

Synthesis and electrical conductivity studies of PEO + LiClO₄ + TiO₂ + MoO₃ nanocomposite solid polymer electrolyte

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Abstract

Titanium oxide nanofillers dispersed PEO + LiClO₄ + MoO₃ nanocomposite solid polymer electrolyte films were prepared by solution cast method. All the prepared samples were investigated by the X-ray diffraction, Fourier transformation infrared spectroscopy and scanning electron microscope with energy dispersive X-ray spectroscopy. Electrical conductivity of all the nanocomposite solid polymer electrolyte films was evaluated by analyzing the measured impedance. The highest conductivity of $1.07 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature is found for the PEO + LiClO₄ + TiO₂ (5 wt%)+ MoO₃ film. Dielectric constant and modulus data were calculated using the measured impedance data for all the prepared films and analyzed. Ionic transference number due to ions for the best conducting nano composite solid polymer electrolyte (PEO+Li⁺+TiO₂+MoO₃) evaluated by the Wagner polarization technique is found to be $t_+ = 0.9967$. The transference number value indicate that the developed NCSPE can be a potential electrolyte for lithium batteries as well as other ionic device applications.

Keywords: TiO₂ nanoparticles, nanocomposite solid polymer electrolyte, XRD, FTIR, SEM-EDX Impedance, Electrical conductivity Ionic Transference Number.

1. Introduction

Nano composite solid polymer electrolytes (NCSPE's) have emerged as promising alternatives to replace liquid electrolytes for various ionic device applications such as batteries and electrochemical capacitors, etc. The most extensively studied polymer for NCSPEs is poly-ethylene oxide (PEO) due to its good mechanical and thermal properties as well as easy processing [1, 2]. In case of PEO solid polymer electrolyte, the transport of Li⁺ cations are coupled with the local relaxation and segmental motion of the PEO chains. Therefore, better transport of Li⁺ ions will occur when PEO is in its amorphous state [3-5]. Hence, various preparative methods have been devised to avoid the crystallinity and to improve the conductivity in the PEO polymer solid electrolyte. Recently, enhancement of both electrical and mechanical properties are obtained by adding

the different types of nano fillers like SiO₂, La₂O₃, Al₂O₃, etc., to the PEO polymer solid electrolyte [6-13]. First, the present paper reports the synthesis of TiO₂ nano particles by sol-gel foam combustion route. The prepared TiO₂ nanoparticles are dispersed in the PEO + LiClO₄ + MoO₃ and prepared the nanocomposite solid polymer electrolyte film by the solution casting route. Phase, structure, micro structure and elemental analysis of the TiO₂ nanoparticles as well as nano composite solid polymer electrolyte films are respectively characterized by the XRD, FTIR, SEM-EDX. Also, studied their electrical conductivity and ionic transport number properties through the impedance spectroscopy and Wagner polarization method.

2. Experimental:

Titanium tetrachloride (Qualigence), citric acid (Qualigence) and urea (Qualigence) precursor chemicals were used for the synthesis of nanocrystalline TiO₂ fillers using sol-gel foam combustion route. The solutions of the above precursors were mixed and continuously stirred at 60 °C till the formation of gel. Further, the formed gel was heated up to 180 °C to form a foam like structure. Pure nano crystalline titanium dioxide fillers were obtained on further heating the foam at 500 °C for 3 h. Precursor solutions of 80 wt% of polyethylene oxide (PEO) (Sigma Aldrich) and 20 wt% of lithium perchlorate (LiClO₄, Aldrich) were prepared separately and mixed under continuous stirring at 40 °C. After 8 h, various weight percentages (1, 3 & 5wt%) of TiO₂ nano particles were dispersed in to the mixed solution and stirred for 20 h in order to achieve a homogeneous mixture. The homogeneous mixtures were poured on Teflon dishes and evaporated slowly at 40 °C in vacuum oven to form the NCSPE films.

2. Result and Discussion

2.1. X-ray diffraction

Figure 1 a & b show XRD patterns of pure TiO₂ alongwith JCPDS data and various polymer samples. From fig. 1a, the observed XRD pattern confirm the formation of pure crystalline TiO₂ phase. From fig.1b, the observed XRD patterns of various polymer samples showed the amorphous

phase of the polymers, which may enable to have high ionic conductivity in electrolytes.

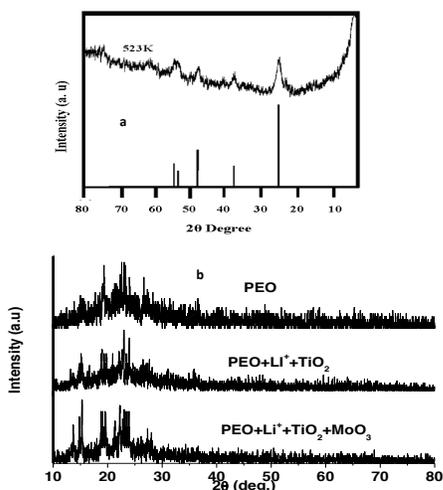


Figure 1 shows XRD patterns of a) Pure TiO₂ with JCPDS data and b) various polymer samples

2.2. FT-IR Analysis:

Fig. 2 shows the IR spectra of PEO, PEO + LiClO₄ + TiO₂ and PEO + LiClO₄ + TiO₂ + MoO₃. From fig.2, the IR band at 2863 cm⁻¹ can be assigned to the C-H stretching mode, and the IR band at 1964 cm⁻¹ is due to an asymmetric stretching mode. The IR bands at 1462, 1143, 951 and 844 cm⁻¹ are assigned to CH₂ scissoring, C-O-C stretching, CH₂ twisting, and CH₂ wagging modes, respectively. In a similar way, the characteristic frequencies of LiClO₄ at 1300 and 920 cm⁻¹ are shifted, respectively, to 1354 and 947 cm⁻¹. The shifts in their corresponding characteristic frequencies are attributed to changes in the environment of ClO₄. Similarly, with the incorporation of TiO₂ in the PEO matrix, the intensity of the band is significantly reduced and is even slightly shifted to 1557 cm⁻¹, which indicate the formation of a complex.

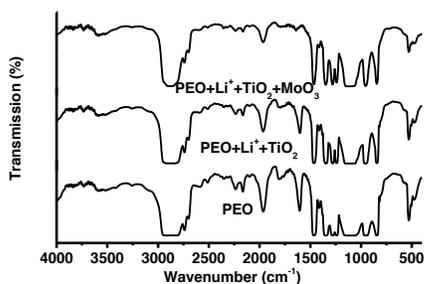


Figure 3 FTIR spectra of all PEO composites

2.3. SEM-EDS:

Fig.3a & b show the SEM image and EDS spectrum of TiO₂. The observed SEM image indicates that TiO₂ particles are in spherical in shape and the average particles size is found to be ~ 45 nm. EDS spectrum of TiO₂ indicates the presence of Ti and O elements in the TiO₂. Hence, the observed SEM image and EDS spectrum confirm the formation of pure TiO₂ spherical shape nano particles. Figures 3c & d, show the SEM images of the nano composite solid polymer electrolyte [PEO + LiClO₄+ TiO₂+MoO₃] at different magnifications. SEM images showed high porosity of the nano composite solid polymer electrolyte film. XRD and SEM results confirmed the formation of pure nano crystalline titanium oxide fillers and also amorphous nature and porosity of the nano composite solid polymer electrolyte film.

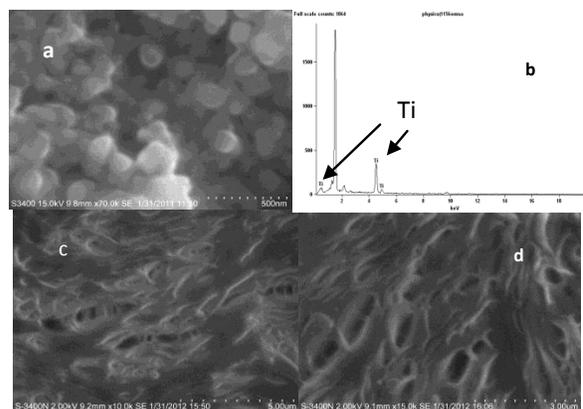


Figure 3: SEM images of a) TiO₂ nanoparticles and b) EDS of TiO₂ nanoparticles c, d) PEO composite.

3. Transport studies

3.1. Impedance:

Fig. 4a shows the impedance plots obtained at room temperature for the PEO + LiClO₄+ TiO₂ films with different TiO₂ concentration. Fig. 4b shows the impedance plots for PEO + LiClO₄+ TiO₂+MoO₃ nano composite solid polymer electrolyte at different temperatures. From fig. 4b, the intercepts of depressed semicircle with real axis (X-axis) gives the best bulk resistance (R_b) of the sample and the intercepts shifts towards origin and the frequency at which the Z'' attains a maximum also shift towards higher frequencies as temperature increases. From fig.4a, the observed inclined straight line at low frequency region of the impedance plot is due to the electrode polarization effect at the electrode and material interface. The conductivity observed at room temperature for PEO + LiClO₄+ TiO₂ (5 wt. %) and PEO + LiClO₄+TiO₂ (5 wt.%) + MoO₃ (1 wt. %) nano

composite solid polymer electrolyte films is found to be $4.33 \times 10^{-5} \text{ S cm}^{-1}$ and $1.07 \times 10^{-4} \text{ S cm}^{-1}$ respectively.

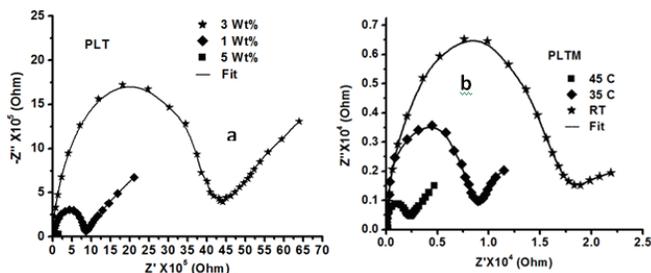


Figure 5: Impedance plots for a) PEO + LiClO₄+ TiO₂ and b) PEO + LiClO₄+ TiO₂+MoO₃ nano composite at different temperatures

3.2. ac Conductivity:

Figure 5a shows the $\log \sigma$ versus $\log \omega$ plots and Arrhenius plot for the NCSPE samples at different temperatures. From fig. 5a, the plateau region corresponds to frequency independent conductivity (σ_0). The σ_0 value is obtained by extrapolating the frequency independent conductivity value to the zero frequency. The observed variation of conductivity with frequency is due to electrode polarization effects at the electrode and material interfaces. As the frequencies decreases, more and more charges accumulation occurs at the electrode and material interface which leads to a drop in conductivity at low frequency. In the intermediate frequency region, the conductivity is almost found to be frequency independent and is supposed to be true dc conductivity. The frequency dependent conductivity at various temperatures in the dispersion region for the NCSPE was analyzed using JUP law [14].

$$\sigma_\omega = \sigma_0 + A\omega^s$$

Where σ_0 is the dc conductivity, A is the pre exponential factor and s the frequency exponent

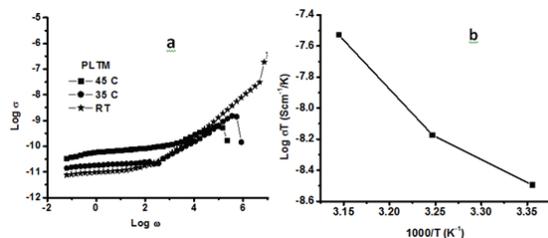


Figure 5: a) $\log \sigma$ versus $\log \omega$ for the NCPE samples and b) $\log \sigma T$ versus $1000/T$ plot for the NCPE sample

Figure 5 b, shows the $\log \sigma T$ versus $1000/T$ of the NCSPE sample. From fig.5b, the activation energy (E_a) is evaluated

from the slope of the $\log \sigma T$ versus $1000/T$ plot and it is found to be 0.90 eV.

Figure 6a, shows the dielectric constant (ϵ') versus $\log \omega$ plots obtained at different temperatures for the NCSPE samples. ϵ' decreases with increasing frequency and temperature. The value of dielectric constant is high at low frequency, which is due to polarization effects at the electrode and the nano composite polymer electrolyte interfaces.

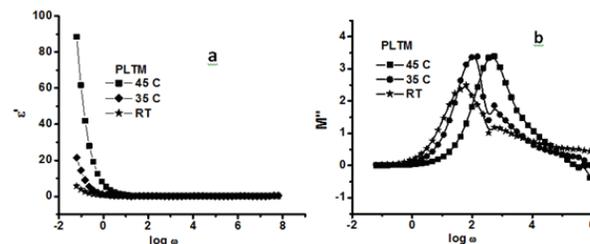


Figure 6: a) Dielectric constant (ϵ') versus $\log \omega$ and b) M'' Vs $\log \omega$ plots for the NCPE samples at different temperatures

Figure 6b shows the modulus versus $\log \omega$ plots obtained at different temperatures for the NCPE sample. From $\log M''$ versus $\log \omega$ plot, the low values of M'' at low frequency indicate negligible of electrode polarization to the electric modulus. From fig.6b, the frequency dependent modulus shows two regions; one is at low frequency and another one is at high frequency regions. In the low frequency region, the charge carriers are mobile over long range distances and at high frequency region the charge carriers are confined to potential wells and are mobile over short distances [17].

Wagner polarization technique was employed for evaluating the lithium ion transference number (t_+) of the nano composite solid polymer electrolyte (PEO+Li⁺+TiO₂+MoO₃). The nano composite solid polymer electrolyte film was sandwiched between silver (Ag) as lithium ion non-blocking electrode and graphite (C) as lithium ion blocking electrode to form a Ag/NCSPE/C for measuring current under the constant applied voltage. Fig. 7, shows the current versus time plot for the best conducting nano composite solid polymer electrolyte (PEO+Li⁺+TiO₂+MoO₃) and the magnified plateau region is shown in insert graph. From fig. 7, the current decreases with time and after some time, it reached to saturation. The initial current (I_T) at $t = 0$ is the total current (I_T) and the current obtained by extrapolating the saturated plateau current to the y-axis is call the electronic current (I_e). The following expressions were used for calculating the cationic transference number (t_{ion}) [18 & 19].

$$I_T = I_e + I_{ion} \quad \text{and} \quad I_{ion} = I_T - I_e \quad \text{----- (1)}$$

$$t_{ion} = I_{ion}/I_T \quad \text{----- (2), where } I_{ion} \text{ is the ionic current}$$

The evaluated ionic transference number due to ions is found to be $t_+ = 0.997$. The transport number value indicate that the developed best conducting nano composite solid polymer electrolyte (PEO+Li⁺+TiO₂+MoO₃) can be a potential electrolyte for lithium batteries as well as other ionic device applications.

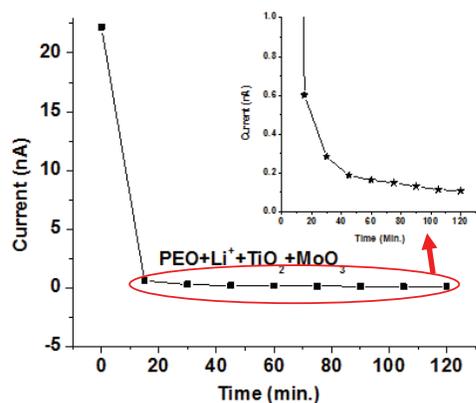


Figure 8: Current Vs. Time plots for the PEO+Li⁺+ TiO₂ + MoO₃ nano composite (Insert graph is expanded view of plateau region)

3. Conclusion

Metal oxide (TiO₂) nanoparticles were synthesized by the sol-gel foam combustion route. The nano composite solid polymer electrolyte (PEO+Li⁺+TiO₂+MoO₃) films were prepared using solution casting process. XRD, FTIR and SEM results confirmed the formation of phase, structure and micro structure of metal oxide (TiO₂) nanoparticles and also nano composite polymer electrolyte films. The bulk resistance (R_b) of PEO+ Li⁺+TiO₂+ MoO₃ obtained from the impedance (Z) plots obtained at different temperatures. The activation energy of Li-ion evaluated from the log σT versus 1000/T plot is found to be 0.90 eV. The ac conductivity results follow power law behaviour. A high degree of dispersion in the permittivity and dielectric loss at low frequency and high temperature suggest that a conduction mechanism of the hopping type is present. The modulus plots are interpreted in terms of the distribution of relaxation times for distinguishable physical process of the sample. Finally, the evaluated ionic transference number due to ions for the best conducting nano composite solid polymer electrolyte (PEO+Li⁺+TiO₂+MoO₃) is found to be $t_+ = 0.9967$. The transference number values indicate that the developed

NCSPE can be a potential electrolyte for lithium batteries as well as other ionic device applications.

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