

Ionic conductivity studies of Nanocomposite solid polymer electrolytes $\text{PEG}_x(\text{NaCF}_3\text{SO}_3): (\text{SiO}_2)_y$

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Abstract: Sodium salts dissociated in polymers are promising for use as solid electrolytes in solid-state rechargeable batteries. However, the magnitude of ionic conductivity in these systems is not high enough and needs to be enhanced for practical applications. Sodium salts complexed with Polyethylene glycol-based solid polymer electrolytes are being examined to investigate their suitability in battery applications. In the present work, we report the investigations carried out on PEG-based solid polymer electrolyte complexed with Sodium Trifluoromethanesulfonate (NaCF_3SO_3). Conductivity profile as a function of salt concentration and nanoparticle content are determined from AC impedance measurements to get an insight into the mechanism of transport of ions in the solid polymer electrolyte and its nanocomposites. The addition of nanoparticles increases the ionic conductivity of the composite system by 1 to 2 orders of magnitude. This is understood as due to the adsorption of anions on to the surface of the nanoparticles which in turn enhances the segmental motion of the polymer chains.

Key words - Solid polymer electrolyte, ionic conductivity, nanocomposite solid polymer electrolyte.

I. INTRODUCTION

Polymer-salt complexes functioning as solid electrolytes have distinct advantages over liquid electrolytes [1, 2]. Host polymer matrix when dissolve inorganic salts, forms the ion-conducting macromolecules known as Solid Polymer Electrolytes (SPEs). Both host polymer and salts together contribute to the electrochemical properties of SPEs. Transport of ions within the polymer matrix-assisted by the segmental motion of polymeric chains leads to the conductivity in SPE systems [2-5]. These SPEs have potential applications in energy storage devices. Solid-state batteries are being developed since the conventional liquid electrolyte based batteries are associated with problems of leakage at electrode-electrolyte junction during the charge and discharge cycle of the batteries. Further, liquid electrolytes are not portable, suffer from lack of processability and have low energy density. These problems can be overcome by using SPEs [2, 6-10]. The optimal ionic conductivity of 10^{-3} Scm^{-1} at ambient temperatures in pristine SPEs is still a dream for the researchers in spite of extensive research over the last three decades. The ionic conductivity in SPEs is governed by the degree of dissociation of salts within the polymer matrix, cation-anion and ion-polymer interaction, and the morphology of the matrix. Morphology of the system is one of the key factor to control the ionic conductivity, as the ion transport is controlled by the segmental motion of the polymeric chains in the amorphous regions of the complex. Fraction of amorphous to crystalline regions in the complex governs the ionic conductivity of these systems. To enhance the ionic conductivity in SPEs, several methods are being adopted such as the addition of plasticizers and inert nanoparticles, exposure to ionizing radiation and quenching at low temperatures [11-14]. The addition of nanoparticles to the SPEs and thus forming nanocomposite solid polymer electrolytes (NCSPEs) is reasonably a good method that enhances the ionic conductivity by a few orders of magnitude [15-18]. The highest ionic conductivity of 10^{-4} Scm^{-1} has been reported with the addition of nanoparticles [18].

Lithium ions as the conducting species in SPEs encounter problems of handling due to their hygroscopic nature and have prompted to explore alternate species like sodium, rubidium, and potassium ions. Sodium salt is considered as a potential alternative to Li salt in SPEs [19-26]. Work related to the sodium-based SPEs and their composites has been reported by several groups across the globe. Deepak et. al., have shown the enhanced ionic conductivity with the addition of SiO_2 nanoparticles from 4.5×10^{-4} to $3.5 \times 10^{-3} \text{ Scm}^{-1}$ in Poly (methyl methacrylate) based sodium ion conducting gel polymer electrolytes [18]. SPEs based on high molecular weight polyethylene glycol (PEG; mol. wt. $\sim 8,000$ and $10,000 \text{ g mol}^{-1}$) complexed with several inorganic salts including LiI, NaI, KI, and CsI have been studied earlier by Shiuli Gupta and they have also

reported the effect of addition of Al_2O_3 nanoparticles [36]. PEG-10,000 complexed with LiBr for the O/Li ratio of 10 at ambient temperature exhibits a maximum ionic conductivity of $3.9 \times 10^{-5} \text{ Scm}^{-1}$ as reported earlier. These systems show a characteristic double peak behavior in the conductivity profile as a function of salt concentration.

Properties of anions like structure, size, and charge also play an important role in determining ionic conductivity [27-29]. Studies show that the size of the anion influences the distance between neighboring cations within the polymeric chain axis and the distance between the cations of the neighboring chains. A wide range of tests have been carried out for salts suitability in SPEs by varying anion species. Increase of conductivity by one order at ambient temperature in Lithium-based salts such as LiBr, LiClO_4 , LiPF_6 , LiBF_4 , LiCF_3SO_3 , and LiTFSI, with the change in anion size has been established [30-34]. On the other hand, sodium-based salts like NaBr, NaI, NaPF_6 , NaNO_3 , NaClO_4 , NaCF_3SO_3 , and NaTFSI exhibits a maximum conductivity of the order 10^{-6} Scm^{-1} at room temperature [19-26].

In this paper, we report the preparation and characterization of SPEs and NCSPEs, namely, $\text{PEG}_x(\text{NaCF}_3\text{SO}_3)$ and $\text{PEG}_x(\text{NaCF}_3\text{SO}_3):(\text{SiO}_2)_y$ where x represents the ratio of number of ether oxygen in a monomer unit of polymer to the number of cations and y represents the weight percent of silica nanoparticles in the SPEs. A low molecular weight PEG ($4,000 \text{ gmol}^{-1}$) which is close to the Rouse region [37] was chosen as a host polymer. The variation of conductivity as a function of salt concentration and the effect of the addition of SiO_2 nanofillers on the conductivity profile has been investigated.

II. EXPERIMENTAL

A. Materials

Polyethylene glycol (PEG) (mol. wt. 3300-4000 gmol^{-1}) from SD Fine Chemicals was used as the host polymer. Sodium Trifluoromethanesulfonate (NaCF_3SO_3) abbreviated as NaTf, from Sigma-Aldrich, is used as the salt for complexation. Fumed silica nanoparticles SiO_2 from Sigma Aldrich (average particle size of $\sim 7 \text{ nm}$) 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. $\text{PEG}_x(\text{NaCF}_3\text{SO}_3)$ and nanocomposite $\text{PEG}_x(\text{NaCF}_3\text{SO}_3):(\text{SiO}_2)_y$ are prepared by solution cast technique. Here $x = 25, 50, 100, 200, 400$ represents oxygen to sodium ratio and $y = 1\%, 3\%$ and 5% represents the weight percent of silica nanopowder. 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.

B. Characterization techniques

$\text{PEG}_x(\text{NaCF}_3\text{SO}_3):(\text{SiO}_2)_y$ samples prepared in various compositions of salt and silica nanopowder are characterized by powder X-ray diffraction (XRD), Infrared (IR) spectroscopy and Differential Scanning Calorimetry (DSC) studies. Rigaku X-ray diffractometer with $\text{Cu-K}\alpha$ 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 $400 - 4000 \text{ cm}^{-1}$. DSC recordings are made using TA Instruments DSC 2920 instrument in the temperature range of $20-100^\circ \text{ C}$. Ionic conductivity measurements are made at room temperature as a function of salt concentration and weight percent of nanoparticles. Bulk ionic conductivity is obtained from AC impedance measurements using a Core Tech impedance analyzer (SA-40) interfaced to a computer for data acquisition. 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.

III. RESULTS AND DISCUSSION

A. X-ray diffraction studies

Figure 1 shows the powder X-ray diffractograms of pure NaTf, and PEG complexed with salt for a selected composition ($\text{PEG}_{100}:\text{NaTf}$). The diffraction peaks corresponding to salt are absent in the polymer-salt complex indicating the dissociation of the salt in the polymer matrix. Figure 2 shows the diffractograms for pure PEG and the polymer-salt complexes with different compositions of the salt. As the salt concentration is increased, there is a decrease in the intensity of the peaks indicated by the decrease in the intensity of the peaks indicating a decrease in the crystallinity of the system. With the addition of

nanoparticles, there is hardly any change in the diffraction peaks (and hence not shown in the graph) indicating that there is no change in the structure of the polymer-salt complex.

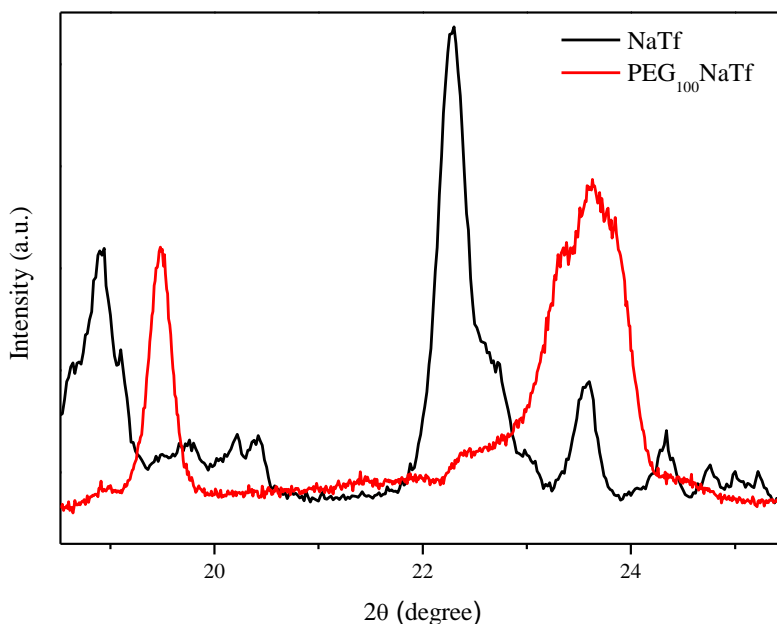


Figure 1. Powder X-ray diffractograms of salt NaTf and polymer-salt complex for $x = 100$.

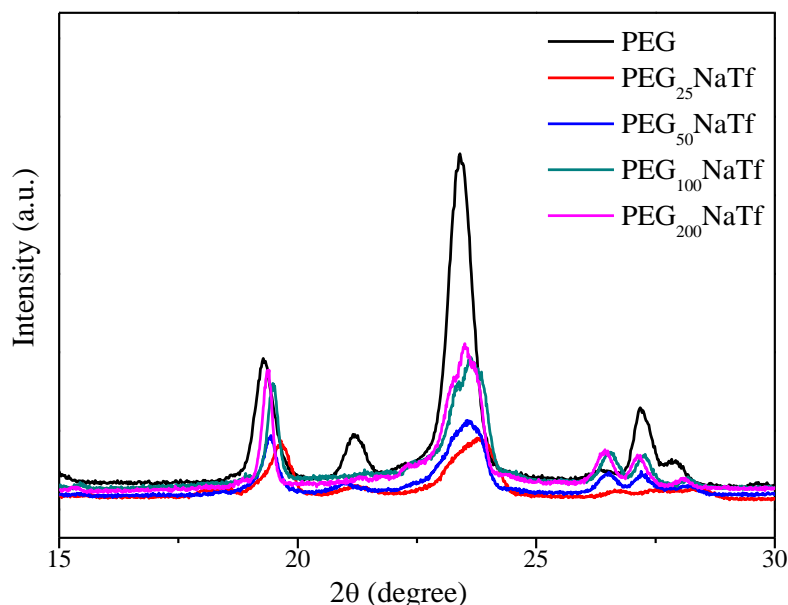


Figure 2. X-ray diffractograms of the pure polymer PEG and polymer-salt complex for different compositions of the salt.

B. FTIR Analysis

FTIR measurements (IR bands) reveal the vibrational modes of the different functional groups present in the polymer matrix. Figure 3 shows the recorded FTIR spectra of pure PEG, PEG-NaTf (for a selected composition $x = 50$) and the spectra with the addition of silica nanofiller (wt. 3%). The band/absorption peak around 3516 cm^{-1} can be assigned to the vibration of 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. In Figure 4, 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 3488 cm^{-1} after the addition of wt. 3% SiO_2 . The shift is shown for one composition of the salt ($x = 50$). Likewise, the O-H stretching band for other compositions of the salt is also shifted to lower frequency after the addition of inert nanofiller. 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 and hence results in shifting of the band peak to lower wavenumber. This, in turn, leads to an enhanced segmental motion of the polymer chain facilitating the transport of conducting ions. This phenomenon can have an impact on the conductivity of the nanocomposite SPE.

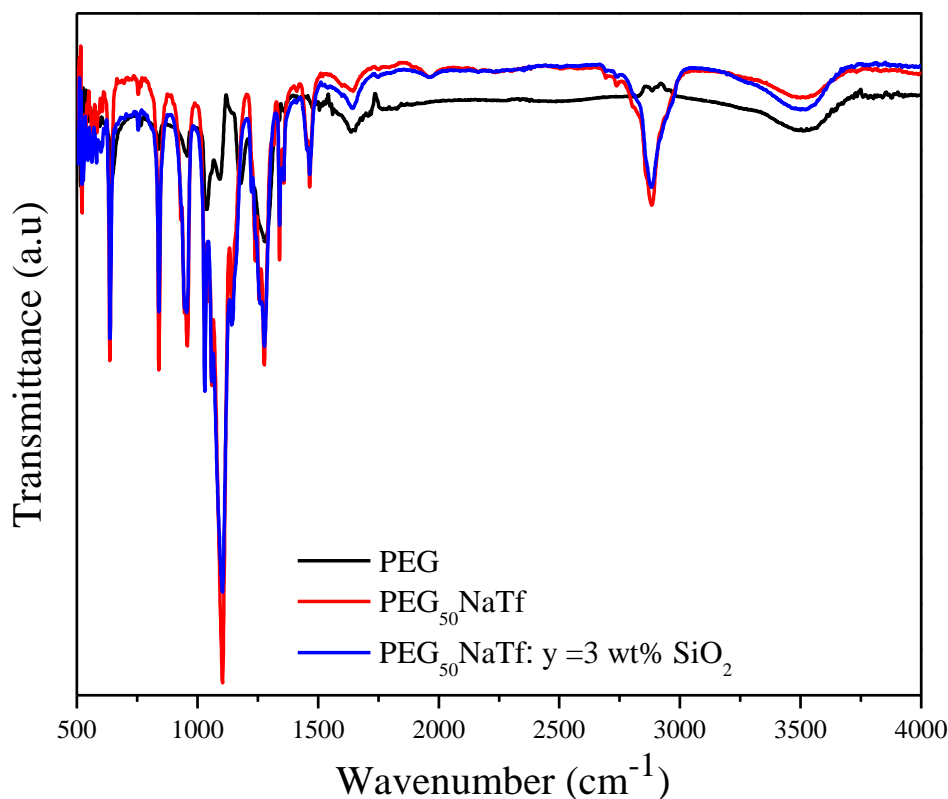


Fig. 3. FTIR spectra of pure polymer PEG, polymer-salt complex for selected composition ($x = 50$) and nanocomposite polymer-salt complex ($y = 3\%$)

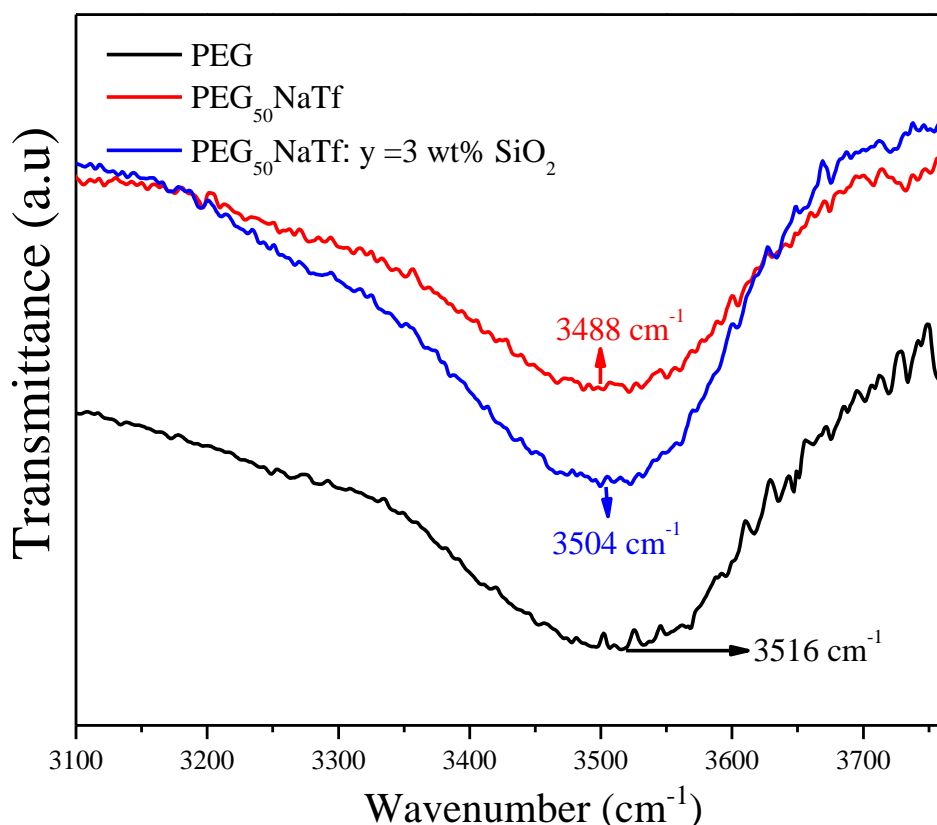


Fig. 4. FTIR spectra of O-H stretching vibration on an expanded scale for PEG, PEG₅₀-NaTf and its nanocomposite ($y = 3\%$)

C. DSC measurements

DSC thermograms are recorded for PEG, NaTf, PEG complexed with NaTf and nano-composites dispersed in SPEs, in the temperature range of 30 °C to 80 °C to study the thermal stability (Figure 5). It is observed that, as the salt concentration is increased (from $x = 400$ to $x = 50$), the melting temperature decreases. But with the addition of 3 wt% nanoparticles, an increase in the melting temperature could be observed for higher salt concentration leading to better stability of the composite system. However, for the lowest salt concentration ($x = 400$) the melting temperature decreases with the addition of nanoparticles.

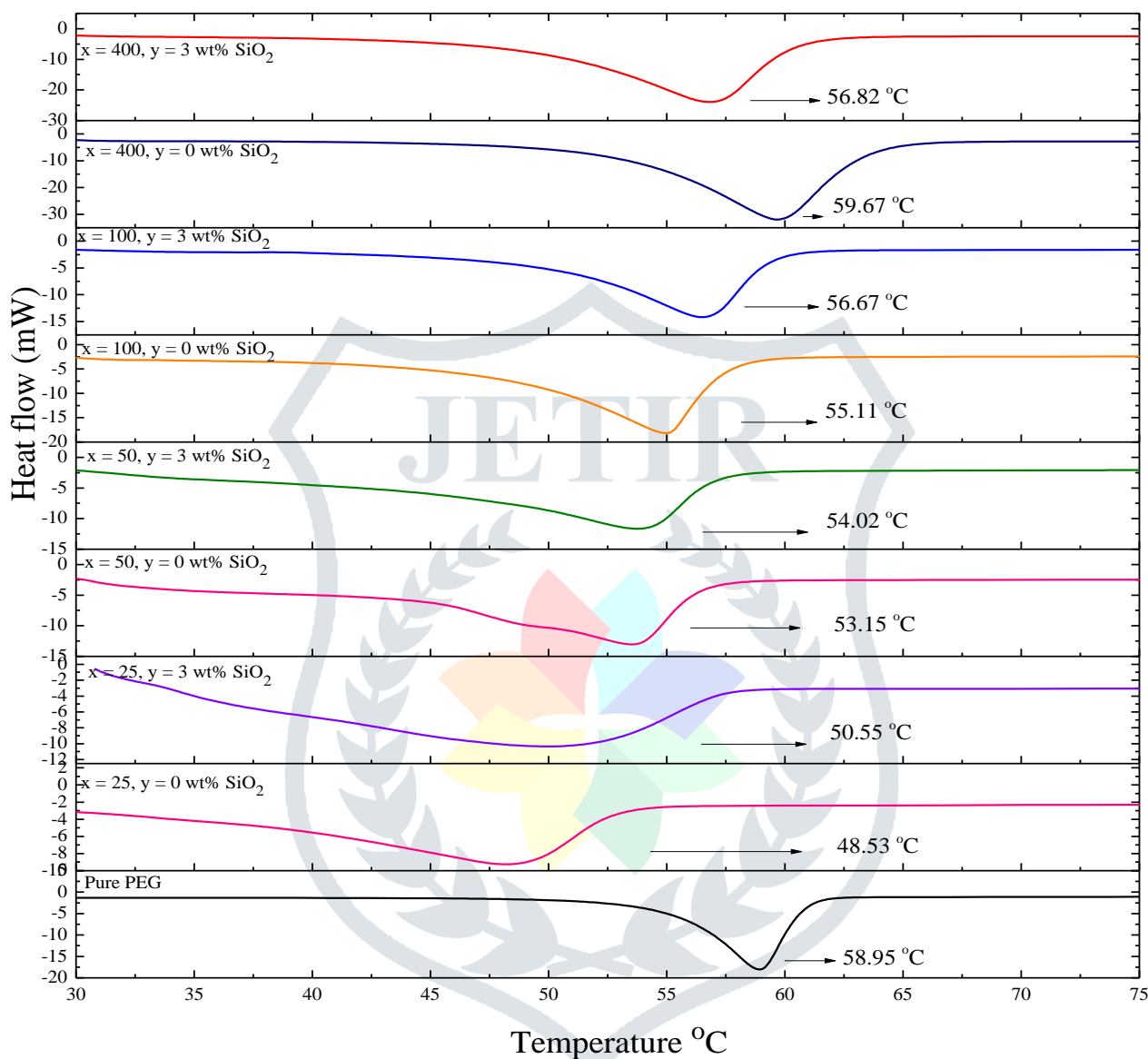


Fig. 5. DSC thermograms of pure PEG, PEG-NaTf and its nanocomposites

D. Conductivity measurements

Complex impedance analysis is made for determining the ionic conductivity of the samples. From the impedance analysis, the Cole-Cole plot is obtained which gives the bulk resistivity of the sample and from the known dimensions of the sample, ionic conductivity is estimated. Ionic conductivity of $\text{PEG}_x(\text{NaCF}_3\text{SO}_3)$ as a function of salt concentration x is as shown in Figure 6. In the conductivity isotherm shown in Figure 6, the conductivity increases as salt concentration increases from $x = 400$ to $x = 100$. 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 many SPEs. As SPEs with higher salt concentrations ($x < 25$) are typically hygroscopic, these compositions are not used for measurement. The highest conductivity of $2.46 \times 10^{-5} \text{ Scm}^{-1}$ was observed for the composition $x = 100$.

Figure 7 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 [35]. 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 (two orders of magnitude).

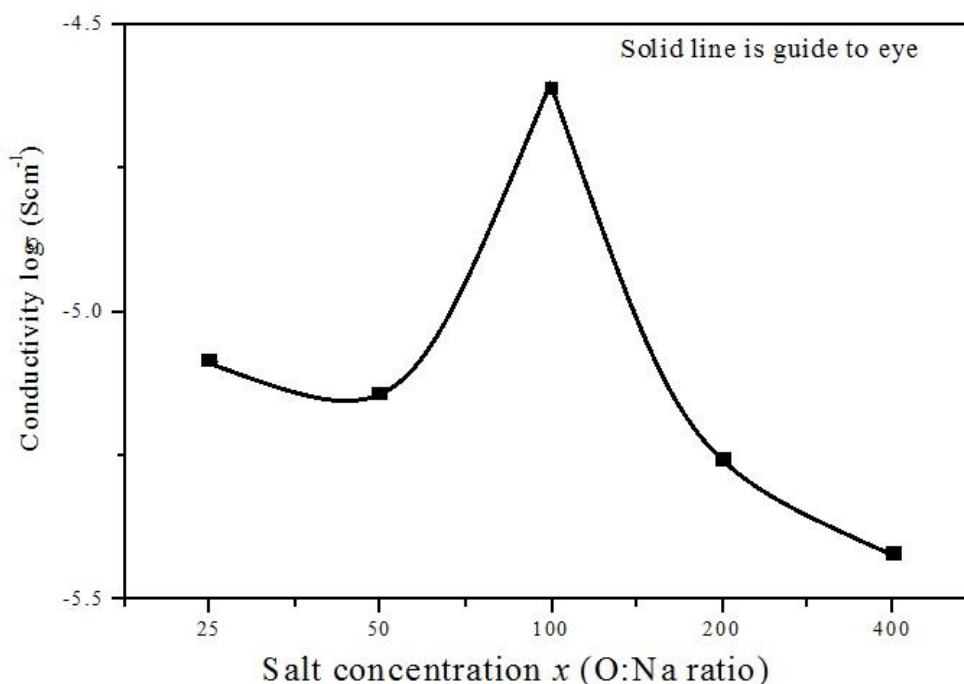


Fig. 6. Variation of ionic conductivity with salt concentration in $(\text{PEG})_x\text{NaCF}_3\text{SO}_3$

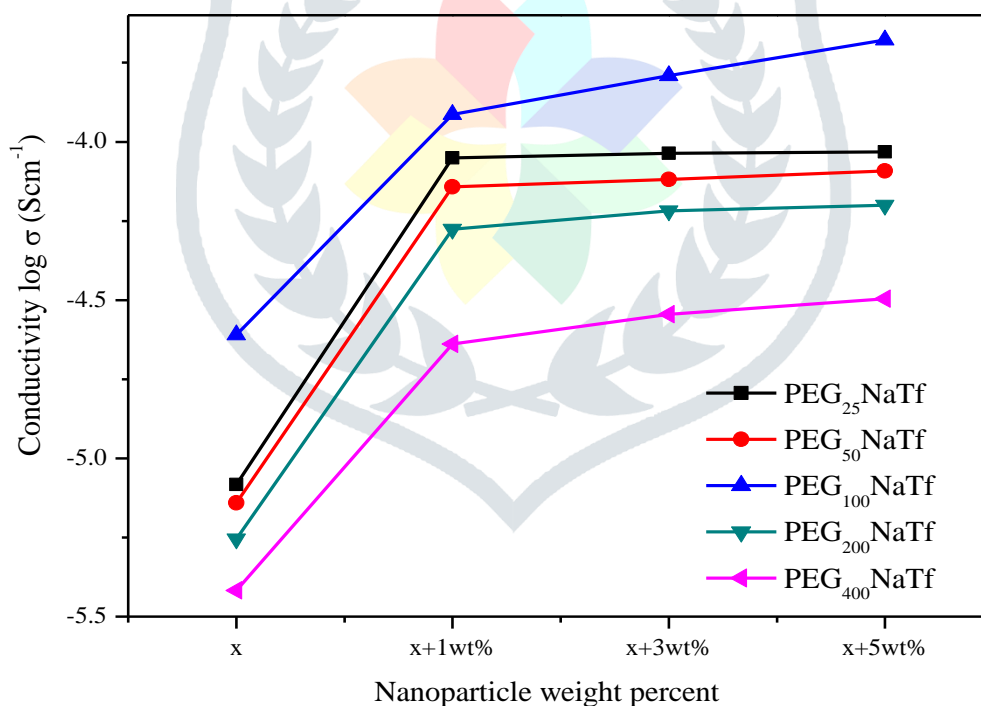


Fig. 7. Ionic conductivity variation with the addition of nanoparticles in $\text{PEG}_x(\text{NaCF}_3\text{SO}_3)$.

IV. CONCLUSIONS

A new solid polymer electrolyte, PEG complexed with NaTf with 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 peak as a function of salt composition typical of an SPE. With the addition of silica nanoparticles, the polymer-salt nanocomposite systems exhibit 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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