Studies on electrical and optical properties of PVP:KIO₄ complexed polymer electrolyte films

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Abstract. Solid polymer electrolytes based on poly (vinyl pyrrolidone) (PVP) complexed with potassium periodate (KIO₄) salt at different weight percent ratios were prepared using solution-cast technique. X-ray diffraction (XRD) results revealed that the amorphous nature of PVP polymer matrix increased with the increase of KIO₄ salt concentration. Electrical conductivity was measured with an AC impedance analyzer in the frequency and temperature range 1 Hz-1 MHz and 303 K-373 K respectively. The maximum ionic conductivity $1.42 \times 10^{-4} S \cdot cm^{-1}$ was obtained for 15 wt% KIO₄ doped polymer electrolyte at room temperature. The variation of ac conductivity with frequency obeyed Jonscher power law. Optical absorption studies were performed in the wavelength range 200-600 nm and the absorption edge, direct band gap and indirect band gap values were evaluated.

1. Introduction

In recent years, solid polymer electrolytes have drawn significant interest due to their theoretical as well as practical applications and hence have been extensively investigated for commercial applications such as high energy density batteries, electrochromic display devices, electrochemical sensors and super capacitors [1-3]. The polymeric electrolytes have many advantages due to their favorable electrical, optical and mechanical properties, ease of fabrication in thin films and ability to form effective electrode-electrolyte contacts. Because of the mechanical stability and suitable conductivity of solid polymer electrolytes, many physicists and chemists have devoted their efforts to study and improve the electrical properties of polymers by doping them with metal salts (ions) [4]. Several types of polymers such as (PMMA),(PVC), (PVDF) and (PEO) etc have been studied to see their potential as electrolytes. Among these polymers, poly (vinyl pyrrolidone) (PVP) deserves a special attention because of its good electrical properties, easy processability, moderate electrical conductivity and charge transport mechanism [5]. The PVP is amorphous polymer, which can permit faster ionic mobility compared to other semi-crystalline polymers, and due to the presence of carbonyl group (C=O) in the side chains of PVP, it forms a variety of complexes with various inorganic salts. It interacts well with several types of ions and enhances the number of free ions in the system. PVP is a potential material having a very high dielectric strength, low scattering loss, good charge storage capacity and dopant dependant electrical properties.

2. Experimental

Thin films (~120 µm) of poly (vinyl pyrrolidone) and various compositions of complexed films of PVP with KIO₄ salt were prepared by solution cast technique [6]. The X-ray diffraction patterns of pure PVP, KIO₄ and KIO₄ complexed PVP polymer electrolytes have been recorded by SEIFERT 3003RT X-ray diffractometer with CuKα radiation ($\lambda=1.54178$ Å operated at 40 KV and 30 mA), in the 2θ range 5-60°. The electrical conductivity measurement of polymer films was carried out by AC impedance spectroscopic technique using computer controlled PSM 1700 (Phase Sensitive Multimeter) meter over the frequency and temperature range 1Hz-1MHz and 303-373K respectively. Optical absorption spectra were recorded at room temperature in the wave length range 200-600 nm using PERKIN ELMER UV-VIS-NIR (model 3100) spectrophotometer.
3. Results and Discussion

3.1 XRD analysis: The XRD profiles of pure PVP, KIO₄ salt and PVP: KIO₄ systems are shown in Fig. 1

![Figure 1 XRD profile of KIO₄ salt doped PVP PVP polymer electrolytes](image)

The XRD profile of KIO₄ salt shows intensive sharp peaks which indicate the crystalline nature of the salt. These peaks are found to be absent in the PVP: KIO₄ systems indicating the complete dissociation of salt in the polymer matrix. For pure PVP a broad peak was observed at \( \theta \) region of 11–18° which can be attributed to the amorphous nature of pure PVP. This peak is broadened and its relative intensity decreases with increase of KIO₄ salt concentration, which indicates the increase in the amorphous nature of the host polymer. The increase in the amorphous nature causes a reduction in the energy barrier to the segmental motion of the polymer electrolyte. This amorphous nature results in greater ionic diffusivity and high ionic conductivity, which can be observed in amorphous polymers having flexible back-bone [7, 8].

3.2 Conductance spectra: The variation of conductivity as a function of frequency at different temperatures for PVP: KIO₄ (95:05) is shown in Fig 2. It is evident from the figure that in the measured frequency range two distinct regions namely, low frequency plateau region and high frequency dispersion region were observed. The low frequency plateau region which describes the electrode-electrolyte interface phenomena is attributed to the space charge polarization at the blocking electrode and is associated with the dc conductivity \( \sigma_d \) of the complexed polymer electrolyte. In the high frequency dispersion region the ionic conductivity increases with increasing frequency which is associated with the ac conductivity of the polymer electrolyte. However, at high frequencies, the conductivity variation with temperature is much less than that at low frequencies. DC conductivity values were obtained by taking the intercept of log σ at zero frequency are listed in table 1.

The total conductivity of polymer electrolytes may be expressed using Jonscher’s universal power law equation [9]

\[
\sigma(\omega) = \sigma_d + \Lambda \omega^{\alpha}
\]

(1)

where \( \alpha \) is the temperature dependent frequency exponent, \( \Lambda \), temperature dependent parameter, \( \sigma_d \) the dc conductivity and \( \omega = 2\pi f \) is the angular frequency.

According to the jump relaxation model reported by Funke [10], the power law exponent \( \alpha \) relates the back hop rate to the site relaxation time:
If $\alpha$ is less than one, the backward hopping is slower than the site relaxation; it results in translational motion of the K$^+$ ion. The conductivity spectra of the polymer electrolyte were fitted to eq (1) using a nonlinear least-square fitting procedure and the evaluated parameter $\alpha$ is in the range from 0.55-0.86, i.e., less than one ($<1$) for PVP: KIO$_4$ (95:05) polymer electrolyte and found to decrease with increase in temperature for all KIO$_4$ salt concentrations.

3.3 Optical Properties: The absorption coefficient $\alpha$ was calculated from the absorbance (A). After correction for reflection, $\alpha$ was determined using the following relation:

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

where $I_0$ and I is the intensities of incident and transmitted radiation respectively, $x$ is the thickness of the sample and A corresponds to $\log(I/I_0)$

![Figure 3 $\alpha$ Vs $h\nu$ plots of PVP:KIO$_4$ polymer electrolyte films](image)

Davis and Shalliday [11] reported that near the fundamental band edge, both direct and indirect transition occur and can be observed by plotting $\alpha^{1/2}$ and $\alpha^2$ as a function of energy $h\nu$ ($\nu$ is the frequency of incident light, and $h$ is Planck’s constant). The position of the absorption edge was determined by extrapolation of the linear portion of $\alpha^{-h\nu}$ curves (Fig.3) to the zero absorption value.

When a direct band gap exists, $\alpha$ has the following dependence on the energy of the incident photon [11-13].

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

where $E_g$ is the band gap and $C = 4\pi\sigma_0/n\epsilon$ is a constant dependent on the specimen structure. For indirect transitions, which require phonon assistance, $\alpha$ has the following dependence on $h\nu$ [11-13]

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

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 direct and indirect band gap values were obtained from the plots of $(\alpha h\nu)^2 - h\nu$ and $(\alpha h\nu)^2 - h\nu^2$ as shown in Figure 4-5.

The values of the absorption edge, direct band gap, and indirect band gap are tabulated in Table 1. It is clear from Table 1 that the direct and indirect band gaps showed a decrease on doping with KIO$_4$

| Sample          | $\sigma$ at 303 K (eV) | Band edge (eV) | Band Gap (eV) |
|-----------------|------------------------|----------------|---------------|
| Pure PVP        | 7.42 10^{-6}           | 5.29           | 5.32          | 5.12          |
| 5wt% KIO$_4$    | 6.66 10^{-6}           | 5.21           | 5.28          | 5.08          |
| 10wt% KIO$_4$   | 3.04 10^{-6}           | 5.18           | 5.19          | 5.01          |
| 15wt% KIO$_4$   | 1.42 10^{-4}           | 5.12           | 5.10          | 4.91          |
4. Conclusions
The XRD patterns of the PVP: KIO₄ electrolyte suggests an increase in the degree of amorphousity with increasing KIO₄ salt concentrations in the polymer matrix. The variation of ac conductivity with frequency obeys Jonscher power law. The optical absorption edge and bad gap (both direct and indirect) showed a decreasing trend with an increased concentration of the dopant.

Acknowledgement: One of the authors Mr. M. Ravi acknowledges the UNIVERSITY GRANTS COMMISSION, NEW DELHI for providing financial support under Research Fellowship for Meritorious Students (RFSMS) scheme to carry out this work.

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