CHAPTER 7

DISCUSSION

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 not yet achieved. The incomplete understanding and lack of experiment data to backing the theory in the conduction mechanism for polymer electrolyte is the main barrier to realization of the usage of solid polymer electrolyte [Alasdair *et al.*, 2005].

Mechanical strength and conductivity are amongst the important properties of solid polymer electrolytes. Various techniques such as blending [Rajendran *et al.*, 2002], modification of polymers [Tan *et al.*, 2006] and incorporation of fillers [Majid *et al.*, 2005] have been employed to improve mechanical strength and enhance conductivity. Examples of polymer modification include natural rubber grafted with methyl methacrylate [Dafader *et al.*, 2006], PVdF grafted with dimethyl acrylamide [Jarvis *et al.*, 2001] and poly(ethylene oxide)–grafted with acrylates [Adebahr *et al.*, 2001]. Natural rubber (NR) has good mechanical properties, but being an insulator, its conductivity at ambient temperature is rather low. NR can be modified by bonding rearrangement, grafting and by attaching new functional groups onto the NR chain [Blackley, 1997 and Ceresa, 1973]. Modified NRs have shown ionic conductivity comparable to glassy or crystalline polymers [Idris *et al.*, 2001]. NR can be grafted with various monomers such as acrylonitrile (AN), methyl methacrylate (MMA), stearyl methacrylate (SMA), divinylbenzene (DVB) and styrene. MMA and styrene are the most suitable monomers for grafting with NR [Hashim *et al.*, 2002 and Arayapranee *at al.*, 2003]. Man *et al.* (2008) studied the styrene– and methyl methacrylate–grafted NR by means of FTIR and SEM. Dafader *et al.*, 2006 investigated the mechanical properties of NR grafted with different types of acrylic monomers including ethylacrylate (EA), n–buthyl methacrylate (BMA) and cyclohexyl methacrylate (CHMA). All these examples show that grafting NR improve mechanical strength. In this work, MG30 is used as polymer host for good mechanical strength.

The effect of high energy radiation on MMA grafted NR was studied using NMR and dynamic mechanical analysis (DMA) by Perera and Rowen, (2000). They found that more extractable PMMA was formed when MG rubber was exposed to high energy radiation. Other than MMA, NR blended with PEO and doped with lithium benzenesulfonate (LiBs) has been reported by Yoshizawa *et al.*, (2000). When 40 wt% of PEO doped with LiBs was added to NR, the ionic conductivity was approximately 10^{-6} S/cm at 50^{o}C. This ratio of rubber elasticity polymer blends provided good ion conducting properties and its mechanical property maintained similar to the NR itself. Klinklai and co–authors (2003) investigated the conductivity of epoxidized natural rubber (ENR) incorporated with lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) and lithium perchlorate ($LiClO_4$), respectively. ENR–LiTFSI electrolyte exhibited conductivity of the order 10^{-6} S cm^{-1} at 323K, whereas ENR–$LiClO_4$ electrolyte exhibited conductivity of the order of 10^{-9} S cm^{-1}. In the work of Mohamed and co–workers (2008), an increase by one order of magnitude in conductivity was observed from 2.0 x 10^{-5} S cm^{-1} to 4.9 x 10^{-4} S cm^{-1}at 303 K when 10 wt. % propylene carbonate (PC) was added into 65 wt. % ENR 50–35 wt.% $LiCF_3SO_3$. Epoxidized natural rubber (ENR) and PMMA–grafted natural rubber contain oxygen atoms with lone pair electrons that serve as sites for coordination with the lithium ions. Studies using synthetic rubber as polymer host have been reported by Matsumoto, (1996). Good mechanical strength and high ionic conductivity polymer blends consisting of poly(acrylonitrile–co–butadiene) rubber (NBR) and poly(styrene–co–butadiene) rubber (SBR) were prepared and an ionic conductivity of 7.2 x 10^{-4} S cm^{-1} is obtained for NBR/SBR 50/50 (w/w) film with 1 M $LiClO_4$ in 50/50 (v/v) γ–butyrolactone (γ–BL) / 1,2–dimethoxyethane (DME) solution. N–ethylimidazolium bis(trifluoromethanesulfonyl) imide (EImTFSI) has been added to nitrile rubber to enhance its conductivity to ~10^{-5} S cm^{-1} at 30 ^{o}C without addition of salt. Imidazolium–type zwitterion i.e. 1–(1–ethyl–3–imidazolio)hexane–6[(6–carbonyl) (trifluoromethanesulfonyl)] imide has been added to 75 wt.% nitrile rubber with 33 % nitrile content–25 wt.% $Li(CF_3SO_2)_2N$ to enhance conductivity of the polymer–salt complex by about 8 times with lithium ion transference number of 0.32 [Marwanta *et al.*, 2005,2007].

Investigations on polymer electrolytes have been primarily focused on the enhancement of ionic conductivity at ambient temperature. Several new techniques have been proposed and developed by earlier researchers on PMMA grafted NR to modulate the ionic conductivity by:

1) Introducing different types of salt
    a) Lithium triflate, $LiCF_3SO_3$
        (i) Idris *et al.* (2001) have discovered 83.3 wt. % MG49 + 16.7 wt. % $LiCF_3SO_3$ exhibits conductivity of 3.7 x 10^{-5} S cm^{-1} at room temperature.
        (ii) Alias *et al.* (2005) discovered 70 wt. % MG49 + 30 wt. % $LiCF_3SO_3$ exhibits conductivity of 1.76 x 10^{-7} S cm^{-1}.

(iii) Ali *et al.* (2006) reported that 65 wt. % MG30 + 35 wt. % $LiCF_3SO_3$ exhibits a conductivity of 8.40 x 10^{-4} S cm^{-1} with activation energy of 0.163 eV.

(iv) Hashim *et al.* (2011) obtained ionic conductivity value of 5.01 x 10^{-5} S cm^{-1} for 65 wt. % MG30 + 35 wt. % $LiCF_3SO_3$ using the same method as that of Ali *et al.*, (2006).

b) Lithium perchlorate, $LiClO_4$

(i) Su'ait *et al.* (2009) obtained ionic conductivity value of 4.0 x 10^{-8} S cm^{-1} for the sample of 85 wt. % MG49 + 15 wt. % $LiClO_4$

c) Lithium tetrafluoroborate, $LiBF_4$

(i) Su'ait *et al.* (2009) obtained ionic conductivity value of 2.3 x 10^{-7} S cm^{-1} for the sample of 80 wt. % MG49 + 20 wt. % $LiBF_4$

d) Ammonium triflate, $NH_4CF_3SO_3$

(i) Kamisan *et al.* (2009) obtained ionic conductivity value of 3.62 x 10^{-3} Scm^{-1} for MG49 + 1.1M $NH_4CF_3SO_3$ in propylene carbonate

2) Introducing different types of plasticizers

a) Ethylene carbonate (EC)

(i) Kumutha *et al.* (2006) incorporated EC into different ratios of $LiCF_3SO_3$ salted MG30 and did FTIR analysis.

(ii) Low *et al.* (2010) reported that 7 wt. % TiO_2 + 12.6 wt. % $LiClO_4$ + 50.4 wt. % MG49+30 wt. % EC exhibits ionic conductivity of 1.1 x 10^{-3} S cm^{-1}

b) Propylene carbonate (PC)

(i) Alias *et al.* (2005) discovered 38.5 wt. % MG49 + 16.5 wt. % $LiCF_3SO_3$+ 45 wt. % PC with conductivity of 1.84 x 10^{-4} S cm^{-1}.

(ii) Ali *et al.* (2008) have reported a value of 3.08×10^{-3} S cm^{-1} for 25 wt. % MG30 + 14 wt. % $LiCF_3SO_3$ + 61 wt. % PC with activation energy of 0.14 eV.

c) EC + PC

(i) Idris *et al.* (2001) reported 32.8 wt. % MG49 + 1.6 wt. % $LiCF_3SO_3$ + 65.6 wt. % EC + PC with conductivity of 4.3×10^{-4} S cm^{-1}.

d) Dimethylene carbonate (DMC)

(i) Hashim *et al.* (2011) reported 2.1 wt. % SiO_2 + 9.9 wt. % $LiCF_3SO_3$ + 18 wt. % MG30 + 70 wt. % DMC with conductivity of 3.5×10^{-4} S cm^{-1} at room temperature.

3) Introducing different types of filler

a) Al_2SiO_5

(i) Kumutha *et al.* (2005) have incorporated EC and Al_2SiO_5 into different ratios of $LiCF_3SO_3$ salted MG30 to do the FTIR analysis.

b) Silicon dioxide, SiO_2

(i) Hashim *et al.* (2011) prepared 7 wt. % SiO_2 + 33 wt. % $LiCF_3SO_3$ + 60 wt. % MG30 and obtained a conductivity of 2.3×10^{-4} S cm^{-1} at room temperature.

c) Titanium dioxide, TiO_2

(i) Low *et al.* (2010) showed that 6 wt. % TiO_2 + 28.2 wt. % $LiBF_4$ + 65.8 wt. % MG49 exhibits a highest conductivity of 1.4×10^{-4} S cm^{-1}

The results shown above prompted the author to extend the study on MG30–$LiCF_3SO_3$ system by adding a second salt $LiN(CF_3SO_2)_2$ to form a double salted system and another system that incorporated a different type of plasticizer, PEG200.

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 [Alasdair *et al.*, 2005]. To the author's knowledge, there is no report on the use of XRD to understand the conductivity behavior of MG30 polymer electrolytes. The XRD patterns for MG30L, MG15L15I and MG30–10P have proven that all these samples are amorphous. After the addition of more than 35 wt. % $LiCF_3SO_3$, the XRD spectra of the MG30– $LiCF_3SO_3$ have shown some peaks at 2θ angles between 21° and 23° and at 2θ angle of 22.7° which are attributed to $LiCF_3SO_3$. These peaks are slightly shifted from the original XRD pattern of $LiCF_3SO_3$. The explanation that can be given to clarify this situation is the "overdose" of $LiCF_3SO_3$ with existence of ion pairs at high salt concentration. Increase in crystallinity of the sample is supported by the XRD pattern in Figure 4.1 and the deconvoluted XRD pattern in Figure 4.2 respectively. These results are again proven correct from the exact prediction in XRD pattern in Figure 4.3 for sample with $LiN(CF_3SO_2)_2$ added. Deconvoluted results in Figure 4.4 shows all the double salted samples are amorphous because broad peaks could be observed between $2θ = 10°$ to 30° which could imply the ability of the MG30 polymer to retain most of the salt within its structure as like MG30L sample. On the other hand, for PEG plasticized samples no significant crystalline peak was observed in the diffractogram, broad hump centered at 22.4° is observed (Figure 4.5). This shows that the addition of PEG200 plasticizer has changed the internal structure of the MG30 polymer. It is expected that the MG30–10P samples which has the smallest percentage of the crystalline phase as deduced by XRD, exhibits the highest conductivity.

Figure 4.7 (a) to (g) depict SEM micrographs of $LiCF_3SO_3$ doped MG30 at 1000 X magnification. MG30 films doped up to 25 wt. % $LiCF_3SO_3$ were observed to have smooth surface with some burnt marks. The sample which contained 30 wt. % $LiCF_3SO_3$ has smooth surface which is consistent with our XRD studies and most importantly the sample exhibits the highest ambient electrical conductivity. The sample doped with 35 wt. % salt contains some pores filled with solid structures that may be attributed to neutral ion aggregates formed from the association of ions that usually occur at high salt concentrations. If these solid structures are the result of neutral ion aggregate formation then a drop in conductivity is expected. The visibility of the solid material at high salt concentration is probably due to the increase in viscosity of the liquid solution which on evaporation after casting was not able to form a continuous surface to cover the neutral aggregates. Thus, a porous surface is formed, which is clearly shown in the micrographs of MG30 sample incorporated with 40 wt. % $LiCF_3SO_3$ where more pores are observed. Some pores are filled with solid matter while some may appear empty. To the authors knowledge no such correlation between surface morphology and ionic conductivity has been used in the study of MG30 polymer electrolytes.

Mohamed *et al.* (2002) have fabricated a PVA–based polymer electrolyte where they have shown some crystalline dendritic structures in a sample with 30 wt. % KOH and these microstructural features are absent in the highest conducting samples. The SEM pictures from Kadir *et al.* (2010) have also shown that when concentration of NH_4NO_3 exceeds 40 wt. % in the PVA–chitosan based electrolyte, the distance between dissociated ions may become too close that they are able to recombine and form neutral ion–pairs which do not contribute to conductivity and protrudes out of the sample. Therefore these SEM results are also comparable with those reported by Mohamad *et al.* (2002) and Kadir *et al.* (2010) where the morphology of the 65 wt. % MG30–35 wt.%

$LiCF_3SO_3$ also consists of micro–structures that have protruded the surface of the film and proves the formation of neutral ion aggregates that leads to a drop in conductivity.

Figure 4.8 (a) to (c) depicts SEM micrographs of $LiCF_3SO_3$ and $LiN(CF_3SO_2)_2$ containing MG30 at 1000 X magnification which is comparable to the surface morphology of MG30L (Figure 4.7 (c)). The film, MG15L15I show some little uneven surface properties but with less solid spherical structures of the thin films. It indicates that a better solubility of salt have been achieved where the double salts liquid solution which on evaporation after casting was able to form a smoother continuous surface. All double salted films exhibit less spherical structures that protrude the smooth surface which may indicate that the recombination rate between the ions are slowed down as compared to single salted samples.

From the FTIR results as studied in Chapter Five, the addition of salt has shifted the most prominent carbonyl band, (C=O) peak of MG30 to a lower wave number from 1731 cm^{-1} to between 1729 and 1724 cm^{-1} proving occurrence of complexation (Figure 5.4, Figure 5.14 and Figure 5.24). This shows that lithium salts are dissolved in the polymer matrix as the polymer–salt complex is formed. The Li^+ cations can form a dative bond with the oxygen atom in the carbonyl group resulting in the downshift of the carbonyl band. This finding is consistent with the observations reported by Kumutha *et al.*, (2005), Kumutha and Alias (2006) and Ali *et al.* (2008).

Another peak in this region that can be observed in previous reports by other researchers but is not much discussed is located at 1663 cm^{-1}. This peak is only noticeable after the lithium salt has been added (Figure 5.4, Figure 5.14 and Figure 5.24). This peak is assigned to C=C polyisoprene stretching vibration. As mentioned, this peak has been detected in other PMMA grafted natural rubber–salt electrolytes by other workers [Alias *et al.*, 2004; Kumutha *et al.*, 2005; Kumutha and Alias, 2006; Ali *et al.*, 2006; Man *et al.*, 2008] but there is no further discussion on the observed band. The existence of this peak, which shows changes with lithium salt concentration, implied the possibility of lithium–olefin complex formation during preparation. The two carbon atom double bonded to each other in natural rubber contributes towards these phenomena. The double bond in the natural rubber is relatively strong and stable thus it is hardly detected as seen in Figure 5.4 (a). The sharing of electron density between lithium and olefin weakens the stable C=C bond in the olefin, thus reducing C=C stretching frequency. The existence of this peak further confirms the existence of interaction between the salt and the NR component of the polymer–host where it has been downshifted from 1663 cm^{-1} to between 1652 and 1648 cm^{-1} (Figure 5.5, Figure 5.15 and Figure 5.25). Such complex formation has been deserved for silver and olefin complexation [Sunderrajan *et al.* (1999) and Kim *et al.* (2003)] and this new idea on MG30 was only reported by Yap *et al.*, (2011).

The highest conductivity value of 1.69×10^{-6} Scm^{-1} has been achieved with a composition of 70 wt. % MG30 + 30 wt. % $LiCF_3SO_3$ in the MG30–$LiCF_3SO_3$ system and the conductivity decreased above that composition. The increase in conductivity was attributed to the increase in the number density of charge carriers as proven from the deconvoluted FTIR results in Figure 5.11, Figure 5.19 and Figure 5.32 which have not been discussed previously by other researchers who studied NR based polymer electrolytes. Rajendran *et al.* (2010) claimed that the increase in conductivity with salt content is attributed to the increase in number of free mobile ions and the decrease in conductivity may be due to ion association, which leads to generate more non–conductive neutral ion. The increase in the value of dielectric constant as the amount of

$LiCF_3SO_3$ salt increases indicates that there is an increase in charge carriers and hence the conductivity (Selvasekarapadian *et al.*, 2005). The dielectric constant of the pure grafted polymer is ~ 1.86.

Further addition of salt after the optimizing composition is reached led to the decrease in conductivity. This has been attributed by some researchers as due to the occurrence of ion association into neutral ion aggregates and/or due to the viscosity of the samples, which could have taken effect at high salt concentration. In theoretical, 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 high salt concentration, the ionic conductivity is strongly dependent on the mobility of ions and ionic conduction pathway (Yu *et al.*, 2007). Ionic conductivity is greatly reduced at high salt concentration due to decreases in availability of vacant coordinating sites besides the formation of ion pairs and ion aggregates. Closeness of the dissociated ions may result in cation–anion recombination to form neutral ion–pairs that do not contribute towards conductivity (Majid and Arof, 2007). The recombination of ions lowers the number density of conducting ions and eventually reduces the conductivity efficiency of polymer electrolytes.

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 MG30 band electrolytes for the first time from the XRD results where some peaks due to the salt has been observed for the samples containing more than 30 wt. %

$LiCF_3SO_3$ (Figure 4.2) and SEM (Figure 4.7) results where we are able to identity some sphere solid on the surface of the high concentration samples. Thus, less mobile charge carriers are produced and then controlled ionic migration.

Double salt polymer electrolytes were studied because systems containing mixed cations or anions were found to give better ionic conductivity than the single salt system Chandra *et al.*, (1994). This is also proven in our study where the conductivity is also found to increase using the double salt system in the PMMA grafted natural rubber. A double salted system approach had been done by Arof and Ramesh (2000) for poly (vinyl chloride) (PVC)–based polymer electrolytes with $LiCF_3SO_3$ and $LiBF_4$ as the ion supplying and they found the ionic conductivity is increased by two orders of magnitude in comparison to single salt system. They suggested that mixed salt have successfully prevented formation of ion aggregates.

A highest conductivity value of 1.46×10^{-5} have been obtained for the sample with 15 wt. % $LiCF_3SO_3$ + 15 wt. % $LiN(CF_3SO_2)_2$ + 70 wt. % MG30. Table 6.3 reveals that the room temperature ionic conductivity is higher after $LiN(CF_3SO_2)_2$ is introduced in to the systems and the activation energy variation decreased gradually when the conductivity increased. This further proved that the mixed salt system has significantly improved the conduction mechanism in the electrolyte system.

It has been suggested that probably double salt systems have prompted the anion–anion interaction through dipole–induced dipole phenomena in polymer electrolyte system which can make some anions immobile and thus make cation motion more favorable. This model theory has been proposed by Ratner *et al.*, (1988) for explaining mixed alkali effect in glass and have been using by Chandra *et al.*, (1994) for the mixed salt polymer electrolytes. The dielectric studies in Figure 6.22 further support the idea for this anion–anion interaction where the dielectric constant and dielectric loss is higher in higher conductivity samples. This is because the dielectric constant and dielectric loss values are always higher than the single salt system electrolytes.

Salts having low lattice energy are generally expected to promote greater dissociation of the salt and providing more ions [Arof and Ramesh (2000)]. Salts that contain large anions usually have low lattice energy and are expected to separate the positive and negative ions more easily in a solid compound. According to the Kapustinskii equation, the lattice energies for $LiCF_3SO_3$ and $LiN(CF_3SO_2)_2$ salts are 735 kJ mol^{-1} and 489.4 kJ mol^{-1} respectively. This offers an explanation as to why conductivity of the MG10L20I is higher than the MG20L10I. This result is also consistent with our finding in the conductivity value and the activation energy. Therefore it is reasonable to say that the $LiN(CF_3SO_2)_2$ salt has a better ability to dissolve and provide more charge carriers in polymer solution which may also cause the increase in the relative dielectric constant and apparently increase in conductivity.

This finding is further supported by FTIR results in Figures 5.19 where more free ions are estimated in MG10L20I rather than the MG20L10I. Results shown in Figure 5.20 are also consistent with the conductivity results whereby MG30 samples which contain both 15 wt. % lithium triflate and 15 wt. % lithium imide (MG15L15I) exhibit ionic conductivity up to 1 order higher than the MG30 sample containing only single lithium triflate salted system (MG30L).

Fig. 6.15 shows the room temperature ionic conductivity plot for MG30– 30 wt. % $LiCF_3SO_3$ with respect to PEG200 concentration. It can be observed that the ionic conductivity of PEG free polymer electrolyte is lower than the PEG200 plasticized MG30–30 wt. % $LiCF_3SO_3$ polymer electrolyte. On addition of PEG, a rapid increase in conductivity is observed and optimized at 10 wt. % PEG with a conductivity of 3.65 x 10^{-4} Scm^{-1} and the conductivity decreased above that composition. This conductivity enhancement with increasing amount of PEG up to 10 wt. % may be due to increase in charge carrier concentration and the occurrence of new pathways for free ions to travel through the material because PEG can provide extra pathways through its ether and hydroxyl groups (Bernson and Lindgren, 1995 and Ferry *et al.*, 1995). This has been proven by Figure 5.33 and Figure 6.25 where more free ions have been detected.

From the plots log σ vs 1000/T for all single salted, double salted and plasticized MG30 systems as depicted in Figure 6.4, Figure 6.14 and Figure 6.24 respectively, it is observed that the conductivity is thermally assisted. The liner behavior in the figures is best represented by the Arrhenius equation where the regression values R^2 for all the lines are almost near to unity. Activation energy (E_a) of all the samples has been calculated using the Arrhenius equation. The highest conducting sample, MG30–10P possessed the lowest E_a value of 0.11eV. The decrease in activation energy supports the suggestion that the PEG200 has created alternative pathways that requires a lower energy for conduction. The lithium transfer number for MG30L–10P sample is calculated as 0.30.