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Polymer Electrolyte Membranes Based on Room Temperature Ionic Liquid: 2,3-Dimethyl-1-octyl imidazolium hexafluorophosphate ($DMOImPF_6$)

S. S. Sekhon,[*1,2] B. S. Lalia,[1] C. S. Kim,[2] W. Y. Lee[2]*

Summary: Room temperature ionic liquid: 2,3-dimethyl-1-octylimidazolium hexafluorophosphate ($DMOImPF_6$) has been incorporated in polyvinylidenefluoride -co-hexafluoropropylene (PVdF-HFP) to develop non-aqueous polymer electrolyte membranes. The conductivity of polymer electrolyte membranes depends upon the composition of ionic liquid and maximum conductivity of 1.35×10^{-3} S/cm at 120 °C has been observed. The addition of plasticizers has been found to enhance the conductivity of polymer electrolytes by one order of magnitude which depends upon the dielectric constant of plasticizer.

Keywords: conductivity; ionic liquid; membrane; plasticizers

Introduction

Room temperature ionic liquids are important materials due to their unique properties such as high ionic conductivity, very low vapour pressure, non-flammability, good thermal and electrochemical stability etc. Due to these properties ionic liquids are being used in various electrochemical devices.[1–5] The first ionic liquid, ethylammonium nitrate, was reported in 1914[6] and since then a large number of ionic liquids have been studied. Ionic liquids containing chloroaluminate anions are air and moisture sensitive and are hence difficult to handle under normal conditions. The report of air and moisture stable non chloroaluminate ionic liquids renewed research interest in these materials. The physical and chemical properties of ionic liquids can be controlled by a proper selection of the cation and anion.[7,8] Despite high conductivity, ionic liquids are generally not preferred in applications due to their liquid nature. One possible approach is to develop solid polymer electrolyte membranes by incorporating ionic liquid in a suitable polymer matrix and this has been attempted in the present work.

In the present study, polymer electrolyte membranes have been prepared by incorporating room temperature ionic liquid: 2,3-dimethyl-1-octylimidazolium hexafluoro phosphate ($DMOImPF_6$) in polyvinylidenefluoride-co-hexafluoropropylene (PVdF-HFP). The dependence of conductivity of different electrolytes on the concentration of ionic liquid, salt, plasticizers and temperature has been studied. The variation of dielectric constant with temperature for polymer electrolytes and its correlation with the conductivity results has also been investigated.

[1] Department of Applied Physics, Guru Nanak Dev University, Amritsar-143005, India
Fax: (+91) 1832258820
E-mail: sekhon_apd@yahoo.com
[2] Polymer Electrolyte Fuel Cell Research Group, Korea Institute of Energy Research, Daejeon, 305-343, Republic of Korea

Experimental Part

PVdF-HFP ($M_w = 130{,}000$, Aldrich), ammonium hexafluorophosphate (NH_4PF_6, Aldrich), 1,2-dimethylimidazole (Merck), 1-bromooctane (Merck), propylene carbonate (PC, Merck), dimethylacetamide (DMA, Merck), acetonitrile (Qualigens) were used as the starting materials in the preparation of ionic liquid and polymer electrolyte membranes containing ionic liquid. 2,3-dimethyl-1-octylimidazolium bromide (DMOImBr) was first prepared by the reaction of 1, 2-dimethylimidazole with 1-bromooctane and then anion exchange reaction was carried out by using ammonium hexafluorophosphate and the ionic liquid having composition: 2, 3-dimethyl-1-octylimidazolium hexafluorophosphate ($DMOImPF_6$) was obtained. The details of preparation procedure has been reported in earlier publications.[9–12] The formation of $DMOImPF_6$ was confirmed by ^1H NMR and mass spectra.

Polymer electrolyte membranes containing ionic liquid were prepared by the solution casting method. In this method, the polymer (PVdF-HFP), ionic liquid ($DMOImPF_6$), and salt (NH_4PF_6), taken in stoichiometric quantities, were dissolved in a mixture of acetonitrile and methanol alongwith continuous stirring to obtain a homogeneous viscous solution, which was then poured in polypropylene dishes. The solvent was allowed to evaporate slowly and polymer electrolytes in the free standing film form were obtained.

The ionic conductivity of electrolytes was measured by impedance method using a cell with platinum electrodes for the ionic liquid and a cell with pressure contact stainless steel electrodes for the polymer electrolytes in the membrane form. The measurements were performed with a computer interfaced Hioki 3532-50 LCR Hi-Tester and HP 4284 A precision LCR meter and details are available in earlier publications.[9–12]

Results and Discussion

The dependence of conductivity of polymer electrolyte (PVdF-HFP:$DMOImPF_6$) membranes (having composition ionic liquid: polymer = 50:50, 60:40, 65:35 wt%) upon the concentration of ionic liquid is given in Figure 1. The conductivity of polymer electrolytes increases with the concentration of $DMOImPF_6$ and maximum conductivity of 4.11×10^{-5} S/cm at 30 °C has been observed for electrolytes containing ionic liquid and polymer in 65:35 weight ratio. Membranes containing ionic liquid more than 65 wt% have not been studied as they possess poor mechanical properties.

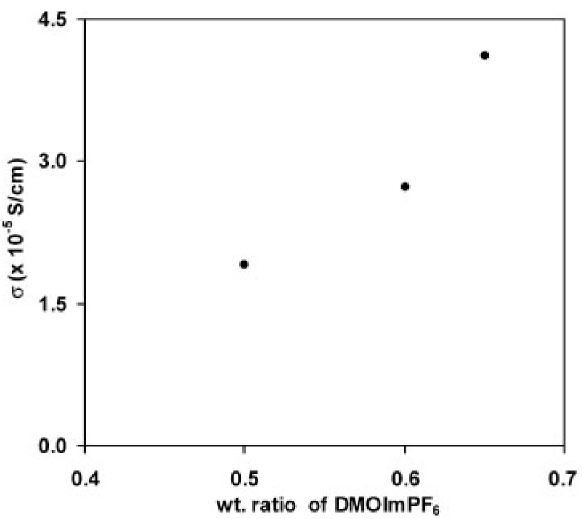

Figure 1.
Variation of conductivity of polymer electrolytes with the concentration of ionic liquid.

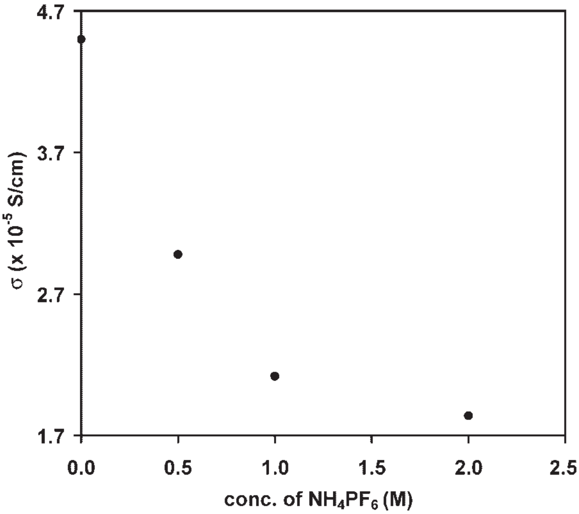

Figure 2.
Variation of conductivity of PVdF-HFP + $DMOImPF_6$ + x(M) NH_4PF_6 at 30 °C with the concentration of salt.

The addition of ammonium hexafluorophosphate (NH_4PF_6) – salt with the same anion as the ionic liquid ($DMOImPF_6$) has been found to lower the conductivity of polymer electrolytes marginally from 4.5×10^{-5} to 1.84×10^{-5} S/cm as shown in Figure 2. The addition of NH_4PF_6 increases the ion concentration in polymer electrolytes resulting in the formation of ion aggregates which do not contribute to conductivity and as a result conductivity decreases.

The addition of plasticizers, having high dielectric constant and low viscosity, namely PC ($\varepsilon = 64.4$, $\eta = 2.53$ cP) and DMA ($\varepsilon = 37.8$, $\eta = 1.94$ cP) has been found to

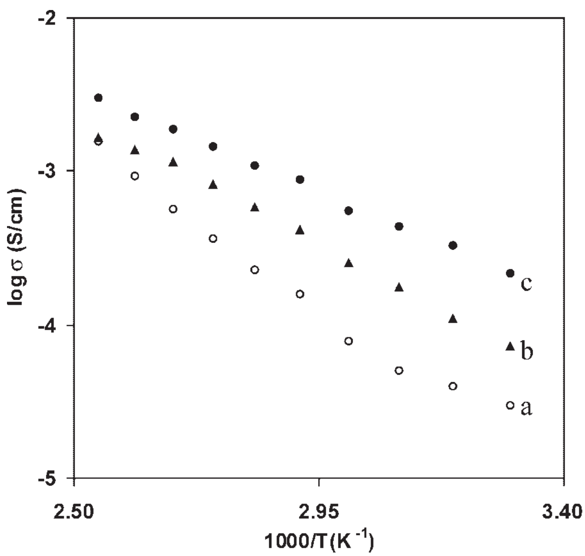

Figure 3.
Variation of log σ with reciprocal temperature for (a) PVdF-HFP + $DMOImPF_6$ + NH_4PF_6, (b) PVdF-HFP + $DMOImPF_6$ + NH_4PF_6 + DMA and (c) PVdF-HFP + $DMOImPF_6$ + NH_4PF_6 + PC.

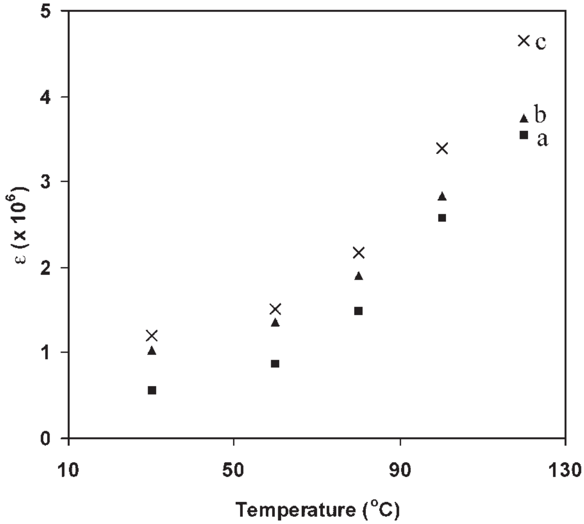

Figure 4.
Variation of dielectric constant with temperature for (a) PVdF-HFP + $DMOImPF_6$ + NH_4PF_6, (b) PVdF-HFP + $DMOImPF_6$ + NH_4PF_6 + 0.1 ml DMA and (c) PVdF-HFP + $DMOImPF_6$ + NH_4PF_6 + 0.1 ml PC.

enhance the conductivity of polymer electrolytes by one order of magnitude. The variation of conductivity of polymer electrolytes with temperature was also studied and is shown in Figure 3. The increase in conductivity of polymer electrolyte membranes PVdF-HFP + $DMOImPF_6$ + 0.5 M NH_4PF_6 with the addition of plasticizers is due to an increase in the dielectric constant of electrolytes, which results in the dissociation of ion aggregates alongwith an increase in mobility (due to the lower viscosity of plasticizers) and both these factors result in an increase in conductivity of polymer electrolytes. The variation of dielectric contant of polymer electrolytes having composition PVdF-HFP + $DMOImPF_6$ + 0.5 M NH_4PF_6 + x ml PC, DMA (x = 0, 0.1) with temperature is shown in Figure 4. The dielectric constant (ε) of polymer electrolytes varies with temperature and follows the order

$$\varepsilon_{\text{with PC}} > \varepsilon_{\text{with DMA}} > \varepsilon$$

The dielectric constant of polymer electrolytes containing PC is higher than those containing DMA at all temperatures. This is also reflected in the variation of conductivity with temperature as given in Figure 3 and the conductivity of polymer electrolytes varies as follows

$$\sigma_{\text{with PC}} > \sigma_{\text{with DMA}} > \sigma$$

at all temperatures. Thus with a proper choice of the concentration of ionic liquid, plasticizer and salt, polymer electrolyte membranes containing ionic liquid with high value of conductivity can be obtained. These membranes being non aqueous in nature can find applications in different devices.

Conclusions

Polymer electrolyte membranes containing $DMOImPF_6$, PVdF-HFP and NH_4PF_6 possess high value of ionic conductivity 1.57×10^{-3} S/cm at 120 °C. The addition of plasticizers (PC and DMA) with high dielectric constant and low viscosity has been found to result in conductivity enhancement. Thus with a proper choice of an ionic liquid, polymer and plasticizers, non aqueous polymer electrolyte membranes with high value of ionic conductivity can be developed.

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