Studies on conductivity and dielectric properties of PEO/PVP nanocomposite electrolytes for energy storage device applications

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Investigations on sodium-ion conducting polymer blend electrolyte systems based on PEO/ PVP, complexed with NaIO$_4$ salt and TiO$_2$ nanofiller, are presented in this report. The complexed polymer blend electrolytes were prepared in the form of dimensionally stable and free-standing films by conventional solution cast technique. Micro Raman and XRD studies confirmed the miscibility between PEO and PVP and the complexation of the salt with PEO/PVP polymer host. TEM measurements were carried out to evaluate size & distribution of the dispersed TiO$_2$ nanofiller. Complex impedance spectroscopy was performed in the 1 Hz – 1 MHz frequency range within the temperature range from room temperature to 343 K. Ionic conductivity of blend electrolytes increased with the increase of TiO$_2$ nanofiller concentration. Electrical conductivity and dielectric properties of NaIO$_4$ salt-complexed blend PEO/PVP/Na+ electrolytes were analyzed as a function of TiO$_2$ nanofiller concentration.

Keywords: Complexed polymer blend electrolytes, NaIO$_4$ salt, TiO$_2$ nanofiller, Ionic and electrical conductivity, Dielectric properties.

INTRODUCTION

Solid polymer electrolytes (SPEs) based on poly(ethylene oxide) (PEO) and complexed with various alkali metal salts have been recognized as potential systems to employ them in solid state rechargeable batteries [1, 2].Amongst the accessible battery chemistries, sodium (Na)-based rechargeable batteries (SIBs) have recently captured much attention because they are environmentally friendly, non-toxic, low-cost and abundant materials [3, 4]. Substantial research efforts, development, and demonstration are currently in progress to replicate the performance of the well-established Li-ion batteries using sodium ion batteries. Compared to the traditional organic liquid electrolytes, SPEs offer enhanced safety, stability and thin-film manufacturability but their low ionic conductivity especially at room temperature has suppressed their development.

Polyethylene oxide (PEO)-based polymer electrolytes have been employed extensively for battery applications since Armand *et al.* demonstrated the feasibility of using PEO as a potential ion-conductive electrolyte [5]. PEO is one of the widely investigated host polymers used for synthesizing SPEs to employ in alkali metal ion-conducting batteries due to its high electrochemical stability, good solvation, complexation and ion dissociation abilities. Several researchers have reported about various sodium salt complexes of PEO-based polymer electrolytes for sodium ion battery applications [6-8]. However, based on previous reports, the semicrystalline nature of PEO at room temperature, subsequently limits its ionic conductivity. The most straightforward approach to overcome this problem is modifying the PEO matrix in order to decrease its degree of crystallinity. One of the most promising alternate choices of enhancing the amorphous phase in PEO- based electrolyte systems is blending of PEO with a suitable higher-amorphous polymer [9]. Polyvinyl pyrrolidone (PVP) has been identified as a compatible partner to PEO, which exhibits higher order of amorphosity. PVP has high glass transition temperature, mechanical and thermal stability, provided its carbonyl group (C=O) enables forming of different complexes of alkali metal ion salts in a wide range of concentrations. In particular, reinforcement of nano-sized materials with polymer electrolyte systems can modify their microstructural properties and enhance their conductivity properties. In the present report, we made an attempt to prepare NaIO$_4$ salt-complexed and 1 wt% nano-sized TiO$_2$ fillers-doped PEO/PVP blend based electrolyte systems, using solution casting technique. X-ray diffraction (XRD), micro Raman and transmission electron microscopy (TEM) were employed to characterize the microstructural properties of the polymer electrolytes.

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Impedance spectroscopy was used to study the ionic conductivity of the 1 wt% TiO_2 nanofiller-doped polymer blend electrolyte as a function of temperature.

EXPERIMENTAL

PEO and PVP of molecular weights of 5×10^6 and 3.6×10^5 respectively, were procured from Aldrich and employed without any further purification to prepare PEO/PVP solid state blend electrolytes. Sodium periodate salt ($NaIO_4$, Sigma Aldrich) and titanium dioxide nanopowder (TiO_2, Sigma Aldrich) were used as additives and methanol (Aldrich) was used as a solvent. Appropriate amounts of PEO and PVP polymers were dissolved in methanol solution, followed by mechanical stirring at room temperature for 15 hours to obtain uniform mixture of blend. In the meanwhile, 10 wt% of $NaIO_4$ salt was dissolved separately in methanol and the solution was added to the prepared viscous PEO/PVP polymer solution to obtain 'PEO/PVP/$NaIO_4$' polymer complex. Nano-sized TiO_2 powder (1 wt%) was dispersed in methanol separately, and the solution was sonicated for 30 min, and added to the 'PEO/PVP/$NaIO_4$(10 wt%)' electrolyte solution to prepare 'PEO/PVP/$NaIO_4$(10 wt%)/TiO_2(1 wt%)' nano composite electrolyte. The as-prepared viscous solutions were poured into polypropylene dishes and the solvent (methanol) was allowed to evaporate slowly at room temperature to harvest free-standing polymer electrolyte films of 150 μm thickness. All electrolyte films were vacuum-dried at 45°C to remove traces of methanol solvent and then kept in desiccators filled with silica gel desiccant for several hours before being characterized to avoid any traces of moisture.

The structural properties of the electrolytes were analysed by recording X-ray diffraction patterns (XRD) in the 2θ range of 10° – 80° with a constant step of 0.02^0, counting time 35s/step on a Bruker D8 Advance diffractometer with Cu Kα radiation and Lynx Eye detector. The Raman spectra were measured on a HORIBA Jobin Yvon LabRAM HR visible spectrometer equipped with a Peltier-cooled CCD detector. The laser beam was focused on a spot of about2 μmusing microscope optics and 633 nm line of He-Ne laser was used for excitation. The spectra were calibrated using the T_{2g} vibrational Raman line of Si at 520.7 cm^{-1}. TEM (HR STEM JEOL JEM 2100 acceleration voltage 80 - 200 kV, maximum resolution – 0.23 nm) measurements were carried out to estimate the size and distribution of doped nano-sized TiO_2 fillers in the matrices of polymer electrolytes. Solid polymer electrolyte films were sandwiched between two copper electrodes and ionic conductivity studies were carried out at room temperature by a.c. impedance measurements using Biologic potentiostat/galvanostat (SP – 200) in the frequency range of 1 Hz - 1 MHz.
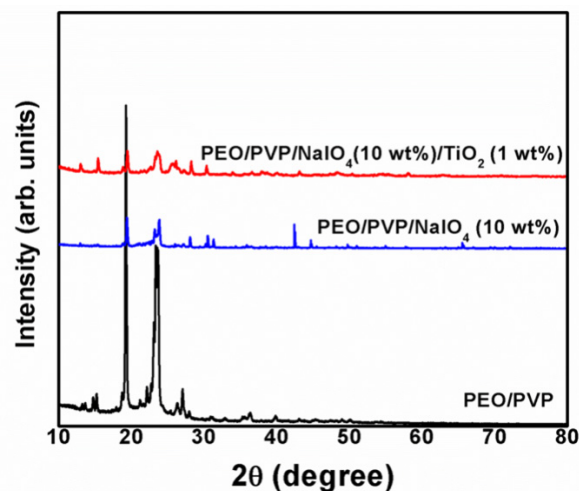
RESULTS AND DISCUSSION

Figure 1. X-ray diffraction patterns for various polymer electrolytes.

Figure 1 presents the X-ray diffractions patterns of pure PEO/PVP, 10 wt% $NaIO_4$ salt-complexed and 1 wt% TiO_2 nanofiller-doped blend electrolyte films. Significantly, the intensity of all crystalline peaks of PEO considerably decreases upon the addition of salt to the polymer blend, suggesting a decrease in the degree of crystallinity of the complexes. This could be due to the disruption of the semicrystalline structure of the film by salt [10]. When salt dissolves in the PEO/PVP polymer host, the interaction between PEO/PVP host matrix and $NaIO_4$ salt leads to an increase of the amorphous region. The relative intensities of sharp peaks of PEO at around 19.2^0 and 23.4^0 in the10 wt% $NaIO_4$ salt-complexed PEO/PVP blend decrease further as a result of doping of 1 wt% of TiO_2 nanofiller, which indicates a decrease of crystallinity in the electrolyte films. It can be attributed to the possible interaction between the polymer chains and TiO_2 nanofiller which leads to a decrease of the intermolecular interaction of polymer chains [11]. This facilitates the possible motion of the polymer chains in the amorphous domain and favors mobility enhancement of the charge carriers in the polymer electrolytes and leads to an increase in ionic conductivity.
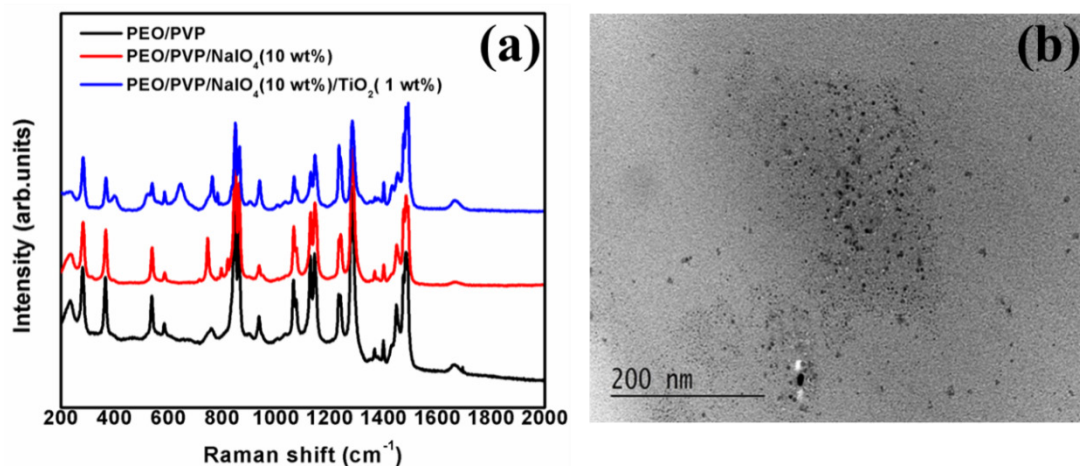
Figure 2. Raman spectra for different polymer electrolytes (a) and TEM image of 'PEO/PVP/NaIO$_4$ (10 wt%)/TiO$_2$ (1 wt%)' electrolyte (b).

Figure 2a shows the Raman spectra of pure, NaIO$_4$ salt-complexed and TiO$_2$ nanofiller-doped PEO+PVP blend electrolytes in the wavenumber region of 200 – 2000 cm^{-1}. Raman spectrum of pure blend displays bands at 759 cm^{-1}, 1229 cm^{-1}, 1231cm^{-1}, 1425 cm^{-1} and 1663 cm^{-1} corresponding to C-N vibration, C-N stretching and C-H bending vibrations of pure PVP, respectively. The characteristic principal bands at 354, 843, 857, 932 and 1062 cm^{-1} are observed corresponding to PEO [12]. The band of lower intensity present at 932 cm^{-1} is assigned to CO stretching mixed with CH$_2$ rocking vibration of PEO. The band is observed at 1480 cm^{-1} and can be attributed to in-phase bending of the CH$_2$ group of PEO [13]. This mode is active in the Raman spectrum and not active in the infrared spectrum. The bands observed at around 1275 cm^{-1} and 1235 cm^{-1} are assigned to the out-of-phase twisting for the CH group of PEO [14]. As a result of addition of 10 wt% of NaIO$_4$ salt to the PEO+PVP blended polymer film, the relative intensity of the spectral band at 1063 cm^{-1} due to C-O stretching and /or rocking modes of CH$_2$ vibrations, is dramatically reduced, which suggests the formation of a complex between sodium ions and PEO+PVP matrix. Further decrease in intensity of the spectral band at 1063 cm^{-1} is observed due to doping of 1 wt% of TiO$_2$ nanofiller. This indicates an increase in the strong interaction between the dissociated salt and the blended polymer matrix as a result of the presence of TiO$_2$ nanofiller and this process leads to a decrease of the semi-crystalline nature of polymer blend. From TEM measurements (Figure 2b) the average size of the nanofiller particles is found to be 10 nm and TiO$_2$ nanoparticles are observed to be uniformly distributed in the matrix of salt-complexed blend electrolytes.

Impedance spectroscopy is a promising method for the investigation of ionic conductivity of solid polymer electrolyte films. The 'PEO/PVP/NaIO$_4$ (10 wt%)/TiO$_2$(1 wt%)' electrolyte films were properly dried and impedance measurements were carried out at room temperature by sandwiching the electrolyte films between two copper electrodes. Figure 3a shows the variation of real and imaginary parts of impedance as a function of applied frequency for 'PEO/PVP/NaIO$_4$ (10 wt%)/TiO$_2$ (1 wt%)' electrolyte film. Figure 3b presents the complex impedance plane plot (Z′ *vs* Z″) for the TiO$_2$ nanofiller (1 wt%)-doped 'PEO/PVP/NaIO$_4$ (10 wt%)' electrolyte film at room temperature. The ionic conductivity of the sample is calculated by the equation $\sigma = \left({}^{t}\!/_{R_b * A} \right)$, where t and A are thickness and area of the electrodes, respectively. The complex impedance plot demonstrates a well-defined semicircle at intermediate frequencies, which can be explained by parallel combination of bulk resistance and bulk capacitance. This could be a result of the migration of ions and the immobile polymer chains, respectively [15]. The bulk resistance is obtained from the intercept of the semicircle at the high frequency side (1 MHz to 1 Hz) of the plot with the real axis. The estimated room temperature conductivity for 'PEO/PVP/NaIO$_4$ (10 wt%)' electrolyte film is 1.57×10^{-7} S/cm. As a result of the inclusion of 1 wt% of TiO$_2$ nanofiller, the corresponding room temperature conductivity increases to 4.56×10^{-7}S/cm. The enhancement of conductivity as a result of inclusion of TiO$_2$ nanofiller could be due to reduction in crystallinity of the polymer chains in the blend polymer electrolyte.
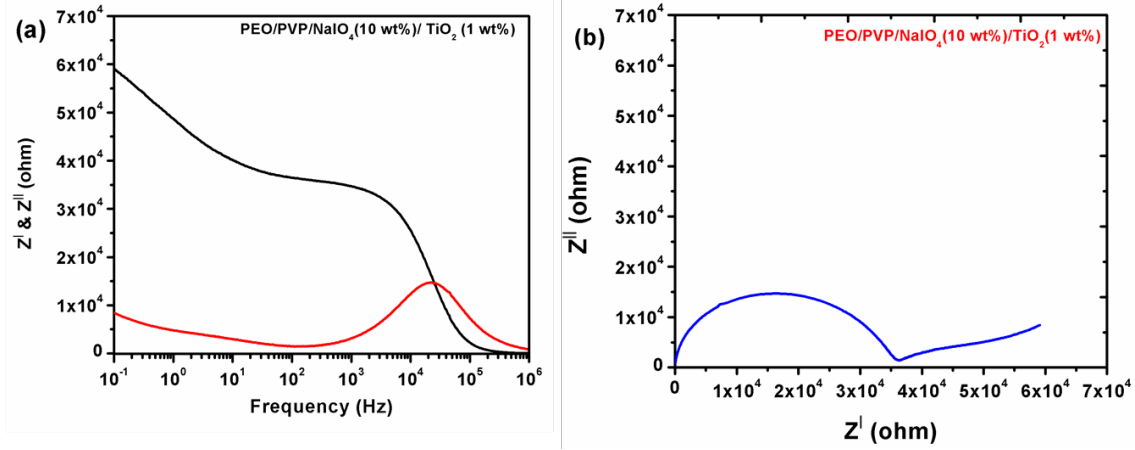
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Figure 3. Variation of real and imaginary parts of impedance as a function of frequency. (a) Cole-Cole plot; (b) for'PEO/PVP/NaIO$_4$ (10 wt%)/TiO$_2$ (1 wt%)' electrolyte film.
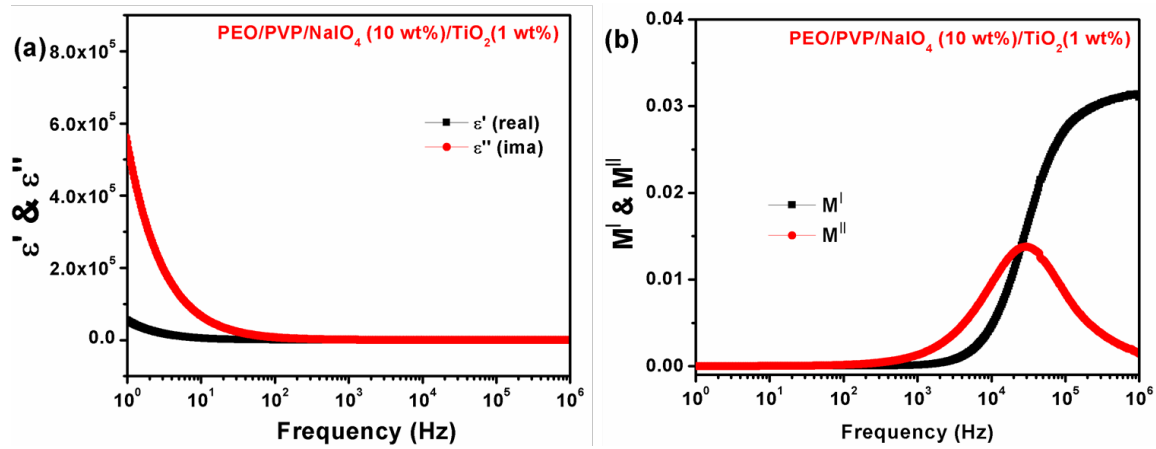

Figure 4. Variation of real and imaginary parts of dielectric permittivity (a) and Variation of real and imaginary parts of dielectric modulus (b) as a function of frequency for 'PEO/PVP/NaIO$_4$ (10 wt%)/TiO$_2$ (1 wt%)' electrolyte film.

This improves the capacity of sodium ion transport in the electrolyte film and hence improves the ionic conductivity of the polymer electrolyte film [16, 17].

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

$$\varepsilon' = \frac{Z_i}{\omega C_0 (Z_r^2 + Z_i^2)} \tag{1}$$

$$\varepsilon'' = \frac{Z_r}{\omega C_0 (Z_r^2 + Z_i^2)}, \tag{2}$$

where C$_o$ is the vacuum capacitance given by $\varepsilon_o A/d$, where ε_o is the permittivity of free space and is equal to 8.85×10^{-12} Fm^{-1}. The angular frequency is given

as $\omega = 2\pi f$, where f is the frequency of applied field. The real part of complex dielectric permittivity 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 cycle, to be returned to the electric field at the end of the cycle.

Figure 4a describes the frequency dependency of real and imaginary parts of dielectric permittivity of nano-composite 'PEO/PVP/NaIO$_4$(10 wt%)/TiO$_2$(1 wt%)' electrolyte. Significantly, nano-composite electrolyte films demonstrate relatively higher dielectric constant values in comparison to the pure and salt-complexed PEO/PVP electrolyte films. This can be explained by the capability of TiO$_2$ nanoparticles that leads to dissociation of undissociated salt/ion aggregates into free ions (anions) in the matrix of PEO/PVP/NaIO$_4$(10 wt%) electrolyte. It also supports the enhancement of dielectric constant values [18, 19]. The dielectric behavior could be easily explained by using the formulation of dielectric moduli. A complex electric modulus was used to investigate the conductivity relaxation phenomena. It suppresses the effects of

electrode polarization to give a clearer picture of electrical property inherited in the polymer electrolyte. Complex electric modulus can be calculated from the impedance data using the following relations:

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \qquad (3)$$

$$M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}. \qquad (4)$$

In the above expressions M', M'' and $\varepsilon', \varepsilon''$ are the real and imaginary parts of the electric modulus and dielectric constants, respectively. The frequency dependence of M' for 'PEO/PVP/NaIO$_4$ (10 wt%)/TiO$_2$ (1 wt%)' electrolyte film is shown in Figure 4b. It is obvious that M' reaches a maximum saturation at high frequency. This is ascribed to the fact that in the high frequency region the dielectric constant values of both pure and salt-complexed PEO/PVP blend electrolytes decrease to a minimum value and thus M' becomes maximum [20]. The imaginary part of modulus (M'') spectra, a distinct relaxation peak is observed which is related to the conductivity processes and it evidences that conduction in polymer electrolytes takes place through charge migration of ions between coordinated sites of the polymer along with the segmental relaxation of polymer [21]. In comparison to salt-complexed electrolytes, TiO$_2$-doped electrolyte films demonstrated better dielectric properties. For the 'PEO/PVP/NaIO$_4$ (10 wt%)/TiO$_2$ (1 wt%)' electrolyte film, relaxation frequency is found to be in a higher frequency region and the corresponding relaxation time is 3.4×10^{-5} sec.

CONCLUSIONS

PEO/PVP blend-based solid polymer blend electrolytes complexed with NaIO$_4$ salt were prepared by solution casting method. The modifications in microstructural properties of pure and salt-complexed PEO/PVP blend electrolytes were studied by XRD and micro Raman techniques. The decrease in intensity of characteristic peaks of PEO reveals the increase in amorphous nature, which supports the increase in ionic conductivity. The presence of well resolved vibrational bands in the micro Raman spectra, corresponding to ether oxygen groups ($C - O - C$) of PEO and carbonyl group of PVP, evidences for co-existence and miscibility of PEO and PVP polymers. The TiO$_2$ nanocomposite 'PEO/PVP/NaIO$_4$ (10wt%)/TiO$_2$ (1 wt%)' polymer blend electrolyte exhibits higher room temperature ionic conductivity of 4.56×10^{-7} S/cm. The increase in the dielectric constant upon addition of TiO$_2$ nanofiller exposes the increase of dissociated ions in the polymer blend matrix. The

distinctive peak in the M'' vs. frequency spectrum suggests that TiO$_2$-doped salt-complexed polymer electrolytes are potential ionic conductors.

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