

ELECTRICAL PROPERTIES OF PEO-LiCF₃SO₃-SiO₂ NANOCOMPOSITE POLYMER ELECTROLYTES

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ABSTRACT

Nanocomposite polymer electrolytes using PEO-LiCF₃SO₃ incorporated with nanosized SiO₂ fillers have been prepared by the solution cast technique. The effects of concentration of filler on the dielectric properties of the electrolytes were studied. Conductivity is observed to increase with filler concentration with two maximas in conductivity observed at 6 wt % and 10 wt % SiO₂ concentration after which the conductivity decreases. Temperature effects on the dielectric properties revealed that the electrolytes to be of the non-Debye type.

INTRODUCTION

Polyethylene Oxide (PEO) based polymer electrolytes have been extensively studied [1-3] due to several advantageous characteristics. High solvating power for lithium ions, complexation ability and ion transport mechanism directly connected with the alkaline salt (Li⁺), are amongst these advantages. However one of its main drawbacks is its semi-crystalline nature at near ambient temperatures.

This structure is not favourable for high ionic conduction since ionic conduction is known to take place in the amorphous phase [4, 5] when local relaxation and segmental motion of the PEO chains increases [6]. Many methods have been employed to inhibit the crystalline phase and increase the amorphous phase in PEO. These include incorporating low molecular weight aprotic solvents such as ethylene carbonate (EC) and propylene carbonate (PC) [6, 7], dibutyl phthalate (DBP) [8, 9], polyethylene glycol (PEG) [10] and/or incorporating inert inorganic fillers such as TiO₂ [11, 12], Al₂O₃ [11, 13], ZrO₂ [14], SiO₂ [15, 16] etc. The latter method is thought to be more effective since it not only enhanced the ionic conductivity but also improved the interfacial contact between electrode and electrolyte while maintaining the mechanical stability of the electrolyte [17, 18].

In this work, the effects of addition of nanosized SiO₂ fillers on the conductivity of PEO-LiCF₃SO₃ polymer electrolyte are investigated by impedance spectroscopy. This paper discusses the dielectric properties of the electrolytes prepared.

EXPERIMENTAL

PEO (molecular weight = $6 \times 10^5 \text{ gmol}^{-1}$) and LiCF_3SO_3 were purchased from Aldrich. The nanoporous SiO_2 powder had a particle size of 80 nm were purchased from Nanostructured and Amorphous Materials Inc. Appropriately weighed quantities of PEO and LiCF_3SO_3 were dissolved in methanol. SiO_2 powders were added to the solution and were magnetically stirred for at least 24 hours until a homogeneous solution was obtained. The amount of filler added was varied from 2 to 12 wt. % of the total PEO and LiCF_3SO_3 weight. The resulting slurry was cast on to Teflon Petri dishes and left to evaporate. After complete drying, the polymer electrolyte films were stored in the dessicator.

Complex impedance measurements were made on disc shaped samples sandwiched between two stainless steel blocking electrodes of diameter 1 cm using a computer controlled HIOKI 3532-50 LCR Hi Tester in the 100 Hz to 5 MHz frequency range. The ionic conductivity and dielectric properties are derived from equations as listed below:

Equation for ionic conductivity:

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where σ is the ionic conductivity, t is the thickness, R_b for the bulk resistance and A is area of cross section. The equations for complex permittivity (ε) and electrical modulus (M) are given by:

$$\varepsilon_r = \frac{Z_i}{\omega \varepsilon_o A / t [Z_i^2 + Z_r^2]} \quad (2)$$

$$\varepsilon_i = \frac{Z_r}{\omega \varepsilon_o A / t [Z_i^2 + Z_r^2]} \quad (3)$$

$$M_i = \frac{\varepsilon_i}{[\varepsilon_i^2 + \varepsilon_r^2]} \quad (4)$$

$$M_r = \frac{\varepsilon_r}{[\varepsilon_i^2 + \varepsilon_r^2]} \quad (5)$$

where Z_r is the real impedance value and Z_i is the imaginary value. ω is the angular frequency. ε_o is $8.854 \times 10^{-14} \text{ Fcm}^{-1}$, ε_r is the real part of the dielectric constant, ε_i is the imaginary part of dielectric constant, M_r is the real part of electrical modulus and M_i is imaginary part of the electrical modulus.

RESULTS AND DISCUSSION

Figure 1 shows the composition dependence at room temperature of the ionic conductivity of PEO-LiCF₃SO₃-SiO₂ (80 nm) system. Initially, the conductivity increases to reach a maximum at SiO₂ concentration of 6 wt. % in region (I). Upon further increase in SiO₂ content to 8 wt. %, the conductivity decreases and increases again to reach another maximum at SiO₂ concentration of 10 wt. % in region(II). For SiO₂ concentration greater than 10 wt. %, the conductivity of the electrolytes decreases with increase in SiO₂ content in region (III). The conductivity of PEO-LiCF₃SO₃-SiO₂ system is optimised at 10 wt. % SiO₂ (80nm) concentration with a value of $7.11 \times 10^{-5} \text{ S cm}^{-1}$. This is an increase of about two orders of magnitude when compared to the filler free sample which is $2.04 \times 10^{-7} \text{ Scm}^{-1}$. The reason for the ionic conductivity behavior in Figure 1 could be attributed to the increase in the number of charge carriers and in the increase in their mobility with addition of SiO₂. Beyond 10 wt. % SiO₂ the decrease in conductivity with further increase in SiO₂ could be attributed to the blocking effect of the conducting pathways due to the presence of a large number of ions. This blocking phenomenon has been reported in a number of works in the literature [19, 20].

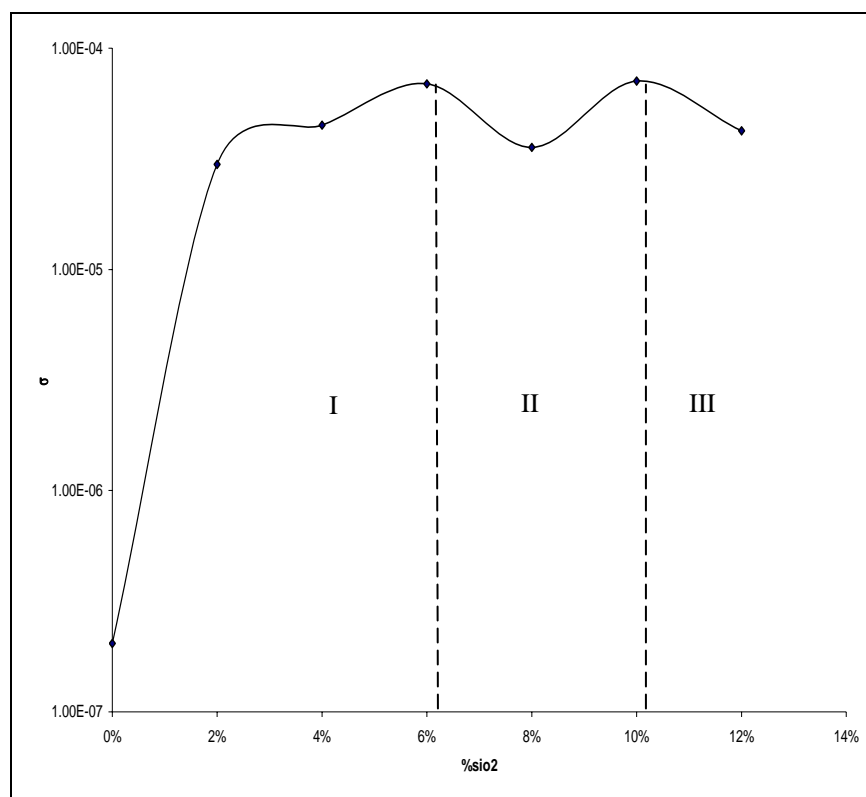


Figure 1: Conductivity variation with SiO₂ (80nm) concentration in nanocomposite polymer electrolyte PEO-LiCF₃SO₃-SiO₂ system.

These two maximas observed in this work may be due to the establishment of percolation pathway in the space-charge region as the filler concentration increases [21,

22]. At the first maxima, surface-charge layer is formed at the polymer-filler interface which provides a conducting pathway for the lithium ions. When the SiO₂ content is further increased, the conductivity tends to decrease but then increases again as the filler content is further increased. The decrease in conductivity as the filler content increases is attributed to the blocking of some of the existing conducting pathways and the possible conglomeration of excess SiO₂ that reduces the polymer-filler interface and hence reduces the conducting pathways. As filler content increases further to the second maxima, conducting pathways are again created but for the conduction of triflate anions. Further increase in filler concentration results in the blocking and the termination of the formation of the conducting pathways. This means that there are two percolation thresholds for polymer electrolytes in this system [22]. The trend in conductivity with two maxima observed in this work is similar to those reported in the literature [23-25].

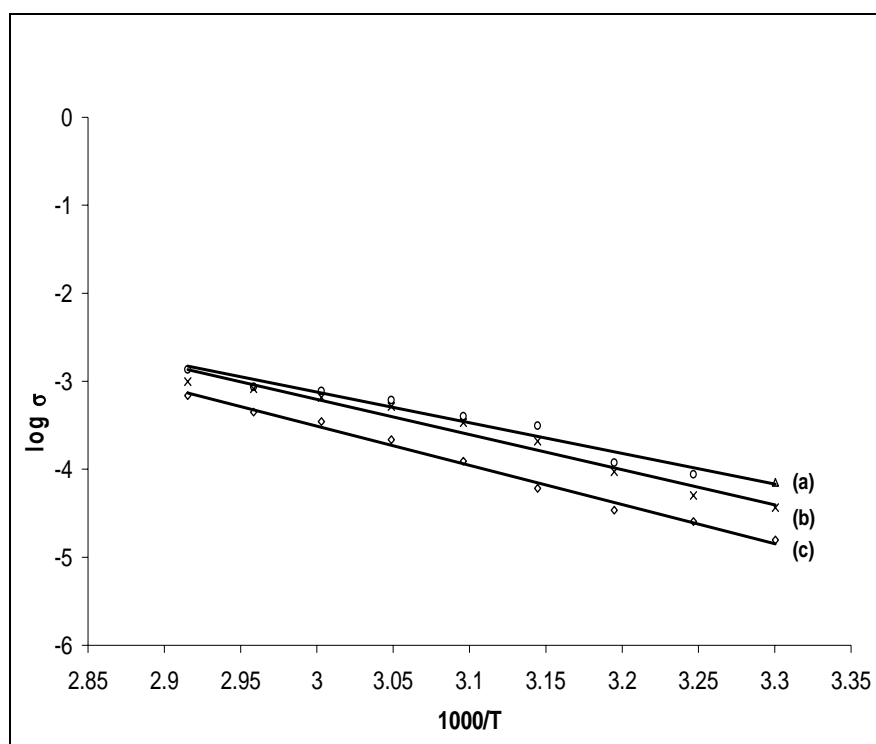


Figure 2: Log σ (S/cm) with $1000/T(1/K)$ for PEO-LiCF₃SO₃-SiO₂ (80 nm) system. (a) 10 wt %, (b) 6 wt % and (c) 2 wt %

Figure 2 presents the logarithmic dependence of conductivity with reciprocal temperature PEO-LiCF₃SO₃- SiO₂ (80nm) electrolytes with filler concentrations of 2, 6, 10 wt% respectively. For SiO₂ concentration of 10, 6 and 2 wt % value of R² were found to be 0.9826, 0.9979 and 0.9893 respectively. It is observed that the ionic conductivity variation with temperature follows the Arrhenius equation with activation energies (E_a) calculated for the temperature range studied (300 K- 343 K) as listed in Table 2. It is found that the activation energies obtained are consistent with conductivity

in that the highest conductivity sample has the lowest E_a . This is attributed to the completely amorphous nature of the polymer electrolyte that facilitates the fast Li-ion motion in the polymer network which further provides a higher free volume in the polymer electrolyte system upon increase in temperature.

Table 2: Activation energy values of PEO-LiCF₃SO₃-SiO₂ polymer electrolytes for 80 nm filler size.

| ELECTROLYTE | SiO ₂ concentration (wt %) | R ² | E _a (eV) |
|--|---------------------------------------|----------------|---------------------|
| PEO-LiCF ₃ SO ₃ -SiO ₂ (80nm) | 10 | 0.9826 | 0.433 |
| | 6 | 0.9979 | 0.440 |
| | 2 | 0.9893 | 0.444 |

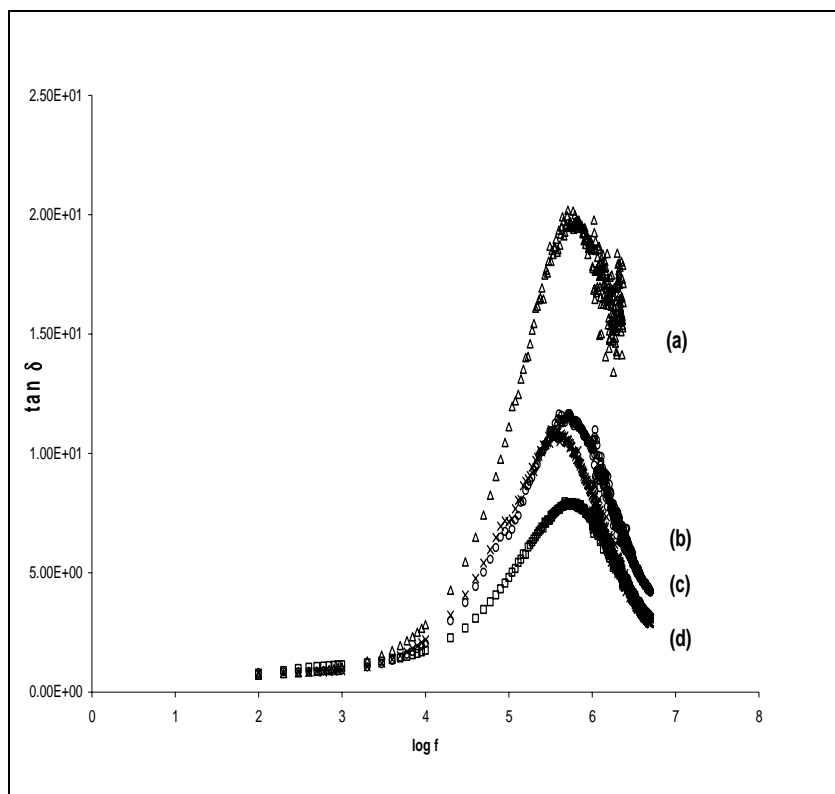


Figure 3: Frequency dependence of $\tan \delta$ for PEO-LiCF₃SO₃-SiO₂ (80nm)10wt.% concentration (highest conductivity) at selected temperatures. (a) 313 K, (b) 308 K, (c) 300 K and (d) 303 K

Relaxation processes of the samples were broadly obtained from a plot of $\tan \delta$ with frequency as shown in Figure 3 for PEO-LiCF₃SO₃- SiO₂ (80nm). It may be observed from Figure 3 that $\tan \delta$ increases with frequency, passes through a maximum value and there after decreases. The increase in loss tangent with frequency is due to free charge build up at the interface between the electrolyte and the electrodes. At higher frequencies, periodic reversal of the electric field occurs so fast that there is no excess of ion diffusion in the direction of the field thus polarization due to charge accumulation decreases. The maxima of $\tan \delta$ shift towards higher frequencies at higher temperatures and so does the height of the peaks. The shift in $\tan \delta$ towards higher frequencies at higher temperatures indicate that there is lower relaxation time at higher temperatures. This means that the ions take a shorter time to hop between conduction sites when the temperature increases showing consistency in results with that obtained from Figure 1.

Apart from the relaxation time, other relaxation behaviour may be obtained from the relaxation of electric field described by the relation:

$$\Phi(t) = \exp [-t/t_M]^\beta \quad (6)$$

Here t_M and β are conductivity relaxation time and Kohlrausch exponent respectively from which β may be calculated from the following equation:

$$\beta = 1.14/\text{FWHM} \quad (7)$$

where FWHM is full width at half maximum. Table 3 lists the values of FWHM and β . It is found that β has an average value of 0.59 for PEO- LiCF₃SO₃-SiO₂ (80 nm). This shows that the relaxation phenomena in the polymer electrolyte system PEO-LiCF₃SO₃-SiO₂ is non- Debye type since values of β obtained are less than 1 indicating deviation from the Debye-type relaxation where $\beta = 1$.

Table 3: Calculated values of β for PEO- LiCF₃SO₃-SiO₂ (80 nm) 10% wt. % concentration

| Temperature (K) | FWHM | β |
|-----------------|--------|---------|
| 300 | 1.750 | 0.651 |
| 303 | 1.9167 | 0.595 |
| 313 | 2.00 | 0.570 |
| 318 | 2.085 | 0.550 |

In order to obtain an estimate of the T_g values of the polymer electrolytes a graph of $\tan \delta$ versus temperature is plotted for 10 wt % and 2 wt % SiO₂ concentration. From the graph, T_g values are obtained from the maximum of $\tan \delta$. These values are tabulated in Table 4, and are found to be consistent with reported results where higher conductivity samples have a lower T_g [26,27].

Table 4: Values of T_g for PEO- LiCF_3SO_3 - SiO_2 (80nm)

| ELECTROLYTE | SiO_2 concentration | $T_g(\text{K})$ |
|--|------------------------------|-----------------|
| PEO- LiCF_3SO_3 - SiO_2 (80nm) | 10 wt % | 323 |
| | 2 wt % | 333 |

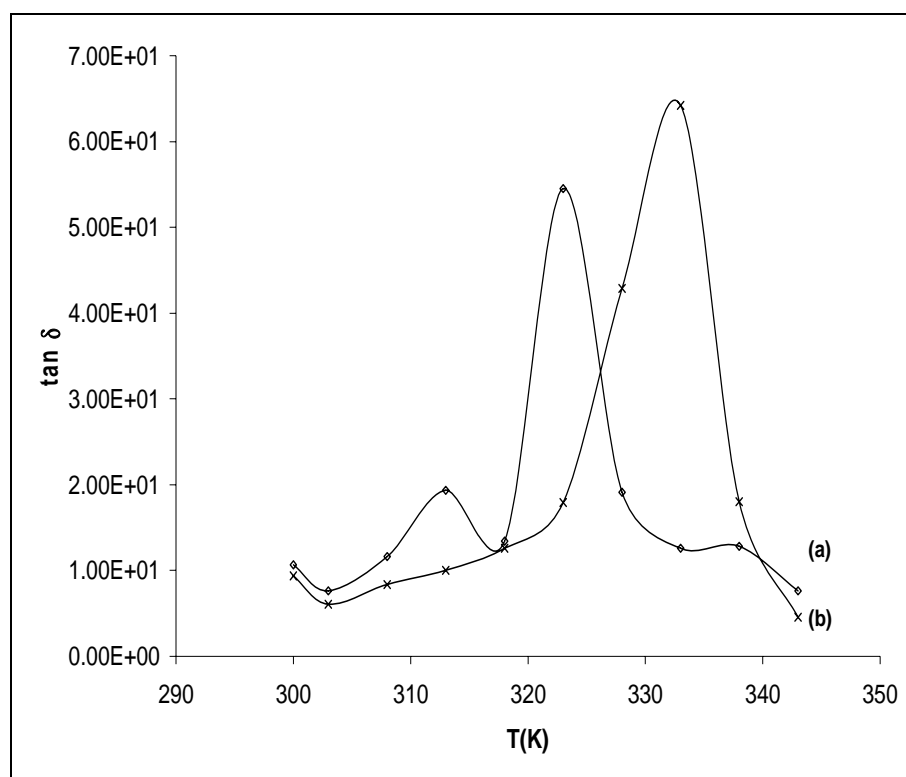


Figure 4: $\tan \delta$ vs temp for 80 nm size filler at SiO_2 concentration: (a) 10 wt % and (b) 2 wt %.

CONCLUSION

The conductivity obtained for PEO- LiCF_3SO_3 - SiO_2 is $7.11 \times 10^{-5} \text{ S cm}^{-1}$ for 10 wt % concentration of SiO_2 . Two maximum in conductivity was observed and these were explained in terms of the percolation theory. The dielectric behaviours of the prepared samples show non-Debye type of behaviour and are strongly dependent on frequency and temperature.

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