CHAPTER 8

DISCUSSION

The science of polymer electrolytes is a highly specialized interdisciplinary field which encompasses the disciplines of electrochemistry, polymer science, organic chemistry, and inorganic chemistry. Many researchers have contributed great effort to synthesize high ion conducting polymer electrolytes over the decades. However, the desired value of conductivity at the ambient temperature is still insufficiently high at room temperature for application in devices. The incomplete understanding on the conduction mechanism for polymer electrolyte is the main barrier that hinders realization of the usage of solid polymer electrolyte. The concept of composite polymeric electrolytes based on a polyether matrix with dispersed inorganic fillers and organic macromolecules is currently being widely explored [Kalita et al., 2007].

Poly(ethylene oxide)-based solid polymer electrolytes have been proposed for used in several applications, due to their low impact on environment, relatively low cost and no risk of electrolyte leakage, good usage safety, as well as good stability [Oleg et al., (2007), Gray, (1991) and Bruce, (1995)]. The great majority of studies on batteries over last two decades have been directed towards the development of highly conductive solid polymer electrolytes**.** A central aspect of research on these electrolytes deals with the mechanism of ion transport. When salt dissolves in polymer and dissociates to ions, it generates carrier ions, which increases ionic conductivity. The effect of anions on conductivity is important, because ionic conductivity is the result of cation and anion flows in opposite directions. In battery application**,** cations from the metal electrode can compensate the polarization of cations, but there is no anion source that can act similarly. If mobile anions are used, the polarization of anions will take place in the system. This polarization causes an anion concentration gradient that affects the conductivity of the system after battery is used. For this reason, it is better to use medium or large anions of relatively low mobility, such as I^-, ClO_4^-, SCN^-, etc. In a carefully chosen polymer system it should be possible to incorporate even larger proportions of salts so that oxygen to metal ratio is reduced to levels where the cations would require to retain part of their own anionic coordination from the pure salts. It should also be possible to alter the polar nature of ionic conduction by incorporating salts with high anionic charges which immobilise themselves due to higher coulombic potential of their own [Schultz et al., (2006)].

In our present study composite polymer electrolytes were prepared using solution casting technique with PEO as a host polymer, LiI as a doping salt and acetonitrile as a solvent. It can be seen that the conductivity increases and reaches the highest value of 1.54×10^{-4} S cm^{-1} for PEO: LiI (90:10) composition. Ionic conductivity of 1.54×10^{-4} S cm^{-1} is recorded at room temperature, increases to 4.08×10^{-3} S cm^{-1} at 80°C. Poly(L-Leucine)-1,3-diamino propane–lithium iodide (LiI) samples reported by Kaus et al., (2009) showed ionic conductivity of 1.20×10^{-4} S cm^{-1} at room temperature, increases to 3.20×10^{-3} S cm^{-1} at 80°C and PEO-$LiClO_4$ reported by Prabharan et al., (1997) also had shown the 10^{-4} S cm^{-1} is recorded at room temperature, increases to 10^{-3} S cm^{-1} at 80°C. The ionic conductivity increased at 80°C temperature because the local environment of the lithium ion is in the liquid state due to the melting temperature of PEO at ~65°C. This observation can therefore be attributed to the availability of conducting ions supplied by the incorporated salt and to the increasing amorphous nature of the material as a result of polymer-salt complexation (Carini et al.,1992). It is well known that ionic conductivity occurs in the amorphous region of the polymer (Berthier et al., 1983, and Wright et al., 1975). However, for higher salt concentrations (LiI > 10 wt %), the conductivity drops due to the ion association, which could lead to the increase in the degree of crystallinity. The crystallinity of the samples at different weight percentages of LiI is measured from the deconvoluted peaks in FTIR studies. This has been attributed due to the occurrence of ion association into neutral ion aggregates. Fig 4.10 depicts the graph of percentage of free ions that shows a maximum at 10 wt% LiI indicating that this sample should exhibit the highest conductivity at room temperature for the PEO-LiI system, based on free ion number density. The ratio of the area of the free ion peak to the total area of both peaks can give the percentage of free ions.

In theory, at low salt concentration, the ionic conductivity is strongly controlled by number of charge carriers and the mobility of ions is relatively unaffected. However, at the lower concentrations, as the temperature increases, the fraction of free anions increases, and the fraction of ion pairs and triplets is a minimum. For the higher concentrations, the fraction of ion pairs increases with increase in temperature, and the fraction of triplets decreases. The oxygen atom in PEO is the backbone to coordinate with the metal cations and facilitate ion-pair separation, which can then favour conduction through ion transport.

From the FTIR studies shown Figure 4.7 the peak of pure LiI is located at 1619 cm^{-1} which is upshifted to 1660 cm^{-1} and gets broader as the percentage of the LiI increases. The complexation might be occurred between the Li^{+} and the oxygen atom in the carbonyl group of polymer. This complexation resulted in increase in amorphousness of the sample that is manifested by the broader peak Golodnitsky, et. al, (2002), in his studies of PEO with $LiClO_4$ also had shown the same type of complexation between polymer and Li^+ . For application in electrochemical devices, amorphous or non-crystalline polymer electrolytes are gaining attention because crystalline polymer electrolytes are believed to be the cause of significant decrease in ionic conductivity.

In Figure 5.1, XRD spectrum of PEO-LiI, it is very clear that when the concentration of salt increases the crystallinity of polymer host decreases. For the pure PEO the peak at 19° gets shifted to 19.3° and the intensity decreases by the addition of different wt. % of LiI salt. This shows on addition of LiI salt into the polymer, a good complexation is formed between Li^+ ions and the oxygen atoms in the polymer PEO, resulting in the reduction of crystallinity of the polymer electrolyte associated with the enhancement of the amorphous phase. Sreekanth et al., (1999), Kuila et al., (2007), and Mohan et al., (2005) were also shown same type of complexation of polymer with Li salts.

Investigation of dielectric behaviour in Figure 7.1: (a), (b) and 7.2 (a), (b) shows, the variations of dielectric constant and dielectric loss as a function of frequency for PEO-LiI at room temperature. ε_r and σ increases with salt concentration due to the increase in concentration of free ions. It can be inferred that ε_r and σ at room temperature increases because of the increase in free ion concentration. ε_r and σ also increase with temperature. This implies that ε_r and σ are interrelated. This should be taken as a further study. As from the figure the dielectric loss and dielectric constant decreases with increase in frequency. This could be explained due to the dipoles formed between Li^+ and the oxygen from the polymer which were not able to follow the variation field at higher frequencies (Bhargav, et al., 2009). The ε_r increase towards low frequencies may be due to dielectric orientation polarization (Ramesh *et al*., 2002) and space charge polarization (Hema *et al*., 2008).

Figure 7.4 (a) and (b) show the variations of ε_r and ε_i with temperature at various frequencies for PEO sample. Both dielectric constant and dielectric loss show temperature dependence and decrease in value of increasing frequency. The dielectric permittivity increases with increase in temperature of polar material due to facilitation in orientation of dipoles (Awadhia *et al.*, 2006) and increasing mobility of charge carriers which tend to move freely as the temperature increase. It can also be seen that as temperature increases, the value of dielectric loss increases. This is due to the contribution of mobility of free ions which increase with their kinetic energy and thermal energy. The dielectric constant and dielectric loss shows a considerable increase when the temperature is increased may be due to polarization effect. The electron exchange interaction results in a local displacement of the electron in the direction of an electric field, which determines the polarization of the PEO-LiI. In other words, increasing the dielectric loss by increasing temperature is owing to the hopping of the charge carriers in the localized state and also due to the excitation of charge carriers to the states in the conduction band.

Figure 7.5 shows the variation of tan δ as a function of log ω for different amounts of salt in PEO polymer electrolytes. It has been observed that tan δ increases with increasing frequency and reaches a maximum. Then it decreases for further increase of frequency. This is due to the increment in number of charge carriers for conduction. The higher the temperature the higher the loss tangent at lower frequency accompanies the less dependence on temperature at higher frequency.

Figure 7.7 (a) and (b) show the real (M_r) and imaginary (M_i) parts of the electric modulus as a function of log ω where the graphs show a significant decrease in intensity with rising temperature. *Mr* and *Mi* plots for PEO-LiI show an increase at high frequency end indicating that the polymer electrolyte films are ionic conductors. As the temperature increases, the possible peak maxima shifts to higher frequencies which indicates that the conductivity of the charge carrier has been thermally activated Ramya et al., (2008).

By adding inorganic filler like SiO_2 can improve the mechanical properties and electrical properties of Li based solid electrolyte Kwang-Sun Ji et al., (2003). It was recognized that the addition of inorganic fillers led to an improvement in the mechanical properties and an increase in the ambient temperature conductivity of electrolytes studied [Yuankang et al., (1986), Linquan et al., (1986) and Plocharski et al., (1989)]. The enhancement in conductivity and the mechanical properties are due to the surface interactions between the PEO and added LiI salt.

To the high conducting 90 wt% PEO-10 wt% LiI system we are added different weight percentage of Al_2O_3 inorganic filler. Table 6.2 shows the ionic conductivity increases by the addition of different weight percentages of Al_2O_3 to the highest conducting PEO-LiI sample. As shown in the table the ionic conductivity increases from 2.98×10^{-4} S cm^{-1} to 3.30×10^{-4} S cm^{-1} in 5 wt.% to 15 wt.% of Al_2O_3 due to interactions between the surface groups of the ceramic particles and both the PEO segments and the lithium salt anions. When the concentration of inorganic filler in the polymer matrix increases, the average separation between dissolved ions decreases which in turn increases the ion-ion interaction and the increase in ion aggregates with increasing concentration of filler (Fuoss and Kraus (1959). Conductivity decreases with further addition of filler due to ion dissociation. There is a decrease in ionic conductivity from 15 wt. % to 25 wt. % of Al_2O_3.

Figure 4.14 FTIR spectra show the change in LiI peak after the addition of Al_2O_3. For the addition of 5 wt. % to 25 wt. % of $Al_2O_{3,}$ the peak shifts from 1619 cm^{-1} to 1659 cm^{-1}. This is due to the complexation of Al_2O_3 with the polymer electrolyte. This happens when oxygen atom in the Al_2O_3 and the donor oxygen in PEO compete to coordinate with the Li^+ions. The Li^+ cations can have interactions with the Al_2O_3 to form complex ions. Such coordination prevents PEO molecules from crystallizing on the one hand, and, on the other, releases more free Li+ ions. Besides, the I^- anions are also bound to the Lewis acidic sites (O vacancies) through coordination, which separates the Li^+I^- pairs. These two modes of coordination produce more dissociated lithium ions as charge carriers and more amorphous region for the carriers to transfer, and finally enhance the conductivity of the polymer electrolyte. This coordination can be explained by the broadening of peak in the spectrum.

Hydroxyl ions coordinated in various ways with aluminum cations constitute the reactive functional groups of alumina surfaces. These hydroxyl groups can have weak dipole dipole interactions with the I^-. If these had happen the conductivity reduces but in our studies the conductivity for PEO-LiI-Al_2O_3 increases than PEO-LiI.

Figure 5.5 shows the XRD patterns after the addition of different weight percentages Al_2O_3 inorganic filler to the highest conducting PEO-LiI system. The characteristic peak at $2\theta = 23^\circ$ has become broader suggesting a reduction in PEO crystallinity (Xi et,al.2005). Moreover, Al_2O_3 may provide more Lewis acid-base interactions with Li^+

and PEO chains yielding new electrolyte properties (Golodnisky et.al.,1998, Ardel et.al., 1996). This complexation agrees well with the FTIR results.

This finding, the increase in the amorphous nature and conductivity is further supported by dielectric studies. Fig 7.8 (a) and 7.8 (b) shows the frequency dependence of the dielectric constant, ε_r and ε_i for PEO-LiI system with Al_2O_3 at different weight percentage at room temperature. As shown in the figure, 15 wt % Al_2O_3 prevails at higher region and this indicates that it has higher mobile charge carriers for migration compared to other electrolyte samples (Mellander et al.,2002). Figure 7.9 (a) and (b) show variation of ε_r and ε_i with log ω for PEO-LiI highest conducting sample with different wt. % of Al_2O_3. It is observed that both the dielectric constant and dielectric loss increase with temperature, which can be attributed to the increase in charge carrier density due to the increase in the dissociation of ion aggregates due to Lewis Acid base interactions of Al_2O_3 and the PEO.

To overcome poor ionic conductivity and low cation transference number there were a lot of strategies used. But up to now none of the strategies was able to simultaneously improve both ionic conductivity and transference number. The addition of anion receptors, supramolecular compounds, which interact with anions by several hydrogen bonds, to the PEO-based electrolytes resulted in the improvement of their conducting properties. The increase in the t_{Li}^+ value after supramolecular polymer electrolyte modification was confirmed experimentally by group of Wieczorek and co-workers for calix4 arenes. The application of this type of receptors as solid polymer electrolyte additives improved t_{Li}^+, however, the conductivity of the membrane was lowered by at least one order of magnitude. This phenomenon could be attributed first of all to the decrease of the charge carriers concentration due to anion trapping and additionally the interactions of calix molecules with the polymer salt system [Kalita et al., (2005)].

In present study we used calix4 and calix6 arenes as organic fillers. To high conducting PEO-LiI system added calix4 and calix6 one at a time. The PEO-LiI has the conductivity of 1.54×10^{-4} S cm^{-1} at room temperature. The decrease in overall ionic conductivity values of PEO-LiI-calix4, 4.56×10^{-5} S cm^{-1} and PEO-LiI-calix6, 2.87×10^{-5} S cm^{-1} at room temperature could be attributed first of all to the decrease of the charge carriers concentration due to anion trapping and additionally, to the high affinity of the carbonyl oxygen atom from the calix arenes to the Li^+ cation. If the complex structures are the result of neutral ion aggregate formation then a drop in conductivity is expected. The possible anion trapping through the dipole interactions is shown in Figure 4.33.

Another important factor that contributes significantly to the conductivity of a material is the number density and mobility of the mobile species and the density number of mobile ions is dependent on the rate of ion association and dissociation. In samples exhibiting higher conductivity values, the rate of ion dissociation should be greater than the rate of ion association. The idea of ion association has been confirmed in calix4 and calix6 arenes conductivity measurements. At higher temperatures, the conductivity of calix4 and calix6 arenes containing samples is similar to the system which does not contain the anion receptor, that is, at higher temperatures the ionic conductivity increases is due to the increase in ion pairs. The fraction of these charge carriers are charge triplets Kalita et al., (2005).

In Figure 4.27, the peak for lithium iodide for the PEO-LiI system appears at 1635 cm^{-1} which originally appeared at 1619 cm^{-1} in pure LiI spectrum. These shifting showed, by the addition of macromolecules to polymer salt system there will be weaker interaction between anions I^- and calix arenes. Calix arenes contains –OH group in the inner rim, the oxygen in the hydroxyl group can have a a stronger interactions with Li^+. In Fig 4.30, the C-O-C vibration of pure calix occurs at 1098 cm^{-1}it gets broader and shifted to 1106 cm^{-1} as the concentration of calix6 increases to 5 wt. % due to the complexation between the linking of polyether chains by van der Waal's forces and due to the weak ionic interactions.

The peaks, far less intense are also found in the FTIR spectra of polymer salt systems with organic additives calix4 and calix6 arenes. In Figure 4.7 the peak at 1652 cm^{-1} can be superposition of peaks attributed to weakly and strongly associated carbonyl group of the calix molecule. The peak at 1700 cm^{-1} corresponds to free carbonyl group of the receptor molecules. It shows that there are interactions between polymer salt system and the additives.

The study of FTIR data of calix6 arenes and calix4 arenes has shown that it has ability to form complexes with polymer-LiI system. The shifting of LiI band has shown that the I^- may be bonded to the -OH group through dipole interactions or through weak van der Waal forces. On the basis of our results obtained in FTIR studies we can assume that calix arene derivatives may be successfully used as receptors to immobilise the I^- anions.

Fig.5.8 and Fig 5.9 show the XRD patterns obtained for calix4 and calix6 arenes added in different weight percentages to the highest conductivity sample in the PEO-LiI system i.e, 90 wt.% PEO:10 wt. % LiI. From the close observation of the peaks at $2\theta = 19^{\circ}$and 23° proves that even high molecular weight polyether somehow interacts with the receptor calix4 and calix6. These interactions can be due to weak inter molecular forces like dipole dipole forces between hydrogen in the hydroxyl group of calix arenes and I^- Another interaction is attributed between polymer and calix arenes. The peak near 2θ =19° and is characteristic for the crystalline phase of the pure polymer Kalita et.al., (2007). The decrease in intensity of the peak at 2θ =19° shows, by the increase in weight percentage of the calix arenes because there is a decreases in weight ratio of the polymer. However the broadness increases. Fig 5.3 shows the percentage of crystallinity peak at 19°, for various PEO-LiI systems. PEO incorporated with 10 wt. % LiI salt shows the lowest percentage of crystallinity therefore this sample is the most amorphous and should exhibit the highest conductivity at room temperature The splitting pattern and the intensity of the peak at 2θ =23° shows the interactions of calix arenes with polymer salt system.

The less intense peak compared to pure calix6 in Fig 5.9, shows the more amorphous nature of the system and the complexation. The complexation related to the lithium cation, which is able to interact with oxygen atoms belonging to different polyether chains and the macromolecule receptors. There are no other new peaks observed in this region, shows the absence of any new crystalline complex.

Fig 5.12 depicts the variation in percentage crystallinity of calix4 and calix6 content in PEO salt complexes measured using Origin software. The least crystallinity was found for system added with 3 wt.% calix4 and system with 3 wt.% calix6, since being the most amorphous. The XRD patterns show that the formation of a less crystalline salt-PEO complex by the addition of Calix4 and Calix6 arenes. It shows a better compatibility between supramolecular receptor and the PEO polymer matrix which agrees with the FTIR results.

From present study we are able to identify the effect of a LiI salt, inorganic filler, Al_2O_3, and macro molecules calix4 arenes and calix6 arenes in improving ionic conductivity in solid polymer electrolyte like PEO. Even though by adding LiI and Al_2O_3 inorganic filler we can improve ionic conductivity and mechanical stability of polymer electrolytes it is not enough for battery applications. Both anions and cations are generally mobile in most polymer electrolytes, whereas restricting the mobility of the anions without affecting the lithium cations is desirable for battery applications. By adding calix arenes we can immobilize I^- anion which can covalently connect to polymer matrix and can trap it through weak van der Waal forces or with electrostatic force of attraction between calix arenes –OH group and I^-. By immobilizing the anions through these weak interactions we can improve the transport properties of this composite polymer system. These immobilization might be the reason of decrease in the ionic conductivity in PEO-LiI-Calix arene system.