Synergetic effect of TiO$_2$ nano filler additives on conductivity and dielectric properties of PEO/PVP nanocomposite electrolytes for electrochemical cell applications

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Abstract. Sodium-ion conducting PEO/PVP blend based solid polymer electrolyte films complexed with NaIO$_4$ salt and nano-sized TiO$_2$ fillers are fabricated by employing a solution casting technique for Na-ion battery applications. Measurements of X-ray diffraction (XRD) and thermogravimetric analysis (TGA) are carried out to investigate the crystallinity and thermal stability of the solid polymer electrolytes. Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM) studies are performed to understand the modifications in surface morphological features and to evaluate the size and distribution of dispersed nano-sized TiO$_2$ fillers. The room temperature ionic conductivities of polymer electrolyte films are investigated by impedance analysis in the frequency range 1 MHz - 1 Hz. The nano-sized TiO$_2$ (3 wt%) filled composite electrolyte of ‘PEO/PVP/NaIO$_4$ (10 wt%)’ demonstrates a maximum room temperature conductivity of 9.82 $\times$ 10$^{-6}$ S/cm. The influence of TiO$_2$ filler on conductivity and dielectric properties are presented in this report.

1. Introduction

Although lithium ion batteries (LIBs) have been recognized as a promising energy storage devices [1-3] their high cost, less abundance, environmental impact and safety limitations impede the widespread implementation of lithium insertion materials in future battery technologies [4-8]. Therefore, there is urgent necessity to search for alternative energy storage system technology capable of complementing the current Li-ion battery technology. 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 [9, 10]. Substantial efforts of research, development, and demonstration are currently in progress to replicate the performance of well-established Li-ion batteries using sodium ion batteries [11-13]. Solid polymer electrolytes (SPEs) have attracted intensive studies during the past decades due to their potential applications in various advanced devices including metal ion batteries, supercapacitors, and stretchable actuators. 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 [14-16].

Polyethylene oxide (PEO) based polymer electrolytes have been employed extensively for battery applications since Armand et al. have demonstrated the feasibility of using PEO as a potential ion conductive electrolyte [17]. 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 [18-25]. Several researchers have reported about various sodium salt complexes of PEO based polymer electrolytes for sodium ion battery applications [26, 27]. However based on previous reports, the semicrystalline nature of PEO at room temperature, subsequently limits its ionic conductivity [28]. 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 suitable higher amorphous polymer [29-32]. 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 stabilities, provided its carbonyl group (C = O) enables to form different complexes of alkali metal ion salts at 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 [33]. Several researchers have reported about micro-or nano-sized ceramic fillers doped sodium-ion polymer electrolytes, such as ZrO2, BaTiO3, Sb2O3, Al2O3 or silica nanoparticles [34, 35]. In the present report, NaIO4 salt complexed and nano-sized TiO2 fillers doped PEO/PVP blend based electrolyte systems are prepared by the solution cast technique and investigated the influence of nano-sized TiO2 fillers on conductivity and dielectric properties of salt complexed PEO/PVP blends solid polymer electrolytes.

2. Experimental

PEO and PVP of molecular weights of 5 X 10^6 and 3.6 X 10^5 respectively, were procured from Aldrich and employed without any further purification to prepare PEO/PVP solid state blend electrolytes. Sodium periodate salt (NaIO4, Sigma Aldrich) and Titanium dioxide nano powder (TiO2, 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 and followed by mechanical stirring at room temperature for 15 hours to obtain uniform mixture of blend. In the meanwhile, 10 wt% of NaIO4 salt was dissolved separately in methanol solution and added to the prepared viscous PEO/PVP polymer solutions to obtain ‘PEO/PVP/NaIO4’ polymer complex. Nano-sized TiO2 powder (3 wt%) was dispersed in methanol solution separately, which was sonicated for 30 minutes, and added to ‘PEO/PVP/NaIO4(10 wt%)’ electrolyte solution to prepare ‘PEO/PVP/NaIO4(10 wt%)/TiO2(3 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. All electrolyte films were, vacuum dried at 45°C to remove traces of methanol solvent and kept in dessiccatos filled with silica gel desiccants 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 0.02°, counting time 35s/step on a Bruker D8 Advance diffractometer with Cu Kα radiation and Lynx Eye detector. SEM (Philips 515 digitalized) images were monitored to study the effect of complexation with NaIO4 salt and additive nano-sized TiO2 filler on surface morphological features of blend electrolytes. TEM (HR STEM JEOL JEM 2100
acceleration voltage 80 - 200 kV, maximum resolution – 0.23 nm) measurements were carried out to estimate size and distribution of doped nano-sized TiO₂ fillers in the matrices of polymer electrolytes. Thermal stabilities of solid polymer electrolytes were studied by TGA carried out under nitrogen gas atmosphere by using TGA Q50 TA operating in the temperature range 303 K to 1073 K and at a heating rate of 10 °C/min. 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 MHz - 1 Hz.

3. Results and Discussion

3.1. Microstructural properties

![Figure 1. X-ray diffraction patterns of pure, salt complexed and nano-sized TiO₂ fillers doped electrolytes.](image)

As evidenced from XRD measurements, PEO/PVP blend electrolyte displays intense diffraction peaks at 2θ = 19.30 and 2θ = 23.40 corresponding to characteristic crystalline peaks of PEO (as shown in figure 1) which originates from the ordering of polyether side chains and strong intermolecular interaction between PEO chains through the hydrogen bonding [36]. The intensity of characteristic diffraction peaks of PEO is noticed to be decreased as a result of addition of NaIO₄ (10 wt%) salt and 3 wt% of nano-sized TiO₂ filler. It evidences for further increase of amorphous portion in the matrix of the electrolytes. This favours for enhancement of mobility of the charge carriers in the polymer electrolytes and leads to increase of ionic conductivity [37]. As evidenced from SEM studies, the surface of pure PEO/PVP blend electrolyte (figure 2(a)) is observed to be relatively rough and composed with micro-void and cracks, when compared to the polymer blend composite, which signifies the crystalline nature. The formation of micro-voids over the surface of films is due to rapid evaporation of the solvent during the preparation of polymer blends. Apparently, surface smoothness
of nano-composite electrolyte films is further increased as a result of incorporating nano-sized TiO\textsubscript{2}
filler in the matrix of salt complexed polymer electrolyte (figure 2(b)).

![Figure 2. (a, b) SEM images of electrolytes, (c) TEM image of TiO\textsubscript{2} nano particles doped salt complexed electrolyte, (d) TGA profiles of different electrolytes.](image)

It evidences for further increase of amorphous portion in the matrix of salt complexed nano composites, which favours for the enhancement of ionic conductivity [38-40]. From the TEM image (figure 2(c)) the average size of nano fillers is found to be 10 nm and dispersed nano particles are observed to be uniformly distributed in the matrix of salt complexed blend electrolytes. The nano-composite polymer electrolytes should have good thermal stability at high temperatures to meet the criteria for employing them as solid electrolytes in sodium ion batteries. Figure 2d represents TGA curves for pure PEO/PVP blend (black line), NaIO\textsubscript{4}(10 wt\%) salt complexed PEO/PVP blend (red line) and nano composite ‘PEO/PVP/NaIO\textsubscript{4}(10 wt\%)’ (blue line) electrolytes. The first weight loss region at lower temperatures (< 100 °C) originates from the loss of water absorbed during the loading of samples and a major weight loss region at higher temperatures (> at above 300 °C) is associated with the decomposition of pure PEO and nano composite matrices [41]. Evidently, nano-sized TiO\textsubscript{2} filler (3 wt\%) doped PEO/PVP/NaIO\textsubscript{4}(10 wt\%) polymer electrolyte is demonstrated appreciable thermal stability.
3.2. Conductivity and Dielectric properties

**Figure 3.** Impedance plots for PEO/PVP (black line), ‘PEO/PVP/NaIO₄(10 wt%)’ (red line) and ‘PEO/PVP/NaIO₄(10 wt%)/TiO₂ (3 wt%)’ electrolytes (inset of figure).

**Figure 4.** $\varepsilon'$ vs frequency plots for ‘PEO/PVP/NaIO₄(10 wt%)’ (blue line) and PEO/PVP (black line), salt complexed PEO/PVP (red line) electrolytes (inset of figure).
The ionic conductivity of the samples is calculated by the equation, \( \sigma = \frac{t}{R\times A} \), where \( t \) and \( A \) represent thickness and area of the electrodes, respectively. 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 (as shown in figure 3). The estimated room temperature conductivity of pure PEO/PVP blend electrolyte is \( 2.24 \times 10^{-9} \) S/cm and associated ionic conductivity for ‘PEO/PVP/NaIO\(_4\) (10 wt%)’ electrolyte increased to \( 1.57 \times 10^{-7} \) S/cm. As a result of inclusion of nano-sized TiO\(_2\) (3 wt%) of filler, the intercept of higher end of semicircle corresponding to ‘PEO/PVP/NaIO\(_4\) (10 wt%)’ electrolyte on the \( Z' \) - axis tends to move towards lower value as shown in inset of figure 3. The corresponding room temperature conductivity of nanocomposite electrolyte is increased to \( 9.82 \times 10^{-6} \) S/cm. The increase in conductivity as a result of inclusion of TiO\(_2\) nano fillers could be due to reduction in crystallinity of the polymer chains in blend polymer electrolyte and improve the capacity of sodium ion transport in the electrolyte film and hence improve the ionic conductivity of the polymer electrolyte film [42, 43]. Dielectric materials are recognized as a media that have an ability to store electrical energy. This property of dielectric materials can be estimate by measuring is the permittivity or di-electric constant of the material. In alternating electric fields the relative permittivity exhibits 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 [44]

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

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

Here \( C_0 \) is the vacuum capacitance and given by \( \varepsilon_0 A/d \), where \( \varepsilon_0 \) is a permittivity of free space and is equal to \( 8.85 \times 10^{-12} \) 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 \( \varepsilon' \) 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 4 describes the variation dielectric constant values of nano-composite ‘PEO/PVP/NaIO\(_4\)(10 wt%)/TiO\(_2\)(3 wt%)’ (blue line) electrolyte. Significantly, nano-composite electrolyte films demonstrate relatively higher dielectric constant values in comparison to pure and salt complexed PEO/PVP electrolytes films (as shown in inset of figure 4). This may be due to capability of TiO\(_2\) nano particles leads to dissociation of undissociated salt/ion aggregates into free ions (anions) in the matrix of PEO/PVP/NaIO\(_4\)(10 wt%) electrolyte and supports for the enhancement of dielectric constant values [45].

4. Conclusions
In the present report, NaIO\(_4\) salt complexed and nano-sized TiO\(_2\) fillers doped free standing PEO/PVP blend electrolyte films were prepared by using conventional solution cast technique. XRD studies revealed the increase of amorphous portion in the matrix of TiO\(_2\) nano composite blend electrolytes. Increase of surface smoothness of blend electrolytes upon doping TiO\(_2\) nano fillers confirmed the enhancement of degree of amorphicity in the blend electrolytes. Relatively, TiO\(_2\) nano composite blend electrolytes showed good thermal stability. The nano-composite ‘PEO/PVP/NaIO\(_4\)(10 wt%)/TiO\(_2\)(3 wt%)’ electrolyte demonstrated higher room temperature ionic conductivity of \( 9.82 \times 10^{-6} \) S/cm. The increase in the dielectric constants as a result of addition of 10 wt% of salt and 3 wt% TiO\(_2\) nano fillers evidenced for increase in number of mobile ions and their mobility in the matrix of PEO/PVP blend electrolytes.

Acknowledgments:
The authors gratefully acknowledges the INERA EU project Research Potential "Research and Innovation Capacity Strengthening of ISSP-BAS in Multifunctional Nanostructures" (FP7 REGPOT-
2012-2013-1) support for his participation at the INERA Workshop “Membrane and Liquid Crystal Nanostructures” (MELINA 2016), 3-6 September, 2016, Varna, Bulgaria.

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