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Investigations on Ionic Conductivity of Nanocomposite Solid Polymer Electrolytes $(PEG)_xLiCF_3SO_3:(SiO_2)_y$

Ravikumar V. Patil, R. Damle*

Department of Physics, Bangalore University, Bengaluru – 560 056, Karnataka, India.

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ABSTRACT

Polymers complexed with lithium salts are promising for use as solid electrolytes in solid-state lithium batteries. However, the key issue is the ionic conductivity and the process of enhancing it for better performance. Polyethylene glycol-based solid polymer electrolytes complexed with lithium salts are being investigated to explore their suitability in battery applications. In the present work, we report the investigations carried out on PEG-based solid polymer electrolyte complexed with lithium trifluoromethanesulfonate ($LiCF_3SO_3$). The ionic conductivity profile as a function of salt content is studied. The effect of the addition of inert nanofiller SiO_2 is also investigated to understand the mechanism of enhancement of ionic conductivity. The preparation of the nanocomposite solid polymer electrolytes and characterization by other techniques like powder XRD, IR spectroscopy, thermal measurements and conductivity profile obtained from AC impedance measurements are discussed to get an insight into the mechanism of ion transport and the influence of the addition of nanofiller.

1. Introduction

Over the past two decades, a fast development of lithium-ion batteries is observed to meet the requirements of power supply in some of the electronic gadgets such as mobile phones, laptops, hybrid electric vehicles, rechargeable batteries, etc. Lithium batteries making use of flammable liquid solvent as electrolyte suffer from risk of fire hazard and can cause difficulties in waste disposal and management. The use of solid polymer electrolyte (SPE) removes this drawback and provides greater energy density and geometrical flexibility. SPE consists of a polymer matrix as a solid solvent along with lithium salt and merely do not contain any volatile organic solvent. SPEs are a class of materials that are flexible so that they can withstand shape changes during the charge-discharge cycle and possess the ability of fabrication into desired shapes. Greater ionic conductivity, high specific energy, leakage proof of electrolyte, wider electrochemical stability, lightweight and ease of preparation are some of the other practical advantages of SPEs [1].

Polar groups in the polymer chain are necessary for dissociating mineral salts, which is common in SPEs. The resulting cations are capable of moving between coordinating sites of one chain or the neighboring chains, promoted by the segmental motion [2]. The ionic conductivity of SPE can be further enhanced by the addition of plasticizers or inert nanofillers as reported earlier. The enhancement in their electrochemical and mechanical properties has also been studied earlier [3-7]. The presence of the plasticizers would also affect the mobility of ionic or/and the interfacial interaction within ionic and polar groups in polymer chains. The addition of plasticizers in the polymer matrix results in a decrease of the glass transition temperature and increased deformability, elasticity, abrasion resistance and elastic recovery in the electrolyte system [8]. Owing to their high ionic conductivity, plasticized polymer electrolytes are considered as promising material for the application as electrolytes. Plasticized SPE at room temperature exhibits higher conductivity than the conventional PEO based polymer electrolyte [9]. Silica-based nanocomposite solid polymer electrolytes (NCSPEs) have been studied in the past [10, 11]. An enhancement of ionic conductivity with the addition of silica nanoparticles has been observed in these studies. With the addition of silica nanoparticles, the conductivity of the order of 10^{-5} Scm^{-1} has been achieved [12].

Poly ethylene glycol (PEG) is a polymeric material that is of significant interest due to its ease of processability and potential applications. PEG complexed with different salts of lithium, sodium, potassium and their modification in structure, optical and electrical properties with additives have been studied in the past. Generally, to modify the permeability of the polymer films, low molecular weight and high dielectric constant additives, such as ethylene carbonate (EC) and propylene carbonate (PC) are used [13]. High molecular weight PEG-based SPEs (molecular weight 8000 and 10,000 $gmol^{-1}$) complexed with various inorganic salts including LiBr, $LiClO_4$, LiCl, LiI, NaI, KI, and CsI are reported earlier. The effect of the addition of Al_2O_3 nanoparticle has also been investigated by the same group. For the O/Li ratio of 10 at room temperature for SPE with PEG-10,000 and LiBr, a maximum ionic conductivity of 3.9×10^{-5} Scm^{-1} was observed. A characteristic double peak behavior is shown for the conductivity variation with the salt concentration. Additional transport properties due to the different viscosity and diffusion behaviors are exhibited with the low molecular weight PEG (Rouse region with mol. wt. < 3,200 $gmol^{-1}$). An increase in ionic conductivity up to three times to that of pure SPEs has been extensively shown in NCSPEs based on PEG, $LiClO_4$ and γ-alumina particles of size 0.3 μm [14].

Trifluoromethanesulfonate, also known by the trivial name triflate, is a functional group with the formula CF_3SO_3-. The anion owes its stability to resonance stabilization which causes the negative charge to be spread over the three oxygen atoms and the sulfur atom. An additional stabilization is achieved by the trifluoromethyl as a strong electron-withdrawing group. Triflates have also been used as ligands for group 11 and 13 metals along with lanthanides. Lithium triflates are used in some lithium-ion batteries as a component of the electrolyte. Different types of lithium-ion conducting polymer electrolytes have been prepared as perfect homogenous mixtures of the components, namely, with PEG as the polymer matrix which is capable of dissolving different alkali metal salts such as lithium trifluoromethanesulfonate ($LiCF_3SO_3$), lithium tetrafluoroborate ($LiBF_4$), and lithium perchlorate [15].

In this paper, we report the preparation and characterization of SPEs and NCSPEs, namely, $(PEG)_xLiCF_3SO_3$ and $(PEG)_xLiCF_3SO_3:(SiO_2)_y$ where x represents the ratio of number of ether oxygen in a monomer unit of polymer to the number of cation and y represents the weight percent of silica nanoparticles in the SPEs. A low molecular weight PEG (4,000 g/mol^{-1}) which is well below the Rouse region was chosen as a host polymer [16]. The variation of conductivity as a function of salt concentration and the effect of the addition of SiO_2 nanofillers on the conductivity profile is described.

*Corresponding Author:ramkrishnadamle@bub.ernet.in(R. Damle)

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2. Experimental Methods

2.1 Materials

Polyethylene glycol (PEG) (mol. wt. 3300-4000 gmol^{-1}) from SD Fine chemicals was used as the host polymer. lithium tri-fluoromethane sulfonate ($LiCF_3SO_3$) abbreviated as LiTf, from Sigma-Aldrich, is used as the salt for complexation. Fumed silica nanoparticles SiO_2 from Sigma Aldrich (average particle size of ~7 nm) is used as a nanofiller. Methanol (AR grade Merck) was used as a solvent. All these chemicals were used for preparation without any further purification. $(PEG)_xLiCF_3SO_3$ and nanocomposite $(PEG)_xLiCF_3SO_3:(SiO_2)_y$ are prepared by solution cast technique. Here x = 25, 50, 100, 200, 400 represents oxygen to lithium ratio and y = 1%, 3%, and 5% represents the weight percent of silica nanopowder. A detailed description of the preparation method is reported elsewhere [17]. The samples are vacuum dried to remove the traces of solvent from the samples. It is observed that, as salt concentration increases, the samples tend to become softer and slightly hygroscopic whereas, with lower salt concentrations, the samples are harder. The samples seemed to gain good mechanical strength by the addition of nanoparticles and are much easy to handle.

2.2 Characterization Techniques

$(PEG)_xLiCF_3SO_3:(SiO_2)_y$ samples prepared in various compositions of salt and silica nanopowder are characterized with powder X-ray diffraction (XRD) studies, infrared (IR) spectroscopy studies, and differential scanning calorimetry (DSC) studies. AC impedance measurements are made as a function of salt concentration and weight percent of nanoparticles. Rigaku X-ray diffractometer with Cu-Kα radiation in the 2θ range from 10° to 80° at a scan speed of 2° min^{-1} is used to record the diffractograms to confirm the salt complexation with the host polymer. IR spectrum of the samples are recorded using Perkin Elmer FT-IR Spectrometer (Frontier) in the wavenumber range of 400-4000 cm^{-1}. DSC recordings are made using TA Instruments DSC 2920 instrument in the temperature of 20-100 °C. AC impedance measurements are made using a Core Tech impedance analyzer (SA-40) interfaced to a computer using Labview. Samples in the form of circular discs dried in an inert atmosphere for more than 8 hours are placed between electrodes of a home-built conductivity rig for AC impedance measurements. Room temperature conductivity was measured as a function of salt concentration and also with the weight percent of SiO_2 nanoparticles.

3. Results and Discussion

3.1 X-Ray Diffraction Studies

Fig. 1 shows the powder X-ray diffractograms of pure polymer PEG, LiTf, and PEG complexed with salt for selected composition and also SPE dispersed with inert nanofiller with different weight percent. Fig. 1(a) shows that the diffraction peaks corresponding to salt are absent in the polymer–salt complex indicating the dissociation of the salt in the polymer matrix. Further, from Fig. 1(b), it is clear that the intensity of diffraction peaks decreases with the increase in salt concentration indicating that, the crystallinity of the complex decreases (Full Width at Half Maximum, FWHM also decreases). With the addition of nanoparticles, there is hardly any change in the diffraction peaks indicating that there is no change in the structure of the polymer-salt complex.

3.2 DSC Measurements

DSC curves are recorded for PEG, LiTf, PEG complexed with LiTf and nanocomposites in the temperature range of 20 °C to 100 °C to study the thermal stability and shown in Fig. 2. It is observed that as the salt concentration is increased (from x = 400 to x = 50), the melting temperature also increases slightly indicating that the thermal stability of the complex slightly increases. But with the addition of nanoparticles, there is only a marginal decrease in the melting temperature for lower salt concentrations (x = 400 and x = 100) whereas there is a decrease in melting temperature by more than 3 °C for higher salt concentration (x = 50). This would mean that the NCSPEs with higher salt concentration tend to be thermally not so stable.

3.3 Infrared Spectroscopic Studies

FTIR spectroscopic measurements reveal the vibrational modes of the different functional groups present in the polymer matrix. Fig. 3 shows the recorded FTIR spectra of pure PEG, PEG-LiTf (for selected compositions x = 25 and 50) and the spectra with the addition of silica nanofiller with different weight percent 3%. The band/absorption peak around 3516 cm^{-1} can be assigned to the terminal O-H group of the host polymer. Various absorption peaks observed between 1100 and 1500 cm^{-1} can be attributed to C-H bending in various planes. The C-H out of plane bending results in a band around 1100 cm^{-1}. An absorption peak around 1500 cm^{-1} may be assigned to the in-plane bending of the CH_2 group of the polymer. It is observed that with the addition of silica nanoparticles, the absorption peak at 3516 cm^{-1} corresponding to O-H stretching is shifted to around 3450 cm^{-1}. For $PEG_{25}LiTf$, the band at 3484 cm^{-1} due to O-H stretching is shifted to 3474 cm^{-1} after addition of 3 wt.% SiO_2. Likewise, the O-H stretching band for other compositions of the salt are also shifted to lower frequency after addition of inert nano filler as shown in Fig. 3(b). This shift to lower wavenumber may be attributed to an increase in the amplitude of vibration of the O-H stretching upon the addition of nanoparticles. Such observation has been reported earlier in PEG complexed with Sodium salts [18]. This phenomenon can be understood as follows: When SiO_2 inert fillers are dispersed in the polymer matrix; the nanoparticles occupy the voids in the complex. The presence of SiO_2 close to the terminal O-H group of the polymer may attract the anion coordinated to the O-H group. It is already established in the reported literature that the addition of nanoparticles to SPEs results in the adsorption of anions on to the surface of the nanoparticles. This adsorption of anions that are coordinated to the terminal O-H group tends to increase the amplitude of the vibration of the O-H stretching of the polymer. This, in turn, leads to an enhanced segmental motion of the polymer chain facilitating the transport of conducting ions. Thus, an increase in the ionic conductivity of the nanocomposite SPEs is supported by the IR spectroscopic measurements.

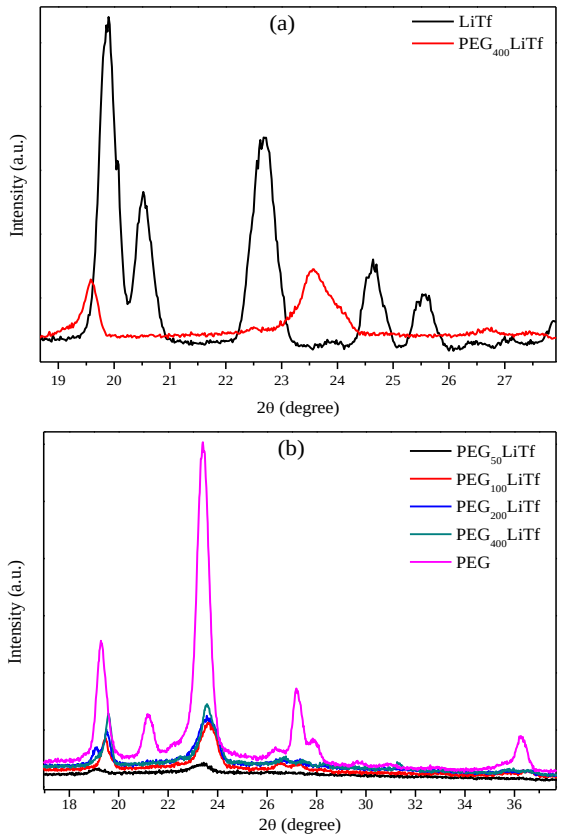

Fig. 1 XRD diffractograms of pure PEG, LiTf, PEG complexed with LiTfand NCSPEs

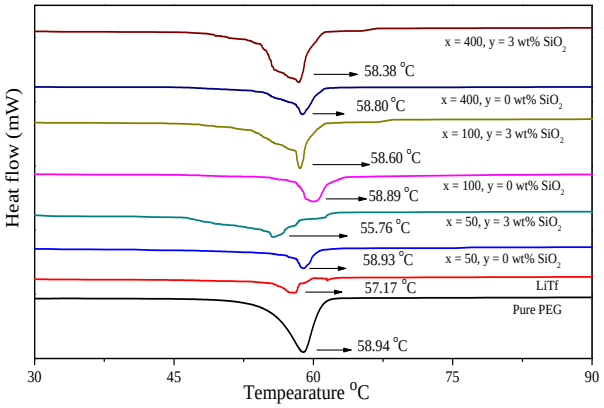

Fig. 2 DSC plots of pure PEG, LiTf, SPEs and NCSPEs

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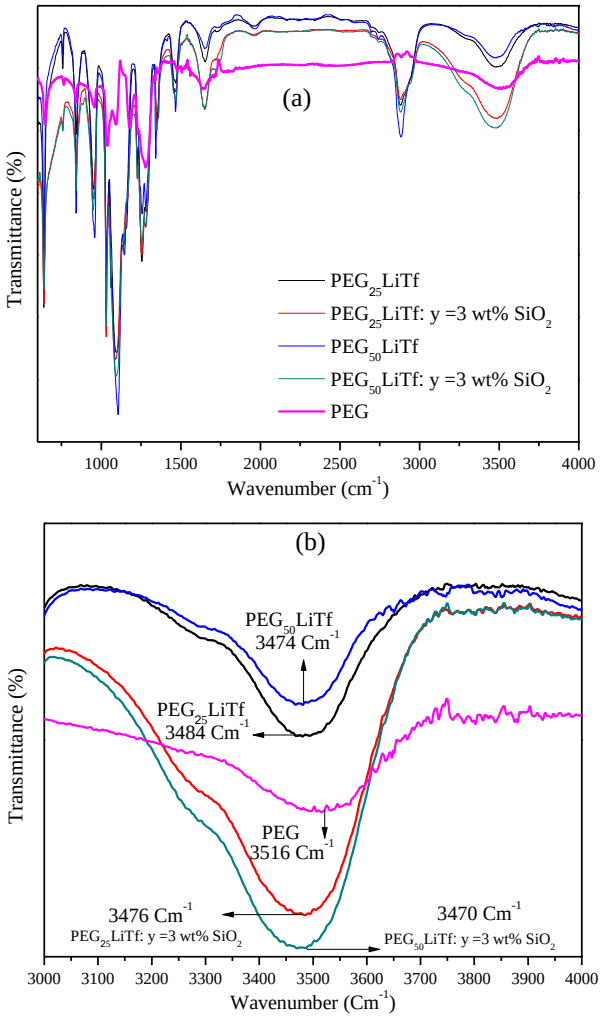

Fig. 3 IR spectra of pure PEG, PEG-LiTf and its nanocomposites

3.4 AC Impedance Studies

Ionic conductivity of the samples is determined from the impedance analysis using the standard technique. From the impedance analysis, the Cole-Cole plot is obtained which gives bulk resistivity of the sample and from the known dimensions of the sample, ionic conductivity is estimated. Ionic conductivity of $(PEG)_xLiCF_3SO_3$ as a function of salt concentration x is as shown in Fig. 4. In SPEs, as the salt concentration increases, available ions for conduction also increases and hence the ionic conductivity increases. In the conductivity isotherm shown in Fig. 4, the conductivity increases salt concentration x = 400 to x = 50. Further increase in salt concentration results in the formation of ion pairs (which are electrically neutral) which would decrease the ionic conductivity as observed. Further increase in salt concentration would result in the formation of triple ion, which carries a net charge. This increases conductivity as observed in the present case. Such a conductivity profile is commonly observed in some SPEs. As SPEs with higher salt concentrations (x < 25) are hygroscopic, these compositions are not used for measurement. The highest conductivity of 1.11×10^{-5} Scm^{-1} was observed for the composition x = 100.

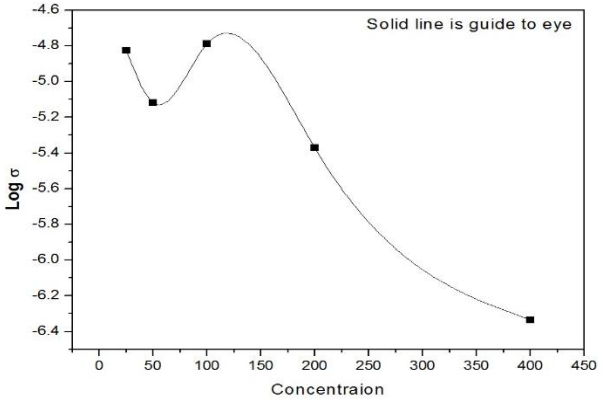

Fig. 4 Variation of ionic conductivity with salt concentration in $(PEG)_xLiCF_3SO_3$

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Fig. 5 shows the variation in the ionic conductivity of the polymer-salt complex with the addition of silica nanoparticles. With the addition of 1 wt.% SiO_2, there is an increase in conductivity by one to two orders of magnitude for all the salt compositions. However, with further addition of nanoparticles, the conductivity almost levels off. This increase in ionic conductivity with the addition of nanoparticles can be attributed to the adsorption of anions on to the surface of the nanoparticles thereby reducing the ion-ion interaction [19]. This reduces the number of ion pairs with net neutral charge. It can be seen from the plot that for x =100 for which the conductivity is maximum, the enhancement in conductivity is also maximum.

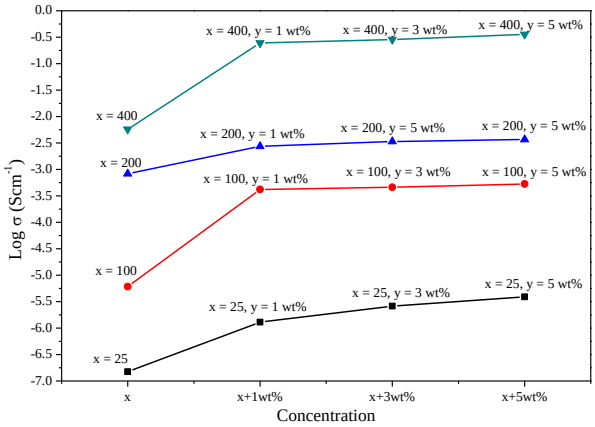

Fig. 5 Ionic conductivity variation with the addition of nanoparticles in $(PEG)_xLiCF_3SO_3$

4. Conclusion

A new solid polymer electrolyte, PEG complexed with LiTf in different compositions of the salt is prepared and characterized. Ionic conductivity of the system with and without the addition of inert nanofiller SiO_2 is measured to investigate the effect on conductivity isotherm. The results indicate that the conductivity isotherm exhibits a single peak as a function of salt composition typical of an SPE. With the addition of silica nanoparticles, the polymer-salt nanocomposite system exhibits an enhancement in ionic conductivity by 1-2 orders of magnitude. This increase in ionic conductivity may be understood by an enhanced segmental motion of the polymer chain due to the adsorption of the anions on to the surface of the nanoparticles.

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