Synthesis and Characterization of Proton Conducting Polymer Electrolyte Based on Poly(N-vinyl Pyrrolidone)

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ABSTRACT: This work aims at developing and characterizing a proton conducting polymer electrolyte based on Poly(N-vinyl pyrrolidone) (PVP) doped with ammonium bromide (NH_4Br). Proton conducting polymer electrolytes based on PVP doped NH_4Br in different molar ratios have been prepared by solution casting technique using distilled water as solvent. The XRD pattern confirms the dissociation of salt. The FTIR analysis confirms the complex formation between the polymer and the salt. The conductivity analysis shows that the polymer electrolyte with 25 mol % NH_4Br has the highest conductivity equal to 1.06×10^{-3} S cm^{-1} at room temperature. Also it has been observed that the activation energy evaluated from the Arrhenius plot is low (0.50 eV) for 25 mol % NH_4Br doped polymer electrolyte. The influence of salt concentration on dc conductivity and activation energy of the polymer electrolyte has been discussed. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Solid polymer electrolytes have become increasingly attractive because of their technological application in the development of solid state electrochemical devices. Polymer electrolytes are generally prepared by dissolving salt/acid in an organic polar solvent with the addition of a suitable polymer. Polymer electrolytes using polymers such as poly(vinyl alcohol) (PVA),[1] poly(acrylonitrile) (PAN),[2] poly(methyl methacrylate) (PMMA),[3] poly(ethylene oxide) (PEO)[4,5] and poly(vinylidene fluoride) (PVdF)[6] are considered as promising candidates for high energy electrochemical devices. The polymer electrolyte properties such as thermal, mechanical, morphological, and electrical properties can be improved at ambient temperature using various methods such as blends,[7] copolymers,[8] block polymers,[9] and cross-linked networks.[10] Among the various types of solid polymer electrolytes, proton conducting polymer electrolytes have attracted the attention of scientists worldwide due to their potential application as solid electrolyte in electro-

chemical devices such as fuel cells, sensors, and electrochromic devices.[11] Based on this view, a variety of proton conducting polymer electrolytes has been developed for solid state applications.

Inorganic acids-doped proton conductors[12–15] have been developed for various electrochemical devices. However, the mechanical and chemical stability of these complexes are relatively poor and chemical degradation is observed after humidification.[14] Proton conducting polymer electrolytes based on PVA,[16–20] poly(vinyl pyrrrolidone) (PVP),[21–23] PESc,[24] PEO,[25,26] CA,[27] PEO-PAAM,[28] chitosan,[29,30] etc. doped with ammonium salts have also been reported. PVP is a vinyl polymer possessing planar and highly polar side groups due to the peptide bond in the lactam ring. It is an amorphous polymer and is soluble in water. The pyrrolidone rings in PVP contain a proton accepting carbonyl group. PVP deserves a special attention among the conjugated polymers because of its good environmental stability, easy processability, and moderate electrical conductivity. In this
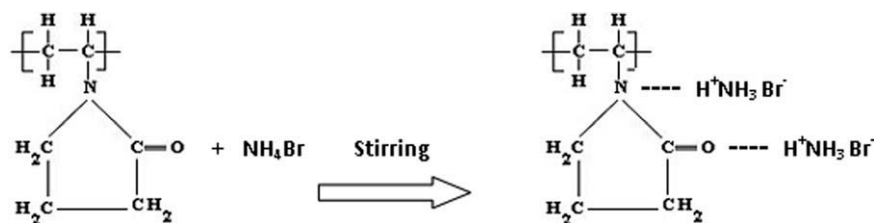
Scheme 1. Possible interaction between PVP and NH$_4$Br.

study, a proton conducting polymer electrolyte based on PVP doped with NH$_4$Br has been synthesized and characterized by XRD, FTIR, and AC Impedance spectroscopic techniques and the results are reported and discussed.

MATERIALS AND METHODS

The polymer PVP of average molecular weight 40,000 (s d fine-chem Limited) has been used as host polymer and ammonium bromide (NH$_4$Br) of molecular weight 53.49 (Spectrum) as dopant in this study. Distilled water has been used as solvent. The proton conducting polymer electrolyte based on PVP : NH$_4$Br has been prepared by solution casting technique. Aqueous solutions of PVP and NH$_4$Br have been prepared in different molar concentrations and kept in the magnetic stirrer for continuous stirring until the solutions become homogeneous. The homogenous solutions have been casted in propylene Petri dishes and the samples have been subjected to an extended drying period in a vacuum oven to remove excess solvent present in the sample. Transparent and flexible films of thickness ranging from 0.017 to 0.024 cm are obtained. The surface area of the film is 1 cm^2.

The X-ray diffraction patterns of the prepared samples have been obtained at room temperature on a Philip's X'Pert PRO diffractometer by exposing them to CuKα radiation in the range of $2\theta = 10$ to $80°$. The FTIR spectra of the polymer electrolytes have been recorded at room temperature in the range of 400–4000 cm^{-1} using a SHIMADZU - IR Affinity-1 Spectrophotometer. The electrical measurements have been carried out at different temperatures ranging from 303 to 343 K in the frequency range of 42 Hz–1 MHz using a computer controlled HIOKI 3532 LCR meter. The polymer sample is sandwiched between two aluminum blocking electrodes which serve as sample holder.

RESULTS AND DISCUSSION

The possible interaction between PVP and NH$_4$Br has been pictorially represented in the Scheme 1 along with the structure.

X-Ray Diffraction Analysis

The XRD patterns of pure PVP and PVP doped with different concentration of NH$_4$Br in mol % are shown in Figure 1. A broad peak around 22.7° which is attributed to the amorphous nature of pure PVP has been found to be shifted in the complex systems. It has also been observed that the relative intensity of this peak decreases and its full-width half maximum increases with increase of salt. This may be due to increase of amorphous nature of the complexed systems. These results can be interpreted in terms of the Hodge et al.[31] criterion which establishes a correlation between the intensity of the peak and the degree of crystallinity. Peaks corresponding to pure NH$_4$Br have been found to be absent in the polymer complexes doped with NH$_4$Br upto 20 mol % indicating the complete dissociation of salt in the polymer matrix. For 25 mol % salt-doped polymer system, the amorphous nature has been found to increase compared to 20 mol % salt-doped polymer sample. However, due to few % of undissociated salt, the peaks corresponding to NH$_4$Br have been observed. These changes reveal the complex formation in the polymer matrices and the increased amorphous nature of the polymer films due to addition of NH$_4$Br.

Fourier Transform Infrared Analysis

FTIR Spectroscopy has been used to confirm the complex formation between the polymer and the salt. Figure 2(a,b) shows the FTIR spectra of pure PVP and PVP doped with different concentration of NH$_4$Br. The absorption bands of pure PVP at 2137 cm^{-1} assigned to C—N stretching is shifted to 2129 cm^{-1} in the 10 and 15 mol % salt added systems. The vibrational band at 1226 cm^{-1} assigned to CH$_2$ bending of pure PVP is shifted to 1250 cm^{-1}, 1242 cm^{-1}, and 1258 cm^{-1} in the 5, 10, and 20 mol %, respectively. The characteristic vibrational band at 1173 cm^{-1} assigned to CH wagging of PVP is shifted to 1188 cm^{-1}, 1180 cm^{-1}, and 1165 cm^{-1} in the 5, 10, and 15 mol %, respectively, in the NH$_4$Br doped polymer complexes. The
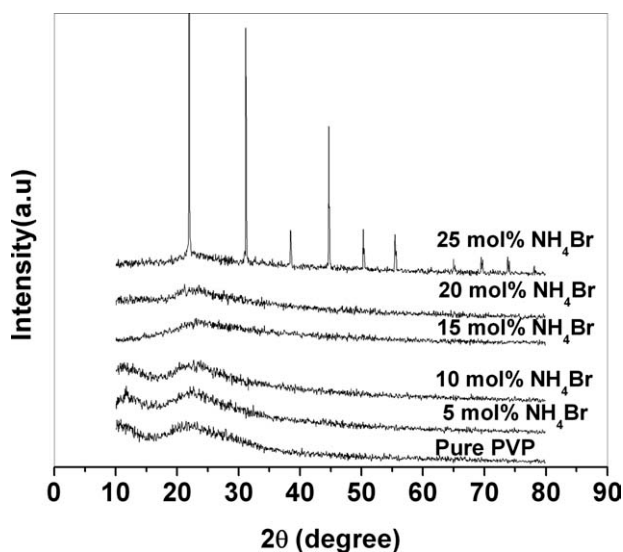

Figure 1. XRD patterns of pure PVP and PVP doped with different concentration of NH$_4$Br.
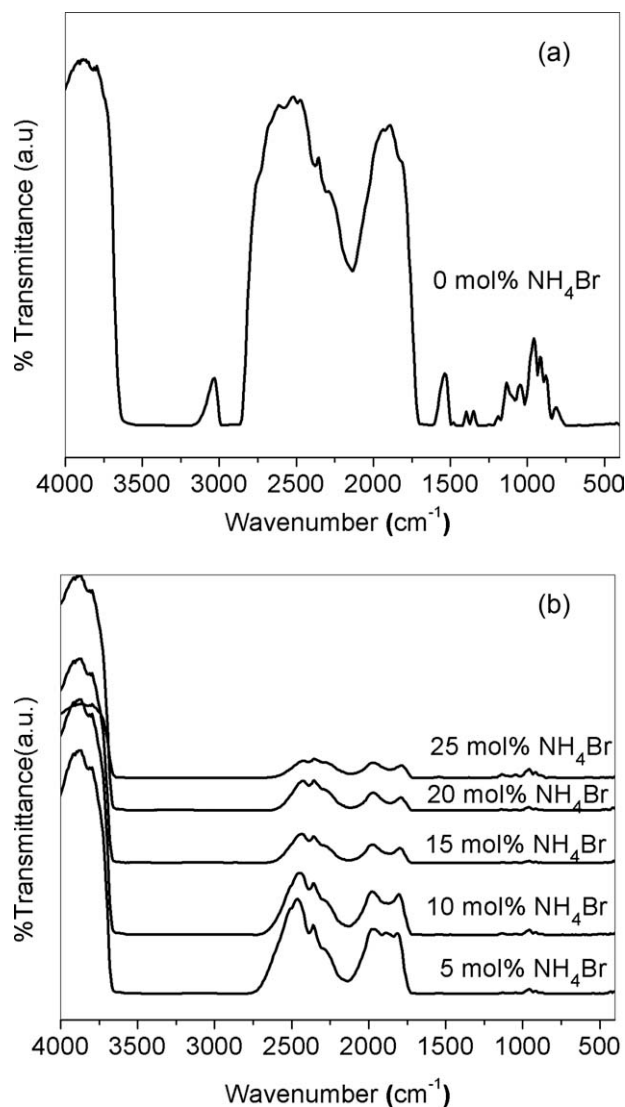
Figure 2. (a,b) FTIR spectra of pure PVP and PVP doped with different concentration of NH$_4$Br.

have been shown in Figure 3(a,b). The impedance plots of the samples show a high-frequency semicircle and a low frequency inclined line. The semicircle arises from coupled resistance/capacitance (R/C) at the electrolyte/electrode interface and the

vibrational band at 1080 cm^{-1} in pure PVP assigned to C—C bonding is shifted to 1088 cm^{-1} and 1072 cm^{-1} in the complexes with 15 and 20 mol %, salt respectively. The band at 841 cm^{-1} attributed to CH$_2$ rocking of pure PVP is shifted to 849 cm^{-1} in the 25 mol % salt-doped system. The bands around 2925 cm^{-1}, 1651 cm^{-1}, and 1451 cm^{-1} attributed to CH$_2$ stretching, C = 0 stretching and CH$_2$ wagging of pure PVP are found to be absent in the polymer complexes. The shift in the positions of absorption bands may be due to the interaction of the salt with the polymer matrix. These results confirm the complex formation between the polymer and the salt.

Impedance Analysis

The behavior of the electrochemical system can be studied by means of impedance plots over a wide range of frequencies at different temperatures by applying an AC voltage or current. The complex impedance plane plots (Cole–Cole plots) for the system PVP doped with NH$_4$Br for different salt concentrations
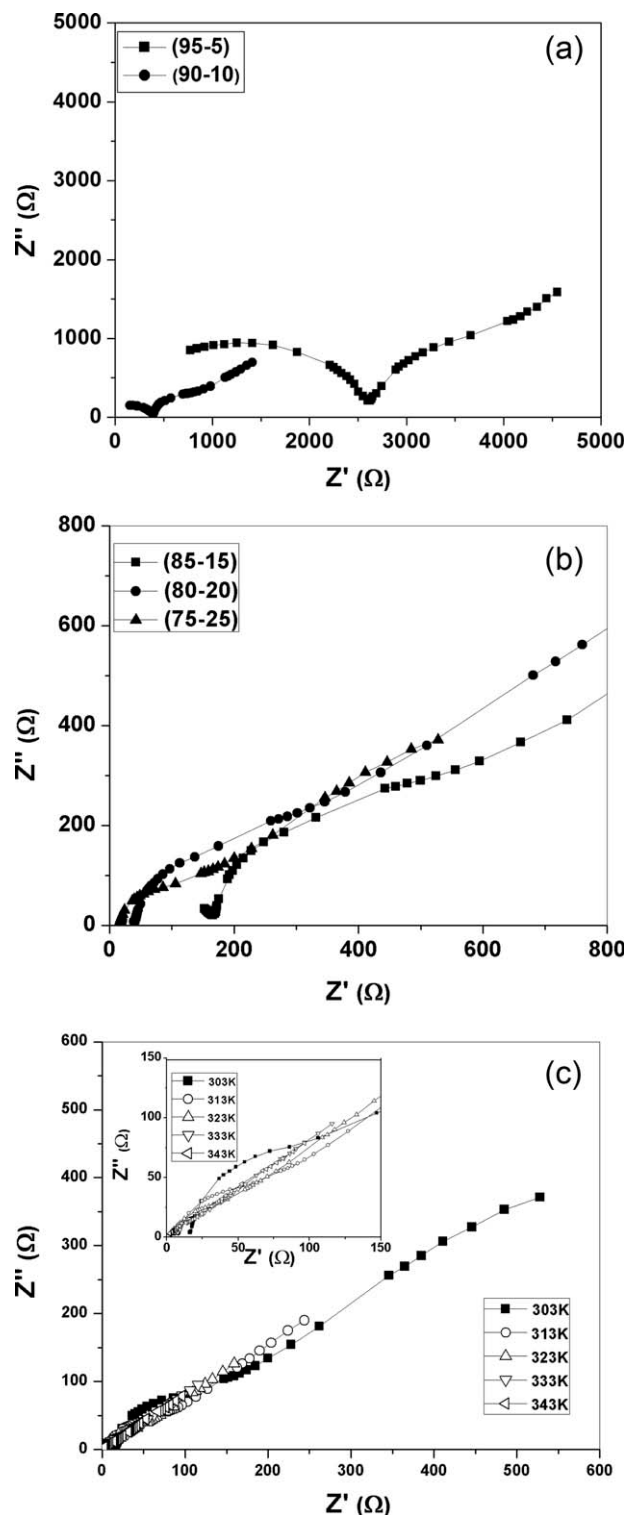
Figure 3. (a,b) Complex impedance plots of PVP doped with different NH$_4$Br concentrations at 303 K. (c) Complex impedance plot for PVP doped with 25 mol % NH$_4$Br at different temperatures.

Table I. Ionic Conductivity Values at Three Different Temperatures and Activation Energy Values of PVP : NH$_4$Br Polymer Electrolytes
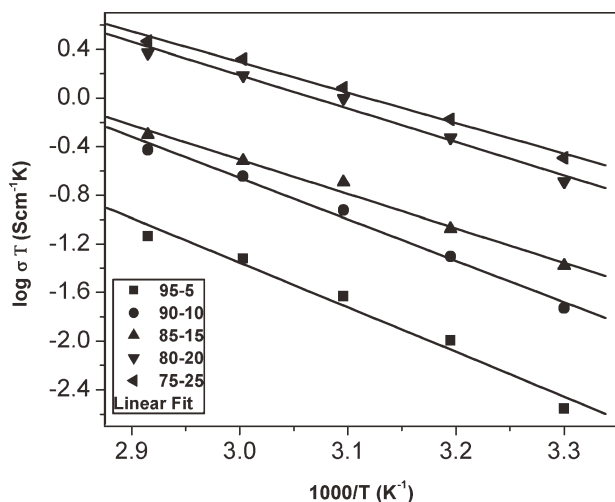
PVP : NH$_4$Br (mol %)	Conductivity, σ (S cm^{-1})			Activation energy, E_a (eV)
	303 K	323 K	343 K	
95 : 5	9.30×10^{-6}	7.27×10^{-5}	2.13×10^{-4}	0.71
90 : 10	6.18×10^{-5}	3.71×10^{-4}	1.11×10^{-3}	0.67
85 : 15	1.40×10^{-4}	6.42×10^{-4}	1.53×10^{-3}	0.57
80 : 20	6.65×10^{-4}	3.19×10^{-3}	6.95×10^{-3}	0.55
75 : 25	1.06×10^{-3}	3.58×10^{-3}	8.89×10^{-3}	0.50

inclined line is due to the effect of the blocking electrodes. The intercept of the semicircle or inclined line with the real impedance (Z') axis gives the bulk electrical resistance (R_b) of the polymer electrolytes. The radius of the semicircle decreases with increase of concentration of the salt and it disappears for the electrolytes with compositions (80–20) and (75–25) indicating the low bulk resistance of the polymer electrolytes. The ionic conductivity has been calculated using the equation $\sigma = l/R_b A$, where l is the thickness of the film and A the surface area of the film. It has been inferred from Table I that the highest ambient temperature conductivity is 1.06×10^{-3} S cm^{-1} for the polymer electrolyte PVP complexed with 25 mol % of NH$_4$Br.

Figure 3(c) represents the impedance plots for the highest conductivity sample (PVP with 25 mol % NH$_4$Br). The disappearance of the high frequency semicircle for the highest conductivity sample indicates that the total conductivity is mainly the result of ion conduction.[32] It has been observed from the Figure 3(c) that the bulk resistance value decreases with increase of temperature resulting in an increase in ionic conductivity.

Temperature Dependence of Ionic Conductivity
Figure 4 shows the temperature dependence of ionic conductivity of the various compositions of PVP : NH$_4$Br polymer electrolytes. It has been observed that the proton conductivity of the electrolytes increases with increasing temperature for all

complexes. The linear variation of ionic conductivity with inverse of absolute temperature reveals the Arrhenius type thermally activated process given by the relation.

$$\sigma = (\sigma_{0/T}) \exp(-E_a/kT) \quad (1)$$

where σ_0 is the pre-exponential factor, E_a the activation energy, T the absolute temperature, and k the Boltzmann constant. The activation energy values are evaluated from the slope of these straight lines and are tabulated in Table I. The activation energy decreases with increase in salt concentration; this is due to the amorphous nature of the polymer electrolyte that facilitates the ionic motion in the polymer network. The activation energy varies from 0.71 to 0.50 eV with the minimum activation energy (0.50 eV) for the composition (75 : 25) that gives the highest conductivity.

Concentration Dependence of Ionic Conductivity
Figure 5 represents the ionic conductivity of polymer electrolytes at room temperature and activation energy as a function of salt concentration. XRD pattern of 25 mol % NH$_4$Br doped polymer electrolyte indicates the increase of amorphous nature compared to 20 mol % salt-doped polymer sample. Due to the few % of undissociated NH$_4$Br in the polymer complex peaks corresponding to NH$_4$Br have been observed. Due to increase of amorphous nature and increase of mobile charge carriers in the

Figure 4. Temperature dependence of ionic conductivity of various compositions of PVP : NH$_4$Br polymer electrolytes.
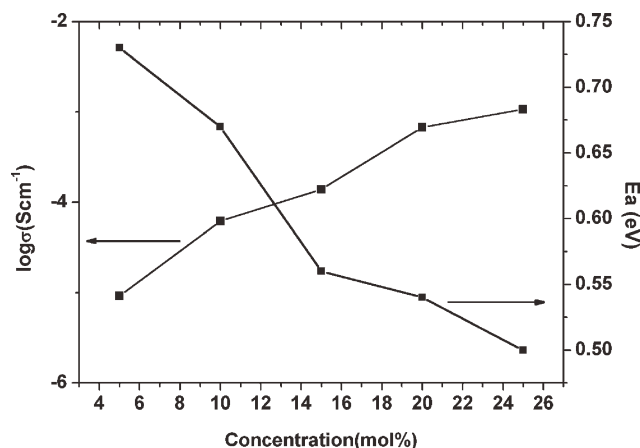
Figure 5. The dependence of ionic conductivity and activation energy on the concentration of the NH$_4$Br in mol %.

25 mol % salt doped polymer, the maximum conductivity has been observed.

It is pertinent to compare the present results with those reported in the literature on the ammonium salts doped proton conducting polymer electrolytes. Maurya et al.[33,34] have reported that the room temperature conductivity values of the proton conducting polymer electrolytes based on PEO-$(NH_4)_2SO_4$ and PEO-NH_4I are 9.3×10^{-7} S cm^{-1} and $\sim 10^{-5}$ S cm^{-1}, respectively. The conductivity of PEO-NH_4SCN polymer electrolyte has been found to be $\sim 10^{-6}$ S cm^{-1},[35] and that of PESc-NH_4ClO_4 has been found to be $\sim 10^{-7}$ S cm^{-1}.[36] Majid and Arof[37] have reported that the NH_4NO_3 doped Chitosan polymer electrolyte exhibits ionic conductivity of 2.53×10^{-5} S cm^{-1} at room temperature. Khiar et al.[38] have studied the $NH_4CF_3SO_3$ doped Chitosan polymer system and reported its conductivity as 8.91×10^{-7} S cm^{-1}. The polymer electrolyte based on Chitosan and NH_4I has been reported to exhibit ambient temperature conductivity of 3.7×10^{-7} S cm^{-1}.[39] Kadir et al.[40] have found that the ionic conductivity of 40 wt % NH_4NO_3 doped PVA-Chitosan polymer is of the order 2.07×10^{-5} S cm^{-1}.

The reported value of the conductivity of the pure PVP is of the order of 10^{-10} S cm^{-1} at ambient temperature and its value increases to 1.06×10^{-3} S cm^{-1} when complexed with 25 mol % NH_4Br. Our aim is to develop proton conducting polymer electrolyte having higher ionic conductivity at ambient temperature. Our group earlier study on proton conducting polymer electrolytes[18,19,21,22,41,42] indicates that the polymer electrolyte PVA : NH_4NO_3 has shown the highest conductivity of 7.5×10^{-3} S cm^{-1} at room temperature. Our earlier work on NH_4Cl-doped PVP has shown ionic conductivity of 2.51×10^{-5} S cm^{-1}.[23] However, our present study on PVP : NH_4Br has shown conductivity of 1.06×10^{-3} S cm^{-1}. This is two orders of magnitude higher than that of PVP doped with NH_4Cl. The associated activation energy of the polymer complexes decreases with the increase of NH_4Br salt content. The low activation energy for 25 mol % NH_4Br polymer electrolytes indicates that all the ions are in mobile state. The highest conductivity observed in this sample is due to the highest mobility of the NH_4^+ cation compared to the Br^- anion. The conduction mechanism is due to hopping of proton from site to site (hopping mechanism).

CONCLUSIONS

The proton conducting polymer electrolyte based on the host polymer PVP doped with ammonium bromide (NH_4Br) in different mol% has been prepared by solution casting technique using distilled water as solvent. Thin, transparent, and flexible films obtained have been characterized by various experimental techniques. The XRD pattern of the prepared polymer electrolytes reveals the increase in amorphous nature of the film with the addition of salt. The shift in the positions of absorption bands observed from the FTIR spectra of the polymer electrolytes which may be due to the interaction of the salt with the polymer matrix confirms the complexation behavior between the polymer and the salt. It has been observed from the conductivity studies that the ionic conductivity of the polymer electrolyte increases with increasing concentration and the highest ionic conductivity has been found to be 1.06×10^{-3} S cm^{-1} at 303 K for the sample 75 mol % PVP- 25 mol % NH_4Br. It has also been observed that the conductivity increases with increasing temperature for all compositions. From the Arrhenius plots, low activation energy equal to 0.50 eV has been obtained for the polymer electrolyte PVP doped with 25 mol % NH_4Br.

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