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Electrical Characterization of Polymer Blend (PVP / PVA) Electrolyte Films Doped with Silver Nitrate

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Abstract: ***Solid polymer blend electrolyte films based on PVP / PVA complexed with $AgNO_3$ were prepared by the solution cast technique. Various experimental techniques such as X-ray diffraction studies and dc conductivity in the temperature range 303-373 K were carried out. The electrical conductivity increased with increasing dopant concentration, which is attributed to formation of charge transfer complexes. The polymer complexes exhibited Arrhenius type dependence of conductivity with temperature.***

Keywords: Polymer blend, Polymer electrolyte film, electrical conductivity

1. Introduction

The development of portable electronic devices, especially mobile phones and laptops, has been remarkable in the last decade leading to a strong need of high-energy batteries. Indeed, the replacement of common liquid electrolytes by an ionic polymer membrane is an important technological development for the lithium ion technology, as it provides the prospect of a favorable combination of high energy and long life [1]. However, at the same time, this remarkable advantage of lithium ion battery can be a practical problem. In a device containing higher energy there is a higher risk of fire explosion. Therefore, safety is a key issue for future application of the lithium ion battery such as large-scale batteries for electronic vehicles and load leveling devices In order to overcome this problem, the development of all solid state batteries using a solid electrolyte may be one solution. A solid polymer is a thin film consisting of ionic salts dissolved in an appropriate polymer which enables ionic conduction at room temperature in the solid state [2]. The ionic conductivity can be enhanced by copolymerization, plasticization, blending, addition of ceramic fillers and addition of ionic salts. The electrical conductivity of polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix.

Although some work has been reported on discharge characteristics of doped polymers [3]-[5], very little work is available on doped poly blend of (PVP+PVA) [6]. PVA is a potential material having a very high dielectric strength, good charge storage capacity and dopant dependent electrical properties. As Ag^+ is a fast conducting ion in a number of crystalline and amorphous materials, its incorporation in a polymeric system may be expected to enhance the electric performance of the blend.

Hence in the present study, the effect of doping with silver nitrate on electrical conduction in PVA / PVP polymer blend electrolyte films has been undertaken.

2. Experimental

Pure (un doped) and $AgNO_3$ doped PVA / PVP polymer blend films of thickness 150 µm were prepared by solution cast technique in different weight ratios (50:50), (47.5:47.5:5), (45.0:45.0:10); (42.5:42.5:15), (40:40:20) using triple distilled water as solvent. Appropriate amounts of PVA, PVP and $AgNO_3$ were dissolved in triple distilled water and the solutions were stirred magnetically for 10-12 hours at room temperature to get homogenous solution and then cast onto polypropylene dishes and evaporated slowly at room temperature. All the films were vacuum dried at 45^0C thoroughly under a vacuum of 10^{-3} torr to remove residual solvent, if any.

The X-ray diffraction studies were performed by means of SEIFERT X-ray diffractometer. The DC conductivities were measured by using a conductivity cell [7], in the temperature range 300 – 400 K.

3. Results and Discussion

3.1 X-Ray diffraction studies

XRD studies were made on (PVP+PVA), $AgNO_3$ and the complexes (fig.1) in order to investigate the influence of the concentration of $AgNo_3$ salt.

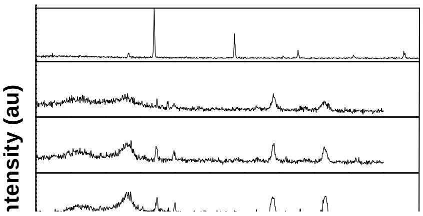

Figure 1

Figure 1 : XRD plots of
(a) pure PVP+PVA (50:50)
(b) PVP+PVA+$AgNO_3$ (47.5: 47.5: 5)
(c) PVP+PVA+$AgNO_3$ (45: 45: 10)
(d) PVP+PVA+AgNO3 (42.5 : 42.5 : 15)
(e) PVP+ PVA+ $AgNO_3$40:40:20)
(f) Pure Salt ($AgNO_3$)

There was a noticeable change in the intensity of XRD peaks of the doped samples in addition to the appearance of additional peaks. Peaks were observed for 2θ values around 23^0, 44^0, and 51^0 for pure (PVP+PVA) blend. The intensity of these peaks decreased with increasing salt concentration and got slightly displaced in complexed polymer blend films. The peaks for 2θ values at 27^0, 38.6^0, 47.7^0, 55.8^0, pertaining to $AgNo_3$ disappeared in polymer complexes which indicate the complete dissolution of the salt in the polymer matrix. This shows that the addition of $AgNO_3$ salt causes a decrease in the degree of crystallinity and simultaneous increase in the amorphosity of the complexed films. This amorphous nature is responsible for greater ionic diffusivity resulting in high ionic conductivity. This observation confirms that complexion has taken place in the amorphous phase.

3.2 DC Conductivity

The variation of DC conductivity (σ), as a function of composition of $AgNo_3$ in (PVP+PVA) for different weight percent ratios of $AgNO_3$ is shown in figure 2 in the temperature range of 300 K – 400 K.

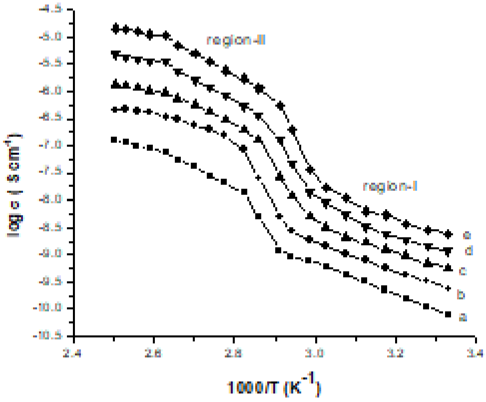

Figure 2

Figure 2: Temperature-dependent conductivity of
(a) pure PVP+PVA (50:50)
(b) PVP+PVA+$AgNO_3$ (47.5 : 47.5 : 5)
(c) PVP+PVA+$AgNO_3$ (45 : 45 : 10)
(d) PVP+PVA+$AgNO_3$ (42.5 : 42.5 : 15)
(e) PVP+PVA+$AgNO_3$ (40 : 40 : 20)

The conductivity of pure blend was $6x10^{-10}$ Scm^{-1} at room temperature and its value increased 10 times on complexing it with 5% $AgNO_3$. It continued to increase with increased dopant concentration, although slowly at higher concentrations. This is due to the formation of ionic aggregates at higher dopant concentrations. These ionic aggregates impede the conduction process [8] and decrease the conductivity. The increase in conductivity at lower dopant concentrations of $AgNo_3$ is attributed to the formation of charge carriers or decrease in the crystallinity of the blend [9]. The conductivity increased with temperature and followed Arrhenius behavior throughout with two regions (region I & region II) having different activation energies. This may be due to a transition from a semi crystalline phase to an amorphous phase [9], [10]. In polymer electrolytes, change of conductivity with temperature is due to the segmental motion, which results in an increase in the free volume of the system [11], [12]. This increase in free volume would facilitate the motion of ionic charge [13]. Similar behavior was observed in a number of other films [9], [14]–[16].

As per Arrhenius relation the dependence of conductivity has the form

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

Where σ_0 is the proportionality constant, E_a, the activation energy, and k is the Boltzmann constant.

The activation energies were calculated from the slope of these plots, and the values are shown in table.

Table

Activation energies (E_a) of (PVP+PVA+ $AgNO_3$) poly blend electrolyte system

Polyblend electrolyte system (wt.%)	*Activation energy (E_a)*	
	Region I (eV)	*Region II (eV)*
(PVP+PVA) (50:50)	0.60	0.49
(PVP+PVA+ $AgNO_3$) (47.5:47.5:5)	0.51	0.28
(PVP+PVA+ $AgNO_3$) (45:45:10)	0.37	0.26
(PVP+PVA+ $AgNO_3$) (42.5:42.5:15)	0.33	0.22
(PVP+PVA+ $AgNO_3$) (40:40:20)	0.24	0.20

These values are found to decrease with increasing concentration of $AgNO_3$. This may be due to the fact that the addition of small amounts of dopant forms charge transfer complexes in the host lattice [16]. These charge transfer complexes increase the electrical conductivity by providing additional charges in the lattice. This results in a decrease of activation energy.

4. Conclusions

The XRD studies showed the amorphous nature of the polymer electrolytes. The conductivity study indicates that the polymer blend can be effectively doped with $AgNO_3$ to improve its conductivity. The increase in conductivity is attributed to the formation of charge transfer complexes.

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