

Characterization of Poly(vinyl alcohol)/Sodium Bromide Polymer Electrolytes for Electrochemical Cell Applications

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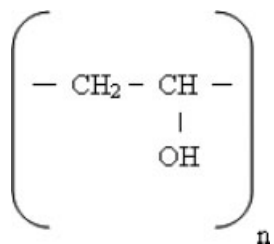
ABSTRACT: Sodium-ion conducting polymer electrolytes based on poly(vinyl alcohol) complexed with sodium bromide were prepared with a solution-casting technique. The structure of these films was determined with X-ray diffraction, and the complexation of the salt with the polymer was confirmed with Fourier transform infrared spectroscopy studies. Electrical conductivity was measured with an alternating-current impedance analyzer in the frequency range of 100 Hz to 1 MHz and in the temperature range of 303–373 K. It was observed that the magnitude of conductivity increased with the increase in the salt concentration as well as the temperature. The nature of the

charge transport in these polymer electrolyte films was determined with both Wagner's polarization technique and the Watanabe technique. The dominant conducting species were found to be ions, particularly anions. Optical absorption studies were performed in the wavelength range of 200–600 nm, and the absorption edge, direct band gap, and indirect band gap values were evaluated. Electrochemical cells were fabricated, and their discharge characteristics were studied. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 510–517, 2008

Key words: conducting polymers; XRD; conductivity; battery

INTRODUCTION

In recent years, polymer electrolytes have been widely investigated because of their potential applications in solid-state batteries, electrochromic windows, sensors, fuel cells, and so forth.¹ Solid polymer electrolytes have many advantages, such as nonleakage, volumetric stability, solvent-free conditions, easy handling, and wide electrochemical stability, over liquid electrolytes.² Because of the mechanical stability and suitable conductivity of solid polymer electrolytes, many physicists and chemists have devoted their efforts to studying and improving the electrical properties of polymers by doping them with metal ions.^{3–5} Poly(vinyl alcohol) (PVA), as one of the most important polymers, has attracted special attention^{6–9} as it has a linear polymer chain and can be treated as a one-dimensional cooperative system in which the rotation of a chain segment is restricted or aided by the neighboring segmental parts:



With increasing polymer temperature, the molecular motion is increased until the polymer behaves like a viscous liquid under conditions in which no thermal degradation takes place.¹⁰ In the amorphous state, the distribution of chains in the PVA matrix is completely random. This allows the onset of molecular motion at temperatures below the melting point. Consequently, as the molecular motion in the amorphous state increases, the sample passes from a glassy state through a rubberlike state to a molten state. These transitions lead to changes in the physical properties and material applications of polymers. Hence, it is very important to examine the physical properties of PVA as a result of the variation in the molecular motion, which is affected directly by the dopant materials. In these investigations, an attempt was made to characterize PVA-based polymer electrolytes by complexation with sodium bromide (NaBr) salt in different weight percentages and to evaluate its potential in electrochemical cell applications.

EXPERIMENTAL

Films of pure PVA and various compositions of complexed films of PVA with NaBr salt were prepared with different weight percentage ratios (90 : 10, 80 : 20, and 70 : 30) by a solution-casting technique with triple-distilled water as the solvent. The solutions were stirred for 10–12 h to get a homogeneous mixture and then were cast onto polypropylene dishes and allowed to evaporate slowly at room

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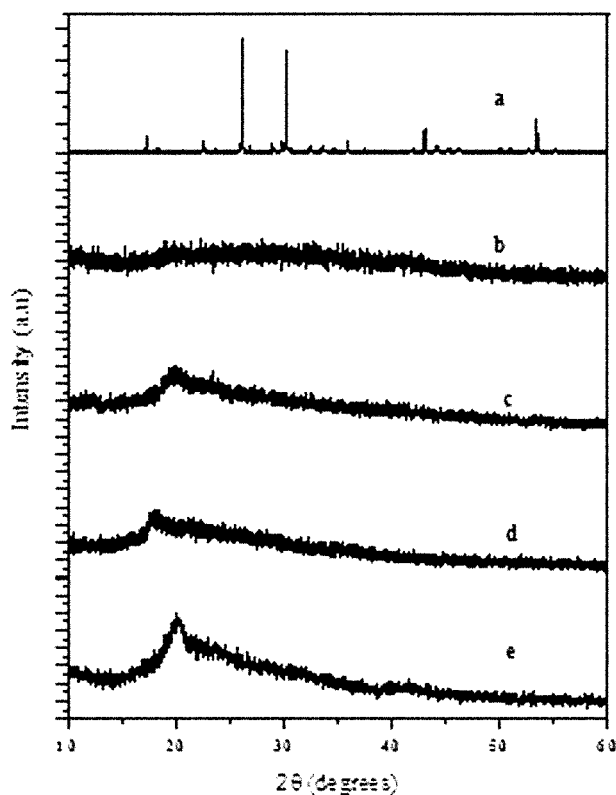


Figure 1 XRD patterns of pure PVA, complexed polymer films with NaBr, and pure NaBr salt: (a) NaBr salt, (b) 70 : 30 PVA/NaBr, (c) 80 : 20 PVA/NaBr, (d) 90 : 10 PVA/NaBr, and (e) pure PVA.

temperature. The final product was vacuum-dried thoroughly before use.

The X-ray diffraction (XRD) patterns of the films were obtained with a HLG4/B-PC X-ray diffractometer with Cu K α radiation and a graphite monochromator at room temperature. Fourier transform infrared (FTIR) spectra were recorded with an EO-SXB IR spectrometer with a resolution of 4 cm $^{-1}$. The measurements were taken over a wave-number range of 400–4000 cm $^{-1}$. The alternating-current (ac) impedance measurements were performed with a Hioki 3532-50 LCR Hi-Tester impedance analyzer in the frequency range of 100 Hz to 1 MHz and in the temperature range of 303–373 K with the sample sandwiched between copper electrodes. The measurement cell was prepared by the polymer electrolyte film being sandwiched between two copper electrodes and was assembled in a homemade sample holder. Transference numbers [ionic transference number (t_{ion}) and electronic transference number (t_{ele})] were evaluated with Wagner's polarization technique. The cationic contribution to the transport number (t_{Na^+}) was evaluated by the Watanabe method, which uses a combination of ac impedance spectroscopy and direct-current (dc) polarization of the Na/(PVA/NaBr)/Na cell. Optical absorption

spectra were recorded at room temperature in the wavelength range of 200–600 nm with a Shimadzu model UV-3100 (Japan) ultraviolet-visible/near-infrared spectrophotometer. Electrochemical cells were fabricated with the Na (anode)/(PVA/NaBr)/(I $_2$ /C/electrolyte) (cathode) configuration, and their discharge profiles were monitored at a constant load of 100 k Ω .

XRD analysis

XRD studies were performed on pure PVA, NaBr salt, and PVA/NaBr complexed polymer electrolyte films to determine the effect of the dopant concentration on the polymer chain (Fig. 1). A semicrystalline peak was observed at 21° in pure PVA films, which corresponded to the orthorhombic lattice structure.^{11,12} The relative intensity of this peak decreased with the increase in the salt concentration. This was a clear indication of a reduction of the crystalline phase in the polymer complex at room temperature. Hodge et al.¹³ established a correlation between the intensity of the peak and the degree of crystallinity. They observed that the intensity of the XRD pattern decreases as the amorphous nature increases with the addition of a dopant. An absence of peaks corresponding to the NaBr salt in the polymer complexes

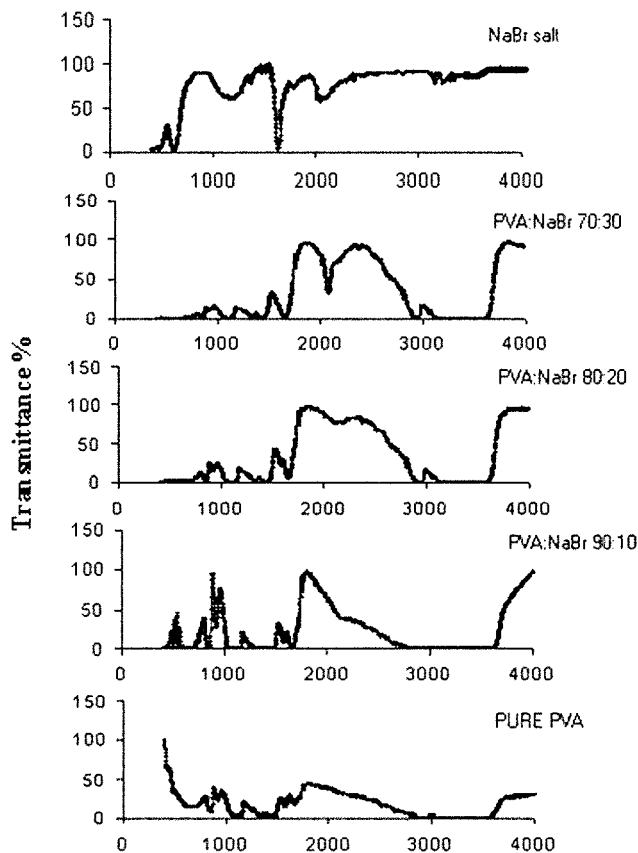


Figure 2 FTIR patterns of pure PVA, complexed polymer films with NaBr, and pure NaBr salt.

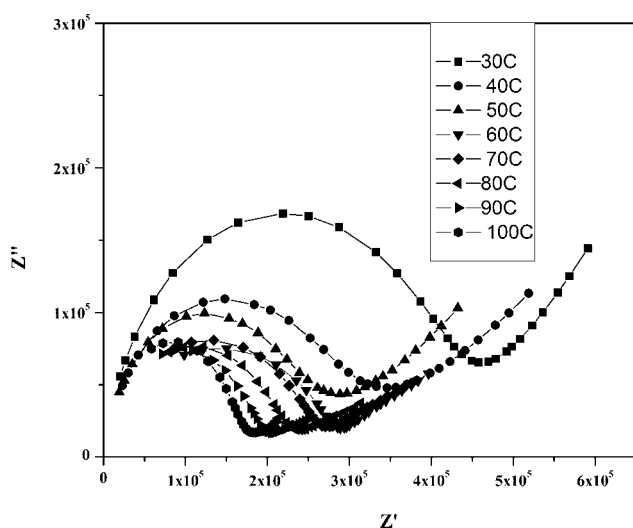


Figure 3 Cole–Cole plots for the PVA/NaBr (80 : 20) polymer electrolyte at different temperatures. Z' is the real part of impedance and Z'' is the imaginary part of impedance.

clearly indicated the complete dissolution of salt in the polymer matrix. This decrease in the intensity of the diffraction peak of the polymer electrolyte with an increase in the salt concentration suggested the amorphous nature of the polymer electrolytes.

FTIR studies

The FTIR spectra of pure PVA, NaBr, and PVA complexed with NaBr are shown in Figure 2. The following spectral features were observed in a comparison of the spectra of complexed PVA with those of pure PVA and NaBr. The O–H stretching band in the IR spectrum is, by far, the most characteristic feature of alcohols and appears in the range of $3538\text{--}3115\text{ cm}^{-1}$ in pure PVA. The hydroxyl band was displaced and reduced in the complexes. This gives a clear indication of the specific interactions in the polymer matrix. C–H stretching of CH_2 showed an absorption band at 2939 cm^{-1} in pure PVA and was slightly shifted to 2953 , 2945 , and 2940 cm^{-1} in the 10, 20, and 30% complexed films, respectively. The vibrational peak at 1445 cm^{-1} was assigned to the CH_2 scissor mode of pure PVA and was shifted to 1424 ,

1418 , and 1411 cm^{-1} in the complexed films. C–C stretching occurring at 1235 cm^{-1} in pure PVA was shifted to 1232 , 1235 , and 1237 cm^{-1} in the complexed films, respectively. The characteristic vibrational band at 1100 cm^{-1} was assigned to C–O stretching of secondary alcohols and was shifted to 1093 , 1095 , and 1097 cm^{-1} in the complexed films, respectively.

The appearance of new peaks along with the changes in the existing peaks (and/or their disappearance) in the IR spectra of the complexed films clearly indicated the complexation of the polymer with the salt.

Electrical conductivity

Ionic conductivity was determined from the ac impedance analysis with copper electrodes. A typical impedance plot of 80 : 20 PVA/NaBr at different temperatures is shown in Figure 3. The bulk resistance (R_b) was measured from the high-frequency intercept on the real axes. The conductivity of the polymer electrolyte (σ) was calculated from the measured resistance, area, and thickness of the polymer film with the following formula:

$$\sigma = L/R_b A$$

where L is the thickness of the polymer electrolyte (cm), A is the area of the blocking electrode (cm^2), and R_b is the bulk resistance of the PVA/NaBr polymer electrolyte. Table I shows the conductivity values of the complexes in the range of $303\text{--}373\text{ K}$. Figure 4 shows the variation of $\log \sigma$ with the inverse absolute temperature for various PVA/NaBr complexes. As the temperature increases, the conductivity also increases for all complexes, and this is in agreement with the theory established by Armand et al.¹⁴ This can be explained on the basis of the free volume model¹⁵ and hopping of charge carriers. Because PVA is a linear polymer with a carbon chain as the backbone, the polymer chains that are less entangled are capable of causing electrical conductivity. Furthermore, PVA, being a polar polymer, ionizes the NaBr salt into anions and cations under the

TABLE I
Conductivity, E_a , and Transference Number Values of PVA and PVA/NaBr Polymer Electrolyte Films

Polymer electrolyte	Conductivity at 303 K (S/cm)	E_a (eV)	Transference number	
			t_{ion}	t_{ele}
Pure PVA	2.07×10^{-9}	0.478	—	—
90 : 10 PVA/NaBr	5.96×10^{-7}	0.392	0.942	0.058
80 : 20 PVA/NaBr	1.062×10^{-6}	0.353	0.952	0.048
70 : 30 PVA/NaBr	1.362×10^{-6}	0.326	0.964	0.036

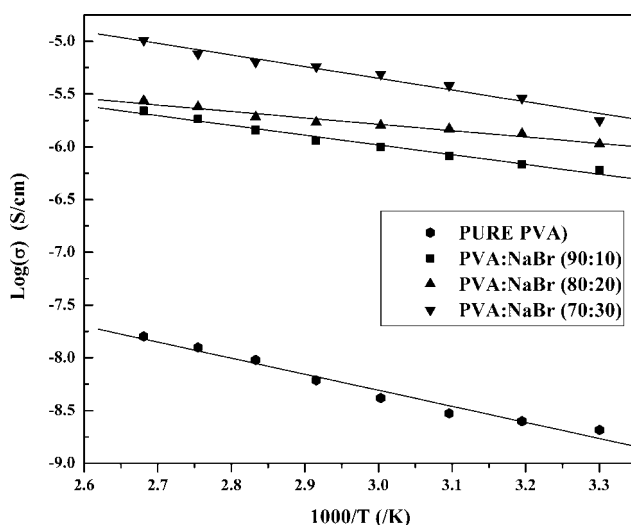


Figure 4 Variation of the conductivity (σ) with the temperature for (a) pure PVA, (b) 90 : 10 PVA/NaBr, (c) 80 : 20 PVA/NaBr, and (d) 70 : 30 PVA/NaBr polymer electrolytes.

influence of the applied electric field and temperature. These ions hop between the localized states and cause the enhanced conductivity. When the temperature is increased, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighboring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur.¹⁶ Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and hence increases the conductivity.

The activation energies (E_a 's) were evaluated from $\log \sigma$ versus $1000/T$ plots with the following Arrhenius equation:

$$\sigma_{ac} = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$

where σ_{ac} is conductivity, σ_0 is a constant, k is the Boltzmann constant, and T is the absolute temperature. These values are listed in Table I. The low E_a value for sodium ion transport is due to the dominant presence of the amorphous nature of the polymer electrolyte, which facilitates the fast motion Na^+ ions in the polymer.¹⁷

Transference number measurements

The ionic transference numbers of the mobile species in the polymer electrolyte were calculated with Wagner's dc polarization technique.¹⁸ The polarization current was monitored as a function of time on the application of a dc potential (1.5 V) across the Na/electrolyte/C cell (Fig. 5).

The total ionic transference number was calculated from plots of the polarization current versus time with the standard equation:

$$t_{\text{ion}} = 1 - I_f/I_i$$

$$t_{\text{ele}} = 1 - t_{\text{ion}}$$

where I_i is the initial current and I_f is the final residual current.

The total ionic transference number was found to be in the range of 0.94–0.96 in these polymer electrolyte systems. This suggests that the charge transport in these polymer electrolytes is predominantly due to ions. t_{Na^+} was evaluated with the combination of ac and dc techniques as proposed by Watanabe et al.¹⁹ In this technique, the sample is held between two reversible electrodes for the cation whose contribution is to be estimated. For this study, because the cation of interest was Na^+ , the sample geometry used was $\text{Na}/(\text{PVA}/\text{NaBr})/\text{Na}$.

t_{Na^+} can be calculated with the following formula:

$$t_{\text{Na}^+} = \frac{R_b}{\left(\frac{V}{I_s}\right) - R_e}$$

where R_b and R_e are the bulk and electrode–electrolyte contact resistances determined from impedance

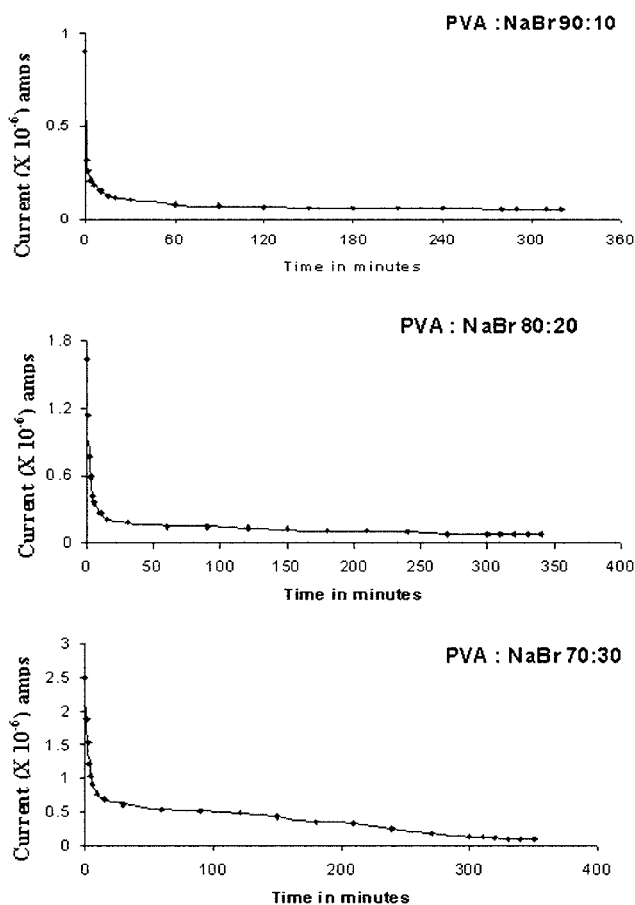


Figure 5 Polarization current as a function of time for PVA/NaBr polymer electrolytes at different concentrations of NaBr.

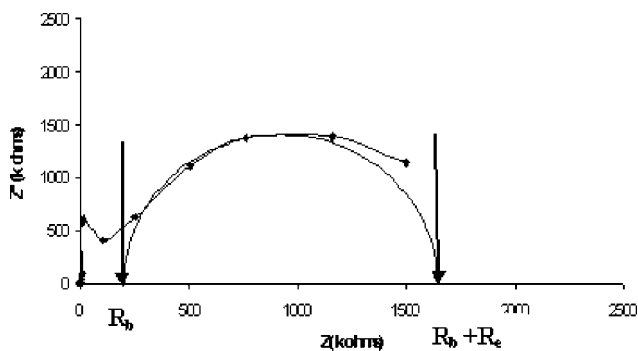


Figure 6 ac complex-impedance plot of the Na/(90 : 10 PVA/NaBr)/Na cell. Z' is the real part of impedance and Z'' is the imaginary part of impedance.

spectra and I_s is the steady-state current under a dc bias of V volts. With this technique, the values of R_b and the electrode–electrolyte charge-transfer resistance were measured from a complex-impedance plot with ion-reversible electrodes. Figure 6 shows a typical impedance plot for determining R_b and R_e . Watanabe et al.¹⁹ pointed out that for calculating the transport number, I_s must be taken from the region in which the I_s – V plot is linear. From these plots (Fig. 7), the value of t_{Na^+} evaluated for the composition with 90 : 10 PVA/NaBr is 0.43. This value of t_{Na^+} suggests that the anionic contribution to the total ionic conduction is significant.

Optical properties

The study of optical absorption gives information about the band structure. Insulators/semiconductors are generally classified into two types: (1) direct band gap semiconductors and (2) indirect band gap

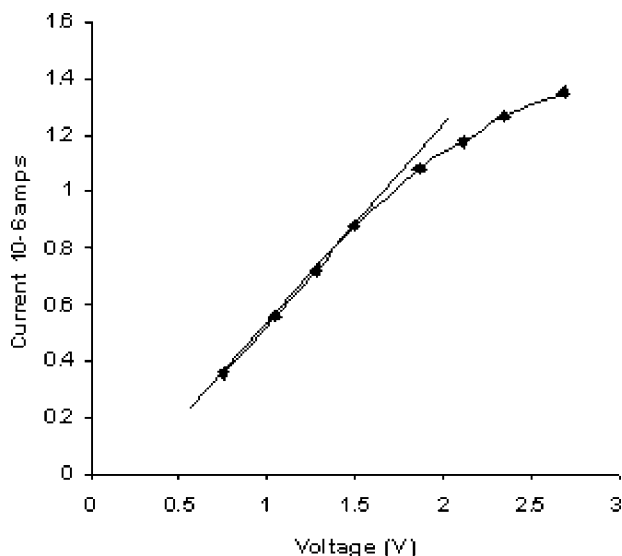


Figure 7 Residual steady-state current (I_s) as a function of the applied voltage across the Na/(90 : 10 PVA/NaBr)/Na cell.

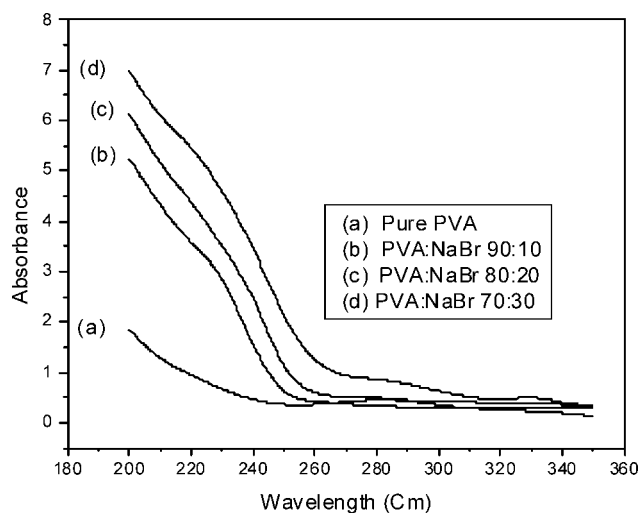


Figure 8 Variation of the absorbance with the wavelength for PVA-based polymer electrolytes.

semiconductors. In direct band gap semiconductors, the top of the valance band and bottom of the conduction band lie at the same zero crystal momentum (wave vector). If the bottom of the conduction band does not correspond to zero crystal momentum, then it is called an indirect band gap semiconductor. In an indirect band gap semiconductor, the transition from the valance band to the conduction band should always be associated with a phonon of the right magnitude. Davis and Shalliday²³ reported that near the fundamental band edge, both direct and indirect transitions occur and can be observed by the plotting of $\alpha^{1/2}$ and α^2 (α is the absorption coefficient).

(α) Vs $h\nu$

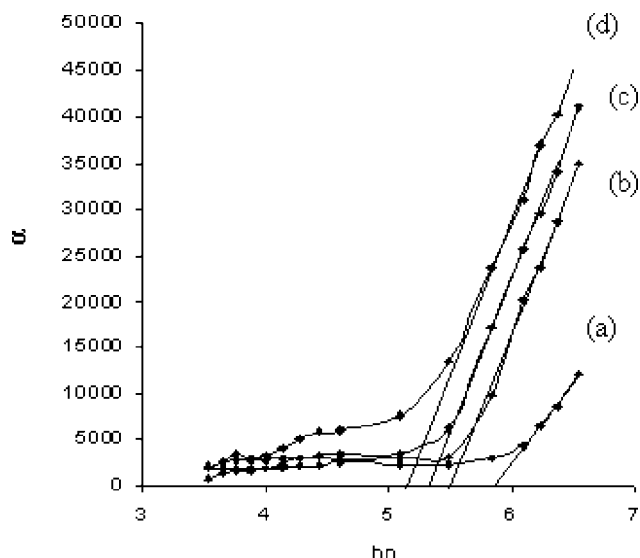


Figure 9 α – $h\nu$ plots of (a) pure PVA, (b) 90 : 10 PVA/NaBr, (c) 80 : 20 PVA/NaBr, and (d) 70 : 30 PVA/NaBr polymer electrolyte films.

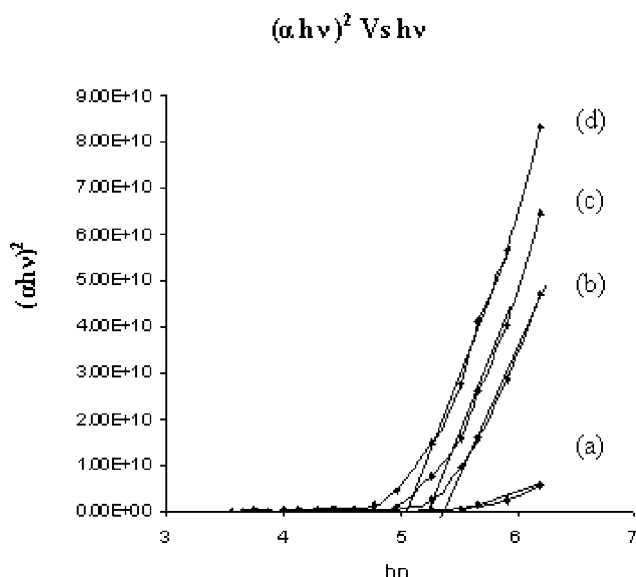


Figure 10 $(\alpha hv)^2-hv$ plots of (a) pure PVA, (b) 90 : 10 PVA/NaBr, (c) 80 : 20 PVA/NaBr, and (d) 70 : 30 PVA/NaBr polymer electrolyte films.

cient) as a function of photon energy $h\nu$ (ν is the frequency of incident light, and h is Planck's constant).

α was calculated from the absorbance (A). The variation of the absorbance with the wavelength is shown in Figure 8. After correction for reflection, α was determined with the following relation:

$$I = I_0 \exp(-\alpha x)$$

where I is the intensity of the incident light and I_0 is the intensity after passing through the material.

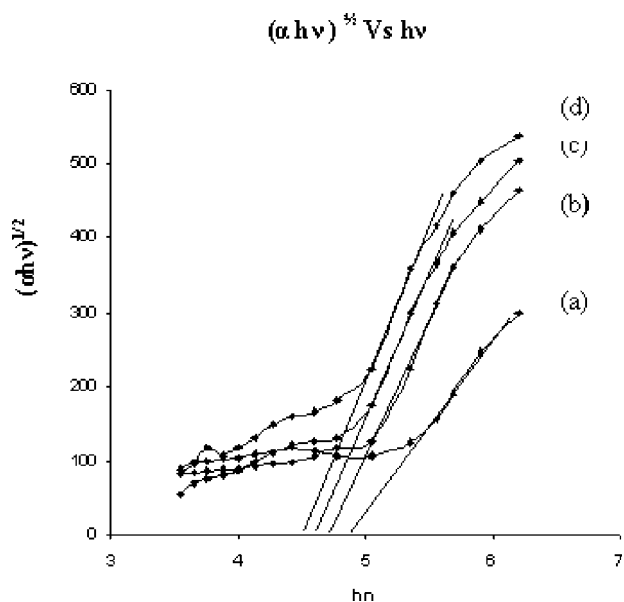


Figure 11 $(\alpha hv)^{1/2}-hv$ plots of (a) pure PVA, (b) 90 : 10 PVA/NaBr, (c) 80 : 20 PVA/NaBr, and (d) 70 : 30 PVA/NaBr polymer electrolyte films.

TABLE II
Absorption Edge and Optical Band Gap (Both Direct and Indirect) of Undoped and NaBr-Doped PVA Polymer Electrolyte Films

Polymer electrolyte	Absorption edge (eV)	Band gap (eV)	
		Direct	Indirect
Pure PVA	5.80	5.40	4.90
90 : 10 PVA/NaBr	5.55	5.25	4.73
80 : 20 PVA/NaBr	5.21	5.18	4.60
70 : 30 PVA/NaBr	5.06	5.03	4.50

which gives

$$\alpha = 2.303/x \log(I/I_0) = 2.303/x A$$

where x is the thickness of the sample.

To determine the nature and width of the band gap, α , $(\alpha hv)^2$, and $(\alpha hv)^{1/2}$ were plotted as a function of $h\nu$.

The position of the absorption edge was determined by extrapolation of the linear portions of $\alpha-h\nu$ curves (Fig. 9) to the zero absorption value. The absorption edge for pure PVA lies at 5.8 eV, whereas for 10, 20, and 30 wt % NaBr doped PVA films, the absorption edge lies at 5.50, 5.21, and 5.06 eV, respectively.

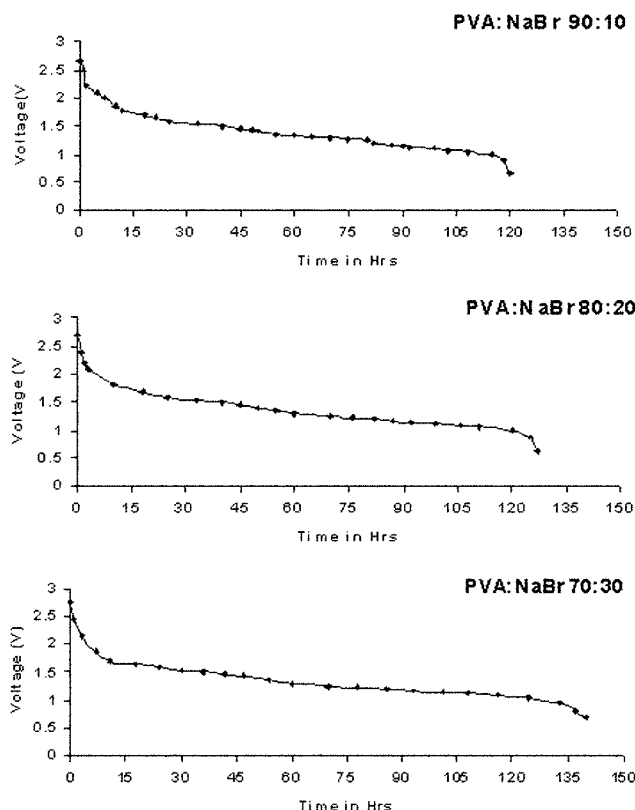


Figure 12 Discharge profiles of PVA/NaBr electrochemical cells at a constant load of 100 kΩ.

TABLE III
Cell Parameters of Na/(PVA/NaBr)/(I₂/C/Electrolyte) Polymer Electrolytes

Cell parameter	90 : 10 PVA/NaBr	80 : 20 PVA/NaBr	70 : 30 PVA/NaBr
Open circuit voltage (V)	2.66	2.70	2.75
Short circuit current (μA)	312	384	495
Area of the cell (cm ²)	1.33	1.33	1.33
Weight of the cell (g)	1.31	1.32	1.34
Discharge time for the plateau region (h)	114	123	133
Current density (μA/cm ²)	235	289	372
Power density (W/kg)	0.633	0.785	1.015
Energy density (W h/kg)	72	96.55	135
Discharge capacity (μA/h)	2.73	3.12	3.721

When a direct band gap exists, α has the following dependence on the energy of the incident photon:^{20,21}

$$\alpha hv = C(hv - E_g)^{1/2}$$

where E_g is the band gap and C (velocity of light) = $4\pi\sigma_0/nc\Delta E$ (ΔE , energy difference) is a constant dependent on the specimen structure.

The direct band gap values were obtained by the plotting of $(\alpha hv)^2 - hv$ curves (Fig. 10). For pure PVA, the optical band gap was observed to be 5.5 eV, whereas for doped films, the values were 5.25, 5.18, and 5.03 eV, respectively.

For indirect transitions, which require phonon assistance, α has the following dependence on hv :^{20,21}

$$\alpha hv = A(hv - E_g + E_p)^2 + B(hv - E_g - E_p)^2$$

where E_p is the energy of the photon associated with the transition and A and B are constants depending on the band structure.

The indirect band gap values were obtained from the plots of $(\alpha hv)^{1/2}$ versus hv as shown in Figure 11. For pure PVA, the indirect band lies at 4.9 eV, whereas for doped films, its value lies at 4.65, 4.60, and 4.50 eV, respectively. The values of the absorption edge, direct band gap, and indirect band gap are tabulated in Table II.

Electrochemical cell discharge characteristics

Solid-state electrochemical cells with the Na (anode)/(PVA/NaBr)/(I₂/C/electrolyte) (cathode) con-

figuration were fabricated, and their discharge profiles were studied and are shown in Figure 12. There was an initial rapid decrease in the voltage, which could be due to polarization and/or the formation of a thin layer of sodium salt at the electrode-electrolyte interface. The open circuit voltage, short circuit current, and other cell parameters of these cells are listed in Table III. From Table IV, it is clear that the short circuit current and discharge time for the plateau region were greater in these 70 : 30 PVA/NaBr cells compared to other cells^{22,23} reported in the literature. This demonstrates the potential application of these polymer electrolytes in solid-state battery applications.

CONCLUSIONS

The complexation of the salt with the polymer was confirmed by XRD and FTIR studies. The increase in the conductivity with an increasing concentration of NaBr was attributed to a decrease in the degree of crystallinity and an increase in the amorphousness. The conducting species in this polymer electrolyte system were found to be predominantly ions, particularly anions. The optical absorption edge and optical band gap (both direct and indirect) showed a decreasing trend with an increased concentration of the dopant. Electrochemical cells fabricated with these electrolyte systems showed better performance than similar cells reported in the literature.

TABLE IV
Cell Parameters of Polymer Electrolyte Batteries

Polymer battery configuration (anode/electrolyte/cathode)	Open circuit voltage (V)	Short circuit current (μA)	Discharge time plateau region (h)	Reference
Na/(PEO/NaNO ₃)/(I ₂ /C/electrolyte)	2.44	240	51	25
Na/(PEO/glass)/(I ₂ /C/electrolyte)	2.45	81.5	98	26
Na/(90:10 PVA/NaBr)/(I ₂ /C/electrolyte)	2.66	312	114	This work
Na/(80:20 PVA/NaBr)/(I ₂ /C/electrolyte)	2.70	384	123	This work
Na/(70:30 PVA/NaBr)/(I ₂ /C/electrolyte)	2.75	495	133	This work

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