SODIUM-ION-CONDUCTING POLYMER NANOCOMPOSITE ELECTROLYTE OF TIO_2/PEO/PVP COMPLEXED WITH $NAIO_4$

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Abstract

Investigation on Sodium-ion-conducting polymer nanocomposite electrolyte system based on the polymer blend of poly(ethylene oxide) and polyvinyl pyrrolidone (PEO/PVP), complexed with $NaIO_4$ salt and nanofilled with TiO_2 of average size ~10 nm, are presented in this report. The salt complexed polymer blend electrolytes were prepared in the form of dimensionally stable and free-standing thin films (150 µm) by conventional solution cast technique. In the polymer blend, the PEO proportion was 70 weight percent (wt%). In PEO/PVP polymer matrix, the salt $NaIO_4$ and the TiO_2 nanofiller were at concentration of 10 wt% and 1 wt%, respectively. 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 the size and distribution of the dispersed TiO_2 nanofillers. The complex impedance spectroscopy in the frequency range 1 Hz – 1 MHz at room temperature shows an enhanced ionic conductivity of the four-component PEO/PVP/$NaIO_4$/TiO_2 nanocomposite Sodium-ion-conducting polymer electrolyte system.

Keywords: *solid polymer electrolytes, complexed polymer blend electrolytes, nanocomposites, $NaIO_4$ salt, TiO_2 nanoparticles, ionic conductivity, electrical properties, dielectric properties*

1. INTRODUCTION

Solid polymer electrolytes based on poly(ethylene oxide) (PEO) and complexed with various alkali metal salts have been recognized as permissible systems to employ them in solid state rechargeable batteries and polymer electronics [1, 2]. At present, Sodium (Na) ion-conducting polymer electrolytes have attracted much attention because this metal exhibits proper complexity properties, is more environmentally friendly, less expensive, more abundant, easily distributed, easy to recycle and easier to extract than lithium [3-6]. Substantial research efforts are currently in progress to enhance the properties of the Na-ion-conducting polymer electrolytes and to search of novel Na-ion-conductor materials in order to satisfy the requirements for efficient electrolyte function and for other advanced applications.

PEO-based polymer electrolytes have been extensively investigated since the demonstration of the feasibility of using PEO as ion-conductive electrolyte [7]. Owing to its high electrochemical stability, good solvation, complexation and ion dissociation abilities, PEO is widely used as a host polymer for synthesizing alkali metal ion-conducting solid polymer electrolytes. Various Na salt complexes of PEO-based polymer electrolytes for Na^+ battery applications have been reported [8-10]. However, the semicrystalline nature of PEO at room temperature subsequently limits its ionic conductivity. This problem can be overcome by modifying the PEO matrix in order to decrease its degree of crystallinity. A successful way for enhancing the amorphous phase in PEO-based polymer electrolyte systems is the

blending of PEO with suitable high-amorphous polymer [11]. For this purpose, polyvinyl pyrrolidone (PVP) has been identified as a compatible partner to PEO. PVP has a relatively high glass transition temperature, mechanical and thermal stabilities. Importantly, the carbonyl group (C=O) in PVP enables forming of different complexes of alkali metal ion salts at wide range of concentrations.

Numerous investigations on Na-ion-conducting polymer blend electrolyte systems based on PEO/PVP blends complexed with different sodium salts have been reported [12-16]. Very recently, we have studied PEO/PVP complexed with the ionic compound sodium metaperiodate ($NaIO_4$) and the microstructural, optical, thermal, electrical and dielectric properties of this solid polymer electrolyte sysytem were thoroughly characterized [17]. The produced PEO/PVP/$NaIO_4$ complexes showed ion-electrolytic properties attractive for electrochemical applications. As a further step, one can try the reinforcement of these polymer electrolyte systems with nano-sized materials in order to modify their microstructural properties and enhance their conductivity properties. Hence, in the present work our investigations are aimed to prepare PEO/PVP blend based electrolyte system complexed with $NaIO_4$ salt and doped with nano-sized TiO_2 nanoparticles. In particular, TiO_2 nanoparticles were incorporated at concentration of 1 wt% in PEO(70 wt%)/PVP(30 wt%) polymer blend complexed with 10 wt% $NaIO_4$. The effect of the inclusion of TiO_2 nanoparticles in the PEO/PVP/$NaIO_4$ on the microstructural, Na^+ conductivity and dielectric properties of the resulting polymer electrolyte was studied by means of transmission electron microscopy (TEM), X-ray diffraction (XRD), micro Raman and electrochemical impedance spectroscopy.

2. MATERIALS AND METHODS

2.1. Materials

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. The salt Sodium metaperiodate ($NaIO_4$, Sigma Aldrich) and Titanium dioxide (TiO_2 nanopowder, Sigma Aldrich) were used as additives. All substances were dissolved in methanol (Aldrich). First, appropriate amounts of PEO and PVP polymers (w/w ratio 70% : 30% in present experiments) were dissolved in methanol, 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 separately dissolved in methanol and this solution was added to the prepared viscous PEO/PVP polymer solution to produce PEO/PVP/$NaIO_4$ polymer complex [17]. Nano-sized TiO_2 powder (1 wt%) was dispersed in methanol solution separately, which was sonicated for 30 minutes, and then added to PEO/PVP/$NaIO_4$ electrolyte solution to prepare PEO/PVP/$NaIO_4$/TiO_2 nanocomposite electrolyte. The as-prepared viscous solutions were poured into polypropylene dishes and the solvent (methanol) was allowed to evaporate slowly at room temperature to obtain free-standing polymer electrolyte films of thickness of 150 µm. The final products of polymer blend electrolyte films were dried at 45°C under vacuum at 10^{-3} mbar pressure to remove traces of methanol solvent. Then the films were kept in desiccators filled with silica gel desiccants for several hours before being characterized, to avoid any traces of moisture.

2.2. Methods

The structural properties of the obtained electrolyte films were analysed by recording X-ray diffraction (XRD) patterns in the 2θ range of 10° – 80° with a constant step 0.02°, counting time 35 s/step on a Bruker D8 Advance diffractometer with Cu Kα radiation and Lynx Eye detector. The Raman spectra were recorded by a HORIBA Jobin Yvon Labram HR visible spectrometer equipped with a Peltier-cooled CCD detector. He-Ne laser beam (wavelength 632.8 nm) was used for excitation. The laser beam was focused on a spot of about 10 µm using microscope optics. The spectra were calibrated using the Raman line of Si at 520.7 cm^{-1}. Transmission electron microscopy (TEM) was used to estimate the size and distribution of nano-sized TiO_2 fillers incorporated in the matrices of polymer electrolytes. The TEM measurements were performed with HR STEM JEOL JEM 2100 at acceleration voltage 100 kV (maximum resolution 0.23 nm). For measurement of the ionic conductivity, the solid polymer electrolyte films were sandwiched between two copper electrodes. The conductivity studies

were carried out at room temperature by complex electrical impedance spectroscopy in the frequency range of 1 Hz – 1 MHz, using BioLogic potentiostat/galvanostat (SP-200).

3. RESULTS AND DISCUSSION

From TEM measurements (Fig. 1), the average size of TiO_2 nanoparticles was found to be ca. 10 nm. The nanoparticles were observed to be nearly uniformly distributed within the $NaIO_4$ salt complexed PEO/PVP blend electrolytes.

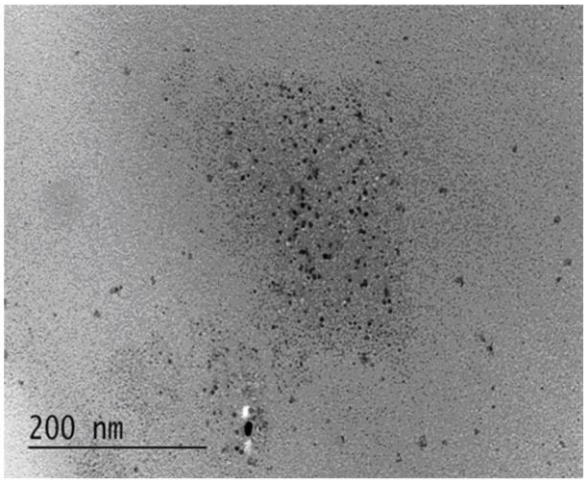


Fig. 1. TEM image of PEO/PVP solid polymer electrolyte complexed with $NaIO_4$ salt (10 wt%) and doped with TiO_2 nanoparticles (1 wt%).

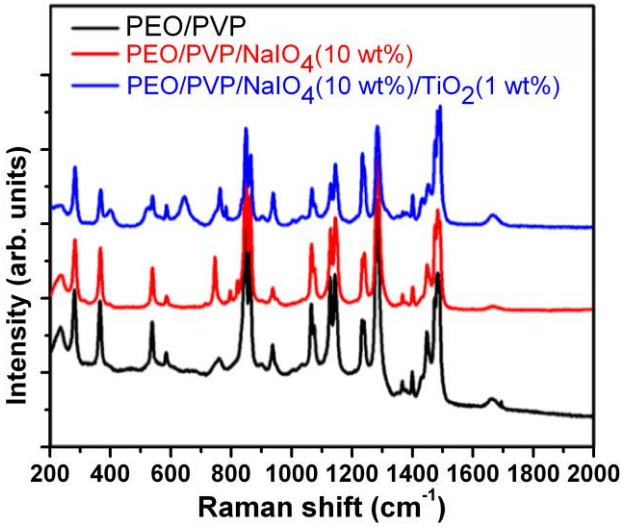


Fig. 2. Raman spectra for polymer blend electrolyte films: undoped PEO/PVP blend; PEO/PVP complexed with 10 wt% $NaIO_4$ and the same PEO/PVP/$NaIO_4$ electrolyte doped with 1 wt% TiO_2.

Figure 2 shows Raman spectra in the wavenumber region 200 – 2000 cm^{-1} recorded for undoped PEO/PVP blend, as well as PEO/PVP complexed with 10 wt% $NaIO_4$ and the same PEO/PVP/$NaIO_4$ electrolyte, but doped with 1 wt% TiO_2. The Raman spectrum of the undoped PEO/PVP polymer

blend displays spectral bands at 759, 1229, 1231, 1425 and 1663 cm^{-1} corresponding to C-N stretching and C-H bending Raman-active vibrations of pure PVP. The characteristic Raman bands corresponding to PEO [18] at 354, 843, 857, 932 and 1063 cm^{-1} are also observed. The Raman band at 932 cm^{-1} is assigned to CO stretching mixed with CH_2 rocking vibration of PEO. The band observed at 1480 cm^{-1} can be attributed to in-phase bending of the CH_2 group of PEO [19]. This mode is active in the Raman spectrum and not active in the infrared spectrum. The bands present at around 1275 cm^{-1} and 1235 cm^{-1} are assigned to the out-of-phase twisting for the CH group of PEO [20]. The presence of well resolved vibrational bands in Raman spectra, corresponding to ether oxygen groups (C–O–C) of PEO and carbonyl group of PVP, evidences the co-existence and miscibility of PEO and PVP polymers. As a result of the addition of 10 wt% $NaIO_4$ salt to the PEO/PVP polymer blend, 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 reduced, which suggests the formation of complex between sodium ions and PEO/PVP matrix. A further decrease in the intensity of the spectral band at 1063 cm^{-1} is observed due to doping of 1 wt% of TiO_2 nanoparticles. This indicates an increase of the interaction between the dissociated salt and the blended polymer matrix due to the addition of TiO_2 nanoparticles. This process leads to decrease of the crystalline nature of polymer blend.

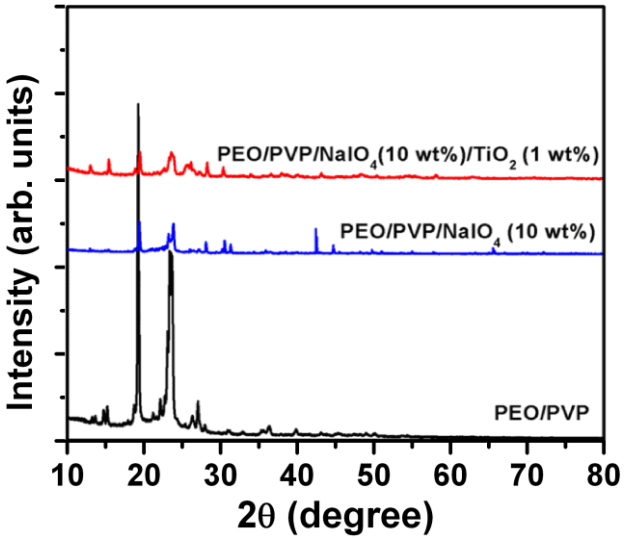


Fig. 3. X-ray diffraction patterns for polymer blend electrolyte films: undoped PEO/PVP blend; PEO/PVP complexed with 10 wt% $NaIO_4$ and the same electrolyte doped with 1 wt% TiO_2.

Figure 3 presents XRD patterns of undoped PEO/PVP, PEO/PVP complexed with 10 wt% $NaIO_4$ and the same electrolyte doped with 1 wt% TiO_2. Significantly, the intensity of the crystalline peaks of PEO at around 19.2° and 23.4° (the two strong peaks well seen in XRD patters of the undoped PEO/PVP blend) decreases considerably upon the addition of the salt $NaIO_4$ to the polymer blend, suggesting a decrease in the degree of crystallinity of the complexes. This is due to the disruption of the semicrystalline structure of the polymer blend by introduction of the salt [21]. Actually, the $NaIO_4$ salt is dissolved in the PEO/PVP polymer host. In fact, the interaction between $NaIO_4$ and the PEO/PVP polymer matrix leads to an increase of the amorphous regions in the latter.

The relative intensities of sharp characteristic crystalline peaks of PEO are further decreased as a result of doping of the same salt complexed PEO/PVP blend with 1 wt% of TiO_2 nanoparticles (Fig. 3), which indicates an additional decrease of crystallinity in the electrolyte films. This effect can be attributed to the possible interaction between the polymer chains and TiO_2 nanofillers which leads to decrease of the intermolecular interaction of polymer chains [22]. 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 increase of ionic conductivity.

The complex electrical impedance spectroscopy is a powerful method for the investigation of ionic conductivity of solid polymer electrolyte films. Figure 4a shows the variation of real (Z') and imaginary (Z'') parts of complex impedance for electrolyte film of the studied PEO/PVP/$NaIO_4$/TiO_2 system as a function of the frequency of the applied electric field. Figure 4b presents the corresponding complex impedance plane diagram, the Nyquist plot (Z' vs Z''). The Nyquist plot demonstrates 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 [23].

The ionic conductivity (σ) of the sample was calculated according to the relation $\sigma = t/(A*R_B)$, where t and A are the thickness of the sample and the area of the electrodes (i.e., the electrically-active area of the electrolyte film), respectively. The bulk resistance R_B was obtained from the intercept of the semicircle with the real axis (Z'). The estimated room temperature conductivity σ estimated by this way for PEO/PVP/$NaIO_4$ (10 wt%) electrolyte film was 1.57×10^{-7} S/cm [17]. As a result of the inclusion of 1 wt% of TiO_2 nanoparticles, the room temperature conductivity increases to 4.56×10^{-7} S/cm. The enhancement of conductivity as a result of inclusion of TiO_2 nanoparticles could be due to reduction in crystallinity of the polymer chains in blend polymer electrolyte, discussed above. Certainly, this improves the sodium ion transport in the polymer electrolyte and hence improves the ionic conductivity of the polymer electrolyte film [24, 25].

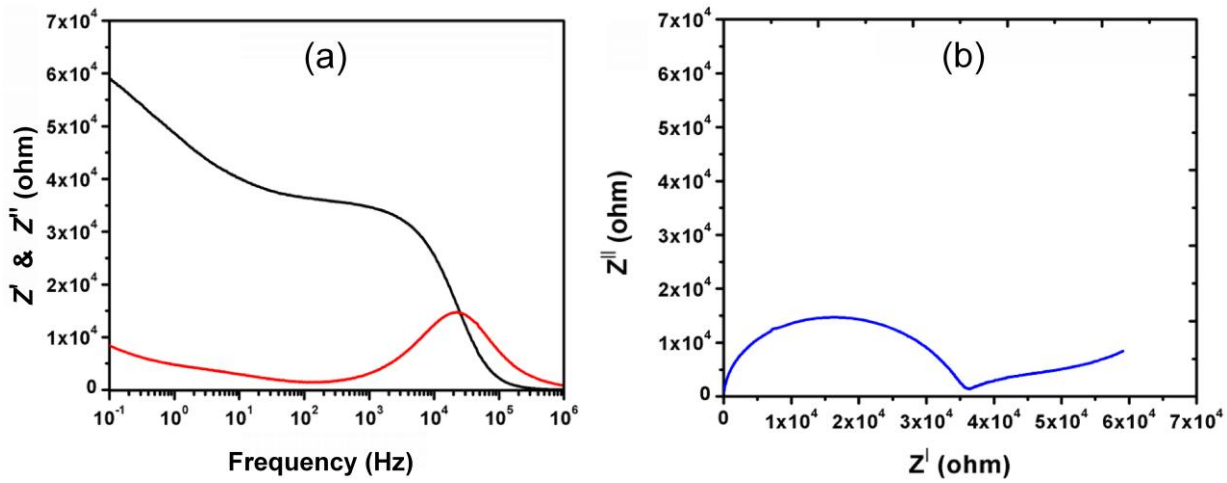


Fig. 4. (a) Frequency spectra of real (Z') and imaginary (Z'') parts of electrical impedance of a film of PEO/PVP/$NaIO_4$ (10 wt%)/TiO_2 (1 wt%) nanocomposite electrolyte measured at room temperature; (b) the corresponding Nyquist complex impedance plot.

Besides the ionic conductivity, the dielectric properties of the considered nanocomposite electrolyte are also of interest because they determine the ability of this dielectric material to store electrical energy. The dielectric properties can be estimated by measuring the dielectric permittivity of the material. In alternating electric field, the relative permittivity is a complex function and is defined by $\varepsilon^* = \varepsilon' - j\,\varepsilon''$. The real ($Z'$) and imaginary ($Z''$) parts of complex impedance are used for the evaluation of real (ε') and imaginary (ε'') parts of dielectric permittivity using the relations [26]:

$$\varepsilon' = -\frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} \quad (1)$$

and

$$\varepsilon'' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)} \quad , \qquad (2)$$

where C_o is the vacuum capacitance ($C_o = \varepsilon_o A/t$, where ε_o 8.85 × 10^{-12} F/m is a permittivity of free space). The angular frequency is given as $\omega = 2\pi f$, where f is the frequency of applied electric field. The real part of complex dielectric permittivity ε' has the same significance as that of the ordinary dielectric constant of the material.

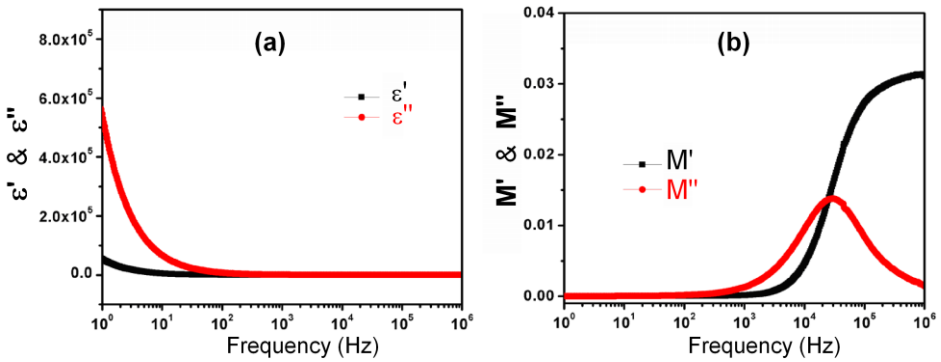


Fig. 5. Frequency spectra of real and imaginary parts of dielectric permittivity (a) and real and imaginary parts of electric modulus (b) for PEO/PVP/$NaIO_4$ (10 wt%)/TiO_2 (1 wt%) nanocomposite polymer electrolyte film.

Figure 5a presents the frequency dependency of the real and imaginary parts of dielectric permittivity of the studied nanocomposite PEO/PVP/$NaIO_4$/TiO_2 electrolyte. Significantly, this material demonstrates a relatively high dielectric permittivity. In comparison to undoped PEO/PVP and $NaIO_4$ salt complexed PEO/PVP polymer electrolytes [17], PEO/PVP/$NaIO_4$/TiO_2 exhibits an enhanced dielectric response. This can be explained by the capability of TiO_2 nanoparticles to do a dissociation of undissociated salt/ion aggregates into free ions (anions) in the matrix of PEO/PVP/$NaIO_4$ electrolyte [27, 28].

The dielectric behavior of the studied nanocomposite PEO/PVP/$NaIO_4$/TiO_2 electrolyte can be complementary characterized by the frequency spectra of its complex electric modulus M^*. The latter can be used to characterize the conductivity relaxation phenomena. The real (M') and imaginary (M'') parts of the electric modulus can be calculated from the dielectric permittivity [29]:

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \qquad (1)$$

and

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

The frequency dependence of M' for the studied PEO/PVP/$NaIO_4$/TiO_2 electrolyte film is shown in Fig. 5b. It is seen that M' reaches saturation at high frequency. This is ascribed to the fact that in high-frequency region the dielectric permittivity values of both PEO/PVP and PEO/PVP/$NaIO_4$ electrolytes decrease to a minimum value. For the imaginary part of modulus (M'' spectra), a distinct relaxation peak is observed. This feature 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 [30]. In comparison to PEO/PVP/$NaIO_4$

electrolytes [17], the TiO_2-doped PEO/PVP/$NaIO_4$ nanocomposite electrolyte considered here demonstrated better dielectric properties and a lower relaxation frequency corresponding to relaxation time of 3.4×10^{-5} s (Fig. 5b).

4. CONCLUSIONS

PEO/PVP blend based solid polymer blend electrolytes complexed with $NaIO_4$ salt have been doped with 1 wt% nanoparticles of TiO_2 with a size of 10 nm. The modifications in microstructural, ion-conducting and dielectric properties of the PEO/PVP/$NaIO_4$ polymer electrolyte system were studied. Raman spectroscopy confirms the salt-polymer-nanofiller interactions. Upon addition of TiO_2, an increase of amorphous nature of the solid polymer electrolyte system was established. This effect supports the increase of the ionic conductivity. The PEO/PVP/$NaIO_4$/TiO_2 polymer blend nanocomposite Na^+-conducting electrolyte exhibits a room temperature ionic conductivity that is about three times higher than that of the undoped PEO/PVP/$NaIO_4$ electrolyte. The increase in the dielectric permitivity upon addition of TiO_2 nanofillers exposes the increase of dissociated ions in the polymer blend matrix. These improved properties indicate that the considered PEO/PVP/$NaIO_4$/TiO_2 polymer nanocomposite electrolyte is a promising ionic conductor.

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