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STUDY OF ION TRANSPORT BEHAVIOR IN IONIC LIQUID BASED POLYMER GEL ELECTROLYTES

Physics

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ABSTRACT

Polymer gel electrolytes were synthesized by incorporating ionic liquid 2,3-dimethyl-1-hexylimidazolium bis(trifluoromethane sulfonyl)imide (DMHxImTFSI)in the polymer network of poly(ethylene oxide) (PEO). High ionic conductivity of the order of 10^{-3} S cm^{-1} has been obtained at 30°C for the polymer gel electrolytes. Ion transport studies revealed that both the cations and anions are mobile in the prepared gel electrolytes.

INTRODUCTION

Polymer gel electrolytes belong to a salt-solvent-polymer hybrid system in which the salt solution is immobilized with the addition of a suitable polymer matrix. Polymer gel electrolytes based on ionic liquids are gaining attention as ionic liquids are advantageous over the conventional salts (such as $LiBF_4$, $LiPF_6$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, NH_4BF_4, NH_4PF_6, etc.) due to their unique properties such as high ionic conductivity, immeasurable vapor pressure, inflammability, good thermal stability and wide electrochemical window etc. The current interest in the polymer gel electrolytes based on ionic liquids is due to their potential to substitute liquid electrolytes for various electrochemical devices such as dye-sensitized solar cells, sensors and actuators, batteries, solid state ultracapacitors, thin film transistors etc. [1-6].

The present work includes the preparation and characterization of non-aqueous polymer gel electrolytes based on ionic liquid 2,3-dimethyl-1-hexylimidazolium bis(trifluoromethanesulfonyl)imide (DMHxImTFSI) and polymer poly(ethyleneoxide) (PEO).

EXPERIMENTAL

Poly(ethylene oxide) (PEO, mol. wt. $5x10^6$, Aldrich)., lithium trifluoromethanesulfonimide (Aldrich), 1,2-dimethylimidazole (Merck), 1-bromohexane (Merck) and propylene carbonate (PC, Merck), were used as the starting materials for the preparation of ionic liquid and polymer gel electrolytes. 2,3-dimethyl-1-hexylimidazolium bromide (DMHxImBr) was first prepared by the reaction of 1,2-dimethylimidazole with 1-bromohexane and then anion exchange reaction was carried out using lithium trifluoromethanesulfonimide and the ionic liquid 2,3-dimethyl-1-hexylimidazolium bis(trifluoromethane sulfonyl)imide (DMHxImTFSI) was obtained. The formation of ionic liquid was checked by ^1H and ^{13}C NMR with JEOL AL-300 MHz NMR spectrometer. The details of the preparation procedure for the ionic liquid is available in earlier publications [7-9]. Polymer gel electrolytes having different concentrations of IL, PEO and PC were prepared by first solvating the ionic liquid in PC and then immobilizing this solution by the gradual addition of polymer along with continuous stirring.

RESULTS AND DISCUSSION

For the preparation of polymer gel electrolytes containing ionic liquid, firstly the liquid electrolytes were prepared by the addition of ionic liquid DMHxImTFSI in PC followed by the incorporation of liquid electrolytes in the polymer matrix PEO. In the case of liquid electrolytes (PC+ x M DMHxImTFSI), the conductivity of the solvent (PC~ 10^{-6} S cm^{-1}) increases by three orders of magnitude (~ 10^{-3} S cm^{-1}) with the addition of even a small amount of IL

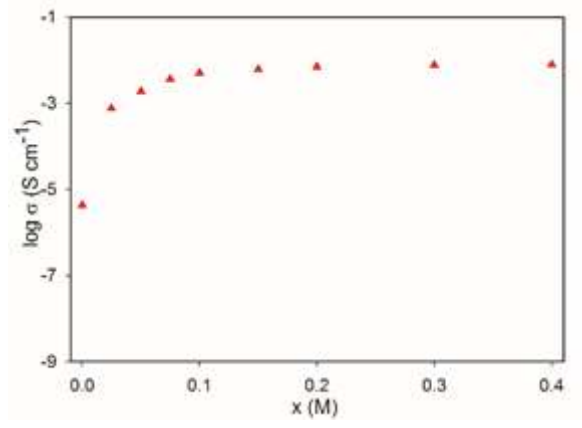


Figure 1 : Ionic conductivity of liquid electrolyte (PC+ xM DMHxImTFSI) as a function of concentration of IL in PC

In the variation of ionic conductivity of liquid electrolyte as a function of concentration of IL in PC (Figure 1)[10], the ionic conductivity increases as the concentration of IL in the electrolyte increases. This is due to the increase in the number of charge carriers provided by the IL. However, this variation is not linear. At higher concentrations of IL (above 0.1M) in PC, the ionic conductivity values do not show much change and reach a saturation value. This behavior has been explained to be due to the formation of ion aggregates at high concentrations of IL. As ion aggregates generally do not take part in the conduction process, hence the saturation in the ionic conductivity is observed [11].

The formation of ion aggregates has been studied qualitatively by mass action considerations [12]. According to this model, the plot between log **σ** and log C (where C is the concentration of ionic liquid) should be a straight line, if all the ions are present as free ions whereas a deviation from the straight line behavior indicates the presence of neutral ion aggregates which do not contribute to conductivity. The variation of log conductivity (log **σ**) with log concentration (log C) for liquid electrolyte (PC-DMHxImTFSI) has been shown in Figure2.

The plot shows a straight line behavior at low concentrations of IL in PC (up to 0.1M), however, a deviation from the straight line is observed as the concentration of IL increases beyond 0.1M IL. This deviation suggests the formation of ion aggregates at high concentrations of IL and hence explains the saturation of ionic conductivity above 0.1M concentration of IL in PC

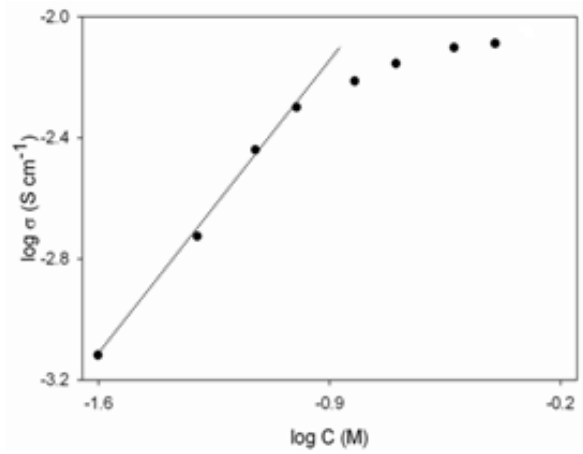


Figure 2 : Log conductivity vs. log concentration of ionic liquid for liquid electrolyte (PC+ x M DMHxImTFSI)

As the value of ionic conductivity shows a saturation above the concentration of 0.1M IL in PC, therefore liquid electrolyte with the composition PC+0.1M IL has been further used for the preparation of polymer gel electrolyte. Figure 3 shows the variation of conductivity and viscosity of the

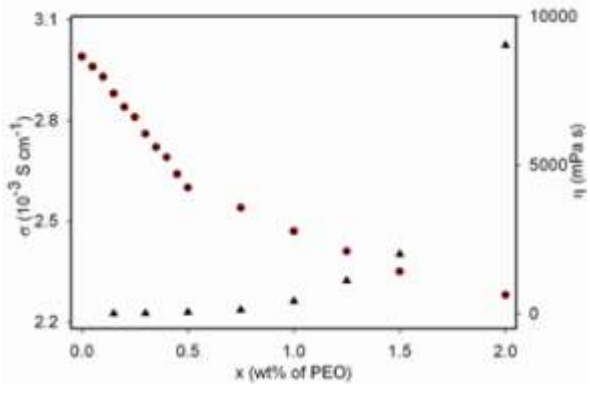


Figure 3 : Variation of conductivity (●) and viscosity (▲) with the concentration of PEO for polymer gel electrolytes (PC+ 0.1M DMHxImTFSI+ x wt% PEO)

electrolyte as a function of concentration of polymer. The ionic conductivity continuously decreases with a corresponding increase in viscosity as the concentration of polymer in liquid electrolyte increases. Polymer gel electrolyte (PC+ 0.1M DMHxImTFSI + 2 wt% PEO) possesses ionic conductivity of $2.28x10^{-3}$ S cm^{-1}at 30°C which increases upto $4.23x10^{-3}$ S cm^{-1} at 70 °C and viscosity of 9030.3 mPa s at 30°C which decreases to 4279.5 mPa s at 70 °C (shown in Figure 4).

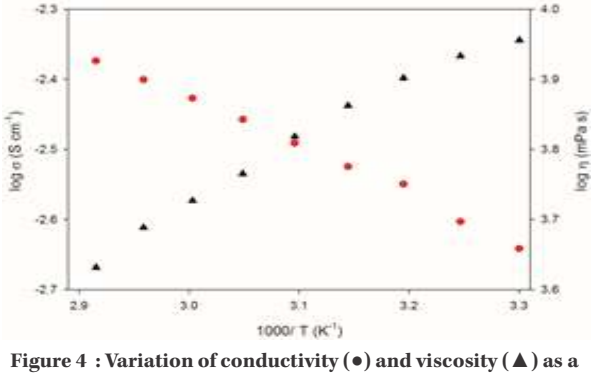
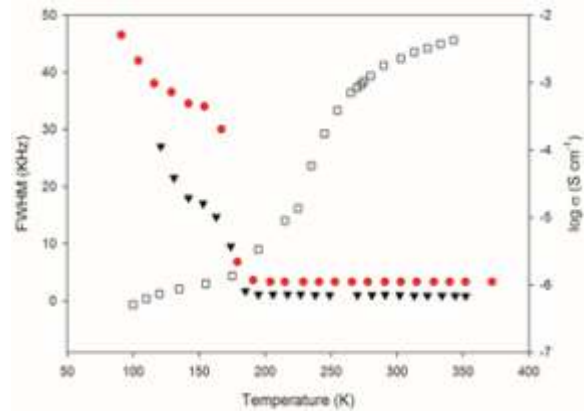


Figure 4 : Variation of conductivity (●) and viscosity (▲) as a function of temperature for polymer gel electrolytes PC+ 0.1M DMHxImTFSI+ 2 wt% PEO

The nature of the mobile species in the polymer gel electrolytes and their ion transport behavior was also studied by ^{1}H and ^{19}F NMR studies in the temperature range 80-350K. The linewidth (FWHM) at different temperatures was calculated and the variation of ^{1}H and ^{19}F NMR lines as a function of temperature is shown in Figure 5



Polymer gel electrolyte show broad lines and a linewidth of 46.5- 30 kHz in the temperature range 90-167 K for ^{1}H NMR line. Line narrowing commences at 167 K with a residual linewidth of 3.3kHz above 200 K. For ^{19}F NMR line, line narrowing begins at 163 K with a residual linewidth of 1 kHz above 190 K. At low temperatures, the broad lines are due to the dipolar and quadrupolar interactions. As the temperature increases, these interactions average out leading to line narrowing. Line narrowing observed in the variation of ^{1}H and ^{19}F NMR line with temperature suggests that both cations and anions are mobile in the polymer gel electrolyte.

The linewidth of NMR line and ionic mobility are inversely related. Line narrowing affects the ionic mobility and hence the ionic conductivity of the electrolyte. For comparison purpose the ionic conductivity has also been observed and included in the graph in the temperature range of 100-350 K. As it can be observed from the graph, the ionic conductivity of the electrolyte shows a sharp increase at the temperature of motional narrowing .This indicates the onset of long range ion diffusional motion at the temperature corresponding to line narrowing.

CONCLUSIONS :

Polymer gel electrolytes based on ionic liquid DMHxImTFSI possesses high ionic conductivity of the order of 10^{-3} S cm^{-1} at ambient temperature. Variation of ^{1}H and ^{19}F NMR line shows that both cations and anions are mobile in the presently investigated gel electrolyte

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