

Conductivity and Dielectric characterizations of nanofiller TiO₂ dispersed PEO – PEG blend Nano Composite Polymer Electrolyte

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Abstract: A set of nanocomposite polymer electrolyte (NCPE) based on poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) blend polymer matrix with cation donor salt lithium perchlorate (LiClO₄) and nano-filler titanium oxide (TiO₂) was prepared by solution casting technique. The frequency-dependent impedance spectroscopy was used to estimate the ionic conductivity of the nanocomposite electrolyte systems. Furthermore the various dielectric parameters with respect to the filler concentration and temperatures were primarily investigated. The maximum ambient temperature conductivity of $6.15 \times 10^{-5} \text{ Scm}^{-1}$ was obtained for the nanocomposite of (72 % PEO–17 % PEG–11 % LiClO₄)–5 % TiO₂ by weight percentage. The dielectric permittivity and loss tangent are reasonably reliable with the conductivity. As obvious, all the composites obey the Arrhenius equation for the conductivity mechanism which confirms that the nanocomposite polymer electrolytes are thermally activated.

Keywords: Nano composite polymer electrolyte; PEO; Impedance spectra, Conductivity; Dielectric loss

1 Introduction

Electrolytes play a crucial role as the ionic conduction medium in various electrochemical devices, such as lithium batteries, supercapacitors, fuel cells, dye-sensitized solar cells and electrochromic devices. Among the different types of electrolytes, solid polymer electrolytes (SPEs) have received great research interest owing to their merits of controllable dimensionality, high potential window, safety, and stability over the conventional liquid electrolytes [1-5]. The PEO was most widely used polymer in lithium polymer battery applications. The PEO has exceptional ability to dissolve the ionic salts with structural suitability for ion dissociation and easily form stable electrolytes in contrast to other polymers [6]. However, PEO incorporated polymer electrolytes endure with low ionic conductivity and poor mechanical strength at ambient temperature. In order to, enhance the ionic conductivity and mechanical stability of solid polymer electrolytes (SPEs), several approach such as insertion of cross-linking agents to form networks, blending of polymers, incorporating low-molecular-weight organic plasticizers, and addition of inorganic fillers (Al₂O₃, SiO₂, TiO₂, BaTiO₃, etc.) [7- 9] have been implemented. Among them, the blend polymer electrolytes demonstrate enhancement in ionic conductivity, and tailored physical properties through simple compositional change. Further, the addition of filler establishes the formation of nanocomposite polymer electrolytes through well known Lewis acid base interactions. The Lewis acid sites on the surface of nanoparticles interact with the base center of ether oxygen in PEO/PEG chains in the formation of complex [6]. The frequency and temperature dependent conductivity and dielectric relaxation are responsive to the ion dynamics in polymers. In the present work, the nano composite polymer electrolyte systems composed of PEO–PEG–LiClO₄ dispersed with different weight percentages of nano-sized TiO₂ ceramic filler have been studied. The conductivity and dielectric parameters of the PEO – PEG blend polymer based electrolytes are investigated using the impedance spectroscopy.

2 Experimental

2.1 Synthesis of nanofiller TiO₂

Typical synthesis of TiO₂ nanoparticles are as follows; simply 10 ml of Titanium (IV) Tetraisopropoxide [Ti(OCH(CH₃)₂)₄] was mixed with the appropriate amount of glacial acetic acid under constant stirring.

ISBN: 978-93-5254-981-8

The white colored precipitate has been formed immediately and it has been diluted by the addition of excess amount of deionized water in order to make the clear glutinous solution. The above solution was stirred constantly for 5 h. After that the solution was kept in the dark for 24 h to complete the nucleation process. At the end the solution was dried at 393 K for 12 h to obtain the TiO₂ crystals. Finally, it was finely ground and calcined at 773 K for 3 h and used directly for nanocomposite preparation [10].

2.2 Preparation of solid polymer electrolyte

PEO ($M_w \sim 7 \times 10^6$) and PEG ($M_w \sim 4000$) were obtained from Aldrich and Merck, respectively, and used as received. LiClO₄ was purchased from Aldrich and it was vacuum dried at 393 K. In the preparation of blend composite polymer electrolytes, 72% PEO, 17% PEG, 11% LiClO₄ and x % ($x = 0, 3, 5$ and 7) of nanoparticle filler TiO₂ by weight percentage were dissolved in anhydrous acetonitrile. The solution was stirred for 36 h at room temperature for complexation. Finally, the gel-like solution was obtained, cast on a polypropylene petri dish and dried by a slow evaporation of solvent in a vacuum oven under the low pressure of 10^{-3} mm of Hg for 48 h. The resulting films were visually examined for their dryness and free-standing nature. The electrical conductivity and dielectric parameters such as permittivity and loss tangent of the polymer complexes at different temperatures were determined from the impedance measurement using HIOKI 3532 LCZ meter in the frequency range 50 Hz to 5 MHz at the temperature range 300–398 K.

3 Results and discussion

3.1 Conductivity

The dc electrical conductivity of polymer electrolytes was determined using the relation

$$\sigma_{dc} = \frac{t}{AR_b} \quad (1)$$

where t and A are thickness and area of polymer electrolyte sample which is placed between stainless steel blocking electrodes. The bulk resistance R_b of polymer electrolyte is determined using impedance measurement. The temperature dependent conductivity of PEO – PEG – LiClO₄ with different weight percentage of TiO₂ over the temperature range from 300 K to 398 K has been shown in Fig. 1. From the figure it can be observed that the conductivity of NCPE increases with temperature upto the melting temperature of PEO/PEG. At the temperature about 333 K, there is a swift rise in conductivity of the NCPE film, which may be due to the semicrystalline to amorphous phase transition of polymer blend matrix.

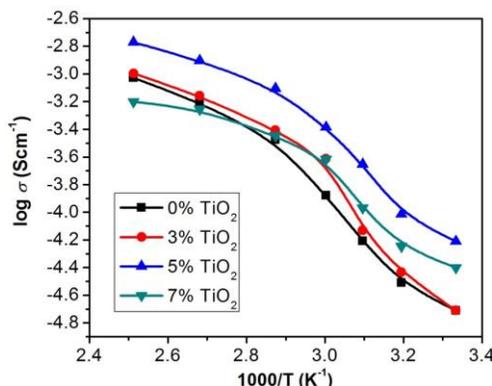


Fig 1. Temperature dependent conductivity of PEO-PEG- LiClO₄ (72:17:11) with differnt wt% TiO₂.

As the temperature increases, the polymer chain gains large amplitude of vibration of internal modes and increase the segmental mobility. This, in turn enhances the inter-chain and intra-chain hopping of ion movements and hence the conductivity of the polymer electrolyte [11]. The NCPE with 5% TiO₂ filler shows the maximum ambient temperature conductivity of $6.15 \times 10^{-5} \text{ Scm}^{-1}$ which is about 3 times more than that of polymer electrolyte without nano filler. The temperature dependent conductivity plot is approximately linear, suggesting the Arrhenius equation could be exploited to fit the observed curve. The addition of nano filler impedes the recrystallization of polymer chains by increasing the amorphous volume fraction. The size of filler particle is adequately small compared to the polymer host; hence it can easily

be penetrate into the polymer matrix and establishes the interaction between filler, Li^+ ions and polymer chain molecules. This in turn produces additional pathways to conduct ions at the surface of TiO_2 nanoparticles, which further increases the conductivity through the enhanced movement of the ions [10].

3.2 Conductivity–frequency dependence

The frequency dependent conductivity of NCPE for different weight percentage of nano filler content at ambient temperature and the same for polymer nanocomposite that exhibits maximum conductivity (72 % PEO–17 % PEG–11 % LiClO_4)–5 % TiO_2 at different temperatures are shown in Fig. 2 and 3, respectively.

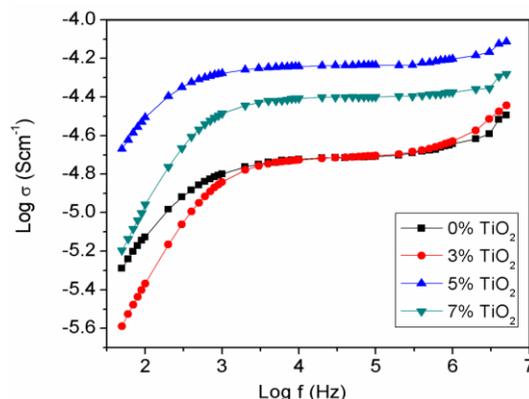


Fig 2. Frequency dependent conductivity of PEO-PEG- LiClO_4 (72:17:11) with different wt % of TiO_2

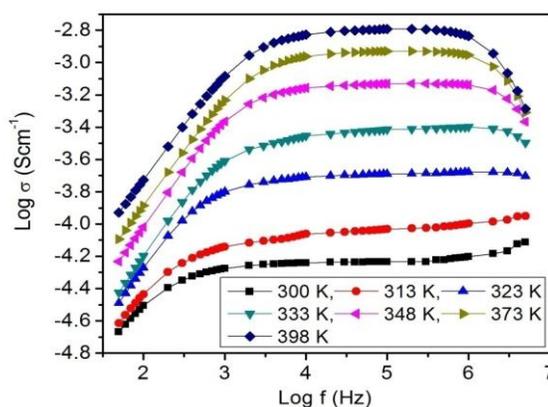


Fig 3. Frequency dependent conductivity of 5 wt% TiO_2 dispersed PNCE at different temperature

The space charge polarization or impedance of the electrolyte at the electrode/electrolyte interface modulates low frequency region of conductivity [11]. In this low frequency of applied field, the ions dwell relatively for a long time and results in accumulation of more charge at the electrode/electrolyte interface. Consequently, mobility of ions is retarded and hence the conductivity drops. The frequency independent plateau region provides the DC electrical conductivity (σ_{dc}) value of the NCPEs. The σ_{dc} determined using ac conductivity curves are consistent with the conductivity obtained from Arrhenius plot (fig 1). The high frequency dispersion in the conductivity is associated to the bulk relaxation phenomenon and faster backward hopping of ions [12]. At very high frequency, the high mobility of lithium ions probably increases conductivity with the frequency well below the melting temperature of PEO/PEG. As above the melting temperature of PEO/PEG, the conductivity decreases with frequency as shown in Fig. 3 which may be attributed to the formation of electric double layer.

3.3 Frequency dependent dielectric behavior

The dielectric behavior of polymeric system may be described by the real and imaginary parts of the complex permittivity ϵ^* , Figure 4 and 5 shows the variation of dielectric constant and dielectric loss as a function of frequency for NCPE with different weight percentage of filler at ambient temperature. As expected, it can be observed that the presence of nano filler may enhance the movement of ions through the Lewis acid base interaction which increases the polarization of ions

effectively. This can also be directly associated with improved amorphous phase volume fraction in the composites system. These observations are well concordance with conductivity as discussed earlier. Interestingly, the well resolved variation of dielectric constant can be noticeable even at high frequency and shows the maximum for 5% TiO_2 dispersed NCPE as shown in inset of figure 4.

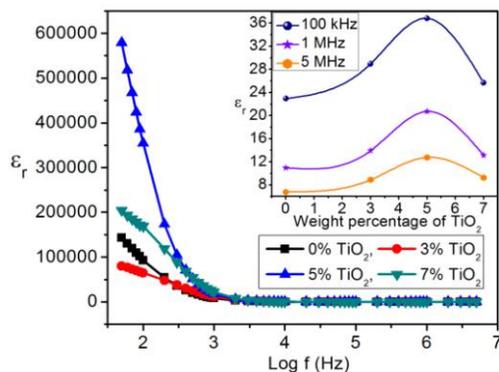


Fig 4. Dielectric constant vs. frequency of PEO-PEG- LiClO_4 (72:17:11) with different wt % of TiO_2

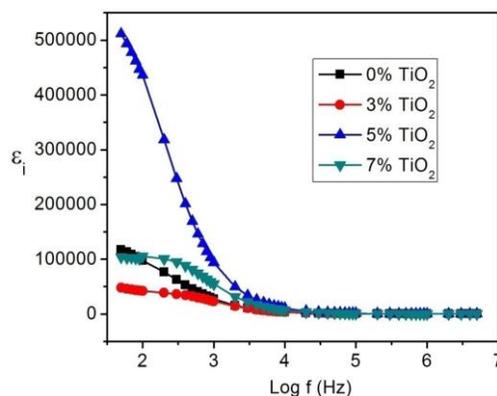


Fig 5. Dielectric loss vs. frequency for PEO-PEG- LiClO_4 (72:17:11) with different wt % of TiO_2

It further supports the proportionality between the permittivity and the conductivity at any given frequency of applied field and suggests both are caused by the same charge carrier i.e., ions in polymer electrolyte. In general, the dielectric constant and loss values are very high at low frequencies and decrease with increase of frequency and attain very low value with small dispersion at higher frequencies. The high ϵ_r and ϵ_i at low frequency are possibly due to the space-charge polarization, which are arising from the accumulation of charge carriers near the electrodes and confirming the non-Debye dependence [12]. Further the dielectric constant and dielectric loss attain maximum at given frequency and temperature for the sample dispersed with 5% nanofiller. At higher frequency, the electric field periodically reverse the direction very rapidly in such a way that there is no excess ion diffusion in the field direction resulting in the decrease in space charge polarization and hence dielectric constant [11, 12].

3.4 Loss tangent

Fig. 6 depicts the loss tangent ($\tan \delta$) as function of frequency at ambient temperature for different weight percentage of TiO_2 dispersed NCPE. It is clearly observed that $\tan \delta$ increases with frequency and reaches a maximum value and thereafter decreases [10, 12]. The loss tangent peak is described by the relation $\omega\tau=1$ where τ is the relaxation time, and $\omega = 2\pi f$ is the angular frequency of the applied electric field corresponding to maximum of loss tangent. The relaxation times and the maximum of $\tan \delta$ vary with filler content and suggest that the presence of relaxation in the polymer electrolytes.

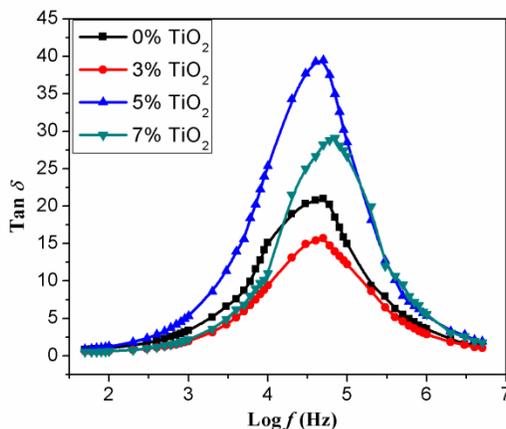


Fig Fig 6. Frequency dependence of $\tan \delta$ for PEO-PEG-LiClO₄ (72:17:11) with different wt % of TiO₂

Conclusion

Nanocomposite polymer electrolytes based on PEO/PEG blend polymer with lithium salt and different weight percentage of TiO₂ nanoparticles were prepared by solution-casting technique. A maximum ambient temperature ionic conductivity $6.15 \times 10^{-5} \text{ Scm}^{-1}$ was obtained for (72 % PEO–17 % PEG–11 % LiClO₄)–5 % TiO₂. The addition of nano filler increases the amorphous phase and establishes Lewis – acid base interaction between filler, Li⁺ ions and polymer chain. This in turn introduces additional pathways to conduct ions at the surface of TiO₂ nanoparticles and increase the number of charge carries and hence increase the conductivity through the enhanced movement of the ions. The conductivity as a function of frequency study revealed that the ionic conductivity at plateau is equal to dc conductivity obtained from Arrhenius plot. The dielectric constant (ϵ_r) and loss (ϵ_i) increase with nanofiller TiO₂ content. The loss tangent as a function of frequency of applied field varies with nanofiller. The conductivity and dielectric permittivity are thermally activated and show Arrhenius behavior.

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