

Dielectric and electrical behaviours of polymeric (PEO/PVP):NaIO₄ composite for solid electrolytes

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Abstract. Composite material prepared from polyethylene oxide (PEO) and polyvinylpyrrolidone (PVP) doped with Sodium (meta)periodate (NaIO₄) salt was studied by complex impedance spectroscopy at room temperature. The polymers PEO and PVP were mixed in a weight ratio 70:30 %, and the concentration of the embedded NaIO₄ compound was 7.5 wt.%. The effect from NaIO₄ filler on the dielectric permittivity of the three-component mixed system was analyzed in the frequency range 0.1 Hz – 1 MHz. As compared with the two-component polymer host PEO/PVP, a distinctly enhanced electrical and dielectrical response and an increase of the value of dielectric constant of the polymeric (PEO/PVP):NaIO₄ composite were present. This suggests the potential of this material for soft electronics and applications such as solid electrolytes.

1. Introduction

Solid polymer electrolytes (SPEs) for solvent-free metal-ion rechargeable batteries are attractive due to their promising advantages, including safety, ease of packing, excellent flexibility and low level of environmental pollution [1,2]. At present, the SPEs become the most appropriate materials for compact design of solid-state ion-conducting electrochromic devices, and in the fabrication of solid-state high energy density rechargeable batteries to run portable electronic equipment for long duration [3,4]. Sodium (Na) based rechargeable batteries (SRBs) have recently captured much attention because they are environmentally friendly, non-toxic, low cost and earth abundant materials [5,6]. Substantial research, development, and demonstration efforts are currently in progress to replicate the performance of well-established Li-ion batteries with sodium ion batteries. SPEs for SRBs simply consist of a sodium salt dissolved in a polymer matrix.

Polyethylene oxide (PEO) based SPEs have been employed extensively for battery applications since Armand et al. [7] have demonstrated the feasibility of using this polymer as an ion-conductive electrolyte. PEO is one of the widely investigated host polymer for synthesizing SPEs for alkali metal ion-conducting batteries due to its high electrochemical stability, good solvation power, complexation and ion dissociation abilities [8].

Several researchers have reported on various sodium salts complexed PEO based polymer electrolytes for SRBs applications [9,10]. Below the melting temperature ($\approx 330^\circ\text{K}$), the pure PEO electrolytes consist of both semi-crystalline and amorphous regions, as well as intermediate regions at



the crystalline/amorphous interphase. The semi-crystalline nature of PEO leads to both amorphous and crystalline phases at room temperature, which subsequently limits its ionic conductivity [11]. The most straightforward approach to overcome this problem is to modify the PEO matrix in order to decrease its degree of crystallinity. The suppression in the degree of crystallinity of the polymer chains improves their mobility, thereby leading to better ionic conduction. Therefore, ion hopping is believed to be predominant in amorphous rich PEO based SPEs [12].

One of the most promising alternative choice of enhancing the amorphous phase in PEO based SPE systems is blending of PEO with suitable amorphous polymer. Polyvinyl pyrrolidone (PVP) has been identified as a compatible partner to PEO which exhibits high-degree amorphosity. PVP demonstrates a high glass transition temperature, mechanical and thermal stabilities, the carbonyl group (C=O) in PVP enables to form different complexes of alkali metal ion salts at a wide range of concentrations [13]. In the work presented here, thin films of pure PEO/PVP and sodium periodate (NaIO_4) salt complexed PEO/PVP blends were prepared by solution casting technique. Their electric and dielectric properties are investigated by applying impedance spectroscopy and related to their microstructural properties.

2. Experimental

Poly(ethylene oxide) (PEO) with an average molecular weight 5×10^6 and Polyvinyl pyrrolidone (PVP) of molecular weight 3.6×10^5 were obtained from Aldrich and were dried in a vacuum oven at 50°C for 24 hours before use. Sodium periodate salt (NaIO_4) was procured from Aldrich and was dried under vacuum at 80°C for 24 hours before use. Methanol (from Aldrich) was used as a solvent without any further purification. Pure and 7.5 wt% NaIO_4 salt complexed PEO/PVP blend electrolyte films of thickness approximately $110\ \mu\text{m}$ were prepared by conventional solution cast technique.

The structural properties of blend electrolytes were analyzed by recording X-ray diffraction (XRD) patterns in the 2θ range of $10^\circ - 80^\circ$ with a constant step 0.02° , counting time 35 s/step on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation and Lynx Eye detector. To understand complexation of additives with the host polymer blend, Fourier-transform infra-red (FTIR) spectra of the films in nitrogen atmosphere were recorded in transmittance mode in the range $400 - 4000\ \text{cm}^{-1}$ with a spectral resolution of $2\ \text{cm}^{-1}$ using Bruker, model Vertex 70' spectrometer. Impedance measurements were performed by Potentiostat/Galvanostat SP-200 (Bio-Logic) set in two electrode configuration. Mechanically pressed two copper plates were placed in contact to the film surfaces forming sandwich structure. The electrode surface was fixed at $1\ \text{cm}^2$. Each sandwich structure was measured from 0.1 Hz to 1 MHz at 20 mV perturbation voltage. The measurements were carried out at room temperature (during the impedance experiments, the temperature of the samples was 20°C).

3. Results and Discussion

3.1. Microstructural properties

Figure 1(a) represents XRD patterns of PEO/PVP and NaIO_4 salt complexed PEO/PVP blend electrolytes. The diffraction pattern of PEO/PVP blend displays characteristic diffraction peaks at $2\theta = 19.30^\circ$ and $2\theta = 23.40^\circ$ corresponding to characteristic crystalline peaks of PEO, which originates from the ordering of polyether side chains and strong intermolecular interaction between PEO chains through hydrogen bonding [14]. The decrease in intensity and increase of broadness of the diffraction peaks due to the complexation of NaIO_4 salt (in our case at a concentration of 7.5 wt.%) reveal the decline in crystalline nature of the blend electrolytes. This could be due to strong interaction of dissolved NaIO_4 salt with the host polymer matrix and intermolecular interaction among the polymer chains of the considered polymer blend electrolytes, which lead to increase of their amorphous phase. Further, FTIR spectra for PEO/PVP and (PEO/PVP): NaIO_4 (figure 1 b) were recorded to understand the complexation properties of these blend electrolytes, such as ion-polymer interactions, intermolecular interactions, and their miscibility.

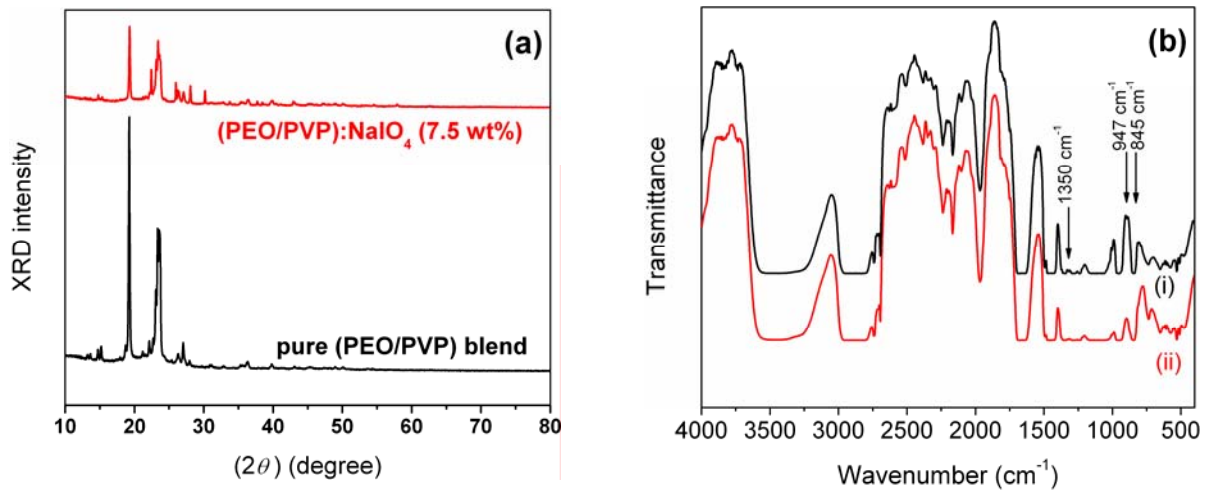


Figure 1. (a) XRD patterns of pure and NaIO₄ salt complexed PEO/PVP blend films obtained under identical experimental conditions; (b) FTIR spectra for polymer electrolyte films: pure PEO/PVP blend (i) and complexed (PEO/PVP):NaIO₄ (ii).

The low-wavenumber region 800 cm⁻¹ – 1000 cm⁻¹ of the FTIR spectra provides information about modifications in local structure of the host polymer due to the interaction of the salt with polymer backbone. The vibrational modes present at around 845 cm⁻¹ and 947 cm⁻¹ (indicated in figure 1 b with arrows) are accountable for CH₂ rocking motion with a little C–O stretching motion and C–O stretching motion with some contribution from CH₂ rocking motions, respectively. The intensities of these two characteristic bands are associated with helical structure of PEO [15,16]. The relatively weak band at 1350 cm⁻¹ signifies the amorphous portion in PEO matrix, whose intensity increased with the salt concentration. It evidences for increase of amorphous portion in the matrix of PEO polymer. In the FTIR spectra, the presence of all allowed vibrational modes and co-existence of well resolved respective band positions corresponding to ether oxygen groups (C–O–C) of PEO and carbonyl groups (C=O) of PVP are in congruent with previous reports in the literature and support the presence of PEO, PVP and their miscibility in resultant blend electrolyte films [17,18].

3.2. Dielectric properties

Dielectric materials are recognized as media that have an ability to store electrical energy. This property can be estimated by measuring the permittivity of dielectric materials. In alternating electric fields, the relative permittivity exhibits complex behaviour and is defined by $\epsilon^* = \epsilon' - j\epsilon''$. The real (Z_r) and imaginary (Z_i) parts of complex impedance (Z^*) can be used for evaluation of real (ϵ') and imaginary (ϵ'') parts of dielectric permittivity by the following equations [19]:

$$\epsilon' = \frac{-Z_i}{\omega C_0 (Z_r^2 + Z_i^2)} \quad (1)$$

and

$$\epsilon'' = \frac{Z_r}{\omega C_0 (Z_r^2 + Z_i^2)} \quad (2)$$

Here, C_0 is the vacuum capacitance of the sample given by $\epsilon_0 A/d$, where $\epsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}$ is the permittivity of free space, A and d are the active area and the thickness of the sample, respectively. The angular frequency is $\omega = 2\pi f$, where f is the frequency of the applied electric field. ϵ' has the same significance as that of the ordinary dielectric constant of the material. It measures the energy stored in the material during each charging cycle, to be returned to the electric field at the end of the cycle.

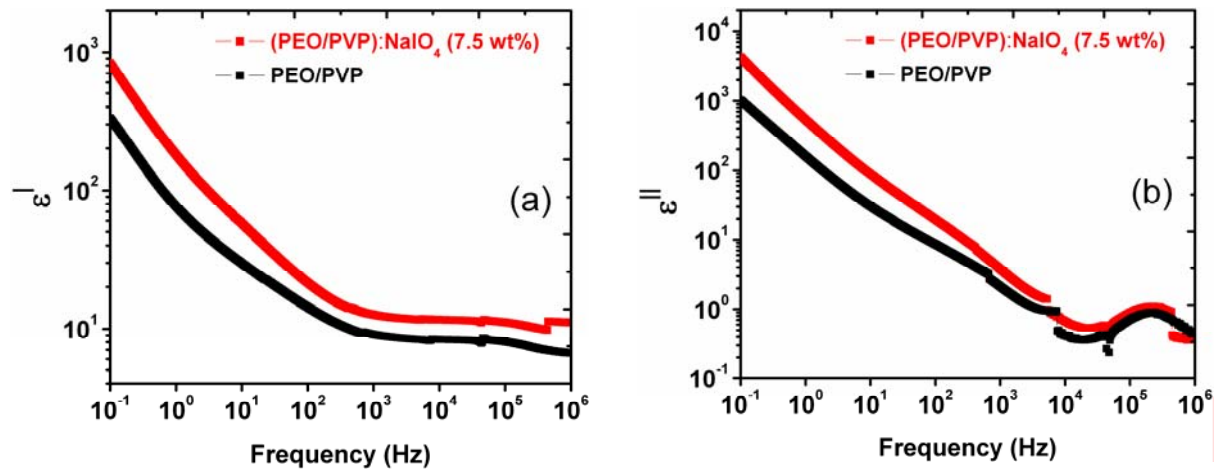


Figure 2. Variation of real (a) and imaginary (b) parts of dielectric constant as a function of frequency for PEO/PVP blend (dark lines) and salt complexed (PEO/PVP):NaIO₄ electrolyte (red lines).

Figure 2(a) shows the frequency dependence of dielectric constants of pure and salt complexed blend films studied here. The high values of the dielectric constant in the low-frequency region can be attributed to a build-up of space charge near electrode/electrolyte interface, which partially blocks the charge transport [20]. The dielectric constant decreases with the increasing frequency, more steeply at lower frequencies and less at higher frequencies. It reveals that, at very high frequencies (e.g., ~ 1 MHz) a periodic reversal of the field takes place so rapidly that the charge carriers will hardly be able to orient themselves in the field direction resulting in the observed decrease of dielectric constant [21].

As seen from figure 2(a), the dielectric constant of (PEO/PVP):NaIO₄ polymeric complex is greater than that of pure PEO/PVP. The increase in the dielectric constant can be attributed to fractional increase in the number of charges due to the addition of salt, resulting also in a higher conductivity. The enhanced dielectric and electric response suggest that the studied (PEO/PVP):NaIO₄ composite is a promising material for soft electronics and applications such as SPEs.

3.2. Electric modulus

Further information about the electrical properties and the conductivity relaxation behaviours of the considered SPEs can be obtained from the complex electric modulus M^* . The real (M') and imaginary (M'') parts of M^* can be calculated from the impedance data using the following relations [22,23]:

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (3)$$

and

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (4)$$

where ε' and ε'' are the real and imaginary parts of the complex dielectric function ε^* that depends on frequency, temperature and structure. At low frequency, both ε' and ε'' are very high due to electrode polarization effect. Namely to minimize the effect of electrode polarization, Macedo et al have established the electric modulus formalism [23]. Generally, in SPEs the movement of ions from one site to another will perturb the electric potential of the surroundings. Motion of the other ions in this region will be affected by perturb potential. Such a cooperative motion of ions will lead to non-exponential decay, or a conduction processes with distribution of relaxation time.

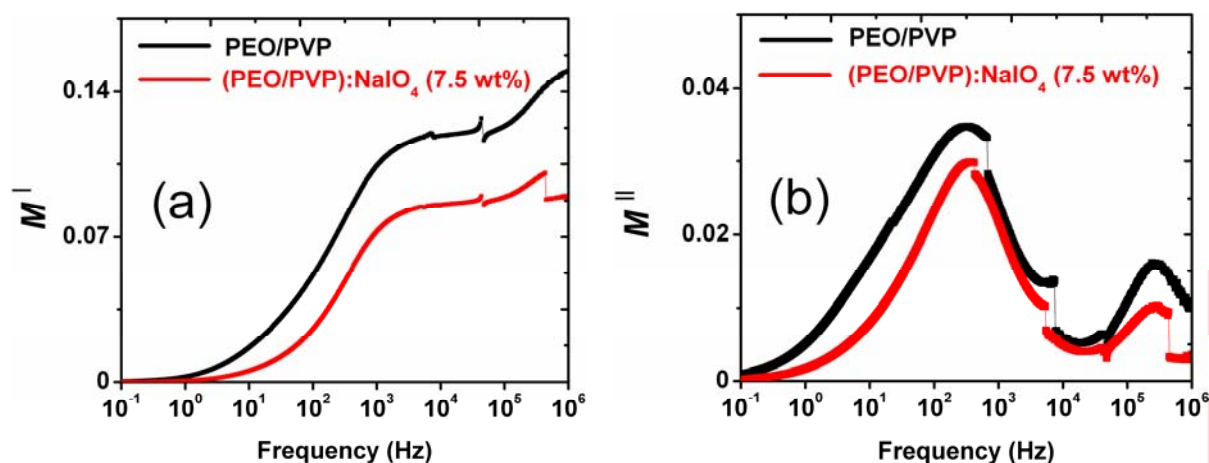


Figure 3. Frequency dependence of real (a) and imaginary (b) parts of electric modulus for pure and NaIO_4 salt complexed PEO/PVP electrolytes.

The frequency dependence of the electric modulus of pure and NaIO_4 salt complexed PEO/PVP blend electrolytes is shown in figure 3. Evidently, the real part (M') of the electric modulus values of the samples increase with an increase frequency and saturate at higher frequency region (figure 3 a). The spectra of the imaginary parts (M'') of the electric modulus of the studied electrolyte samples displayed distinct relaxation peaks (figure 3 b), which are related to the conductivity processes, whereas no corresponding feature can be seen in the dielectric loss spectra as depicted in figure 2(b). It evidences, that ionic and polymer segmental motions are strongly coupled. The presence of relaxation peaks in M'' spectra indicate that the considered materials are potential ionic conductors. The low-frequency side of the peaks represents the range of frequencies in which charge carriers are mobile over long distances. The high-frequency side of the M'' peaks represents the range of frequencies in which the ions are spatially confined to their potential wells and the ions can make only short-range motion with in the wells. The frequency range where the peak occurs is indicative of the transition from long-range to short-range mobility by increasing frequency of the applied electric field [24]. The low value of M'' in the low-frequency region suggests that the electrode polarization makes negligible contribution to electric modulus. The broad nature of the M'' peaks can be interpreted as being the consequence of distribution of relaxation time. Thus, the electric modulus studies could be used to detect the percolation threshold phenomena [25].

4. Conclusions

Pure and NaIO_4 (7.5 wt.%) salt complexed PEO/PVP blend electrolyte films prepared by solution cast technique were studied by means of impedance spectroscopy. Measured under identical experimental conditions, thin films of $(\text{PEO/PVP})\text{:NaIO}_4$ exhibit an enhanced dielectric response as compared to pure PEO/PVP. The distinct peaks present in the spectra of imaginary parts of electric modulus can be

attributed to a strong coupling between ionic and polymer segmental motions. The clear effect from the inclusion of the NaIO₄ salt resulting in the increasing value of dielectric constant of the studied (PEO/PVP):NaIO₄ blends, indicates their usefulness as a material for SPEs. A further advantage of this flexible polymeric composite is the possibility to be relatively easily optimized (compositionally and structurally) in order to enhance its SPE performance, e.g., by increase of the concentration of NaIO₄ salt complexed in the PEO/PVP, thereby increasing the amorphous portion in the (PEO/PVP):NaIO₄ SPE.

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