or more) glass formers and mixing salt having same of different cations etc. Studies on addition of ILs into the glass matrix are very recent development in the field of solid state ionics. Addition of IL into the glassy system leads to tremendous enhancement (Hayashi *et al.*, 2010). Room temperature ionic liquids (RTILs) exhibits good thermal and electrochemical stability, negligible vapor pressure and non-flammability that may be useful to increase the ionic conductivity in solid electrolyte (Hayamizu *et al.*, 2001; Hayamizu *et al.*, 2004).

In the present study, we have synthesized ionic liquid –glass composite solid electrolyte. The ionic liquid used is 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF<sub>4</sub>]. Preliminary investigation on electrical conductivity-temperature cycles, impedance spectroscopy and stability are reported here.

### MATERIALS AND METHODS

The glassy samples of 50Li<sub>2</sub>O-50P<sub>2</sub>O<sub>5</sub> were prepared by conventional melt-quenching method. Solid lithium oxide and ammonium hydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>), in powder form, are mixed and heated to 450 °C in a muffle furnace for 2 hour and melted at 900 °C followed by rapid quenching using heavy copper plates. The glass is then ground into a fine powder.

The ionic liquid [BMIM][BF<sub>4</sub>] was synthesized by the reaction of 1-methylimidazole with 1-bromobutane followed by anion metathesis with NaBF<sub>4</sub>. In the first step 1-methylimidazole (5 mmol) was mixed with 1-bromobutane (6 mmol) and refluxed at 80°C for 12 hr. After completion of the reaction solution becomes viscous this was then washed with diethyl ether (3 × 20 mL) to remove unreacted 1-bromobutane. The 1-butyl-3-methylimidazolium bromide [BMIM][Br] layer was dried on rotatory evaporator. In the second step the bromide ion was substituted with the BF<sub>4</sub><sup>-</sup> ion. The [BMIM][Br] (1.0 g) was dissolved in anhydrous acetone (10 mL) and added NaBF<sub>4</sub> (0.6 g) and stirred at room temperature



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for overnight. The reaction mass was filtered. The filtrate was concentrated, dissolved in dichloromethane and washed with water ( $2 \times 20$  mL). The organic layer was dried with anhydrous sodium sulfate and rotovaped to give ionic liquid [BMIM][BF<sub>4</sub>]. The prepared IL, viz. [BMIM][BF<sub>4</sub>] is then added drop wise to the fine glass powder followed by thoroughly manual grinding. This uniform mixture is pelletized and cylindrical pellets are used for the measurement. The conductivity-temperature cycles were studied using computer controlled HIOKI 3532-50 LCR meter and Librathern PID temperature controller.

### RESULTS AND DISCUSSION

To investigate the electrical properties, conductivity( $\sigma$ ) –temperature (T) cycles are obtained at a controlled heating rate of 1 °C/min. Fig 1 shows the electrical conductivity as function of temperature for IL-glass composite. The electrical conductivity shows Arrhenius behavior with low activation energy in the range 0.16-0.18 eV.

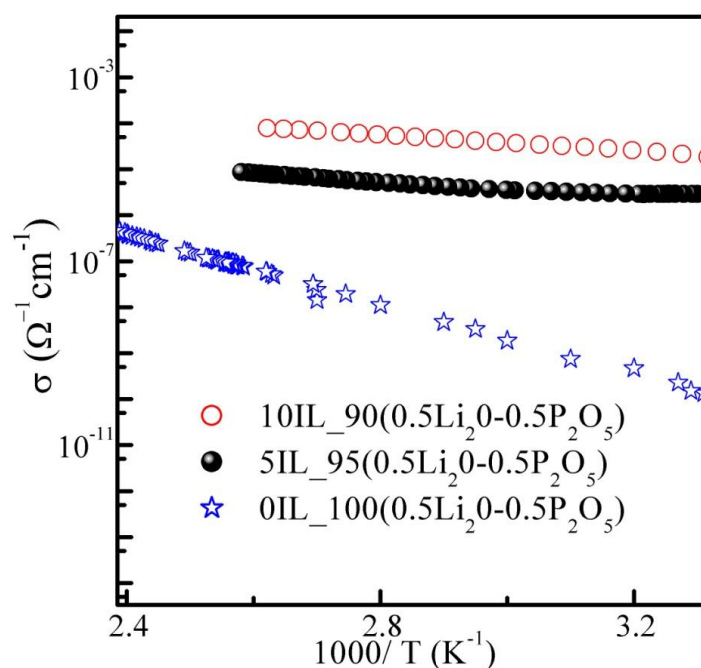
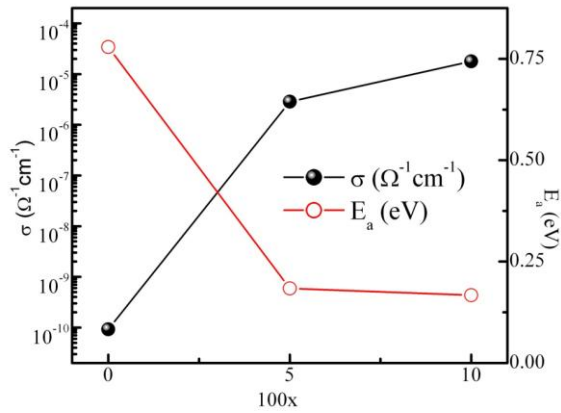


Figure 1: Temperature dependence of the conductivity

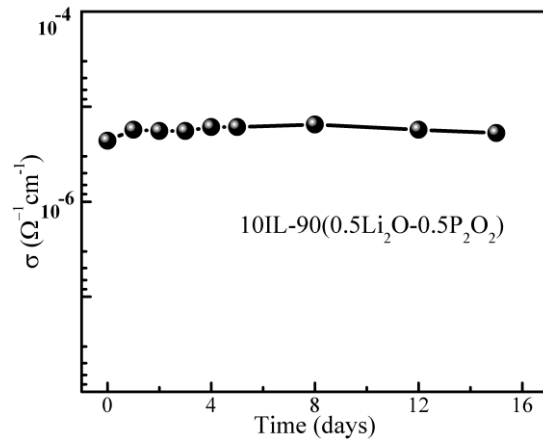
As apparent in Fig. 2, the electrical conductivity also increases notably with IL content. It was not possible to further incorporate IL into glass matrix for  $x > 10$  wt %. The conductivity is cycled between room temperature to 100 °C and observed as a function of time for 15 days after each cycle. As shown in Fig. 3 the conductivity almost remains constant with time up to 100 °C.

The Nyquist plots (Fig. 4) at different temperatures for the 10IL -90(0.5Li<sub>2</sub>O-0.5P<sub>2</sub>O<sub>5</sub>) glass sample consists of one depressed semicircle followed by a characteristic spike in low frequency region that is due to the blocking electrode capacitance due to the accumulation of free mobile charges at the interface. The equivalent circuit (as shown inset of Fig. 4) of spectra consisted of  $R_b$ ,  $C_p$  and  $C_d$ , where  $R_b$  is bulk resistance, CPE is constant phase element and  $C_d$  represents interface capacitance due to blocking electrodes. The diameter of the semicircle decreases as function of temperature that suggests the predominant ionic behavior.

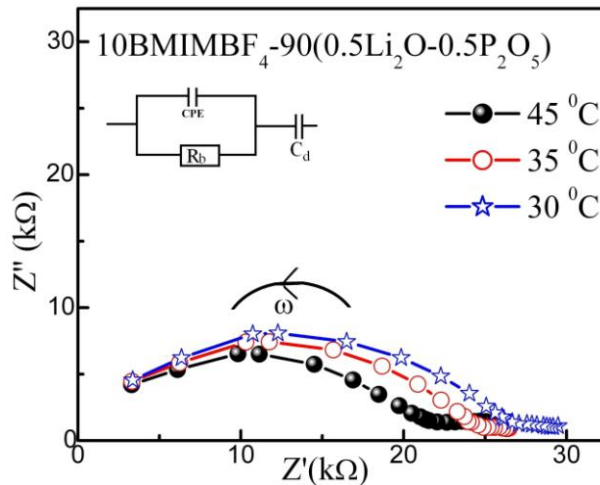
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**Figure 2: Conductivity and activation energy as function of IL content.**



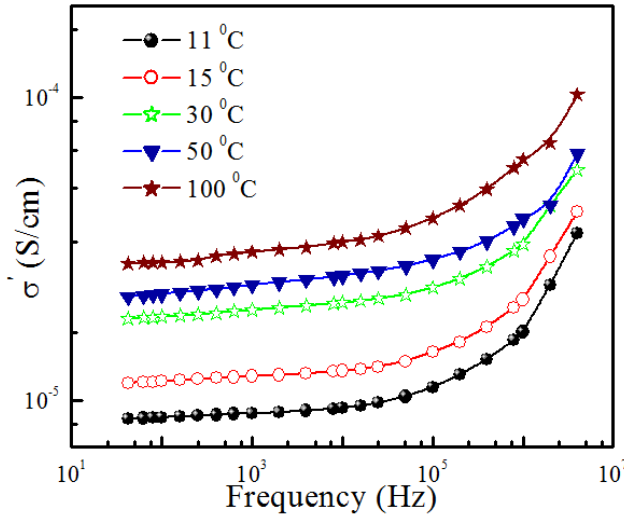
**Figure 3: Room temperature conductivity as function of time for 10 IL -90(0.5Li<sub>2</sub>O-0.5P<sub>2</sub>O<sub>5</sub>) compositions.**



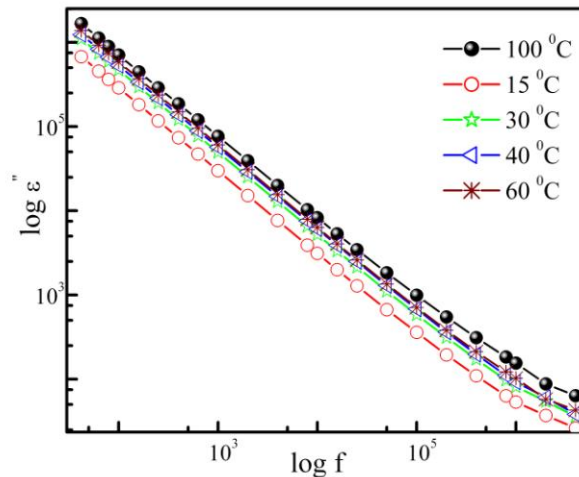
**Figure 4: Impedance spectra for 10 IL -90(0.5Li<sub>2</sub>O-0.5P<sub>2</sub>O<sub>5</sub>).**

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Fig. 5 shows frequency dependence of the conductivity for the 10IL-90(0.5Li<sub>2</sub>O-0.5P<sub>2</sub>O<sub>5</sub>) sample at different temperatures. In lower frequency region, the conductivity is independent of frequency but at higher frequency conductivity increases as function of frequency and exhibits power law behavior.



**Figure 5: Frequency dependence of  $\sigma(\omega)$  for the 10 IL -90(0.5Li<sub>2</sub>O-0.5P<sub>2</sub>O<sub>5</sub>) composition.**



**Figure 6: Frequency dependence of log loss in dielectric for the 10IL-90(0.5Li<sub>2</sub>O-0.5P<sub>2</sub>O<sub>5</sub>) composition.**

As shown in Fig. 6, the dielectric loss decreases as function of frequency and tends to saturate at higher frequencies which is typical behavior of ionic glasses as reported earlier (Anantha *et al.*, 2005).

Ionic transport number for all the samples is measured by dc polarization. The composite sample is sandwiched between blocking graphite electrodes and the current is measured on different applied voltages as a function of time. The ionic transport number is measured by using the following results

$$t_i = (1 - I_s / I_0) \quad (1)$$

where  $I_s$  is the saturated current,  $I_0$  is current at time  $t = 0$ . The transient current vs time is shown for one of the sample containing 5 wt% of IL in Fig. 7. Apparently, the current drops abruptly initially and

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saturates subsequently which confirms the dominant ionic behaviour. The ionic transport number is calculated using equation number (1) is found to be  $\sim 0.78$ - $0.80$  for all the samples.

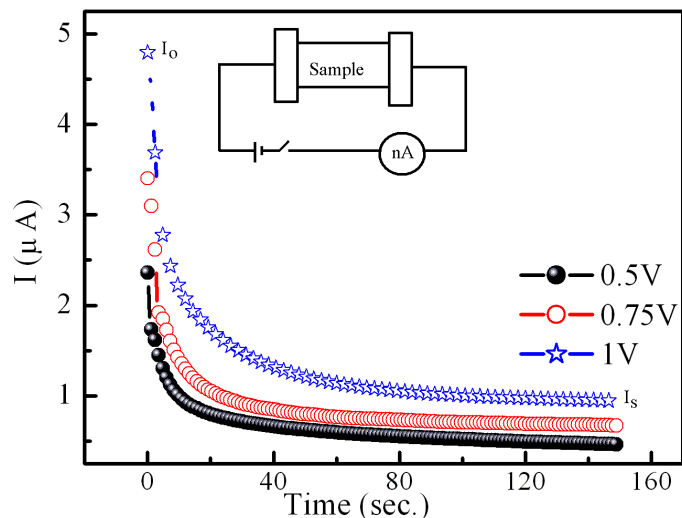


Figure 7: Current as a function of time for the sample 5 IL-95 ( $0.5\text{Li}_2\text{O}-0.5\text{P}_2\text{O}_5$ )

### CONCLUSIONS

Addition of [BMIM] [BF<sub>4</sub>] ionic liquid to a Li<sup>+</sup> ion conducting oxide glass matrix enhances the conductivity significantly. The composite samples are thermally stable at least upto 100 °C and predominantly ionic in nature. Efforts are on to understand the mechanism and to further enhance the electrical transport in the composite.

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