**CHAPTER 8**

**DISCUSSION**

In the present work, $Al_2TiO_5$ filler has been prepared using the sol-gel method. Formation of aluminium titanate at low temperatures, over 600 $^o$C can be achieved via nonhydrolytic synthesis [Andrianainarivelo et al., 1997] and around 800 $^o$C by a synthesis with alkoxides stabilized with acetylacetone [Coury et al., 1994]. The formation of aluminium titanate at low temperatures is attributed to a diffusion-limited crystallization process, which takes place in conditions of high homogeneity at the molecular level reached in the material [Lange et al., 1994]. The sol-gel process is undoubtly the simplest and the cheapest one. The method is based on the phase transformation of a sol. The advantages of the sol-gel method are its versatility and the possibility to obtain high purity materials, the composition of which is perfectly controlled. The basis of choosing the $Al_2TiO_5$ as the filler is because of its low thermal expansion, high thermal shock resistance and high melting point. Due to these reasons, it is believed that $Al_2TiO_5$ should be able to serve as a good filler. Ammonium thiocyanate, $NH_4SCN$ has been chosen to make the electrolyte a proton conductor. As mentioned, the $NH_4^+$ is believed to be responsible for the ionic conduction. The conducting species in the chitosan-$NH_4SCN$ system is $H^+$ from the acids used to dissolve the polymers, which is acetic acid. The addition of $NH_4SCN$ enhances the conductivity of chitosan-$NH_4SCN$ from $1.60 \times 10^{-10}$ S cm$^{-1}$ to $1.38 \times 10^{-4}$ S cm$^{-1}$. Srivastava and Chandra (2000) have proven that in the PESc:$NH_4ClO_4$ system, the conducting species is $H^+$ ion. The $H^+$ ion originates from the ammonium ion. Due to thermal energy, the $NH_4^+$ ions is able to rotate and the fourth hydrogen in the $NH_4^+$

ions is then released as a proton when it hops to another site. This rotation continues until an $H^+$ ion from another site takes the place of the emigrant proton. Conduction thus occurs by a Grotthuss mechanism, i.e. the conduction occurs through the exchange of protons between polymer-salt complex sites. The Grotthuss mechanism [Majid and Arof, 2005], consists of internal free rotation of $NH_4^+$ ion followed by proton hopping leaving in a vacancy in the $NH_4^+$ ion. This is then filled by incoming $H^+$ [Shuhaimi et al., 2008].

The conductivity value of the pure chitosan acetate is $1.67 \times 10^{-10}$ S cm$^{-1}$. Pure chitosan then has been added with NH$_4$SCN. With the addition of 40 wt. % NH$_4$SCN, the conductivity value of chitosan-NH$_4$SCN system has increased to a maximum value of $1.38 \times 10^{-4}$ S cm$^{-1}$. The conductivity value of the polymer electrolyte system which consists of chitosan – 40 wt. % NH$_4$SCN – 5 wt. % Al$_2$TiO$_5$ was obtained at $2.10 \times 10^{-4}$ S cm$^{-1}$. The increased in the conductivity is believed to be influenced by the increased in the number of charge carriers supplied by NH$_4$SCN salt and the nature of the materials i.e. the degree of amorphousness/crystallinity is proven from the XRD and morphology studies.

Ionic conductivity of polymer electrolytes can be increased by dispersion of nano-sized inorganic ceramic filler particles (Al$_2$O$_3$, SiO$_2$, TiO$_2$, ZrO$_2$) in the polymer host matrix [Croce et al., 2001; Dissanayake et al., 2003; Ahn, et al., 2003; Appetecchi et al., 2000; Jayathilake et al., 2002; Lin et al., 2005; Xi et al., 2005; Chung et al., 2001; Croce et al., 2006]. Other technique is the addition of low molecular weight plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and polyethylene glycol (PEG) into the conventional PEO-LiX systems [Nicotera et al., 2002; Bandara et al., 1998; Qian et al., 2002; Chintapalli et al., 1996]. The addition of

fine inorganic fillers such as $\gamma$-Al$_2$O$_3$, SiO$_2$, $\gamma$-LiAlO$_2$, Zeolite and Nasicon into the polymer electrolyte has been widely recognized to lead to an improvement in the mechanical properties and at the same time an increase in the electrical conductivity [Liquan, 1986; Plocharski et al., 1988; Capuano et al., 1991; Munichandraiah et al., 1994]. The use of plasticizers tend to make the electrolyte more liquid-like. There are so many parameters governing the conductivity in the composite electrolyte that the mechanism of conductivity enhancement remains uncertain at the present time. In several composite electrolytes however, the additives such as $\alpha$-Al$_2$O$_3$, lithium borosulfate glass and $\gamma$-LiAlO$_2$ have been found to have a negligible or a small depressing effect on the conductivity [Weston et al., 1982; Panero et al., 1992; Kumar et al., 1994]. Croce et al., (1998), suggested that the inorganic fillers help to increase the ionic conductivity of PEO-based electrolytes in two ways; increasing the ratios of the amorphous phase of PEO and providing Li$^+$ conducting pathways at the fillers' surface through Lewis acid-base interactions, among different species in the CPE.

Another important feature of filler is its size. The size of filler can also determine the degree of enhancement and conductivity. It has been shown that increasing the particle size for the same volume concentration of barium titanate increases the nonlinear AC conduction as the electrical field is increased. The addition of barium titanate into acrylic resin can produce a material with an electrical field dependent permittivity, whilst having a low DC conductivity [Robertson and Varlow, 2004]. This therefore results in higher permittivity at zero field and also a higher increase in permittivity as the electric field strength is increased and has been reported that an increase in the particle size and filler concentration does not significantly increase the DC conductivity. In this study, from Scherrer length calculation, the crystallite size of the Al$_2$TiO$_5$ particle is 123.75 nm.

Pitawala and co-workers (2007) concluded from their study on $(PEO)_9LiTf$ that the ionic conductivity enhancement observed in the $(PEO)_9LiTf:EC:Al_2O_3$ polymer electrolyte evidently results from the combined effect of the plasticizer and the filler. Both of these would increase the amorphous phase content in the electrolyte as evident from their thermal data. An additional mechanism, directly associated with surface interactions of the filler with ionic species also appears to contribute to the conductivity enhancement. One possible explanation for this can be the creation of favourable conducting pathways through Lewis acid–base type interactions of ionic species with O/OH surface groups on alumina filler grains. The presence of O/OH surface groups on $Al_2TiO_5$ has been inferred from FTIR studies presented in Chapter 6. $H^+$ ions from the salt can hop along the oxygen atom of the OH groups and in doing so conduct charge. Evidence of $Al_2TiO_5$ acting as transit pathways in the lower activation energy of the composite produced in this work.

According to Jeon et al., (2006), the ionic conductivity of polymer electrolyte increases up to 1.5 wt.% $TiO_2$ in a viscous electrolyte, and when the $TiO_2$ is added further the conductivity begins to decrease. This decrease is probably due to aggregation of $TiO_2$ nanoparticles. The conductivity shows a maximum value of $5.1\times10^{-5}$ S cm$^{-1}$ at 25 $^{\circ}$C compared with $3.2\times10^{-5}$ S cm$^{-1}$ for a polymer electrolyte without $TiO_2$.

Transport parameters such as number density of ions and mobility of charge carriers were the other alternative way in order to understand the increase and decrease in conductivity value. In the present study, it has been shown that the use of aluminium titanate as a filler is able to improve the electrical conductivity of the chitosan-$NH_4SCN$ system from $1.38 \times 10^{-4}$ S cm$^{-1}$ to $2.10 \times 10^{-4}$ S cm$^{-1}$, as the $Al_2TiO_5$ concentration

increases from 1 to 5 wt. %. Further addition of $Al_2TiO_5$ decreased the conductivity decreases. According to Choi et al., (1996) the enhancement of ionic conductivity in PEO-LiClO$_4$ filled with SiC was achieved when the content of SiC is between 5 and 10 wt. %. This is attributed primarily to the enhancement of PEO segmental motion. Park et al., (2003) have reported on conductivity studies of PEO-LiClO$_4$-Al$_2$O$_3$ and observed that the increase of ionic conductivity with Al$_2$O$_3$ content is attributed to a reduction of crystallinity of composite polymer electrolyte as is also observed in the present study. A reduction of crystallinity arises from the random distribution of fine Al$_2$O$_3$ powder which may increase the disorder domain in the polymer electrolyte. A polymer chain in the amorphous phase or the less ordered regions is more flexible, which results in an increase of segmental motion of the polymer. For more than 12 wt.% Al$_2$O$_3$, the ionic conductivity decreases, because the inorganic fillers tend to impede ionic movement by acting as an insulator or an agglomerates. In this work the conductivity decreased after more than 5 wt.% Al$_2$TiO$_5$. Probably, at this composition the dielectric effect of Al$_2$TiO$_5$ is more dominant over its insulating effect. Park and co-workers also claimed that the conductivity values of the composite polymer electrolytes prepared with two fillers are higher than those of the composite polymer electrolytes prepared with one filler (Al$_2$O$_3$ or BaTiO$_3$). In the composite polymer electrolytes doped with two fillers (Al$_2$O$_3$ or BaTiO$_3$), a role of ferroelectric BaTiO$_3$ is to enhance the charge carrier generation and Al$_2$O$_3$ is to reduce the crystallinity of the composite polymer electrolyte. Table 8.1 below shows examples of conductivity for some composite polymer electrolytes.

**Table 8.1 : Examples of conductivity of composite polymer electrolytes.**

| Composition | Conductivity ( S cm$^{-1}$) | Reference |
|---|---|---|
| PEO-LiClO$_4$-Al$_2$O$_3$ | > 1.0 x 10$^{-7}$ | Park et al., 2003 |
| PEO-LiClO$_4$-Al$_2$O$_3$-BaTiO$_3$ | 1.5 x 10$^{-7}$ | Park et al., 2003 |
| PEO-LiClO$_4$-$\alpha$-Al$_2$O$_3$ | ~ 10$^{-4}$ | Tambelli et al., 2002 |

The conductivity also can be correlated to the dielectric constant, $\varepsilon_r$ of the samples. The decrease in conductivity should be due to the decrease in the number of free mobile ions due to ion association. This can be reflected from the dielectric constant, $\varepsilon_r$ versus frequency curve for different Al$_2$TiO$_5$ concentration, Fig. 5.6. The dielectric constant reflects the capacitive nature at the electrode-electrolyte interface. The higher the value of the dielectric constant, the higher the capacitance value. The higher the capacitance value indicates the larger number of ions existing at the electrode-electrolyte interface [Yahya, 2002] and in the material in general.

The conductivity studies on chitosan-NH$_4$SCN and chitosan-NH$_4$SCN-Al$_2$TiO$_5$ is conclusive that the conductivity is affected by temperature. The plots can be considered linear and hence obey Arrhenius rule. The dielectric constant, $\varepsilon_r$ of the system is also affected by the temperature. Temperature has influenced the dissociation of ions which leads towards conductivity enhancement. From the plot of $\varepsilon_r$ versus log frequency of the chitosan-NH$_4$SCN-Al$_2$TiO$_5$ system in Fig. 5.7 at various temperature (298 K – 393 K), it is observed that as the temperature increases the $\varepsilon_r$ also increases.

The dielectric properties of composites comprising polyvinylidene fluoride (PVDF) and calcium copper titanate (CCTO) particles have been investigated by Yang et al., (2011). The effective dielectric constant of the composite containing 40 vol.% nanosized CCTO filler is over $10^6$ at $10^2$ Hz and room temperature, which is substantially higher than that of the composite containing microsized CCTO, where $\varepsilon_r$ value is 35.7 (with 40 vol.%). The $\varepsilon_r$ decrease with temperature for the composite containing nanosized CCTO, while the one with microsized CCTO shows the opposite tendency. For the composite with nanosized CCTO, the conductivity decreased sharply with increasing temperature in the low frequency range ($100\text{-}10^4$ Hz) and slightly increased in the high frequency range, while the conductivity of the composite with microsized CCTO is nearly independent of temperature. The theoretical calculations demonstrate that the activation energies of the composites containing nano- or microsized CCTO are -0.52 and 0.051 eV, indicating active interfaces and insulated grain boundaries in these two composites, respectively. Theoretical analysis also shows that the dielectric performance of the composite with nanosized CCTO does not follow the conventional mixing rules and the giant dielectric constant comes mainly from the interfacial polarization.

From XRD studies, the filler is expected to be randomly distributed in the polymer. It can be shown that the composite samples are quite amorphous compared to on filler samples. XRD patterns also depict crystalline features on the surface of the sample when the $Al_2TiO_5$ content is more than 5 wt. %.

The SEM micrograph for chitosan-$NH_4SCN$-$Al_2TiO_5$ system shows that the surface morphology of the samples is denser and more amorphous as compared to other

samples. The XRD pattern has also proved that the samples is amorphous. After the addition of more than 5 wt.% $Al_2TiO_5$, the conductivity of the system has decreased. The best inference that can be made about the decrement phenomena in the system is that the $Al_2TiO_5$ has made the sample more crystalline and less amorphous as shown by the XRD pattern and SEM micrograph in Fig 7.3. This phenomena agreed with Park et al., (2003) in their work on $PEO-LiClO_4-Al_2O_3$ system. The $Al_2O_3$ powders are observed to be uniformly distributed within sample when an $Al_2O_3$ composition is less than 12 wt.%. The $Al_2O_3$ agglomeration is observed in the sample containing 14 wt.% of $Al_2O_3$. According to them, the $Al_2O_3$ content should be properly maintain to prevent phase discontinuities in the composite polymer electrolytes. Therefore, the composite polymer electrolyte with high $Al_2O_3$ content may exhibit a tendency to form phase into separation. From the results, they concluded that an addition of $Al_2O_3$ is necessary to reduce crystallinity of the polymer electrolyte, but a proper $Al_2O_3$ content should be maintained to assure a highly distribution of the powder in the composite polymer electrolyte.

The present study is also in agreement with Jeon et al., (2006) on effect of $TiO_2$ on P(VdF-HFP)/P(EO-EC) membranes. At low $TiO_2$ loadings, it is clear that there is good dispersion of nanoparticles in the porous membranes. At higher $TiO_2$ loadings ($\geq$30 wt.%), however, $TiO_2$ nanoparticles start to agglomerate. This accounts for the decrease in uptake of viscous electrolyte in the porous membranes. With increase of $TiO_2$ content in porous membranes, the titanium distribution gradually increases.