ELSEVIER

Short communication

Thermal, electrical and optical studies on the poly(vinyl alcohol) based polymer electrolytes

G. Hirankumar [a], S. Selvasekarapandian [a, *], N. Kuwata [b], J. Kawamura [b], T. Hattori [b]

[a] *Solid State and Radiation Physics Laboratory, Department of Physics, Bharathiar University, Coimbatore, Tamil Nadu 641046, India*
[b] *Institute of Multi Disciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan*

Abstract

Solid polymer proton conductors comprising of poly(vinyl alcohol), ammonium acetate and water have been prepared by solution cast method for different NH_4^+/OH^- ratios. The XRD spectra for the electrolyte indicate that the amorphous nature of PVA increases with the concentration of ammonium acetate. The DSC curves show the low glass transition temperature for the ratio $(NH_4^+/OH^-) = 0.25$ which relates to higher conductivity of the sample. The ionic conductivity at room temperature depends strongly on NH_4^+/OH^- ratios. The variation of electrical conductivity with temperature showed two regions of activation above and below glass transition temperature. The optical absorption studies show the similar trend for pure PVA and salt-doped PVA with different absorption intensity. The direct and indirect band gap energy is observed to be constant for pure PVA and salt-doped PVA samples and found to be 5.4 eV and 4.8 eV, respectively. The dc polarization measurement shows that the conductivity is mainly due to ions.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Proton conductor; Poly(vinyl alcohol); Differential scanning calorimetry; Conductivity analysis; Transport number; Optical absorption

1. Introduction

In the recent years, extensive research efforts have been devoted to the development of amorphous polymeric materials with high ionic conductivity at room temperature as well as good mechanical, optical and thermal properties. One of the methods to obtain amorphous nature of the electrolyte is dissolving the salt in the immobilized polymer matrix. The electrical and optical properties of the polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix. Proton conducting membranes such as Nafion have been reported as a very successful host polymer but its applications are limited due to its high cost. Many researchers have studied the behaviour of acid-based polymer electrolyte complexes as proton conductors and their applications in solid state devices, at room temperature, have been demonstrated [1]. Poly(vinyl alcohol) (PVA) is one of the most important polymeric materials as it has many applications in industry and is of relatively low cost [2]. PVA is a potential material having a very high dielectric strength, good charge storage capacity and dopant-dependent electrical and optical properties. The electrical conductivity of the PVA blend with inorganic acids and water has been already reported by R.A. Vargas and the co-workers [3–5]. It is reported that the water content in the PVA based electrolyte enhanced the conductivity while preserving the dimensional stability of the electrolyte [6]. Literature studies reveal that the ammonium salts are excellent proton donors to the polymer matrix and ammonium salts doped with PVA are rare. In the present work, the polymer electrolytes based on poly(vinyl alcohol) doped with ammonium acetate have been prepared with water as a solvent. The XRD has been carried out to confirm the amorphous nature of the electrolyte. The polymer electrolytes have been

* Corresponding author. Tel.: +91 422 2422222x422;
fax: +91 422 2422387.
E-mail address: sekarapandian@yahoo.com (S. Selvasekarapandian).

characterized by DSC, ac impedance and UV–vis spectroscopic techniques.

2. Experimental

Thin films of polymer electrolyte (200 μm) of pure poly(vinyl alcohol) (Merck, $M_w = 1{,}25{,}000$) (degree of hydrolysis = 88%) and poly(vinyl alcohol) doped with ammonium acetate have been prepared for different NH_4^+/OH^- ratios (i.e., ratio of number of ammonium ions to the hydroxyl groups in PVA) (0.09, 0.25, 0.43, 0.67) by a solution cast technique. Aqueous solutions of poly(vinyl alcohol) and CH_3COONH_4 mixtures were thoroughly stirred to obtain a homogeneous mixture. The mixtures were then poured on to a glass plate and evaporated slowly at room temperature. The smooth, uniform thin films, which are transparent to visible light and good mechanical properties, have been obtained. The final product was vacuum dried. X-ray diffraction (XRD) patterns have been obtained using Cu Kα radiation. The thermal behaviour of the polymer electrolytes have been characterized by MAS-5800. The DSC thermograms have been taken with increasing temperature at a heating rate of $10 \, K \, min^{-1}$. The optical absorption measurements of the samples have been recorded in the range 175–600 nm by using a CARY 500 Scan UV–vis–NIR spectrophotometer. The transmittance of the samples have been recorded by using GENESYS-2 THERMO SPECTRONIC in the wavelength range 200–700 nm. The electrical conductivity study of the polymer electrolytes has been carried out in the temperature range of 301–373 K over a frequency range of 42 Hz–1 MHz using a computer controlled HIOKI 3532 LCR meter with a cell having stainless steel electrodes.

3. Results and discussion

3.1. XRD analysis

Fig. 1(a–c) shows the XRD pattern of pure PVA and PVA doped with CH_3COONH_4 having different mole ratios. It is observed from the Fig. 1a, a broad peak between 17° and 27° can be associated with the amorphous behaviour of pure PVA. This peak corresponds to (1 1 0) reflection. The decrease in the relative intensity of this diffraction peak with increase of CH_3COONH_4 concentration has been noted. This may be due to the further increase of amorphous nature of poly(vinyl alcohol) with addition of salt. Hodge et al. [7] established a correlation between the intensity of the peak and the degree of crystallinity. They observed that the intensity of XRD pattern of PVA decreases as the amorphous nature of PVA increases with addition of water. No peaks corresponding to pure CH_3COONH_4 appeared in the polymer complex, which indicates the complete dissociation of the salt in the polymer matrix. This change in intensity and broad nature of polymer electrolyte with increase of salt
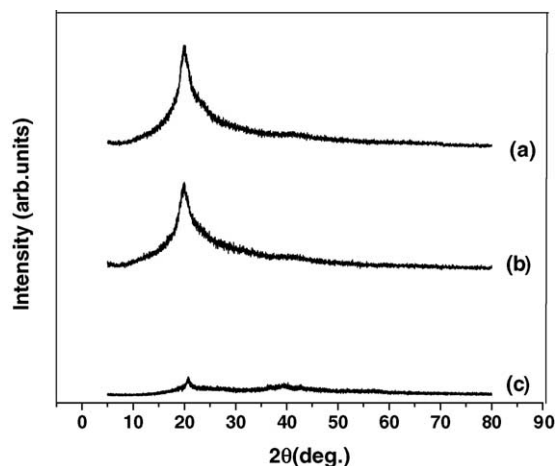

Fig. 1. XRD pattern for PVA/CH_3COONH_4 with concentration NH_4^+/OH^- (a) 0.00, (b) 0.09 and (c) 0.25.

concentration suggests the amorphous nature of the polymer electrolyte.

3.2. Thermal analysis

Fig. 2 shows typical plot of the DSC curves for pure PVA film and PVA doped with ammonium acetate which have been recorded on the heating run from 173 K to 373 K. The glass transition of the pure PVA is found to be 344 K, which is less than the reported value (358 K) and this reduction of the glass transition temperature may be due to the plasticization of PVA by water. R.A. Vargas et al. [4] have observed that the membranes prepared by dissolving PVA in water with no acid content has got low glass transition temperature compared to pure PVA. Iwamoto et al. [8] has observed that water destroys crystallinity in PVA. The destruction of crystallinity of PVA has also been confirmed by XRD analysis. It is also observed that the addition of salt, further decreases the glass transition temperature (T_g) of PVA. The sample doped with 12.5 mol% ammonium acetate has a minimum T_g. Fig. 3 shows the DSC curve of all the samples in the vicinity of the glass transition
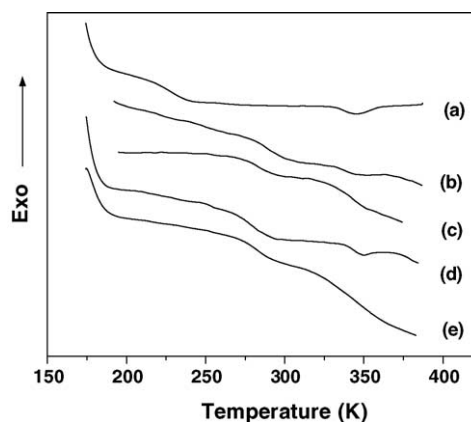

Fig. 2. DSC curves for PVA/CH_3COONH_4 with concentration NH_4^+/OH^- (a) 0.00, (b) 0.09, (c) 0.25, (d) 0.43 and (e) 0.67.
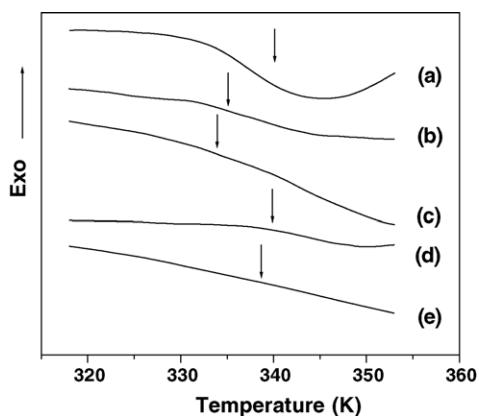
Fig. 3. DSC curves for PVA/CH₃COONH₄ with concentration NH₄⁺/OH⁻ (a) 0.00, (b) 0.09, (c) 0.25, (d) 0.43 and (e) 0.67 in the vicinity of the glass transition.

Fig. 4. Isotherms of the electrical conductivity vs. NH₄⁺/OH⁻ in the PVA/CH₃COONH₄ system.

temperature. Table 1 gives the thermal parameters of interest from the general analysis of the DSC data for all the samples, Δh is the height of the step change which is measured between the extrapolated onset and the extrapolated end of the glass transition region.

Higuchi et al. [9,10] proposed that water is present in three states such as non-freezable bound water, freezable bound water or intermediate water and free water in hydrophilic polymer (PVA) matrices. The freezable bound water in the polymer matrix crystallizes at a temperature lower than 273 K, while the free water crystallizes at 273 K, which can be identified by DSC curve. A small endothermic step is observed at 269 K for NH₄⁺/OH⁻ = 0.25 ratio, may be attributed to the melting of the freezable bound or intermediate water in the system. The lowering of the freezable bound water melting point causes an increase in the over all hydrogen bonding ability of the polymer matrix [11]. For higher temperatures, the DSC traces of all samples show a rapid downward variation indicating a fast endothermic process in the samples that may be associated with the liberation of water by the gels.

3.3. Conductivity analysis

The variation of logarithmic conductivity of PVA/CH₃COONH₄ polymer electrolyte as a function of CH₃COONH₄ concentration expressed as NH₄⁺/OH⁻ ratio at different temperatures is shown in Fig. 4. It is observed that the conductivity of the pure PVA at room temperature, increases with the addition of CH₃COONH₄

Table 1
Thermal parameters for different NH₄⁺/OH⁻ ratios

NH₄⁺/OH⁻ ratio	T_g (K)	Δh (Wg⁻¹)
0.00	344.0	0.29
0.09	333.4	0.31
0.25	331.1	0.88
0.43	339.3	0.22
0.67	335.7	0.75

and reaches a maximum value of 5.62×10^{-6} S cm⁻¹ corresponding to a NH₄⁺/OH⁻ ratio equal to 0.25. The higher conductivity for NH₄⁺/OH⁻ = 0.25 is consistent with the DSC curve and can be explained by the low glass transition temperature that causes the greater segmental mobility of the polymer matrix and an increase in the overall hydrogen bonding ability due to the increased dissociation of the ion pairs in the films. It is noteworthy that the conductivity of the complexes at room temperature is about four orders greater in magnitude in comparison to the conductivity of pure PVA $(2 \times 10^{-10}$ S cm⁻¹). Enhancement in the ionic conductivity with increasing salt concentration up to the ratio NH₄⁺/OH⁻ = 0.25, can be related to the increase in the number of mobile charge carriers. The conductivity follows a non-linear behaviour above the ratio NH₄⁺/OH⁻ equal to 0.25 and may be explained due to aggregation of the salt. The conductivity increases with temperature in pure and salt-doped polymer electrolytes. It is clearly shown that the conductivity for all isotherms follows almost the same pattern of variation with salt concentration.

The temperature dependence of the conductivity for all polymer electrolyte samples is shown in Fig. 5. The experimental data has been fitted with Arrhenius equation by using least squares analysis, a good straight line fit (regression > 0.95) has been obtained for all the samples above (region II) and below (region I) the glass transition. At lower salt concentration, the highly conducting phase would exist in small domains disconnected from each other. When the optimal concentration is reached, the separate domains have grown enough to link up and form continuous highly conducting phase. This separate conducing phase might also explain why the electrolytes have an apparently Arrhenius-like behaviour. As amorphous regions progressively increases in the region II, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This in turn, favours hopping inter-chain ion movements, and accordingly, the conductivity of the polymer electrolyte becomes high. Due to the amorphous nature of the electrolyte above the glass
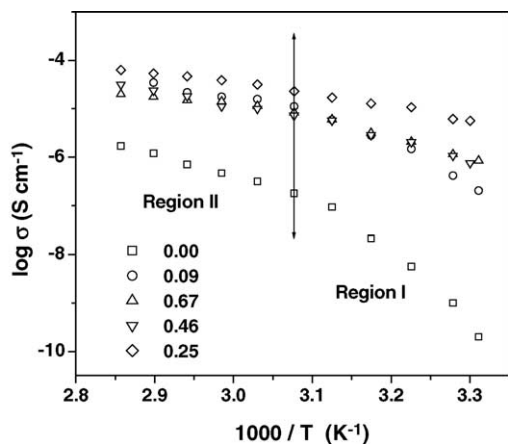
Fig. 5. Temperature dependence of the conductivity for complexes PVA/CH$_3$COONH$_4$ with variable NH$_4$$^+$/OH$^-$ ratios.
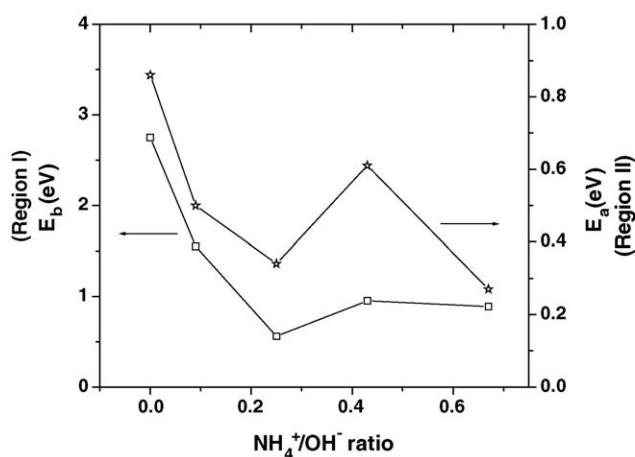

Fig. 6. Variation of activation energy in region I and region II with NH$_4$$^+$/OH$^-$ ratio.

transition temperature of all samples, the order of variation in the conductivity is small. Table 2 gives the dc conductivity at ambient temperature and activation energies above (E_a) and below (E_b) the glass transition of all complexes as calculated from the fitting parameter according to the Arrhenius model,

$$\ln(\sigma_{dc}) = \ln(\sigma_o) + \left(\frac{E_a}{kT}\right) \tag{1}$$

The calculated activation energy as a function of NH$_4$$^+$/OH$^-$ ratio in the polymer electrolyte is shown in Fig. 6.
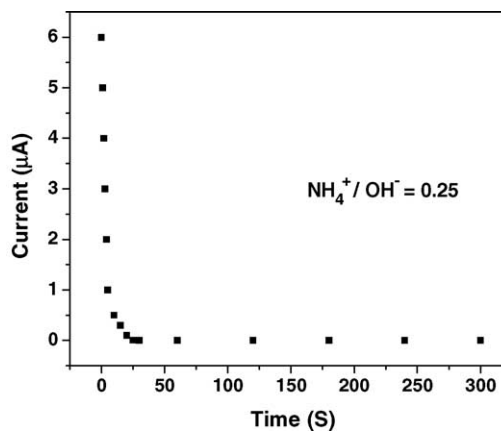

Fig. 7. Transference number measurement for NH$_4$$^+$/OH$^-$ = 0.25.

Fig. 7 shows the variation of polarization current as a function of time. The ionic transference number of the mobile species in the polymer electrolyte has been calculated by Wagner's dc polarization method [12]. This dc polarization measurement has been used to analyse the mobile species in the electrolyte is either ions or electrons. The polarization current has been monitored as a function of time on application of dc potential (0.8 V) across the cell Ag/electrolyte/Ag. The total ionic transference number has been calculated from the plot using the standard equation,

$$t_{ion} = \frac{I_i - I_f}{I_i} \tag{2}$$

where I_i is the initial current and I_f is the final residual current. The total ionic transference number has been found 0.96 for NH$_4$$^+$/OH$^-$ = 0.25. This shows that the charge transport in this polymer electrolyte is mainly due to ions.

3.4. UV–vis characterization

Fig. 8 shows optical absorption spectra recorded for different NH$_4$$^+$/OH$^-$ ratios in the region 175–350 nm. In the UV region, the band at 188 nm have been observed for pure PVA and PVA doped with different concentration of ammonium acetate with different absorption intensity. This absorption peak may be attributed to the n $\rightarrow$ σ^* transition which is very sensitive to hydrogen bonding. The absorption bands at 282 nm and 320 nm with different absorption intensity may be assigned as $\pi \rightarrow \pi^*$ which comes from unsaturated
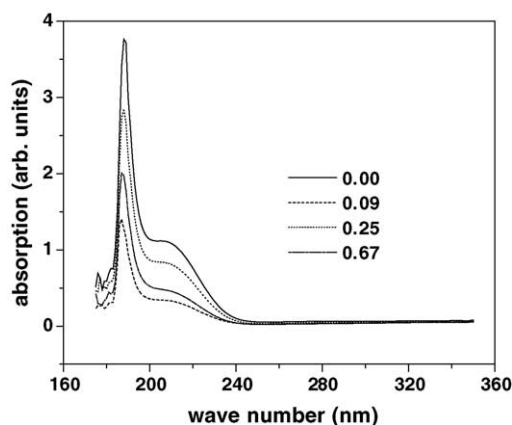
Table 2
Conductivity values and activation energies for different NH$_4$$^+$/OH$^-$ ratios

NH$_4$$^+$/OH$^-$ ratio	$\sigma_{301\,K}$ (S cm^{-1})	$\sigma_{345\,K}$ (S cm^{-1})	<T_g		T_g	
			E_b (eV)	R	E_a (eV)	R
0.00	2.00×10^{-10}	1.20×10^{-6}	2.75	0.994	0.86	0.998
0.09	2.04×10^{-7}	3.47×10^{-5}	1.55	0.991	0.50	0.950
0.25	5.62×10^{-6}	5.37×10^{-5}	0.56	0.985	0.34	0.998
0.43	7.59×10^{-7}	2.40×10^{-5}	0.95	0.994	0.61	0.987
0.67	8.51×10^{-7}	1.78×10^{-5}	0.89	0.998	0.27	0.991

Fig. 8. Optical absorption spectra for different NH_4^+/OH^- ratios.

Table 3
Band gap energy for PVA/CH_3COONH_4 complexes with different NH_4^+/OH^- ratios

NH_4^+/OH^- ratio	Band gap energy (eV)	
	Direct	Indirect
0.00	5.44	4.84
0.09	5.45	4.83
0.25	5.43	4.81
0.43	5.50	4.79
0.67	5.44	4.80

bonds, mainly C=O and C=C, which are present in the anion (CH_3COO^-) in CH_3COONH_4 and tail head of the polymer, respectively. The small peak around 206 nm for pure PVA can be attributed to the n → π* transition and has been observed for all salt concentration of the samples.

Fig. 9 shows optical transmittance spectra for different NH_4^+/OH^- ratios in the region 200–700 nm. One can observe for pure and all composition of salt added PVA films, nearly zero transmission intensity in the wavelength range 200–220 nm. Then, the transmission intensity starts increasing at 220 nm until it reaches 64% at 250 nm. Then, the intensity decreases up to a wavelength 278 nm and the transmission intensity gradually increases up to 400 nm and reaches a constant value around 80% in the region 400–700 nm. It is also observed in the wavelength region 220–250 nm, a pure film attains the maximum transmission intensity than the salt-doped samples.

In order to evaluate the optical band gap energy, the absorption coefficient have been determined from the spectra using the formula,

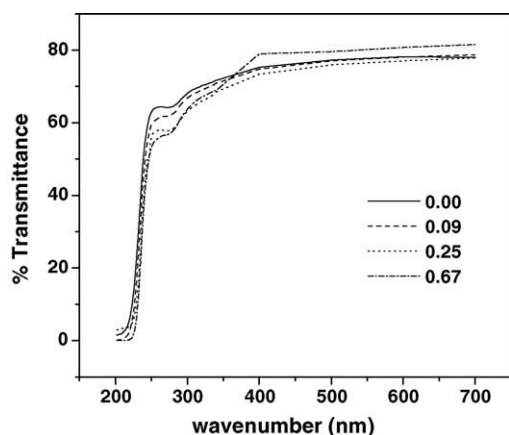$$\alpha = \frac{\ln(1/T)}{d} \quad \text{or} \quad \alpha = \frac{A}{d} \tag{3}$$

where T is the transmittance, A the absorbance and d is the thickness of the film under investigation. To determine the width of the band gap, $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ have been plotted against the photon energy ($h\nu$) (not shown). The direct and indirect optical band gap are calculated from the plot ($h\nu$) versus $(\alpha h\nu)^2$ and ($h\nu$) versus $(\alpha h\nu)^{1/2}$, respectively, and values are tabulated in Table 3. The direct optical band gap for pure PVA is found to be 5.44 eV and remains the same for the salt-doped samples within the experimental error. Similarly, the indirect band gap for pure PVA is found to be 4.84 eV and remains the same for the salt-doped samples. These indicate that there is no charge transfer complexes arises between the host polymer and the ammonium acetate salt.

4. Conclusion

The electrical study indicates that PVA can be effectively doped with ammonium acetate to enhance its conductivity and the maximum conductivity has been obtained for a dopant concentration–polymer ratio (NH_4^+/OH^-) of 0.25. The Arrhenius plot shows two regions, having different activation energies above and below the glass transition. The XRD study reveals the amorphous nature of the electrolyte. The DSC measurement shows the minimum glass transition temperature for (NH_4^+/OH^-) = 0.25. The dc polarization measurement shows that the conductivity is primarily due to ions. The UV–vis studies show that there is no charge transfer complex between the salt and pure PVA.

Fig. 9. Transmittance spectra for different NH_4^+/OH^- ratios.

References

[1] K.C. Gong, H.S. Cai, in: G. Wazari, R.A. Huggins, D.F. Shriver (Eds.), Solid State Ionics, Materials Science Society, Pittsburg, 1989, p. 377.
[2] M. Krumova, D. Lopaz, R. Benavente, C. Mijangos, J.M. Perena, Polymer 41 (2000) 9265.
[3] M.A. Vargas, R.A. Vargas, B.E. Mellander, Electrochim. Acta 44 (1999) 4227.
[4] M.A. Vargas, R.A. Vargas, B.E. Mellander, Electrochim. Acta 46 (2001) 1699.
[5] M.A. Vargas, R.A. Vargas, B.E. Mellander, Phys. Stat. Sol. 220 (1) (2000).
[6] M.A. Vargas, R.A. Vargas, B.E. Mellander, Electrochim. Acta 45 (2000) 1399–1403.

[7] R.M. Hodge, G.H. Edward, G.P. Simon, Polymer 37 (1996) 1371.

[8] R. Iwamoto, M. Miya, S. Miya, J. Polym. Sci. B Polym. Phys. 17 (1979) 1507.

[9] A. Higuchi, T. Iijima, Polymer 26 (1985) 1207.

[10] A. Higuchi, T. Iijima, Polymer 26 (1985) 1833.

[11] Z.H. Ping, Q.T. Nguyen, S.M. Chen, J.Q. Zhou, Y.D. Ding, Polymer 42 (2001) 8461.

[12] J.B. Wagner, C.J. Wagner, Chem. Rev. 26 (1957) 1597.