

Electrical conductivity studies on polymer Electrolyte Films doped with NaIO₄

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Abstract:

Polymer electrolyte system based on polyvinyl alcohol (PVA) complexed with NaIO₄ has been prepared using solution cast technique. DC conductivity of the films were measured in the temperature range 303–398 K. The electrical conductivity increased with increasing dopant concentration, which is attributed to the formation of charge transfer complexes. The polymer complexes exhibited Arrhenius type dependence of conductivity with temperature. The total ionic transport number was evaluated by means of Wagner's polarization technique. Transport number for Sodium ion is ranged from 0.91 to 0.96 depending on the composition. The features of complexation of the electrolytes were studied by X-ray diffraction.

Keywords — Polymer electrolyte, Electrical conductivity, Transport number, X-ray diffraction

1. Introduction

Polymer electrolytes have been the subject of increasing interest because of their potential applications in batteries, fuel cells, and other electrochemical devices [1-2]. These electrolytes show good thermal stability, high electrical conductivities. Electrical conductivity and Mechanical stability are, in general, the most important properties of materials to be used as electrolytes in solid state devices. The major efforts in this field have remained concentrated in developing new polymer electrolytes having high ionic conductivity and high mechanical, thermal and electrochemical stability. Polymer electrolytes are commonly doped with alkaline salts in order to achieve high ionic conductivity (3-6). The ionic conductivity of a polymer electrolyte is highly dependent on the concentration of the added salt (7-8). Conductivity in these polymeric system is essentially associated with ion migration between coordination sites, but also with segmental motions of the polymer chains (9-10).

In the present investigation, polymer electrolytes composing of PVA as host polymer, NaIO₄ as a salt have been prepared. We report here the results of our investigation on the Electrical conductivity, transport and electrochemical nature of polymer electrolyte films.

2. Experimental

Polymer electrolyte films (thickness ~120 μm) of pure polyvinyl alcohol (PVA) and various compositions of complexed films of PVA with NaIO₄ salt were prepared in the weight percent ratios (95:5), (90:10), (85:15) and (80:20) by solution cast technique using tetrahydrofuran as a solvent. The solutions were stirred for 8-10 h to get a homogeneous mixture and were then, cast onto polypropylene dishes and evaporated slowly at room temperature followed by vacuum drying.

In order to investigate the nature of these polymer electrolyte films, X-ray diffraction studies were carried out using Seifert X-ray diffractometer at room temperature. The dc conductivity was measured by means of an in-house conductivity set-up [11] in the temperature

range 303-398 K. The total ionic transport number was evaluated by means of Wagner's polarization technique [12]. In this technique, freshly prepared polymer electrolyte films were polarized in the configuration Na/polymer electrolyte/C under a dc bias (step potential of 1.5V). The resulting current was monitored as a function of time.

3. Results and discussion

3.1 Temperature dependent DC conductivity

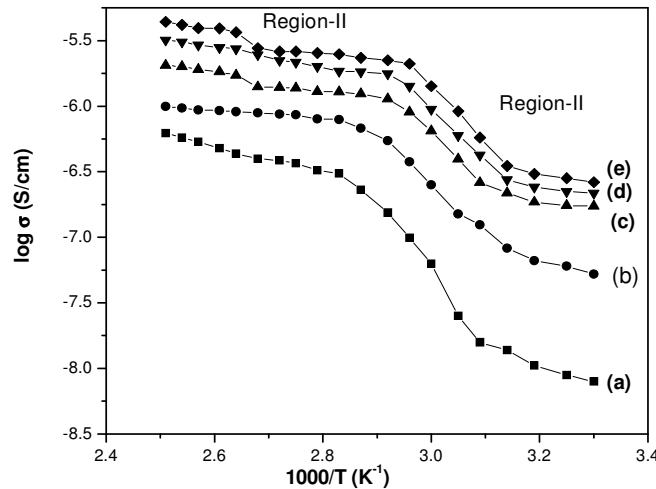


Fig 1. Temperature dependent conductivity of (a) Pure PVA (b) PVA+NaIO₄ (95 :5) (c) PVA+NaIO₄ (90 :10) (d) PVA+NaIO₄ (85 : 15) (e) PVA+NaIO₄ (80 :20)

Fig. 1 shows the variation of dc conductivity as a function of inverse temperature for different composition of (PVA+NaIO₄) polymer electrolyte in the temperature range of 303-398 K. From the plots it is clear that the conductivity is found to increase with increase of temperature in pure polymer film as well as in all the compositions of (PVA+NaIO₄) polymer electrolyte. With the addition of dopant, the conductivity was found to increase when compared to pure films. The increase in degree of ionic segmental mobility and interaction between Na ions and the polymer chains induced the higher ionic conductivity in polymer electrolyte system. This promotes localized amorphous regions and thus enhance the Na ions transport in the amorphous polymer electrolytes [13].

The temperature –dependent conductivity plots follow an Arrhenius behaviour throughout with two regions having different activation energies. A slow rate of increasing conductivity in first region may be due to the available thermally activated mobile ions, while the fast rate of rising conductivity in second region can be linked to the phase transition of the electrolyte system from semi-crystalline to amorphous. The conductivity σ may be expressed as

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad \dots\dots\dots (1)$$

where σ_0 is the pre-exponential factor, E_a , the activation energy, k , the Boltzmann constant and T is the absolute temperature.

The increase in the conductivity with temperature plots may be attributed to the transition from crystalline/semi-crystalline phase to amorphous phase. The increase in conductivity with temperature is interpreted in terms of a hopping mechanism between coordination

sites, local structural relaxation and segmental motion of polymer [14-15]. As the amorphous region increases, however, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion that results in increased conductivity [16]. The activation energies evaluated from the slopes of $\log \sigma$ versus $1000/T$ plots, for both the regions are given in the Table 1. From the table it is clear that the activation energies in both the regions decrease with the increase of salt concentration in all the samples. Increase in the electrical conductivity and decrease in the activation energy values of polymer electrolytes can be explained on the basis that the polymer films are known to be a mixture of amorphous and crystalline region and the conductivity behavior of such films may be dominated by the properties of the amorphous regions.

Table 1. DC conductivity and Activation energies of (PVA+NaIO₄) polymer electrolytes

Polymer electrolyte system (wt %)	Conductivity (Scm ⁻¹)			
	303 K	333 K	363 K	398 K
Pure PVA	7.91×10^{-9}	6.29×10^{-8}	3.67×10^{-7}	6.22×10^{-7}
PVA+NaIO ₄ (95:05)	5.24×10^{-8}	2.51×10^{-7}	8.59×10^{-7}	9.96×10^{-7}
PVA+NaIO ₄ (90:10)	1.73×10^{-8}	6.48×10^{-7}	1.38×10^{-6}	2.06×10^{-6}
PVA+NaIO ₄ (85:15)	2.19×10^{-7}	9.46×10^{-7}	2.17×10^{-6}	3.21×10^{-6}
PVA+NaIO ₄ (80:20)	2.65×10^{-7}	1.43×10^{-6}	2.69×10^{-6}	4.41×10^{-6}

Polymer electrolyte	Activation energy (E _a)	
	Region I (eV)	Region II(eV)
Pure PVA	0.40	0.24
PVA+ NaIO ₄ (95:05)	0.36	0.12
PVA+ NaIO ₄ (90:10)	0.29	0.11
PVA+ NaIO ₄ (85:15)	0.19	0.10
PVA + NaIO ₄ (80:20)	0.15	0.06

3.2. Transport numbers

The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport were evaluated using the Wagner’s polarization technique [11]. In this technique, the current is monitored as a function of time on the application of a fixed DC potential of 1.5 V across the cell. The transference numbers were calculated using the following equation

$$t_{ele} = i_s/i_t \quad \dots\dots\dots (2)$$

$$t_{ion} = 1 - \frac{i_s}{i_T} \quad \dots\dots\dots (3)$$

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

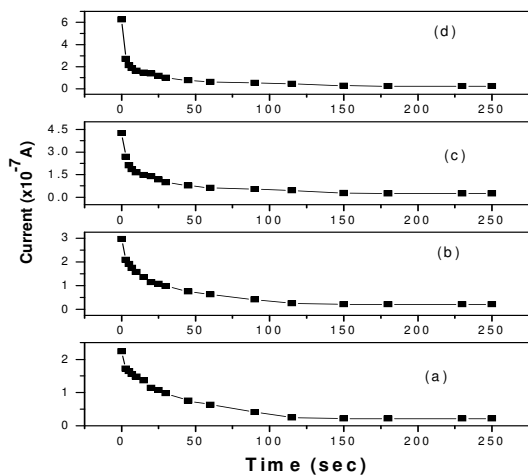


Fig.2 Current vs time plots of (a) PVA+NaIO₄ (95 :5) (b) PVA+NaIO₄ (90 :10) (c) PVA+NaIO₄ (85 : 15) (d) PVA+NaIO₄ (80 :20)

Figure 2 shows the variation of current as a function of time upon the application of a DC voltage of 1.5 V across the (Na/electrolyte/C) cell. The transference numbers evaluated from the plots are given in Table 2. The ionic transference number was found to be in the range 0.91–0.96 in these polymer electrolyte systems. This suggests that the charge transport in these polymer electrolytes is predominantly due to ions, with negligible contribution from the electrons. The conductivity measurements are inadequate if performed without the information on the possible type of charge carriers.

Table 2: Transference numbers of NaIO₄ doped polymer electrolytes

Polymer electrolyte system (wt %)	Transference numbers	
	t_{ion}	t_{ele}
PVA+ NaIO ₄ (95:05)	0.91	0.09
PVA+ NaIO ₄ (90:10)	0.93	0.07
PVA+ NaIO ₄ (85:15)	0.94	0.06
PVA + NaIO ₄ (80 : 20)	0.96	0.04

Composite polymer electrolytes thus offer an interesting alternative to other reported electrolyte system for room temperature solid –state batteries [17-19].

3.3. X-ray diffraction Analysis

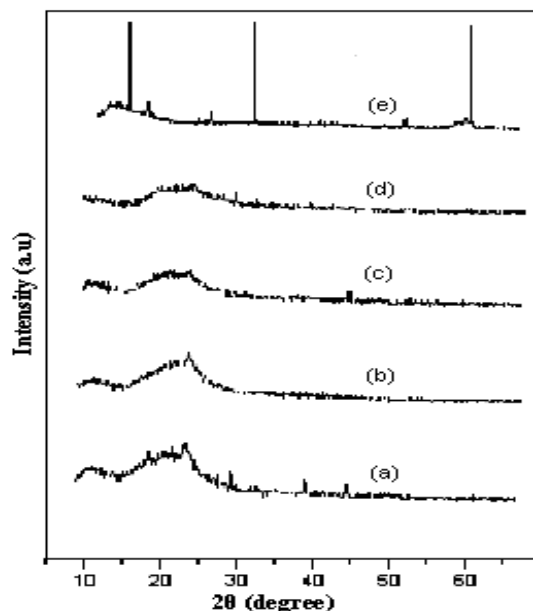


Fig 3. XRD patterns of (a) Pure PVA (b) PVA+NaIO₄ (95 :5) (c) PVA+NaIO₄ (90 :10) (d) PVA+NaIO₄ (85 : 15) (e) NaIO₄ salt.

To investigate the influence of sodium salt on PVA structure, XRD studies were performed. Fig 3 (a-e) shows the X-ray diffraction (XRD) patterns of pure PVA, PVA complexed with NaIO₄ and NaIO₄ salt. Comparison of the XRD pattern of complexed PVA films with those of pure PVA and NaIO₄ reveals the following differences: Peaks observed for 2θ values around 23° are less intense in complexed PVA films compared to those in pure PVA films. This indicates that the addition of NaIO₄ salt causes a decrease in the degree of crystallinity and simultaneous increase in the amorphosity of the PVA complexed films [20]. This change in intensity and broadening of the peak with increase of salt concentration suggests the amorphous nature of the complexed polymer electrolyte. The crystalline peaks for 2θ values at 15, 32 and 62° corresponding to NaIO₄ are absent in complexed PVA. This indicates the absence of any excess (uncomplexed) salt in the complexed polymer electrolyte films. Absence of sharp peaks at higher concentration of NaIO₄ salt indicates the dominant presence of amorphous phase. This amorphous nature is responsible for greater ionic diffusivity resulting in high ionic conductivity [21-22]. These observations confirmed that complexation has take-place in the amorphous phase.

4. Conclusions

The XRD study reveals the amorphous nature of the polymer electrolytes. The introduction of salts has proved to be a convenient method to increase the ionic conductivity at ambient temperatures. The value of activation energy decreases with increasing dopant con-

centration . The charge transport in these polymer electrolytes is predominantly due to ions, with negligible contribution from the electrons. The electrolyte films exhibit better performance, which indicates that such electrolytes are more suitable for fabricating solid-state batteries.

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