Investigating the Ionic Conductivity and Thermal Stability of Ionic Liquid Based Polymer Gel Electrolyte

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Abstract—*Ionic conductivity and thermal behavior of ion conducting polymer gel electrolyte containing ionic liquid 2,3-dimethyl-1-hexylimidazolium triflate (DMHxImTf), polymer poly(ethylene oxide) (PEO) and solvent propylene carbonate (PC) have been studied. Polymer provides the physical structure while DMHxImTf provides the ions for conduction. The dependence of ionic conductivity on the concentration of ionic liquid, polymer and temperature has been investigated. Polymer gel electrolyte has been found to show conductivity of the order of 10^{-3} Scm^{-1} at 30°C. TGA/DSC studies show that polymer gel electrolyte is stable up to 100°C.*

1. INTRODUCTION

Polymer gel electrolytes are a type of quasi solid state electrolytes in which a salt solution (liquid electrolyte) is trapped in a polymer network. Significant amount of liquid electrolyte can be entrapped in a polymer network and this hybrid network structure imparts the cohesive properties of solids and the diffusive transport properties of liquids to polymer gel electrolytes, hence, making them advantageous over both solid electrolytes and liquid electrolytes. Recently, room temperature molten salts or ionic liquids have replaced 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. Polymer gel electrolytes containing ionic liquids are being employed in various electrochemical devices such as dye-sensitized solar cells, batteries, supercapacitors, actuators, thin film transistors etc [1-6].

In the present work, polymer gel electrolytes containing ionic liquid 2,3-dimethyl-1-hexylimidazolium triflate (DMHxImTf), polymer poly(ethylene oxide) (PEO) and solvent propylene carbonate (PC) have been prepared and characterized for their ionic conductivity and thermal stability.

2. EXPERIMENTAL

The starting materials used for the preparation of ionic liquid and polymer gel electrolytes are Poly(ethylene oxide) (PEO, mol. wt. $5x10^6$, Aldrich)., lithium triflate (Aldrich), 1,2-dimethylimidazole (Merck), 1-bromohexane (Merck) and propylene carbonate (PC, Merck). Synthesis of the ionic liquid was carried out in a two-step reaction. Firstly, 2,3-dimethyl-1-hexylimidazolium bromide (DMHxImBr) was prepared by the reaction of 1,2-dimethylimidazole with 1-bromohexane and then anion exchange reaction was carried out using lithium triflate and the ionic liquid 2,3-dimethyl-1-hexylimidazolium triflate (DMHxImTf) was obtained. The formation of the ionic liquid was checked by ^{1}H and ^{13}C NMR with JEOL AL-300 MHz NMR spectrometer. The details of the preparation procedure for the ionic liquid are available in earlier publications [7-10]. 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.

3. RESULTS AND DISCUSSION

Ionic Conductivity and Viscosity

Polymer gel electrolytes containing ionic liquid were prepared by firstly solvating the ionic liquid DMHxImTf in an organic solvent propylene carbonate (PC) followed by the immobilization of this liquid electrolyte using a polymer matrix PEO. For these gel electrolytes, the variation of ionic conductivity as a function of concentration of ionic liquid, polymer and temperature has been studied.

In the variation of ionic conductivity of liquid electrolyte as a function of concentration of ionic liquid in PC (Figure.1), the ionic conductivity increases as the concentration of ionic liquid in the electrolyte increases. This is due to the increase in the number of charge carriers provided by the ionic liquid.

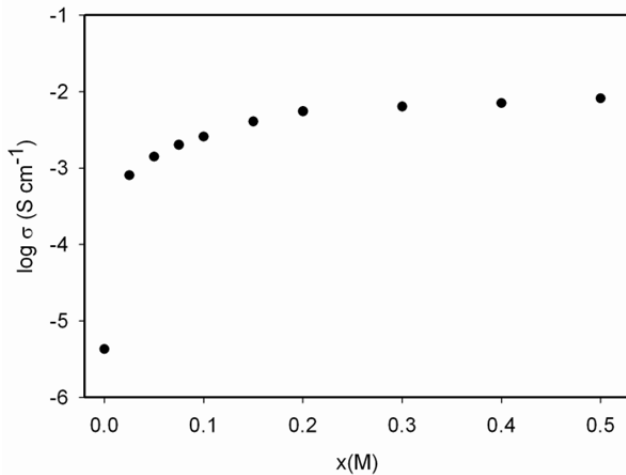However, this variation is not linear. At higher concentrations of IL

Fig. 1: Ionic conductivity of liquid electrolyte (PC+ xM DMHxImTf) as a function of concentration of DMHxImTf

(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 ionic liquid, ion aggregates are formed because of the increased coulombic interactions between the ions. Theses ion aggregates are neutral and generally do not take part in the conduction process, hence the saturation in the ionic conductivity is observed [11].

The conductivity of polymer gel electrolytes containing different amounts of PEO has been measured at 30°C and variation of conductivity with the concentration of PEO (expressed as wt% of liquid electrolytes) has been given in Fig. 2.
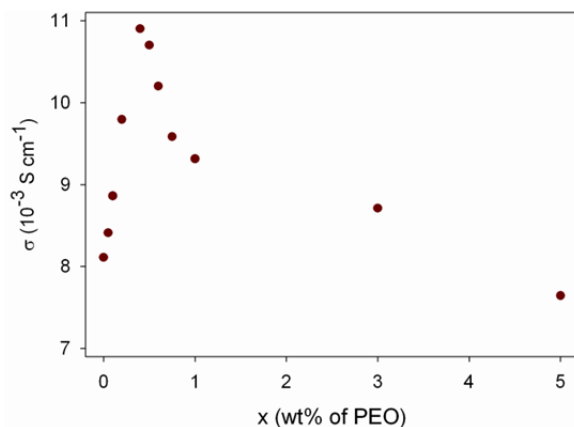

Fig. 2: Variation of ionic conductivity of PC+ 0.5(M) DMHxImTf+ x wt% PEO with concentration of PEO.

The conductivity of liquid electrolytes increases with the addition of polymer, reaches a maximum value of 1.09×10^{-2} S cm^{-1} at 0.4 wt% PEO, and then shows a small decrease at higher concentrations of PEO. The electrolyte having composition PC+ 0.5M IL+ 5 wt% PEO, which has been used for further characterizations possesses ionic conductivity of 7.65×10^{-3} S cm^{-1} at 30°C which is only slightly lower than the value observed for liquid electrolytes. The increase in conductivity at low PEO concentrations is due to an increase in free ion concentration with the dissociation of ion aggregates present in liquid electrolyte PC+0.5M IL [12-15], and as a result polymer gel electrolytes with conductivity higher than the corresponding liquid electrolytes have been obtained. Further addition of polymer to the liquid electrolytes increases the viscosity of the electrolyte. As viscosity and mobility are inversely related to each other, increase in viscosity with the increasing concentration of polymer reduces the mobility of ions and hence a decrease in ionic conductivity is observed at high concentration of PEO.
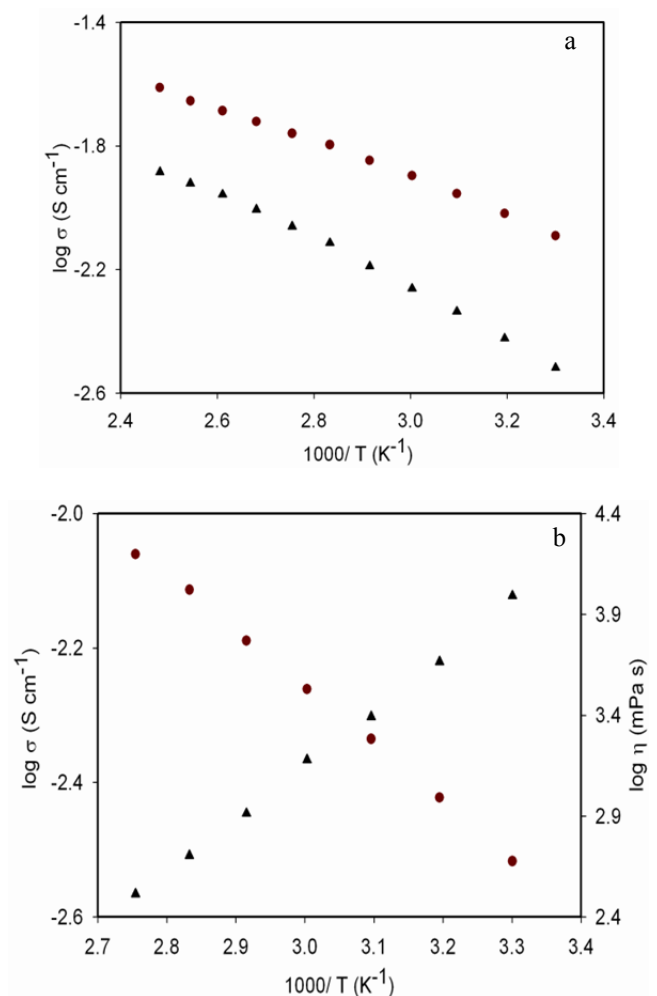

Fig. 3: Variation of log conductivity with reciprocal temperature for liquid electrolyte (PC+ 0.5M DMHxImTf) and polymer gel electrolyte (PC+ 0.5M DMHxImTf+ 5 wt% PEO) (a) and variation of log conductivity and log viscosity with reciprocal temperature for polymer gel electrolyte (PC+ 0.5M DMHxImTf+ 5 wt% PEO) (b)

The variation of conductivity as a function of temperature for liquid electrolyte (PC+0.5M DMHxImTf) and polymer gel electrolytes (PC+0.5M DMHxImTf+ 5 wt% PEO) has been given in Fig. 3 (a).

The ionic conductivity of gel electrolyte PC+0.5M DMHxImTf+ 5 wt% PEO increases from 7.65×10^{-3} S cm^{-1} (30°C) to 9.70×10^{-3} S cm^{-1} (90°C). The increase in conductivity with temperature also corresponds to the decrease in viscosity of gel electrolytes. The variation of log viscosity with reciprocal temperature for the polymer gel electrolyte has been shown in Fig. 3 (b).

For PC+0.5M DMHxImTf + 5 wt% PEO, the viscosity varies from 9817.6 mPa s (30°C) to 326.7 mPa s (90°C). The ionic conductivity of liquid and gel electrolytes increases with increase in temperature. The variation of conductivity with temperature for gel electrolytes is similar to the variation for liquid electrolytes which suggests liquid like behavior of gel electrolytes. However, the conductivity of gel electrolytes is lower than the corresponding liquid electrolyte at all temperatures which is due to their high viscosity. As the temperature increases, the viscosity of the gel electrolyte decreases. Also the charge carriers are thermally activated and the free volume increases due to the expansion of polymer chains assisting the motion of charge carriers. Both these factors lead to increase in mobility of ions which in turn increases conductivity.

The conductivity of the neat ionic liquid has been observed to increase with temperature, which is due to a decrease in viscosity, which enhances ionic mobility and conductivity. At room temperature the addition of PC to the ionic liquid results in an increase in conductivity and electrolytes having composition PC + 0.5 M IL + 5 wt% PEO show higher conductivity than for the ionic liquid and solvent free polymer gel electrolyte at all temperatures. The increase in conductivity with the addition of PC is due to its lower viscosity as compared with ionic liquid and higher dielectric constant and both these factors contribute to higher conductivity.

4. DSC/TGA

The thermal stability of polymer gel electrolyte PC+ 0.5 M IL+ 5 wt% PEO has been studied by simultaneous DSC/TGA/DTG measurement in 25-550°C temperature range at a heating rate of 10°C/min under nitrogen atmosphere. The DSC/TGA/DTG plot of electrolytes has been given in Fig. 4.

For polymer gel electrolyte (PC+ 0.5M IL + 5 wt% PEO), the TGA curve shows the stability of electrolyte upto 100°C and there is a weight loss of only 3.7% upto this temperature. However, above 100°C, first major weight loss step caused by the evaporation of PC, commences. This step involves a weight reduction of 67.6% over the temperature range of 100-210°C. It also corresponds to an endothermic peak in the DSC curve at 181°C. The second weight loss step at 350°C in the

TGA curve is due to the decomposition of ionic liquid which also leads to an exothermic peak at 444°C in the DSC
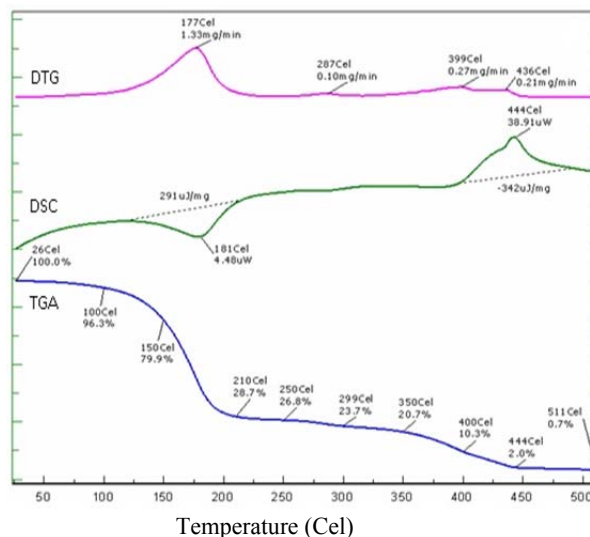

Fig. 4: DSC/TGA/DTG curves for polymer gel electrolyte PC+ 0.5M DMHxImTf+ 5 wt% PEO

curve. Imidazolium based ionic liquids, decompose to produce both volatile acids from anion and carbene derivatives of cation [16]. The high thermal stability of ionic liquid is attributed to the heteroatom- carbon and heteroatom- hydrogen bonds.

5. CONCLUSION

Polymer gel electrolyte containing ionic liquid DMHxImTf exhibits ionic conductivity value of 7.65×10^{-3} S cm^{-1} and viscosity of 9817.6 mPa s at 30°C. The electrolyte has been found to be thermally stable upto 100°C

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