Synthesis and ac conductivity studies of PEO + $LiClO_4$ + La_2O_3 + MoO_3 nanocomposite polymer solid electrolyte

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Abstract

Synthesized La_2O_3 nano particles are suspended in the polyethylene oxide + $LiClO_4$ + MoO_3 to form the nano composite polymer solid electrolyte film by the solution casting method. Phase, structure and micro structure of the nano composite polymer solid electrolyte films are respectively characterized by the X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The DC conductivity of the polyethylene oxide (PEO) nano composite polymer solid electrolyte is evaluated by analyzing the measured impedance data. Also, frequency dependence of conductivity, dielectric constant and modulus properties are evaluated and studied. The effective cationic conductivity is evaluated using the Wagner polarization method.

1. Introduction

Polymer solid electrolytes are getting important for various electrochemical device applications, due to their high ionic conductivity, high mechanical and thermal stability. In the PEO polymer solid electrolyte, the transport of Li^+ cations are coupled with the local relaxation and segmental motion of the PEO chains and better transport of Li^+ ions can occur when PEO is in its amorphous state. Hence, the observed conductivity enhancement in the PEO polymer solid electrolyte can be attributed to the increase in the amorphous regions, which are responsible for the high conduction of Li^+ ions [1-8]. However, PEO often shows relatively high crystallinity and in such cases, its ionic conductivity is lower than 10^{-7} S cm−1 at room temperature. 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 various types of nano fillers like SiO_2, TiO_2, Al_2O_3, etc., in the PEO polymer solid electrolyte[9-11]. The present paper reports the synthesis of PEO+$LiClO_4$+La_2O_3+MoO_3 nano composite polymer electrolyte film and its characterization by the X-ray diffraction (XRD), Fourier transformation infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The conductivity studies of polymer solid electrolyte at different temperatures were made through impedance measurements.

2. Experimental

The nano composite polymer solid electrolyte (NCPSE) film of PEO+$LiClO_4$+La_2O_3+MoO_3 was prepared by the solution casting method. First, nanocrystalline metal oxide (La_2O_3) particles as nano fillers were synthesized by the sol gel combustion route. In sol gel combustion, lanthanum nitrate (Qualigence), citric acid (Qualigence) and urea (Qualigence) precursor chemicals were used for the synthesis of nanocrystalline La_2O_3 fillers. Frist, the solutions of all the required precursors were mixed under continuous stirring at 80^0C up to the formation of the gel and it was heated up to 180^0C. The gel was expanded like foam, whose volume is 20 times of the gel. Pure nano crystalline lanthanum oxide fillers were obtained on further heating the foam up to 1000^0C for 3hr. The polymer solid electrolyte films were prepared using poly ethylene oxide (PEO) (National chemicals) and alkali metal salt, lithium perchlorate ($LiClO_4$) (Aldrich). First, polyethylene oxide solution was prepared using methanol as solvent under continuous stirring at 40^0C. After 8hr, the prepared 1 weight percentage of La_2O_3 nano particles were suspended in to the solution and stirred for 8 hours in order to achieve a homogeneous mixture. Finally, molybdenum trioxide is added to the solution and stirred another 10 hr. The solutions thus obtained was cast in a polypropylene dishes and allowed to evaporate slowly to form the polymer solid electrolyte film.

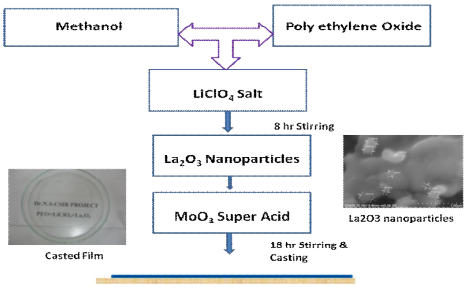

Figure 1 Flowchart of total solution casting process for the preparation of nanocomposite polymer solid electrolyte (PEO + $LiClO_4$ + La_2O_3 + MoO_3) film.

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3. Characterization

The powder X-ray diffraction patterns were recorded on thin transparent polymer films using PANanalytical Xpert Pro Xray diffractometer with Cu Kα radiation of wavelength =1.5418 Å and scanned from 80-10^0 deg. FTIR Spectra were recorded on thin transparent films using shimadzu FTIR/8300/8700 spectrophotometer in the range of 4000-400 cm^{-1} with 2 cm^{-1} resolution for 20 scans. The micro structures of PEO+ Li^+ based polymer solid electrolyte and size of the La_2O_3 nano particles were obtained through SEM measurements using Hitachi S3400N Scanning electron Microscope. Impedance data were measured for the PEO+$LiClO_4$+La_2O_3+MoO_3 nano composite film by using the frequency analyzer, NOVOCONTROL, Germany and Ac conductivity was calculated using measured impedance data obtained at different temperatures.

4. XRD

Fig.2.shows XRD patterns of the all the prepared PEO based electrolyte films. From fig.2, the peak free XRD patterns of the Pure PEO, PEO+$LiClO_4$ (PL),PEO+$LiClO_4$+La_2O_3(PLL), PEO+$LiClO_4$+La_2O_3+MoO_3 (PLLM) polymer films confirm the amorphous nature.

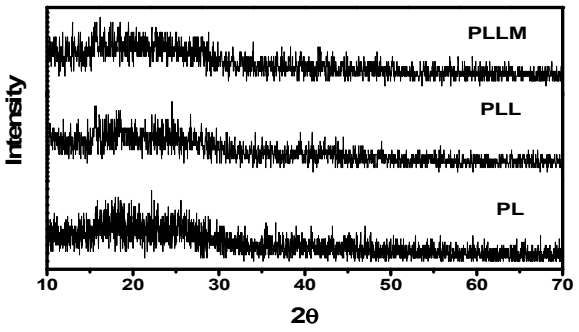

Figure 2. XRD patterns of the prepared polymer films

5. FT-IR

Figure 3 shows the FTIR spectra of PEO, PEO + LiClO4, and PEO+$LiClO_4$+La_2O_3+MoO_3. The band in PEO that appears at 2863 cm^{-1} can be assigned to the C-H stretching mode and the peak at 1964 cm^{-1} is due to an asymmetric stretching mode. The peaks at 1462, 1143, 951, and 844 cm^{-1} are assigned to -CH_2- scissoring, -C-O-C- stretching, -CH_2 twisting, and -CH_2- wagging modes respectively. In a similar way, the characteristic frequencies of $LiClO_4$ 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 -ClO_4 -. Similarly, with incorporation of La_2O_3 in the PEO matrix, the intensity of the peak is significantly reduced and is even slightly shifted to 1557 cm^{-1}, which indicate formation of a complex in the system.

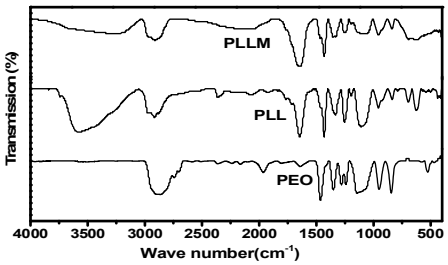

Figure 3. FTIR spectra of all polymer films

6. SEM

Fig.4a-d show the SEM pictures of La_2O_3 and PEO+Li^++La_2O_3+MoO_3 nano composite polymer electrolyte samples.. From the fig.4a, b, agglomerated particles of the La_2O_3 are observed. The particles size is ~ 95nm. XRD, FTIR and SEM results confirmed the formation of pure nano crystalline lanthanum oxide fillers prepared by foam combustion route. Fig.4c, d, show the SEM images of the PEO+Li^++La_2O_3+MoO_3 nano composite polymer electrolyte at different magnifications.

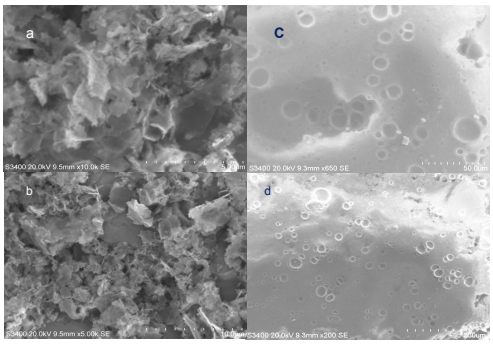

Figure 4 a, b. SEM images of La_2O_3 nanoparticles and 4 c,d NCPSE

7. Impedance

Fig.5. shows that the impedance plots for the PEO+Li^++La_2O_3+MoO_3 nano composite polymer solid electrolyte (NCPSE) film obtained at different temperatures. In fig.5a,b the intercepts of each 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. The

bulk resistance (R_b) obtained from the analyzed impedance data and the film dimensions were used to calculate the bulk conductivity of the NCPSE samples measured at various temperatures. From fig.5, the impedance plot, observed as straight line at low frequency region is due to the electrode polarization effect at the electrode and material interface. Fig.6.shows the Arrhenius plot (log σT versus 1000/T) of the NCPSE sample. From fig.6, the slope of the plot gives activation energy (Ea) and it is found to be 0.14 eV.

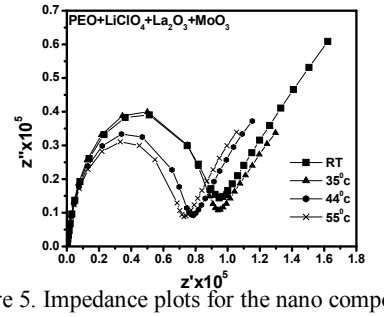

Figure 5. Impedance plots for the nano composite polymer solid electrolyte.

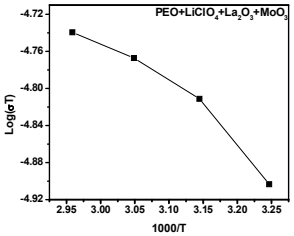

Figure 6. Arrhenius plot (log σT versus 1000/T) of the NCPE sample

8. ac Conductivity

Fig.7.shows log σ versus log ω plots obtained for the NCPSE sample. From fig.7, it is observed that the frequency dependence of conductivity shows two distinct regions, within the measured frequency window, (i) the low frequency plateau region and (ii) high frequency dispersion region. The plateau region corresponds to frequency independent conductivity (σ_0).

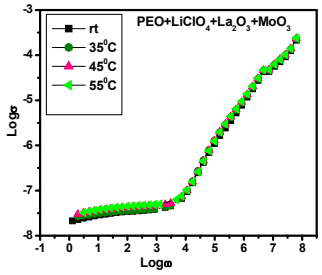

Figure7. log σ versus log ω plots for the NCPSE sample

The σ_0 value is obtained by extrapolating the conductivity value to the zero frequency. The frequency dependent conductivity at various temperatures in the dispersion region for the NCPSE was analyzed using JUP law [12].

Fig.8a shows the dielectric constant (ε') versus log ω plots for the NCPSE samples obtained at different temperatures. ε' is also decrease with increasing frequency and increasing with temperature. The value of dielectric constant at low frequency is high due to the free charge motion within the nano composite polymer solid electrolyte. It is also reflects the reorientation process of the dipoles in polymer chains, which showed a relaxation peak in dielectric loss spectra. As temperature increases, the viscosity of the polymer materials decreases and hence, dielectric loss (ε'') increasing with temperature due to dipole rotation in the presence of applied electric filed [13, 14]. Fig.8b shows the plot between dielectric loss (ε'') and log ω for the NCPSE samples at different temperature.

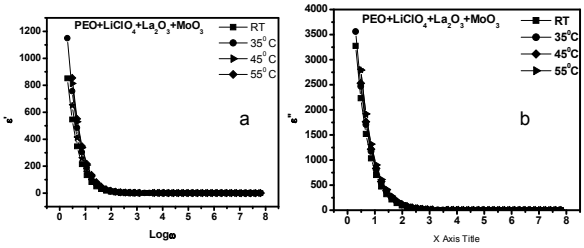

Figure 8 a). Dielectric constant (ε') versus log ω plots b) Dielectric loss (ε'') versus log ω plots for the NCPSE

Fig.9 shows the modulus versus log ω plots for the NCPSE samples obtained at different temperatures. In M'' versus log ω plot, the low values of M'' at low frequency indicate negligible of electrode polarization to the electric modulus.

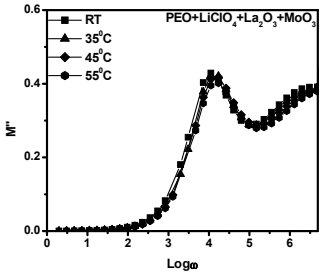

Figure 9. M'' Vs. Log ω plots of NCPSE sample

From fig.9, it is obtained that the frequency dependent modulus shows two regions one is low frequency and another one is high frequency region. 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 [15] The

broadness of the M'' versus log(ω) curves is interpreted in terms of the distribution of relaxation times for distinguishable physical processes.

Fig.10 shows the current Vs time graph obtained for the NCPSE sample by using Wagner polarization method. The Lithium ion transference number "t_+" of the PEO+Li^++La_2O_3+MoO_3 nano composite polymer solid electrolyte was measured by using Wagner polarization method. The Nano composite polymer solid electrolyte film was sandwiched between lithium ion blocking and unblocking electrodes to form a polymer electrolyte cell then constant voltage source applied. Initially, measured current (I_T) decreases with time after some time, it reached the saturation as a plateau. The amount of electronic current (I_e) is obtained by extrapolating the plateau to the Y-axis and substituting the above values in following equation for obtaining the cationic transference number "t_+"

$t_+ = I_+/I_T$

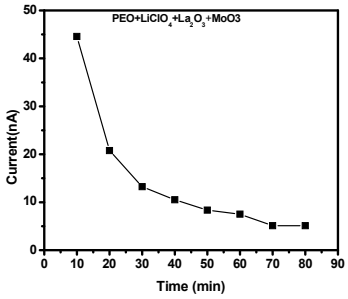

Figure 10 show the current Vs time graph of NCPSE

The initial current (I_T) across the cell, when applied DC voltage. The effective cationic conductivity (σ_+) is generally expressed by the following relation [16, 17].

$\sigma_+ = t_+ \sigma_T$

Where σ_T is the total conductivity.

5. Conclusion:

The PEO+Li^++La_2O_3+MoO_3 nano composite polymer solid electrolyte film was prepared by using the solution casting method. XRD, FTIR and SEM results respectively confirmed the formation of Phase, structure and micro structure of PEO+Li^++La_2O_3+MoO_3 nano composite polymer solid electrolyte. Electrical conductivity is calculated from the analysis of the measured impedance data obtained at different temperatures for the NCPSE film. The activation energy of Li-ion is calculated from Arrhenius plot and it is found to be 0.14 eV. 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. The effective cationic conductivity obtained from the Wagner polarization method.

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