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Ionic Conductivity behavior of a Novel (PEO+PVP) Polymer Composite Electrolyte Complexed with NaF

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ABSTRACT

This paper presents the preparation and characterization of a series of (PEO+PVP) composites with different ratios of NaF salt. New Na^+ ion conducting polymer blend electrolyte films based on semicrystalline polymer poly (ethylene oxide) PEO and poly (vinyl pyrrolidone) PVP complexed with NaF salt were prepared using the solution-cast technique. The features of the complexation and structure of the electrolytes were studied by X- ray diffraction (XRD) and FTIR techniques. Frequency dependent conductivity were obtained from complex impedence (cole-cole) plots. It was observed that the magnitude of conductivity increased with increasing temperature and followed Arrhenius behavior throughout with three regions having different activation energies. The activation energy values were found to decrease with increasing concentration of NaF.

1.Introduction

Now a days intensive attention has been focused on polymer salt complexes among the various ion-conducting materials due to their possible applications like thin film formation, interfacial contacts, desirable size etc., as solid polymer electrolytes in advanced high-energy electrochemical devices [1- 2]. Various approaches such as blending [3], [4], co-polymerization [5], plasticization [6], addition of ceramic fillers [7] etc. have been made to enhance the ionic conductivity of polymer electrolytes [8, 9]. For the present study, we have adopted one of the above techniques, namely, blending because of the ease of preparation and easy control of physical properties within the compositional regime, which thus reduces development costs. In the present study, the effect of doping with sodium fluoride (NaF) on electrical conductivity of (PEO+PVP) polymer blend electrolyte films has been undertaken. Several experimental techniques such as XRD, FTIR and electrical characteristics were performed to characterize these polymer blend electrolytes.

2. Experimental

Films (thickness~150 μm) of (PEO+PVP) blend and NaF salt complexed (PEO+PVP) blend were prepared in weight ratios (45:45:10), (40:40:20), (35:35:30) and (40:40:20) by solution cast technique using methanol as the solvent. The X-ray diffraction studies of these films were performed by means of a SEIFERT X-ray diffractometer system with Ni-filtered CuKα radiation. The IR spectra were recorded with the help of Perkin Elmer FTIR spectrophotometer in the range 4000 - 400 cm^{-1}. The impedance measurements were performed using a complex controlled phase sensitive multimeter (PSM 1700) in the frequency range 1 Hz – 1 MHz and temperature range 303 – 373 K.

3. Results and Discussions

3.1 x-ray diffraction studies

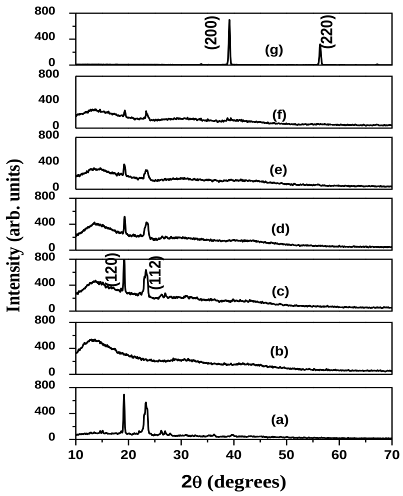

Fig. 1 XRD patterns of (a) Pure PEO (b) Pure PVP (c) PEO+PVP (50:50) (d) PEO+PVP+NaF (45:45:10) (e) PEO+PVP+NaF (40:40:20) (f) PEO+PVP+NaF (35:35:30) polymer films and (g) NaF salt.

XRD studies were made on pure (PEO+PVP), and their complexes (Fig. 1) in order to investigate the complexation and influence of the concentration of NaF salt. The XRD patterns of pure (PEO+PVP) blends exhibited two peaks at 19.1° and 23.3° which are indicative of the crystalline nature of the blend. As PEO is crystalline and PVP is amorphous in nature, the blend showed a combination of the structures of both PEO and PVP. Upon the addition of NaF salt to the polymer blend, the intensity of all crystalline peaks decreased gradually suggesting a decrease in the degree of crystallinity of the complex. No sharp peaks corresponding to salt were observed in all doped (PEO+PVP) films, indicating the absence of excess salt (uncomplexed) in the doped polymer samples i.e. there was complete dissolution of salt in the

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polymer and giving rise the dominant presence of amorphous phase [10].

3.2 IR Spectra

The IR spectra of pure (PEO+PVP) and NaF complexed (PEO+PVP) are shown in Fig. 2. The small ether oxygen band at 1800 cm^{-1} is found to smoothen gradually with the increase of salt concentration, which suggests that PEO is disrupted by dopant salt. The CH_2 wagging mode exhibited at around 1360 cm^{-1} in pure PEO is shifted to 1349, 1342 and 1334 cm^{-1} in 10, 20 and 30 wt% NaF salt complexed films, respectively. In the region 1708 – 1620 cm^{-1} a strong band appeared at around 1675 cm^{-1} is assigned to free C=O stretching of PVP in uncomplexed (PEO+PVP) blend. Upon the addition of salt this band gradually broadens and shifted to lower wave number. This is a result of coordination between the Na^+ cation and the oxygen atom of carbonyl groups of PVP [11].

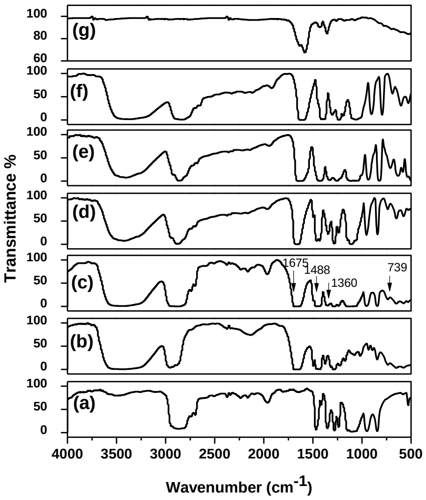

Fig 2 .IR spectra of (a) Pure PEO (b) Pure PVP (c) (PEO+PVP) blend(d) (PEO+PVP+NaF) (45:45:10) (e) (PEO+PVP+NaF) (40:40:20)(f) (PEO+PVP+NaF) (35:35:30) (g) NaF salt.

3.3 AC impedance studies

3.3.1 Impedance polts

Typical impedance plots (Z' vs Z") for pure (PEO+PVP) blend and NaF doped (PEO+PVP) composite electrolytes in the temperature range 303– 373 K are shown in Fig. 3.

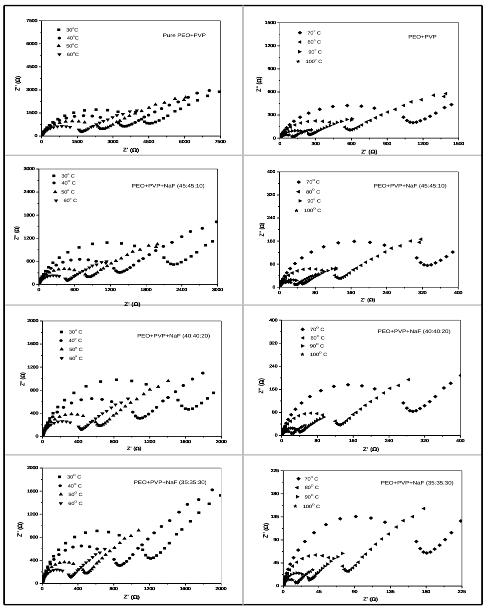

Fig 3 .Impedance (Cole-Cole) plots of (PEO+PVP) blend and (PEO+PVP+NaF) polymer blend films at different temperatures

Figure shows normal impedance behaviour such as a depressed semicircular portion followed by a spike (residual tail). In the complex impedance representation, the low frequency response appears as an inclined spike and such a spike (tail-like) is characteristic of a blocking double-layer capacitance. The high frequency semicircle corresponds to the bulk response of the films. These results suggest that the migration of ions may occur through the volume of polymer matrix, which can be represented by a resistor [12].

3.3.2 Composition dependence of conductivity

The variation of conductivity (σ), as a function of NaF salt concentration in (PEO+PVP) is shown in Fig. 4, in the temperature range of 303 – 373 K. From the figure, it is seen that the conductivity of pure (PEO+PVP) is about 2.62 X 10^{-6} Scm^{-1} at room temperature and increases to 5.62 X 10^{-6} Scm^{-1} for 10 wt% NaF. The increase in conductivity becomes flatter on further addition of NaF to the polymer upto 30 wt%. The increase in conductivity at lower dopant concentrations of NaF is attributed to the formation of charge transfer complexes or decrease in the crystallanity [13], while the slow increase at higher dopant concentrations is due to the formation of ionic aggregates. For further increase of the salt concentration (40 wt% of NaF to the polymer) the conductivity decreases. This may be due to the increasing influence of the ion pairs, ion triplets and higher ion aggregations, which reduces the overall mobility and degree of freedom [14]. Similar behavior can be seen for all temperatures. The conductivity data of pure and complexed PEO at all temperatures are presented in Table 1.

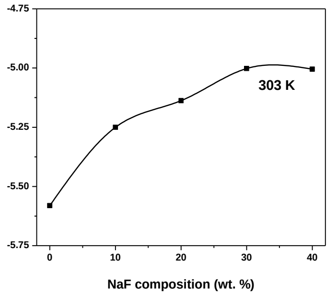

Fig 4. Composition dependence of conductivity of (PEO+PVP+NaF) polyblend polymer electrolyte system at room temperature.

Table1.Conductivity data of (PEO+PVP+NaF) polyblend electrolyte system at different temperatures

Polymer blend electrolyte system (wt %)	Conductivity (Scm^{-1})			
	303 K	323 K	343 K	363 K
Pure PEO+PVP	2.62 X 10^{-6}	5.11 X 10^{-6}	1.14 X 10^{-5}	4.65 X 10^{-5}
PEO+PVP+NaF (45:45:10)	5.62 X 10^{-6}	1.40 X 10^{-5}	3.46 X 10^{-5}	2.14 X 10^{-4}
PEO+PVP+NaF (40:40:20)	7.28 X 10^{-6}	1.90 X 10^{-5}	4.61 X 10^{-5}	2.88 X 10^{-4}
PEO+PVP+NaF (35:35:30)	9.95 X 10^{-6}	2.53 X 10^{-5}	6.80 X 10^{-5}	3.77 X 10^{-4}
PEO+PVP+NaF (30:30:40)	2.16 X 10^{-6}	2.20 X 10^{-5}	5.40 X 10^{-5}	2.64 X 10^{-4}

3.3.3 Temperature dependence of conductivity

The variation of conductivity as a function of temperature for pure and different concentrations of NaF salt in (PEO+PVP) is shown in Fig. 5 over a temperature range 303–373 K. In the temperature range of study, the conductivity increased with temperature and followed Arrhenius behavior throughout with two regions (regions I and II) having different activation energies. This may be due to a transition from a semicrystalline phase to an amorphous phase [15]. In polymer electrolytes, change of conductivity with temperature is due to segmental motion, which results in an increase in the free volume of the system [16, 17].

As per Arrhenius relation the dependence of conductivity has the form

$$\sigma = \sigma_0 \exp(-{}^{E_a}/_{kT})$$

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

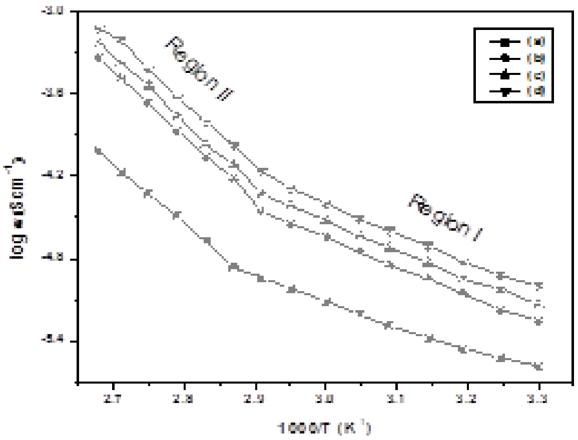

Fig 5. Temperature – dependent conductivity of (a) Pure PEO+PVP(b) PEO+PVP+NaF (45:45:10) (c) PEO+PVP+NaF (40:40:20) and(d) PEO+PVP+NaF (35:35:30)

3.3.4 Activation energies

The activation energies were evaluated from the slope of these plots (log σ vs 1000/T) and the values are given in Table 2. From the table, it is clear that the activation energy in both regions decreases with increase of salt concentration in all the samples. Increase in the electrical conductivity and decrease in activation values may be due to the fact that the addition of small amounts of dopant forms charge transfer complexes in the host lattice [19, 20].

Table 2. Activation energies of (PEO+PVP+NaF) polymer blend electrolytes.

Polymer electrolyte	Activation energies	
	Region I	Region II
PEO+PVP (50:50)	0.43	0.96
PEO+PVP+NaF (45:45:10)	0.42	0.95
PEO+PVP+NaF (40:40:20)	0.41	0.92
PEO+PVP+NaF (35:35:30)	0.35	0.86

4. Conclusions

A new Na^+ ion conducting (PEO+PVP) solid polymer blend electrolyte membrane: (PEO+PVP+NaF) has been synthesized. Diffraction peaks less in NaF complexed (PEO+PVP) films vis-à-vis pure (PEO+PVP) films indicating that the addition of NaF salt causes a decrease in the degree of crystallinity of the polymer. The intensity of the bands in pure (PEO+PVP) was found to decrease and shifted to lower wavenumbers in complexed films, indicating complexation. The AC impedance studies showed that the conductivity of the complexed samples increased with the addition of salt to the polymer electrolyte. The conductivity followed Arrhenius behavior throughout with the regions having different activation energies. The activation energy values were found to decrease with increasing concentration of NaF.

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