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Dielectric Study of Hot-Pressed Nanocomposite Polymer Electrolytes[1]

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Abstract—Ion-conducting nanocomposite polymer electrolyte films based on poly(ethylene oxide)–$NaPO_3$ 3 : 1 with up to 15 wt % of SiO_2 have been prepared using recently developed hot-press technique instead of conventional solution cast method. With 7 wt % of SiO_2, the film conductivity has been enhanced by an order of magnitude. The materials have been characterized by Fourier transform infrared spectrometry and thermogravimetric analysis. For the composition with the highest conductivity, the temperature dependences of ionic mobility, mobile ions concentration, ionic transference number, and ionic drift velocity have been determined. Dielectric constant and dielectric loss have been measured. The conductivity enhancement has been discussed on the basis of existing theories of dielectrics.

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The development of new ion conducting polymeric electrolytes including solid polymer electrolytes (SPE) and nanocomposite polymer electrolytes (NCPE) is one of the important areas of research in the field of energy technologies. NCPEs are promising electrolyte systems to fabricate all solid-state electrochemical devices (batteries, fuel cells, supercapacitors, memory devices, electrochromic displays, etc). In order to prepare NCPEs, nanoparticles like TiO_2, SiO_2, Al_2O_3, ZrO_2 and others are incorporated in solid polymeric matrices. The idea of dispersing nanosized inert ceramic fillers into the host polymeric matrix was proposed originally by Weston and Steele [1]. Such nanocomposite polymer electrolytes are advantageous over conventional solid polymer complexes: they are mechanically stronger, exhibit higher ionic conductivity and better electrolyte interfacial stability [2–9]. The high ionic conductivity of NCPEs is due to the high fraction of amorphous phase in the polymeric host material. Polymer electrolyte films are conventionally formed via the solution-cast or sol-gel routes. However, recently, an alternate hot-press technique has been developed for preparation of completely dry polymer electrolyte films [7–14]. The sodium salt electrolyte has several advantages over other alkali compounds, in particular over lithium salts. Sodium salt is more readily available and cheaper than lithium salts [10, 13, 15]. In this contribution, we report on materials characterization and dielectric studies of Na^+ ion conducting hot-pressed nanocomposite polymer electrolytes based on poly(ethylene oxide)–$NaPO_3$ (75 : 25) containing up to 15 wt % of SiO_2. The important characteristics of the prepared materials were determined as function of temperature: ionic drift velocity, ionic mobility, mobile ion concentration, and ionic transference number.

EXPERIMENTAL

The AR grade chemicals: poly(ethylene oxide) PEO (M_w = 10^5 MW, Aldrich), $NaPO_3$ (> 98%, Merck), and SiO_2 (> 99.8%, particle size cca. 8 nm, Sigma) were used for preparation of NCPEs. The samples were coded as follows: $(1 - x)$[75PEO : $25NaPO_3$] : $xSiO_2$ ($0 < x < 15$ wt %), meaning that the composition of PEO and $NaPO_3$ (3 : 1) was modified with a certain fraction of SiO_2. The details of NCPEs preparation by hot-press method are to be found in our previous communication [12]. The materials properties were elucidated by means of FTIR (Shimadzu-8400) and TGA (SDT Universal). The ionic mobility was

[1] The text was submitted by the authors in English.

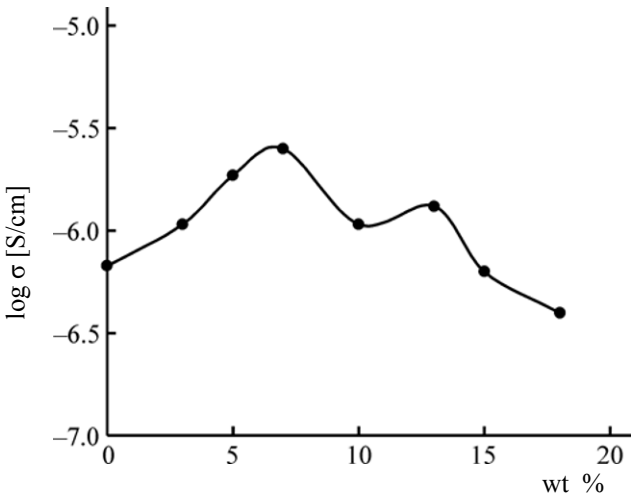


Fig. 1. The nanocomposite ionic conductivity as function of the SiO_2 nanofiller content (adopted from [12]).

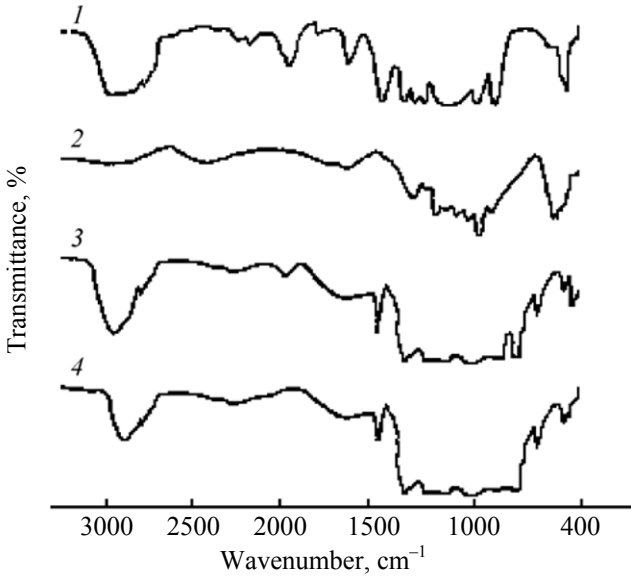


Fig. 2. FTIR spectra of pure PEO (*1*), pure $NaPO_3$ (*2*), the hot-pressed SPE host (*3*), and the SiO_2-filled nanocomposite (*4*). Details of the samples composi-tion are to be found in the Experimental section.

determined at different temperatures taking advantage of the following equation:

$$\mu = d^2/(V\cdot\tau)\ [\mathrm{cm^2\ V^{-1}\ s^{-1}}] \quad (1)$$

with d, sample thickness; V, the applied external dc potential; τ, time of flight. The time of flight τ was determined directly, employing the dc polarization transient ionic current (TIC) technique by using an *x–y–t* recorder (Graphtec WX 2300-1L, Japan) [16]. The mobile ions concentration n was evaluated at different temperatures from the conductivity σ and ionic mobility μ data using the known relation:

$$\sigma = n\cdot q\cdot\mu\ [\mathrm{cm^{-3}}] \quad (2)$$

with q, charge of the mobile ion. The ionic transference number (t_{ion}) was evaluated at different temperatures using dc polarization technique via the following equation:

$$t_{ion} = 1 - (I_e/I_T) \quad (3)$$

with I_e, electronic current and I_T, total current through the [SS // NCPE // SS] cell [16].

The ionic drift velocity (v_d) of the mobile ion was evaluated at different temperatures using the following well-known equation:

$$v_d = l_T/(A\cdot n\cdot q) \quad (4)$$

with A, cross-sectional area of the polymeric film.

The dielectric constant (ε^*) and dielectric loss (ε_l) of NCPE were determined using the equations:

$$\varepsilon^* = \frac{Z_i}{\omega C_0(Z_r^2 + Z_i^2)} \quad (5)$$

and

$$\varepsilon_l = \frac{Z_r}{\omega C_0(Z_r^2 + Z_i^2)} \quad (6)$$

with $C_0 = \varepsilon_0\cdot A/d$ (ε_0, the permittivity of vacuum) and $\omega = 2\pi f$ (f, frequency in Hz).

RESULTS AND DISCUSSION

The ionic conductivity of nanocomposite polymer electrolytes (NCPE) was determined at different filler concentrations at room temperature (Fig. 1). Two conductivity maxima were revealed with 7 and 13 wt % of SiO_2. The conductivity enhancement was of about an one order of magnitude ($\sigma \approx 2.5\times10^{-6}$ S/cm) at 7 wt % of the nanosized SiO_2 filler, as compared with the unfilled analog. That NCPE film composition, 93 [75PEO : 25$NaPO_3$] : 7SiO_2 was therefore considered the optimum conducting composition. The increase in conductivity was likely due to the decrease of crystallinity degree and the effect of the interaction between the mobile charge double layer with the Lewis acid-base O/OH sites [17, 18].

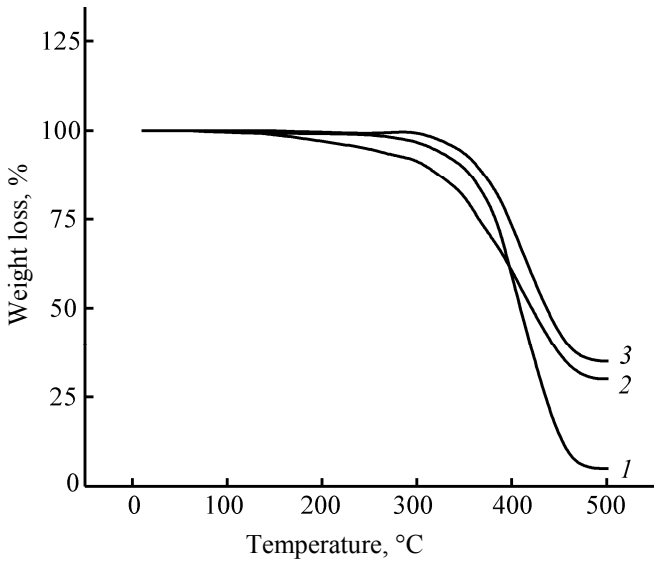


Fig. 3. TGA curves of (*1*) pure PEO, (*2*) the hot-pressed SPE host, and (*3*) the SiO_2-filled nanocomposite. Details of the samples composition are to be found in the Experimental section.

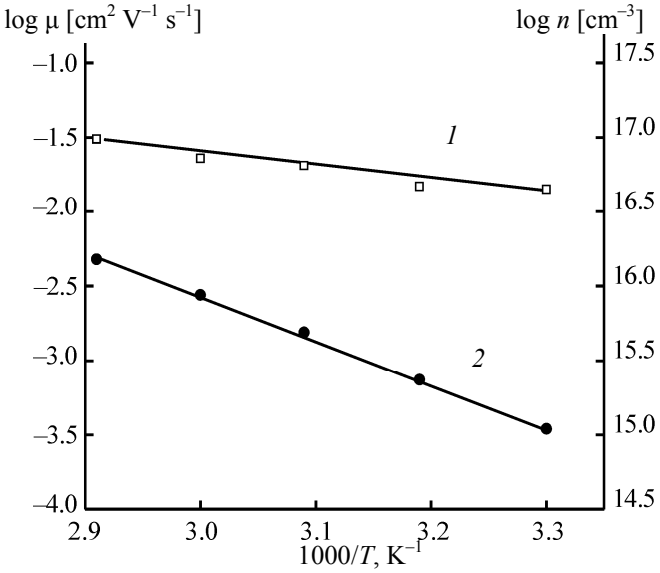
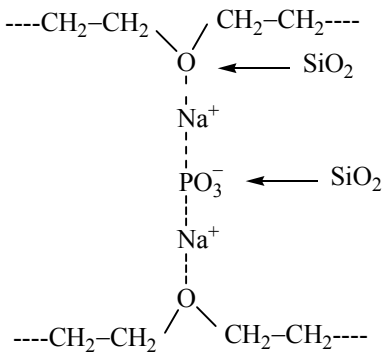


Fig. 4. (*1*) Ionic mobility and (*2*) concentration of the mobile ions of the SiO_2-filled nanocomposite, as function of temperature. Details of the sample composition are to be found in the Experimental section.

The prepared materials were characterized by XRD, SEM, DSC, FTIR, and TGA; XRD, SEM, and DSC data on the hot-pressed NCPEs was reported previously [12]. Fig. 2 shows FTIR spectra of the pure SPE host, 75PEO:25$NaPO_3$, its components, PEO and $NaPO_3$, and the NCPE modified with the optimized amount of the filler, 93(75PEO : 25$NaPO_3$) : 7SiO_2. In the SiO_2-filled composites, two types of cation-cation and cation-anion cross-linking were possible, as illustrated in the scheme below:



The observed vibrational spectra changes were seemingly due to the complexation of Na^+ ion to the ether oxygen of PEO. As clearly seen from the spectra, the C–O–C (around 1100 cm^{-1}) and C–H (around 2900 cm^{-1}) stretching bands became narrower after addition of the salt. The changes of symmetrical and asymmetrical ether vibrational bands confirmed the complexation of sodium ions to PEO, as suggested in the literature [19–21].

The TGA curves of pure PEO, pure SPE host, 75PEO : 25$NaPO_3$, and the NCPE modified with the optimized amount of the filler, 93(75PEO : 25$NaPO_3$) : 7SiO_2, are shown in Fig. 3. The total weight loss in the case of pure PEO was larger as compared to both the pure SPE host and the NCPE. In particular, the total weight loss in the cases of NCPE and of SPE host was of about 65% and 70%, respectively, being of about 95% in the case of pure PEO. The thermal stability of pure polymer was improved by addition of SiO_2 nanofiller. Figure 4 shows the ionic mobility μ and the mobile ions concentration n in the case of 93(75PEO : 25$NaPO_3$) : 7SiO_2 as function of temperature. The temperature behavior of the above-mentioned characteristics obeyed the Arrhenius law as expressed by Eqs. (7) and (8).

$$\mu(T) = 42.9\exp\left(-\frac{0.21}{kT}\right)\ [\mathrm{cm^2\ V^{-1}\ s^{-1}}], \qquad (7)$$

$$n(T) = 7.73\times10^{25}\exp\left(-\frac{0.66}{kT}\right)\ [\mathrm{cm^{-3}}] \qquad (8)$$

with 0.21 and 0.66 (eV) are the energies assigned to the thermally activated processes of mobile ions migration E_m and formation E_f, respectively. Both ionic mobility and the mobile ions concentration

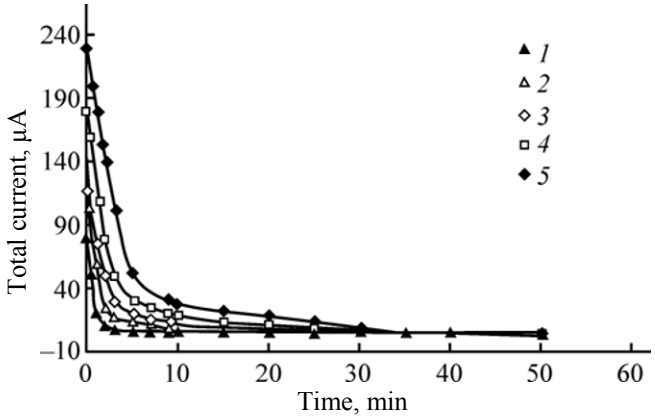


Fig. 5. Kinetics of the I_T change in the case of the SiO_2-filled nanocomposite, at different temperatures, °C: (*1*) 30, (*2*) 40, (*3*) 50, (*4*) 60, and (*5*) 70. Details of the sample composition are to be found in the Experimental section.

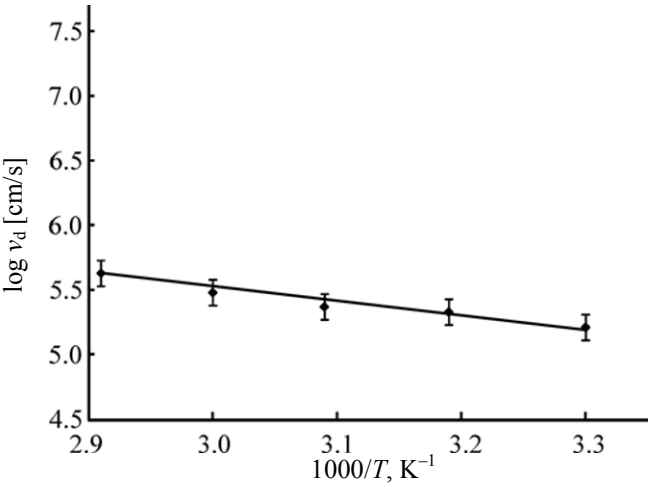


Fig. 6. Ionic drift velocity of the SiO_2-filled nanocomposite, as function of temperature. Details of the sample composition are to be found in the Experimental section.

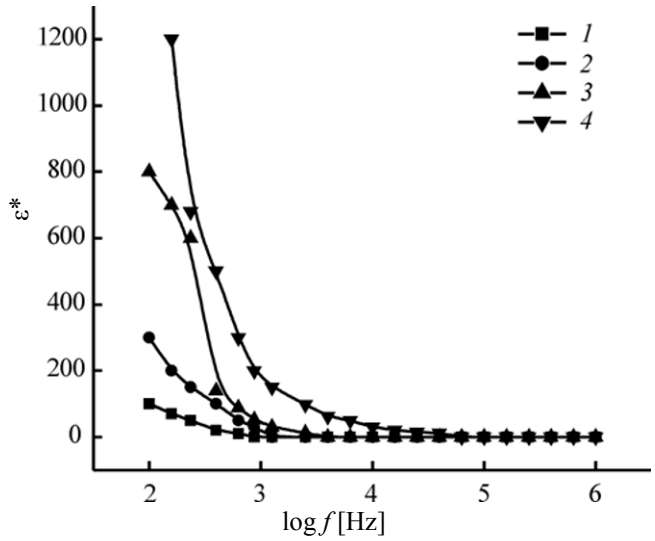


Fig. 7. Dielectric constant of the SiO_2-filled nanocomposites, as function of frequency, Hz: (*1*) 0, (*2*) 3, (*3*) 5, and (*4*) 7. Details of the sample composition are to be found in the Experimental section.

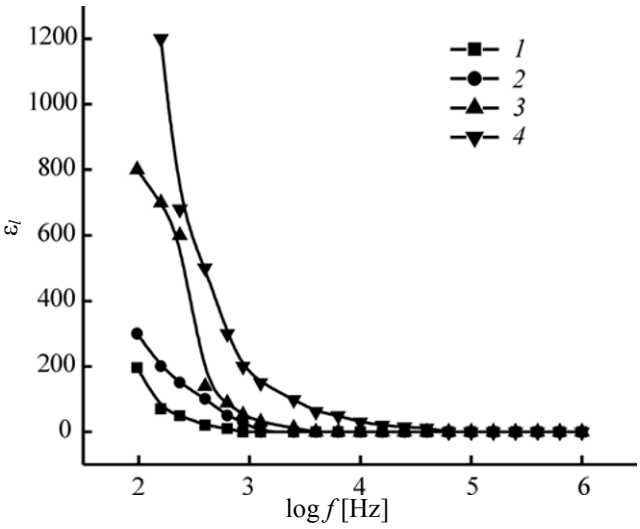


Fig. 8. Dielectric loss of the SiO_2-filled nanocomposites, as function of frequency, Hz: (*1*) 0, (*2*) 3, (*3*) 5, and (*4*) 7. Details of the sample composition are to be found in the Experimental section.

increased with temperature due to more efficient Na^+ mobile ions formation and to more of the available conduction paths. The ionic transference number t_{ion} the SiO_2-filled composite was evaluated as function of temperature as well. Fig. 5 shows kinetics of I_T changes at different temperatures. From the results it followed that t_{ion} was of 0.95 at all the temperatures; hence, the charge transport in the studied system was of predominantly ionic nature with negligible contribution of electronic one. The ionic drift velocity v_d was determined at different tempera-tures in the case of the 93(75PEO : 25$NaPO_3$) : 7SiO_2 nanocomposite; as shown in Fig. 6, the drift velocity followed the Arrhenius law as well [Eq. (9)].

$$v_d(T) = 3.89\times10^8 \exp\left(-\frac{0.20}{kT}\right) \text{ [cm s}^{-1}\text{]} \qquad (9)$$

with 0.20 eV, the drift energy E_d of the thermally activated process. Theoretically, v_d should be directly proportional to μ at fixed external dc electric field. This was clearly indicated and verified in the case of the studied system by the almost identical E_d and E_m reflecting the two separate thermally activated

processes (Figs. 4 and 6). The increase in ionic conductivity of NCPEs could also be understood from dielectric studies. Figures 7 and 8 show the frequency dependence of dielectric constant ε* and dielectric losses ε_l in the case of the 93(75PEO : 25$NaPO_3$) : 7SiO_2 nanocomposite. As could be clearly noted, both dielectric constant and dielectric losses increased sharply due to the electrode polarization and the effect of mobile charges, as reported in come previous contributions [22, 23]. The explanation of the effect could be as follows. At low frequencies, there was enough time for the charges to build-up at the electrode–electrolyte interface before the applied field changed direction. At higher frequencies, rapid reversal changes of the electric field prevented the build-up at the interface. The addition of the SiO_2 nanofiller caused increase of dielectric constant and dielectric losses. That was indicative of increasing the number of mobile ions in the polymeric electrolytes, being as well responsible for the overall increase in the conductivity of the studied nanocomposite.

To conclude, novel Na^+-conducting nanocomposite polymer electrolyte was prepared by the hot-press process. In terms of the conductivity, the nanocomposite containing 7 wt % of the SiO_2 nanofiller was the most promising, and its important characteristics (including the temperature behavior of the electrophysical parameters) were studied in detail. The studied composition is attractive for using in the solid state devices fabrication.

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