Nanocomposites of TiO_2-Doped PEO/PVP/$NaIO_4$ Polymer-Ion Complexes for Na^+ Electrolyte Applications

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Abstract. The ion conductivity of TiO_2-doped nanocomposite polymer electrolytes based on two-polymer blend of poly(ethylene oxide) (PEO) and polyvinyl pyrrolidone (PVP), being complexed with $NaIO_4$ at concentration of 10 wt%, is studied. The polymer-ion complexes PEO/PVP/$NaIO_4$ are doped with small amount (up to 3 wt%) TiO_2 nanoparticles of average size ~ 10 nm. Thin films of PEO/PVP/$NaIO_4$/TiO_2 nanocomposite polymer electrolytes with a thickness 150 µm are formed using conventional solution-cast technique. The ionic conductivity of these nanocomposites is measured as dependent on the concentration of the included TiO_2 nanoparticles by applying complex electrical impedance spectroscopy in the frequency range 0.1 Hz – 1 MHz. The obtained results indicate that the Na^+-ion conductivity of PEO/PVP/$NaIO_4$/TiO_2 nanocomposite polymer electrolytes is enhanced with the addition of TiO_2 nanoparticles. Such nanocomposites are attractive for Na^+ electrolyte applications.

Keywords: Polymer-ion nanocomposite electrolytes, TiO_2 nanoparticles, $NaIO_4$, ionic conductivity, electrical impedance spectroscopy.

1. INTRODUCTION

Nowadays, the nanocomposites produced from polymers by inclusion of nanoparticles (NPs) have been attracted significant interest in both academic and scientific sectors. In such advanced materials having often unusual, but very useful properties, the presence of unique ‘polymer-nanofiller’ interfaces can tailor the type of conformations, thereby modifying in desirable and controlled way the key properties of the nanocomposites. The same apply to the polymer nanocomposite electrolytes (NCPEs) that have been gaining vital significance in view of their improved properties that match the outstanding technological achievements (Yuan et al., 2014, Lee et al., 2015, Deng et al., 2016, Suthanthiraraj et al., 2016, Zhan et al., 2018)

In particular, the incorporation of NPs into polymer matrix of NCPEs may substantially improve their ionic conductivity (Johan et al., 2011, Suthanthiraraj et al., 2016, Koduru et al., 2018, Johnsi et al., 2018, Sharma et al., 2019, Koduru et al., 2019). This occurs through interfacial interactions in a length scale of nanometer range dimensions between polymer chains and inorganic nanofillers having high surface area (Bertasi et al., 2014, Suthanthiraraj et al., 2016, Kumar et al., 2016, Koduru et al., 2018, Koduru et al., 2019).

In the present work, our investigations are focused on a NCPE system based on a blend of poly(ethylene oxide) (PEO) and polyvinyl pyrrolidone (PVP) complexed with the ionic compound sodium metaperiodate ($NaIO_4$). This polymer-ion system showed ion-electrolytic properties attractive for electrochemical and other applications (Koduru et al., 2017, Hadjichristov et al., 2019). The PEO/PVP/$NaIO_4$ polymer electrolyte was doped with nano-sized TiO_2 at concentration of 1, 2 and 3 wt%, and the effect from TiO_2

nanofillers on the ionic conductivity of PEO/PVP/$NaIO_4$/TiO_2 polymer-ion complexes was studied by means of complex electrical impedance spectroscopy.

2. MATERIALS AND METHODS

2.1 Materials

PEO and PVP (Fig. 1) of molecular weights of 5×10^6 and 3.6×10^5, respectively, Titanium dioxide (TiO_2) nanopowder and the salt Sodium metaperiodate ($NaIO_4$) (all from Sigma Aldrich) were used to prepare the polymer blend electrolytes. The mean size of TiO_2 NPs was 10 nm.

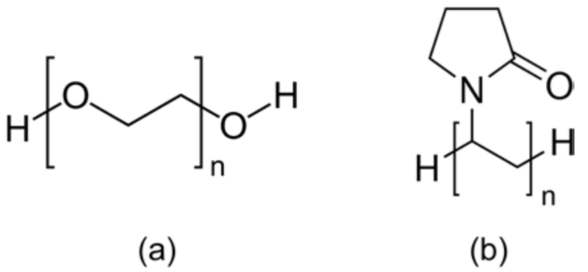

Fig. 1 Molecular structure of: (a) poly(ethylene oxide) (PEO); (b) polyvinyl pyrrolidone (PVP).

The procedure of preparation of NCPEs PEO/PVP/$NaIO_4$/TiO_2 follows the one described by (Koduru et al. 2018). Methanol solution of TiO_2 was added to the methanol solution of the salt-complexed polymer blend solution. The incorporation of TiO_2 NPs in the polymer blend solution was achieved drop-by-drop. The concentration of the salt $NaIO_4$ in the PEO/PVP/$NaIO_4$/TiO_2 nanocomposite blend solution was kept at 10 wt%. TiO_2 NPs were included in the polymer blend at three concentrations: 1, 2 and 3 wt%.

2.2 Methods

For ionic conductivity measurements, the produced solid polymer electrolyte films of PEO/PVP/$NaIO_4$/TiO_2 NCPEs of a thickness 150 μm were sandwiched between two copper electrodes. The conductivity studies were carried out at room temperature by complex electrical impedance spectroscopy in the frequency range 0.1 Hz – 1 MHz, using potentiostat/galvanostat BioLogic SP-200. The voltage amplitude applied to the polymer electrolyte films was fixed at 0.5 V_{RMS}. The ionic conductivity (σ) of the samples was calculated according to the relation:

$$\sigma = \frac{t}{AR_B} \quad (1)$$

Here t and A are the thickness of the samples and the area of the electrodes, respectively. The bulk resistance R_B of the samples was determined through impedance spectra.

3. RESULTS AND DISCUSSION

As an example, Fig. 2(a) shows the real (Z') and imaginary (Z'') parts of complex electrical 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. Fig. 2(b) presents the corresponding complex impedance plane diagram, the Nyquist plot (Z' vs Z'').

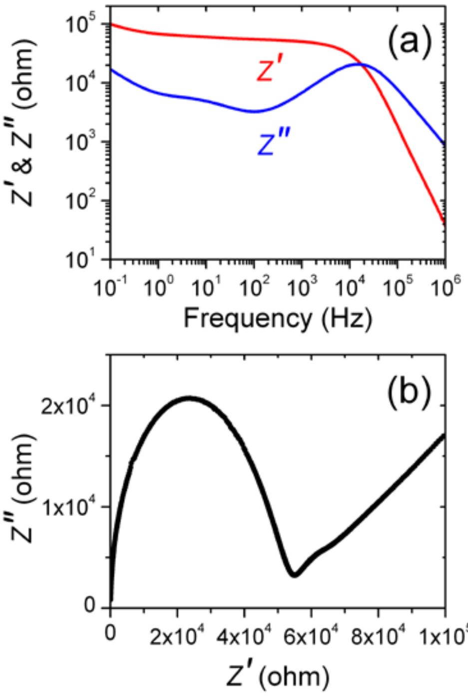

Fig. 2 Data obtained by electrical impedance spectroscopy: (a) real (Z') and imaginary (Z'') parts of complex electrical impedance Z measured for PEO/PVP/$NaIO_4$/TiO_2 NCPE containing 1 wt% TiO_2 NPs; (b) the corresponding Nyquist complex impedance plot relevant to data given in (a).

The Nyquist plot demonstrates a well-defined semicircle at intermediate frequencies, which can be relevant to parallel combination of bulk resistance and bulk capacitance (Barsoukov et al., 2005). This could be a result from the migration of ions (Papke et al., 1982, Barsoukov et al., 2005).

The bulk resistance R_B of the TiO_2-doped $PEO/PVP/NaIO_4$ films was determined as the intercept of the semicircle with the real axis (Z'). Then the ionic conductivity (σ) of TiO_2-doped $PEO/PVP/NaIO_4$ was calculated by Eq. (1). The room-temperature σ of the studied NCPEs (Fig. 3) was considerably higher than that of undoped $PEO/PVP/NaIO_4$ electrolyte ($\sigma = 1.57 \times 10^{-7}$ S/cm reported by Koduru et al. (2017)). This shows the large effect from the inclusion of TiO_2 NPs. By increasing concentration of TiO_2 from 1 wt% to 3 wt%, σ of TiO_2-doped $PEO/PVP/NaIO_4$ increases nonlinearly (Fig. 3).

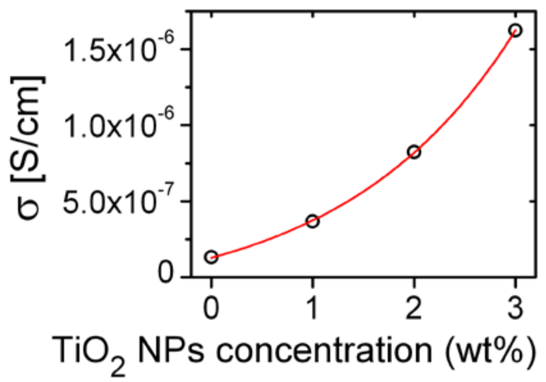

Fig. 3 Ionic conductivity (σ) of the studied $PEO/PVP/NaIO_4/TiO_2$ NCPEs vs the concentration of TiO_2 NPs.

The conductivity enhancement due to inclusion of TiO_2 NPs results from the reduction in crystallinity of the polymer matrix of polymer-ion electrolyte $PEO/PVP/NaIO_4$. Due to high interfacial interactions between the organic moieties of both polymers and TiO_2 NPs (Suthanthiraraj et al., 2016) the sodium ion transport in the polymer electrolyte is improved and hence the ionic conductivity is enhanced (Carlier et al., 2001, Lin et al., 2012), Suthanthiraraj et al., 2016).

4. CONCLUSIONS

The change in ion-conducting properties of PEO/PVP blend-based solid polymer electrolytes complexed with $NaIO_4$ salt was studied upon addition of TiO_2 NPs of a size ~ 10 nm. As compared to undoped electrolyte $PEO/PVP/NaIO_4$, Up to TiO_2 concentration 3 wt%, these nanofillers lead to increase of the Na^+-ion conductivity of $PEO/PVP/NaIO_4/TiO_2$ NCPEs. This agrees with other reported results regarding NCPEs and does characterize the TiO_2-doped $PEO/PVP/NaIO_4$ NCPE system as a promising ionic conductor.

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