Studies on proton conducting polymer electrolytes based on poly(ethylene oxide)/poly(vinyl pyrrolidone) with NH$_4$SCN

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Attempted a work based on poly(ethylene oxide) (PEO) and poly(vinyl pyrrolidone) (PVP) with constant salt ratio of NH$_4$SCN were prepared by the solution casting technique. The ionic conductivity of the PEO/PVP host polymer was discussed. The dissociation of the ammonium salt and the interaction between the polymer salt complexes was confirmed by X-ray diffraction analysis. Atomic force microscope is an excellent tool to measure the roughness factor, pore size and also two and three dimensional topographic images of the sample. Topography studies have been image of the sample PS4 having maximum ionic conductivity in 3D image. The maximum room temperature ionic conductivity was found to be 8.31×10^{-4} S cm^{-1} for the film containing NH$_4$SCN as the complexing salt.

Keywords: Poly(ethylene oxide) (PEO), poly(vinyl pyrrolidone), ionic conductivity, polymer, interaction.

Introduction

Solid proton conducting polymer electrolytes are a class of ion conductors and are formed by the dissolution and complexation of alkali salts in a polymer. Solid proton conducting polymer electrolytes are material evidence of several advantages such as rechargeable batteries, fuel cells, super capacitor, sensors, and optical displays[1,2]. Highly proton conductive solid materials display a great potential for the total solidification of electrochemical power devices such as fuel cells, metal hydrate batteries and super capacitors. For most potential applications it is desirable that the solid polymer electrolytes display a reasonable proton conductivity, mechanical strength, flexibility and thermal stability. Polymers that have been used in the producing of proton conducting films include poly(ethylene oxide) (PEO), poly(acrylic acid) (PAA), poly(vinyl alcohol) (PVA), poly(N-vinyl pyrollidone) (PVP)[3-6]. Proton conducting polymer electrolytes can be obtained by doping the polymer either with alcohol, amine, strong acids and ammonium salts. Several ammonium salts such as NH$_4$I, NH$_4$SCN, NH$_4$SO$_3$CF$_3$ and NH$_4$ClO$_4$ were used as doping salts[7-10]. PEO is a semi crystalline polymer that displays both amorphous and crystalline phases at room temperature[11]. Complex formation in poly(ethylene oxide)-salt is ruled by competition between salvation energy and lattice energy of the polymer and the inorganic salt[12]. This polymer in its pure form is chemically and electrochemically stable since it contains only strong unstrained C-O, C-C and C-H bond[13]. Poly(N-vinyl pyrrolidone) (PVP) is a biocompatible polymer used as a blood plasma expander for trauma victims[14]. Poly (N-vinyl pyrrolidone) is used as humidity sensor in the doping of iodine and cobalt[15]. PVP is an amorphous polymer, which can permit faster ionic mobility when compared to other semi crystalline polymers. It presence of carbonyl group (C=O) in the side chain of PVP, it complexes with various inorganic solids. It has good thermal stability, easy processability cross linking, high dielectric strength, low scattering loss, good storage capacity, and dopant dependent electrical properties and is highly soluble in water and methanol[16,17]. Poly(ethylene oxide) is a semi crystalline polymer having (T_g) of about –57°C is chosen as a host polymer. Poly(N-vinyl pyrrolidone) is an amorphous polymer having (T_g) of 69°C. So these two polymers compatible in nature. Poly(ethylene oxide) is chosen to blend with poly(N-vinyl pyrrolidone). Ammonium thiocyanate is chosen since it shows

hygroscopic crystalline solid and soluble in polar groups such as water, methanol. Many literatures related to PEO-PVP blends are reported and these examples include PEO-PVP-LiClO$_4$[18], PEO-PVP-NaBr[19] and PEO-PVP-Sm^{3+}+EU^{3+} [20]. To the best of our knowledge, there has been no previous study of proton conducting solid polymer electrolyte based on poly(ethylene oxide) and poly(N-vinyl pyrrolidone) prepared by solvent casting technique.

Experimental

Materials:

Poly(ethylene oxide), poly(N-vinyl pyrrolidone) was purchased from Sigma-Aldrich and the average molecular weight M_w ~ 100,000 and 360,000. The ammonium thiocyanate and methanol were obtained from SRL, Mumbai have been used in the system.

Preparation of proton conducting polymer electrolytes:

The polymer poly(ethylene oxide) (PEO) of average molecular weight 8,000 and poly(vinyl pyrrolidone) (PVP) of average molecular 3, 60,000 and salt (NH$_4$SCN) were obtained from Sigma-Aldrich Chemicals Limited, USA. The obtained PEO-PVP and NH$_4$SCN were dried at 50°C for 12 h to remove moisture. The polymer PEO, PVP and NH$_4$SCN were dissolved at room temperature respectively. After that the polymer salt complex was stirrer and degassed to remove air bubbles and poured on a well cleaned Petri dish. The solvent methanol was allowed to evaporate slowly at room temperature. Flexible thin films with thickness of about 0.1–0.5 mm were obtained. The X-ray diffraction pattern of the polymer electrolytes has been taken using X'Pert PRO Analytical X-ray diffractometer. The complex formation between the polymer and the salt has been confirmed by FTIR spectra by using SPECTRA RXI, Perkin-Elmer spectrophotometer in the range of 400–4000 cm^{-1}. The AC conductivity studies were carried out with the help of stainless steel blocking electrode using by computer controlled microautolab type III Potentiostat and Galvanostat in the frequency range of 100 Hz–300 KHz over the temperature range 303–353 K. Polymer electrolytes of uniform thickness having an area of 1 cm^2 have been placed in between two stainless steel plates which act as blocking electrodes. The surface morphology and surface roughness factor of the sample were observed by AFM (A100SGS).

Characterization techniques:

X-Ray diffraction analysis:

Fig. 1 shows that the poly(ethylene oxide), poly(N-vinylpyrolidone) and the prepared polymer electrolytes respectively. The pure poly(ethylene oxide) having two peaks at 2θ = 19.2° and 23.5° corresponding to the reflection of (120) and (010) plane respectively; confirm the semi crystalline nature of poly(ethylene oxide)[21]. The broad peak around 19° from Fig. 1b can be connected with amorphous nature of pure PVP[22]. The peak corresponding to 2θ = 24° and 26° (JCPDF 23-0029)[23], corresponding to pure NH$_4$SCN have been found to be absent in the salt-doped polymer complex indicating in complete dissociation of the salt in the polymer matrix. The characteristic peaks of PEO-PVP complex show variation in intensity suggesting that the ordering of the PEO polymer crystallinity is disturbed due to the coordination interactions between NH$_4^+$ ions and etheric oxygen. In Fig. 1 it is observed that with the addition of ammonium salt to the polymer blend the intensity of these peaks decreases gradually and becomes relatively broader suggesting a decrease in the degree of crystallinity of the complex. Absence of relating to ammonium thiocyanate salt in the complexes indicates that complete dissolution of salt in the polymer matrix.
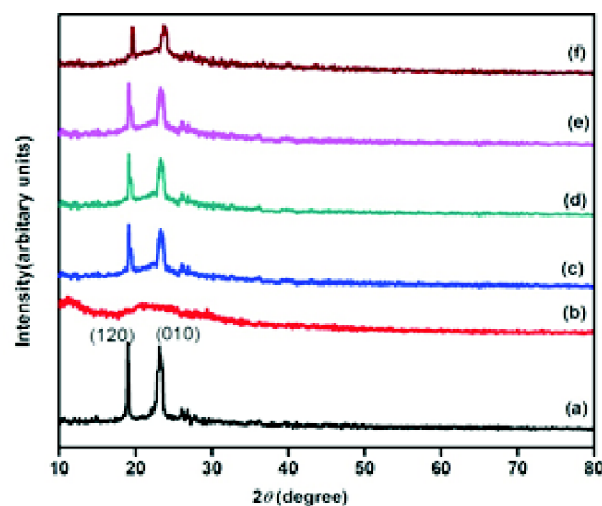

Fig. 1. XRD patterns of pure PEO, PVP, NH$_4$SCN and blended polymer electrolytes.

FT-IR spectroscopic analysis:

Fig. 2 explains the FTIR spectra in the range of 4000–400 cm^{-1} of PEO-PVP and NH$_4$SCN concentrations. The vi-
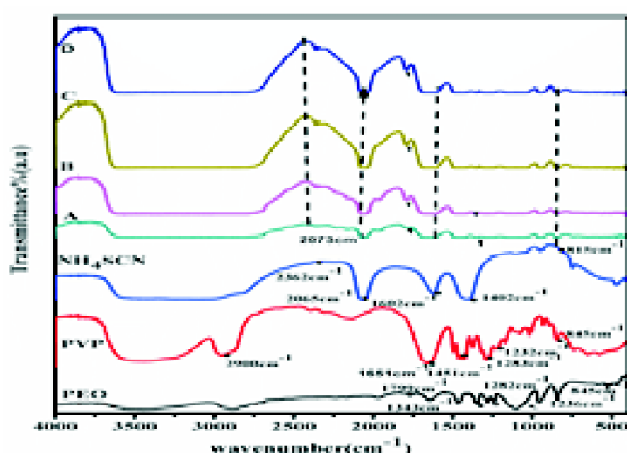
Fig. 2. FTIR spectra of pure PEO, PVP and NH$_4$SCN blended polymer electrolytes.

brational bands observed at 1343, 1282 and 1236 cm^{-1} are ascribed to CH$_2$ bending symmetric twisting and symmetric twisting vibration of PEO respectively and these bands are shifted to small humps such as 1344, 1345, 1348 and 1349 cm^{-1} [24,25]. The vibrational band of PEO at 1282, 1236 cm^{-1} is a small hump present in all prepared polymer electrolytes. The absorption band of PEO at 1799 cm^{-1} is corresponding to ether oxygen and these bands is shifted to 1790, 1792, 1793, 1794 cm^{-1} in the complexes respectively. The vibrational band at 1100 cm^{-1} is assigned to C-O-C symmetric and anti symmetric is not present in all prepared sample. Here pure PEO has the *trans*-T (CC-OC), *trans*-T (CO-CC), *gauche*-G (OC-CO) conformation. The spectral feature between 1000 and 700 cm^{-1} is very sensitive to any conformational change in PEO. In the present PEO-PVP-NH$_4$SCN the vibrational band between 1000 and 700 cm^{-1} shows that the bands related to *gauche* conformation of PEO are only present in the system. The vibrational band 2073 cm^{-1} indicates that the contact ion pair aggregation, this result indicates that the hydrogen bonds between NH$_4^+$ and ether oxygen. This result is also confirmed that wrap of hydrogen bonds toward the contact ion pairs. The vibrational band observed at 2900 cm^{-1} is ascribed to aliphatic C-H stretching of pure PVP is hidden in all prepared polymer electrolytes. The sharp vibrational band at 2365 cm^{-1} which is shifted to 2368, 2371, 2372 and 2375 cm^{-1} in the system. The vibrational band between 1675–1663 cm^{-1} corresponds to symmetric and asymmetric of C=O stretching modes of PVP. The bands at 1651 cm^{-1} and 1451 cm^{-1} are ascribed to C=O stretching

and CH$_2$ wagging of pure PVP[26]. The intensity of the peak corresponding to C=O stretching at 1651 cm^{-1} is decreases with increase of salt concentrations. This indicates the strong interaction of SCN^{-1} anions with the carbonyl group. The absorption peak of PVP corresponding to wave number 1283 cm^{-1} is ascribed to CH$_2$ wagging mode. The band at 845 cm^{-1} is ascribed to CH$_2$ rocking mode of pure PVP. The vibrational band H-N-H bending peak of NH$_4^+$ at 1393 cm^{-1} is occurred small shifting in the system. The new peak 2073 cm^{-1} is present in all prepared polymer electrolytes. From the above analysis the polymer-salt complex formation and proton interaction are confirmed.

AC impedance analysis:

The real (Z') and imaginary part (Z'') of the complex impedance is calculated from the measured values of Z and θ and the complex impedance plots were obtained using Nyquist plot from Fig. 4. At low frequency the impedance should exhibit a straight line parallel with the imaginary axis, but the double layer at the blocking causes the sloped line[27–29].
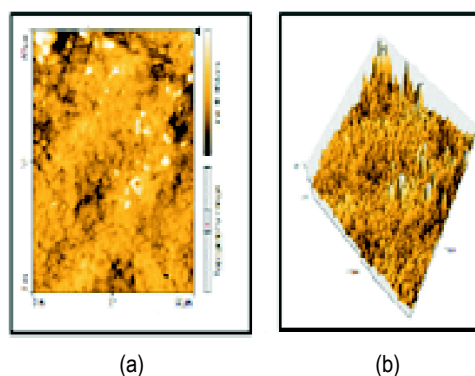

Fig. 3. Topography image of the maximum ionic conductivity sample, (a) 2D image and (b) 3D image.

This feature indicates that the conductivity is mainly due to the ions. The ionic conductivity values are determined by using the formula $\sigma = \ell/(AR_b)$, where ℓ is the thickness of the film, A is the surface area of the film and R_b is the bulk resistance of the film. The highest ionic conductivity value is found to be 5.61×10^{-3} at 70°C for (0.6PEO:0.2PVP:0.2NH$_4$SCN) in the system. Table 1 shows the conductivity values of the complexes in the temperature range of 303–343 K. From Table 1; we can under that the temperature increases, the ionic conductivity also increase for all complexes. The increase in the ionic conductivity with increasing salt concentration can

Table 1

Sample code	Wt% composition of PEO/PVP/NH$_4$SCN	Ionic conductivity values (σ) at different temperatures (K)					Activation energy
		303	313	323	333	343	
PS1	67.5:22.5:5	3.01×10^{-8}	2.21×10^{-7}	2.81×10^{-6}	2.92×10^{-6}	3.23×10^{-6}	0.56
PS2	65:25:10	3.53×10^{-5}	3.81×10^{-5}	4.19×10^{-5}	5.16×10^{-5}	1.01×10^{-4}	0.47
PS3	62.5:27.5:15	2.32×10^{-4}	4.52×10^{-4}	6.12×10^{-4}	7.11×10^{-4}	7.32×10^{-4}	0.45
PS4	60:20:20	8.31×10^{-4}	1.01×10^{-3}	2.42×10^{-3}	3.61×10^{-3}	5.61×10^{-3}	0.31

be related to the increase in the number of mobile charge carriers. At high temperatures, the semicircle disappears indicating the prevailing of the resistive component of the electrolyte system.

Atomic force microscopy:

Tapping mode AFM was used to obtain nodule size and surface roughness of the membrane. In the present study two and three dimensional topographic images of the sample PS$_4$ having a maximum conductivity are shown in Fig. 2. The topographic images clearly show the presence of pores and cavities which are responsible for maximum ionic conductivity. The roughness factor has an important role in the ionic conduction. In the present study the roughness factor is low, so the ionic conduction is high. The root mean square roughness of the topographic image over the scanned area is found to be 50 nm. It could not see any small particles on the surface, indicating that the NH$_4$SCN had been dispersed evenly into the host polymer. This result is in accordance with XRD analysis.

Conclusion

New proton conducting polymer electrolytes PEO-PVP complexed with NH$_4$SCN salt were prepared by using the solvent casting technique. The XRD spectra of the polymer electrolytes indicate the increase in amorphous nature of the polymer with increase of salt concentration. The complex formation between polymer and ammonium salt has been confirmed by vibrational spectroscopy. The ionic conductivity has been calculated by AC impedance spectroscopy. The surface morphology of the polymer has been studied and the presences of the pores are identified by using AFM analysis.

Acknowledgements

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