Complex electrical impedance and dielectric spectroscopy of Na⁺-conducting PEO/PVP/NaIO₄ solid polymer electrolyte with incorporated nano-sized Graphene Oxide

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Abstract. Being of significant interest as electrolytic materials for mini-mobile energy storage devices, we have studied solid-state polymer-based electrolytic systems – nanocomposites, in particular, NaIO₄ salt-complexed poly(ethylene oxide) (PEO)/polyvinyl pyrrolidone (PVP) polymer blends doped with nano-sized Graphene Oxide (GO). The GO monolayer average size and thickness were 5 μm and 2 nm, respectively. In the PEO/PVP polymer blend, the PEO:PVP ratio was 70:30 weight percent (wt.%), the concentration of the salt sodium metaperiodate NaIO₄ was 10 wt.%. The nano-sized GO was dispersed with concentration of 0.2; 0.4 and 0.6 wt.%. Thin films (150 μm) of GO/PEO/PVP/NaIO₄ Na⁺ ion-conducting nanocomposites were produced by solution casting technique. They were studied by complex electrical impedance and dielectric spectroscopy in the frequency range 0.1 Hz – 1 MHz of the applied electric field. The room-temperature ion conductivity, the complex dielectric function, dielectric loss and AC conductivity of GO/PEO/PVP/NaIO₄ at various concentration of GO were obtained, and the effect from the GO nanofillers was estimated.

1. Introduction

The studies on solid polymer electrolytes have received great attention due to their electrical applications in electrochemical devices such as solid-state rechargeable batteries and supercapacitors, electrochromic display devices, vehicular systems, and polymer electronics and mechatronics, and etc. [1]. Such ion-conducting materials were prepared using various polymer hosts for achieving high conductivity and thermal and mechanical stability [2]. PEO (polyethylene oxide)-based polymer electrolytes are of current interest for high energy density and high power Li⁺ and Na⁺ batteries due to the easy formation of complexes of PEO with alkali salts, that provide high mobility of charge carriers, stable chemical properties, etc. The polymer nanocomposite electrolytes are even more important (and will be in the future). At present, their production technology is well developed, dealing with various nano-sized inorganic and organic fillers [3–9]. Thus, one can obtain advanced and prospective multifunctional nanocomposite materials with improved and unique useful properties having versatile applications [6,9].

Recently, we have synthesized and investigated novel Na⁺-ion-conducting solid-state polymer electrolytes based on blends of poly(ethylene oxide) (PEO) and polyvinyl pyrrolidone (PVP), as complexed with the inorganic ionic compound sodium metaperiodate (NaIO₄). The produced...
PEO/PVP/NaIO₄ materials showed enhanced ion-electrolytic and dielectric properties attractive for electrochemical and other applications [10,11]. In the present work, we studied PEO/PVP/NaIO₄ electrolytic system, but doped with nano-sized Graphene Oxide (GO). Such nano-structural modification of PEO/PVP/NaIO₄ solid-state polymer electrolytes [12] aims at a suitable enhancement of their ion conductivity and dielectric properties that are of importance for the applications in energy storage systems. In the work [12] we have examined the microstructural properties and ionic conductivity of PEO/PVP/NaIO₄ doped with 0.4 wt.% nano-sized GO, as depending on the concentration of the salt NaIO₄. In our present study, PEO(70 wt.%)/PVP(30 wt.%) polymer blend was complexed with 10 wt.% NaIO₄, and nano-sized GO were incorporated in the polymer blend at concentration ranging from 0.2 to 0.6 wt.%. The effect from the inclusion of GO on the electrical conductivity and dielectric properties of GO/PEO/PVP/NaIO₄ nanocomposite solid polymer electrolytes was estimated by means of complex electrical impedance spectroscopy and dielectric spectroscopy. Our previous investigation of GO/PEO/PVP nanocomposites produced by the same technology indicated that at concentration 0.6 wt.% of GO these materials have shown excellent microstructural, thermo-mechanical and conductivity properties [13]. The same applies to the GO/PEO/PVA/NaIO₄ polymer nanocomposite electrolytes we have recently studied [14].

2. Experimental

The details to materials, samples’ preparation and experiments using complex impedance spectroscopy are given elsewhere [13] but may be reported briefly here. The salt Sodium metaperiodate (NaIO₄) and nano-sized Graphene Oxide (GO) were used as additives in the PEO/PVP polymer blend (PEO:PVP = 70:30 wt.%). This composition was found to be an optimized composition [10]. The mean size of GO was ca. 5 μm, their thickness was ~ 2 nm (given from manufacturer). The concentration of the salt NaIO₄ in the GO/PEO/PVP/NaIO₄ nanocomposites was 10 wt.%. The nano-sized GO was included in the polymer blend at three concentrations: 0.2; 0.4 and 0.6 wt.%. Thin films (150 μm) of PEO/PVP/NaIO₄ and GO-doped PEO/PVP/NaIO₄ polymer complexes were produced by solution casting technique. The complex electrical impedance spectra of the studied nanocomposites were measured over the frequency range 0.1 Hz –1 MHz of the applied electric field (voltage 0.5 V RMS), using impedance-meter BioLogic SP-200, at ambient temperature (in our case, 27°C).

3. Results and discussion

Figure 1 reports the frequency spectra of the real ($Z'$) and imaginary ($Z''$) parts of complex electrical impedance of the studied GO/PEO/PVP/NaIO₄ nanocomposites, and figure 2(a) presents the corresponding Nyquist plots (complex impedance plane diagrams, $Z''$ vs $Z'$). For all our samples, the Nyquist plots demonstrate well-defined semicircles attributed to the presence of parallel combination of bulk resistance and bulk capacitance. The ionic conductivity ($\sigma$) of the samples was calculated according to the relation $\sigma = d/(A*R_b)$, where $d$ 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. $R_b$ is the bulk resistance of the samples. Intercept of the low-frequency spike at the $Z'$ axis of the Nyquist plot gives the value of $R_b$. Figure 2(b) shows the values of $\sigma$ for GO/PEO/PVP/NaIO₄ as depending on the concentration of incorporated GO. Up to 0.6 wt.% content of GO, $\sigma$ is increasing with increasing concentration of GO and reaches value of $3 \times 10^{-6}$ S/cm at 0.6 wt.% GO. As compared to GO-free PEO/PVP/NaIO₄ electrolyte [10], this is an enhancement of about 20 times.
Figure 1. The frequency spectra of the real ($Z'$) and imaginary ($Z''$) parts of complex electrical impedance of the studied GO/PEO/PVP/NaIO$_4$ system composed with nano-sized GO incorporated at concentrations 0; 0.2; 0.4 and 0.6 wt.%. The impedance spectra of PEO/PVP blend at the same compositional ratio (PEO:PVP = 70:30 wt.%) are also given for comparison (dashed lines). All spectra were recorded at room temperature upon the same experimental conditions.

Figure 2. (a) The Nyquist complex impedance plots for GO/PEO/PVP/NaIO$_4$ at various concentration of GO (data from figure 1). The insert: the Nyquist plot for PEO/PVP blend. (b) Room-temperature ionic conductivity ($\sigma$) of the studied polymer electrolyte nanocomposites GO/PEO/PVP/NaIO$_4$ vs the concentration of the nano-sized GO. The insert: $\sigma$ – linearly scaled.

The enhancement of ionic conductivity resulting from the incorporated GO is due to the well known effect of high interfacial interactions of the nanodopants with the polymer chains, in our case – with certain functional groups of both PEO and PVP [13,14]. It is well known, that such interactions at the nano-level (in nanometer ranges) lead to improvement in both amorphicity and flexibility of the polymer matrix. This effect leads to increase in the segmental motion of the polymer chains in the amorphous phase regions in the polymer matrix of nanocomposite polymer electrolytes, thereby the charge carriers’ mobility is enhanced, thus increasing the ionic conductivity [6,13–16]. Reasonably, the nature of GO plays significant role for the increase of Na$^+$-ion conductivity. The large number of oxygen-containing functional groups in GO, such as carboxylic acid, epoxy and hydroxyl, certainly improve the charge carrier mobility and, thereby, the ionic conductivity.

The spectra of the real ($\varepsilon'$) (figure 3a) and imaginary ($\varepsilon''$) (figure 3b) parts of the dielectric permittivity of the studied GO/PEO/PVP/NaIO$_4$ nanocomposites were calculated from their impedance data. They are defined as follows:

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

where $C_0$ is the vacuum capacitance ($C_0 = \varepsilon_0 A/d; \varepsilon_0 = 8.85 \times 10^{-12} \text{ F/m}$ is the permittivity of free space), $\omega = 2\pi f$ is the angular frequency, where $f$ is the frequency of applied electric field. The dielectric properties are of interest because they determine the ability of the dielectric material to store
electrical energy. $\varepsilon'$ is the lossless permittivity that represents the ability of the dielectric material to store energy during each charging cycle and returned to the electric field at the end of the cycle. $\varepsilon''$ represents the dielectric loss (the energy dissipated by conduction).

**Figure 3.** (a) The frequency-dependent real (a) and imaginary (b) parts of the dielectric function of GO/PEO/PVP/NaIO$_4$ NCPEs containing 0; 0.2; 0.4 and 0.6 wt.% GO nanofillers. The spectra of the dielectric function of PEO/PVP blend at the same compositional ratio (PEO:PVP = 70:30 wt.%) are also given for comparison (dotted lines). The inserts: the frequency-dependent increment of the dielectric function $\Delta\varepsilon'$ and $\Delta\varepsilon''$ (see the text).

It is known that the increase of dielectric permittivity at low frequency is related to the electrode polarization effect, which occurs due to the formation of electric double layers that are built up by the free charges at the electrolyte/electrode interface [17]. In our case, most important is that the GO-doped PEO/PVP/NaIO$_4$ exhibits a considerably enhanced dielectric response as compared to the undoped electrolyte PEO/PVP/NaIO$_4$ (figure 3). At concentration 0.6 wt.% of GO, the enhancement of the dielectric permittivity $\varepsilon'$ (dielectric constant) and the dielectric loss $\varepsilon''$ of GO-doped PEO/PVP/NaIO$_4$ over given frequency ranges can reach a factor of 60 and 12, respectively, as compared to the undoped PEO/PVP/NaIO$_4$ electrolyte (see the inserts in figure 3 (a) and (b), respectively).

Using the calculated $\varepsilon$ spectra (figure 3), by expressions [18,19]

\[
\sigma'_{AC} = 2\pi f \varepsilon_0 \varepsilon''
\]
(2)

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]
(3)

we obtained the real part of AC conductivity ($\sigma'_{AC}$) (figure 4a) and the dielectric loss tangent ($\tan \delta$) (figure 4b), respectively, for the studied GO/PEO/PVP/NaIO$_4$ nanocomposite solid polymer electrolytes. The gradual increase of $\sigma'_{AC}$ toward to the higher frequencies is usual behaviour for similar solid polymer electrolyte systems and signifies the increment of displacement currents owing to attenuation of capacitive reactance [20]. The enhancement in $\sigma'_{AC}$ by doping with GO (figure 4a) is attributed to increased conduction pathways resulting from the structure modification by the GO nanodopants. This effect is well known for the nanocomposite solid polymer electrolytes [6,21,22]. As compared to the undoped electrolyte PEO/PVP/NaIO$_4$, the enhancement of $\sigma'_{AC}$ at 0.6 wt.% GO is the same as the increment $\Delta\varepsilon''$ shown in the insert in figure 3(b).
Figure 4. (a) The frequency dependence of the real part of AC conductivity for the studied nanocomposite electrolyte systems at room temperature, as calculated by Eq. (2); (b) The dielectric loss tangent $\tan \delta$ as a function of the frequency, as calculated by Eq. (3) for the studied GO/PEO/PVP/NaIO$_4$ nanocomposite electrolytes at various concentration of the incorporated GO.

The quantity $\tan \delta$ is directly related to the dielectric losses and is relevant to the electrode polarization. The peak of $\tan \delta$ frequency spectrum corresponds to dielectric relaxation frequency. The frequency-dependent loss tangent calculated for the studied nanocomposite solid polymer electrolyte system GO/PEO/PVP/NaIO$_4$ (figure 4b) clearly shows a shift of $\tan \delta$ peak towards higher frequency by doping of PEO/PVP/NaIO$_4$ with GO. Simply, this means a reduction of the dielectric relaxation time of the polymer chains, i.e., the doping of PEO/PVP/NaIO$_4$ with GO leads to enhanced mobility of polymer chains. As mentioned above, this occurs due to the improvement in the amorphous phase and flexibility of the polymer network owing the high interfacial interactions of the nanodopants with the polymer chains, a fact commonly reported for this kind of nanocomposite solid polymer electrolytes [6,21,22] and found, in particular, by microstructural investigation of the GO/PEO/PVP/NaIO$_4$ nanocomposite electrolytes studied here [12]. This effect actually supports the mobility enhancement of the charge carriers in these electrolytic materials, thus increasing the ionic conductivity.

4. Conclusion
The results obtained using data collected by impedance spectroscopy and further by dielectric spectra, indicate that the studied GO-doped PEO/PVP/NaIO$_4$ nanocomposite electrolytes have improved ionic-electrolytic and dielectric properties. Upon addition of nano-sized GO (in our case, up to 0.6 wt.%), the Na$^+$-ion conductivity, AC conductivity and dielectric permittivity of these polymer electrolyte materials are enhanced. The increased value of electrical conductivity suggests an improvement in amorpicity and flexibility of GO/PEO/PVP/NaIO$_4$ salt-complexed blend electrolyte system due to high interfacial interaction of nano-sized GO with the matrix of the polymer PEO/PVP blend, as well as an increase in segmental motion of polymer chains – a fact that was evidenced by behaviour of the dielectric tangent loss spectra. As compared to the undoped electrolyte PEO/PVP/NaIO$_4$, at 0.6 wt.% GO the ion conductivity and the AC conductivity of GO-doped PEO/PVP/NaIO$_4$ were enhanced by a factor of 20 and 12, respectively, and the enhancement of the real part of dielectric permittivity can reach a factor of 60. Thus, these Na$^+$-ion-conducting nanocomposites with GO nanodopants are attractive for use in sodium ion secondary batteries, electrochemical applications, in organic electronics, as well as in sensors and mechatronics.

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