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Enhancement of ionic conductivity of Poly (vinylidene fluoride-hexafluoropropylene) based solid polymer electrolyte by the incorporation of 1-methyl-3-propylimidazolium iodide

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Abstract : Ionic liquid incorporated solid polymer electrolyte was prepared with an aim to achieve good ionic conductivity for the application of batteries, sensors and actuators. The solid polymer electrolyte prepared by solution casting technique comprises a solution of sodium trifluoromethane sulfonate (NaTf) in a room temperature ionic liquid 1-methyl-3-propylimidazolium iodide (MPII) immobilized in poly (vinylidene fluoride-hexafluoropropylene) (PVdF-HFP). Different structural and electrical studies demonstrate promising characteristics of the polymer electrolyte films suitable as electrolyte in rechargeable sodium batteries. Fourier Transform Infra-red (FTIR) and X-ray diffraction techniques indicate possible conformational/structural changes in the polymer (PVdF-HFP) due to the addition of MPII and MPII-NaTf. The content of IL was found to affect the ionic conductivity and the maximum ionic conductivity value of $1.377 \times 10^{-3} \text{ S cm}^{-1}$ was achieved for (40wt %) of IL. The temperature dependence of electrical conductivity of the sample exhibit the metallic behaviour of the sample.

Keywords: Polymer electrolyte, Sodium triflate, ionic liquid, ionic conductivity.

1. Introduction

Recent development in polymer electrolyte which combine ionic conductivity in the solid state with mechanical flexibility making them ideal replacements for liquid electrolyte in electrochemical cells. However, the transport and interfacial properties of newly developed polymer electrolytes should approach those of conventional liquid solutions. Many research was done on high molecular weight polymer PEO blended with lithium salt, LiX where X is preferably a large soft anion, eg. $[\text{ClO}_4]^-$ or $[\text{N}_9\text{CF}_3\text{SO}_2\text{O}_2]^-$ [1,2]. Despite major improvements in the conductivity of high molecular weight polymer electrolytes, the conductivities at room temperature and below are often not sufficient for use in applications where relatively high rates are required. An alternative method of achieving high conductivity while retaining the useful properties of polymer electrolyte is to use ionic liquids (ILs) either as the main conductivity medium supported in a polymer membrane or as a plasticizing component in polymer electrolyte. The material with IL as the main conducting medium and the polymer as the supporting matrix has been pioneered by the groups of Watanabe[3,4] and Forsyth and MacFarlane[5-8] and have termed either “polymer in ionic liquid electrolytes (PILS)” or “ion gels”. For example studies on the effect of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) on the properties of PEO-EC-LiBF₄ electrolyte were reported[8] showing a decrease in the degree of crystallinity of the

polymeric component and a subsequent fivefold increase in conductivity for a material containing 0.2mol of EMIBF₄ IL. The key parameter to improve the transference number is closely related to the free energy of polymer electrolytes containing ILs and is significantly affected by the type of cation and anion. The common cations in ILs fall into one of the following three categories: alkyl pyrrolidiniums, alkyl imidazoliums and alkyl sulfoniums. The types of anions vary. Of the most commonly used IL architectures, the imidazolium architecture has the highest conductivity and thus makes it an ideal starting point for the development of an electrolyte. We report here our recent results on dimensionally stable solid polymer electrolyte produced by incorporating room temperature ionic liquid 1-methyl-3-propylimidazolium iodide(MPII) into a poly(vinylidene fluoride-hexafluoropropylene) copolymer [P(VdF-HFP)] and sodium triflate as electrolyte. Many investigations have been done on ionic liquid based polymer electrolytes composed of P(VDF-HFP) which provide structural integrity while at the same time allowing for the formation of ionically conducting channel.

2. Experimental

2.1 Materials:

Poly(vinylidene fluoride-co-hexafluoropropylene) of molecular weight 130,000g/mol⁻¹, and Sodium triflate from ALDRICH and room temperature ionic liquid 1-methyl-3-propylimidazolium iodide from HIMEDIA were purchased. Acetone obtained from MERCK was used as solvent. All the chemicals were used as received.

2.2 Sample preparation:

Ionic liquid incorporated polymer electrolyte samples were prepared by keeping polymer-salt ratio as 70:30 with varying weight percentage of ionic liquid. Initially, P(VdF-HFP) was allowed to swell in acetone by mechanical stirring for 10h. Then the required amount of sodium triflate [P(VdF-HFP):NaTf = 70:30] was dissolved in various weight ratios(20, 40, 60) of ionic liquid was mixed with PVdF-HFP and stirred for another 4-5 hrs. The obtained solutions were then poured in glass petri-dishes and allowed to dry to obtain stable translucent free standing thick films. The weight ratios of P(VdF-HFP):NaTf:MPII are shown in Table 1.

Table 1: The weight ratios of PVdF-HFP:NaTf:MPII

Designation	Weight ratios (wt%)		
	P(VdF-HFP)	NaTf	MPII
PSIL0	70	30	0
PSIL2	56	24	20
PSIL4	42	18	40
PSIL6	28	12	60

2.3 Instrumentation:

XRD patterns of the sample were recorded using XPERTPRO X-Ray diffractometer using Cu-K α radiation in the Bragg angle (2θ) ranging from 10 to 60°. Fourier transform Infra-Red(FTIR) spectrum were recorded with the help of SHIMADZU 8400S FTIR spectrophotometer. The electrical conductivity measurement of the samples was carried out by AC impedance analyzer, PSM1735 supplied by Newton 4th Ltd, London over the frequency range from 1 Hz to 1MHz, Thickness of the samples (L) was determined using micrometer screw gauge. The temperature dependence of the ionic conductivity was performed in the temperature range from 30°C to 90°C.

3. Results and Discussion

3.1 XRD

X-ray diffraction study is used to determine the degree of crystallinity of the samples in a qualitative manner and also to detect the presence of excess salt.

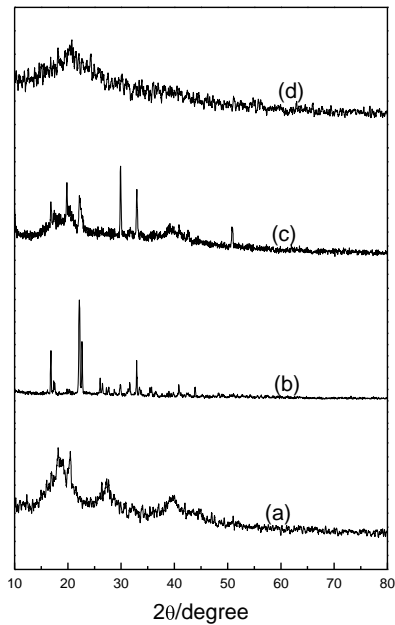


Fig. 1. XRD patterns of (a) pure P(VdF-HFP), (b) NaTf, (c) P(VdF-HFP) + NaTf, (d) P(VdF-HFP) + NaTf + MPII(60wt%)

Figure 1 shows the XRD pattern of P(VdF-HFP) film, NaTf and the samples PSIL0 and PSIL6. The broad peaks at $2\theta=18, 20, 27$ and 39° and other minor peaks of P(VdF-HFP) confirmed its semicrystalline nature. The presence of sharp crystalline peaks in Figure 1b reveals that sodium triflate is polycrystalline in nature. In the sample PSIL0, the crystalline peaks of NaTf dominates the amorphous region of P(VdF-HFP) with the disappearance of some of the peaks of NaTf. This indicates that certain amount of sodium triflate remain as free salt and does not complex with polymer because of excess amount of it. These peaks may also arise from large ion clusters that are formed by strong interaction of ions and the ordering of large ion clusters concerning with ion percolation paths, is accelerated with salt concentration [10]. When 60 wt% of IL was added to the polymer electrolyte, the peak of P(VdF-HFP) at 18° and 20° merged together to form single broad peak at 20° . Disappearance of peak corresponding to NaTf and broadening of polymer peak shows the plasticising action of IL which helps the better dissolution of NaTf.

3.2 Fourier Transform Infrared Spectroscopy

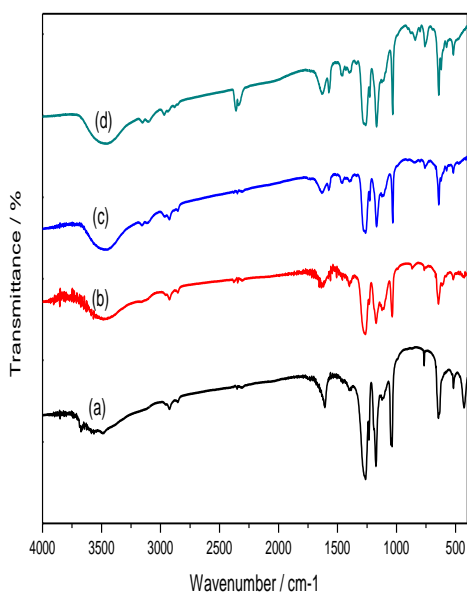


Fig.2. FTIR spectra of (a) P(VdF-HFP) + NaTf, (b) P(VdF-HFP) + NaTf + MPII(20wt%), (c) P(VdF-HFP) + NaTf + MPII(40wt%), (d) P(VdF-HFP) + NaTf + MPII(60wt%)

FTIR spectroscopy is vital in the examination of interactions taking place between the individual constitutions of the polymer electrolyte system. Figure 2 shows the FTIR spectrum of the samples PSIL0, PSIL2, PSIL4 and PSIL6. Prominent peaks of pure PVdF-HFP at 528, 737, 757, 821, 886 and 950 cm^{-1} indicates the α phase of semicrystalline of P(VdF-HFP). The peak at 886 cm^{-1} corresponds to the amorphous phase of the polymer. The peak 528 and 737 cm^{-1} disappeared when NaTf was added to the polymer and a new peak was obtained at 763 cm^{-1} . For NaTf, symmetrical stretching of CF_3 is observed at 766 cm^{-1} , symmetrical stretching of SO_3 at 1037 cm^{-1} , asymmetrical stretching of SO_3 at 1173 and 1261 cm^{-1} , symmetric vibration of CF_3 at 1233 cm^{-1} and characteristic peak of Tf⁻ anion at 1608 cm^{-1} . The peak 766, 1037, 1173, 1261, 1233 and 1608 cm^{-1} does not show prominent change in ionic liquid free polymer electrolyte. But as the content of MPII is raised from 20wt% to 60wt%, the peak at 766 cm^{-1} was shifted to 761 \rightarrow 757 \rightarrow 756 cm^{-1} , the peak at 1173 cm^{-1} get shifted to 1172 \rightarrow 1168 \rightarrow 1168 cm^{-1} and the peak at 1608 cm^{-1} is shifted to 1652 \rightarrow 1629 \rightarrow 1627 cm^{-1} . Shifting of NaTf peaks which is not observed in the P(VdF-HFP)-NaTf are prominently observed after the addition of MPII. The dissolution of NaTf is enhanced by the addition of MPII. These observations indicate the plasticizing nature of MPII which is in good agreement with XRD result.

3.3AC Impedance Spectroscopy

3.3.1 Dependence of ionic conductivity on the concentration of IL

From the measurement of resistance using ac impedance spectrometer, bulk resistance of the sample was estimated by drawing the cole-cole plot for samples PSIL0, PSIL2, PSIL4 and PSIL6 and the figure 3 depict the same. Spectra of PSIL0 and PSIL2 consist of a flat quasi-semicircle followed by a short straight line at the low frequency region. The bulk resistance (R_b) was obtained from the point of intersection of the semicircle on the horizontal axis. But for PSIL4 and PSIL6, the plot shows a straight line inclined towards the real axis representing the electrode/electrolyte double layer capacitance behaviour. This response reveals a major contribution towards total resistance from bulk resistance (R_b) and only a minor contribution from grain boundary resistance. The ionic conductivity was calculated from the equation $\sigma = \frac{L}{AR_b}$

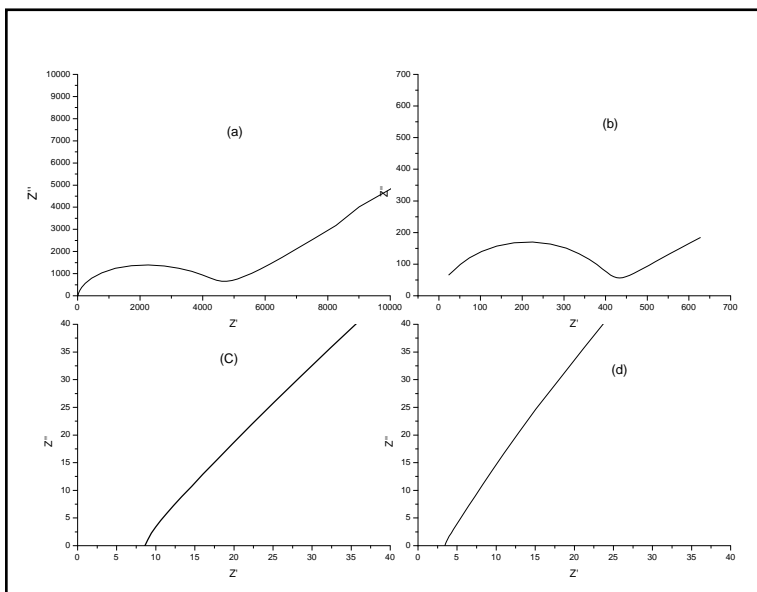


Fig.3. Cole-Cole impedance plot of samples of (a) P(VdF-HFP) + NaTf, (b) P(VdF-HFP) + NaTf + MPII(20wt%), (c) P(VdF-HFP) + NaTf + MPII(40wt%), (d) P(VdF-HFP) + NaTf + MPII(60wt%)

Table2: Variation of ionic conductivity at room temperature

Sample	Compositon [PVdF-HFP:NaTf:MPII]	ionic conductivity at 30°C (σ Scm^{-1})
PSIL0	70:30:00	2.61×10^{-6}
PSIL2	56:24:20	4.102×10^{-4}
PSIL4	42:18:40	1.377×10^{-3}
PSIL6	28:12:60	8.00×10^{-4}

The variation in ionic conductivity at room temperature against the addition of ionic liquid is given in Table 2. The ionic conductivity increased with the amount of MPII and reached a maximum of $1.377 \times 10^{-3} \text{ Scm}^{-1}$ for 40wt% of MPII and then decreased with further addition of MPII. The increase in ionic conductivity is strongly due to the production of large number of mobile charge carriers as ionic liquid provides MPI^+ and I^- [11]. High concentration of charge carriers enhanced the dissociation of NaTf and thus favours the ionic hopping mechanism. Another perspective is the weakening of the interaction between the polymer matrices upon inclusion of ionic liquid. Addition of ionic liquid softened the polymer backbone and enhances the flexibility of polymer system, accelerating the polymer segmental mobility and ionic transportation by providing more conducting pathways. Ionic liquid also destroyed the ordered arrangement of the polymer backbone and thus decreased the crystallinity of the polymer matrix. This proves the strong plasticizing effect of MPII. Increase in MPII content from 40wt% to 60wt% reduces the ionic conductivity due to the space charge of mobile ions and hence leads to the formation of ion pairs. These ion pairs inhibit the mobility of free charge carriers and thus prevent the passage of ions in the polymer matrix.

3.3.2 Temperature dependence of ionic conductivity

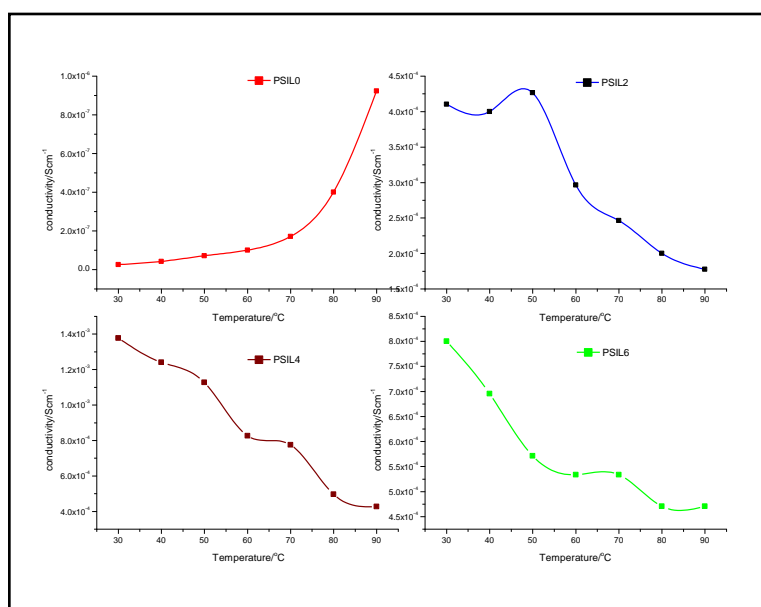


Fig.4. Temperature dependence conductivity of (a) P(VdF-HFP) + NaTf, (b) P(VdF-HFP) + NaTf + MP II (20wt%), (c) P(VdF-HFP) + NaTf + MPII(40wt%), (d) P(VdF-HFP) + NaTf + MPII(60wt%)

The temperature dependence of ac-conductivity of all the samples is shown in figure 4 in the temperature range from of 30°C to 90°C. The conductivity of MPII free polymer electrolyte increased with increase in temperature which could be attributed to the enhancement of free volume of the polymer electrolyte medium [12]. This in turn enhanced the segmental motion of the polymer host. The segmental motion permitted the ions to hop from one site to another site by providing a pathways for ions to move[2]. The conductivity of PSIL2 slightly initially increased and decreased after 60°C. The samples PSIL4 and PSIL6 showed decreasing conductivity with rise in temperature. Decrease in conductivity with increase in temperature indicates metallic behaviour of the sample. Due to the presence of MPII, loop-like microstructures are plenty due to the presence of supramolecular interactions (eg., dipole-dipole, ion-dipole, H-bonding, etc.)[13], and this causes abolishing partial delocalisation of electrons showing higher conductivity. With the increase in temperature, these bonds gradually break, abolishing the loop-like microstructure. This decreases the delocalization of electrons, and hence, conductivity decreases. The decrease is more prominent in higher concentration of MPII.

4 Conclusion

Ionic liquid incorporated Sodium ion based P(VdF-HFP) free standing polymer electrolyte samples were successfully synthesised for three concentrations of ionic liquid. Highest ionic conductivity of $1.337 \times 10^{-3} \text{ Scm}^{-1}$ was achieved for sample containing 40wt% of IL. MPII free polymer electrolyte shows an increase in conductivity with increase in temperature due to the enhancement of free volume while MPII incorporated polymer electrolyte shows decrease in ionic conductivity with increase in temperature due to the breaking of

supramolecular interactions. Sodium triflate which remain undissociated in the IL free polymer matrix, get dissolved in the presence of MPII which was revealed in the XRD pattern. The above result was conformed from the FTIR analysis.

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