CHAPTER 7

DISCUSSION

The increasing attention being given to develop polymer electrolytes of appropriate conductivity is stimulated by the development in various electrochemical devices such as batteries, fuel cells, sensors, electrochromic windows and capacitors. Ion conducting polymers could be defined as membranes that posses transport properties comparable to that of liquid electrolytes [Ganesh *et al*., 2008]. Although liquid electrolytes are widely used in commercial and industrial applications especially in lithium ion batteries, it has its drawbacks such as being toxic, prone to leakage and dangerous to the environment. The development of high conducting polymer electrolytes with good mechanical and electrochemical stability, low cost and compatible with electrode materials is attempts to replace liquid electrolytes. Polymer electrolytes such as PEO and PMMA - based in large amounts are harmful to the environment [Kumar and Bhat, 2009]. To overcome this issue or at least to minimize it, biodegradable materials are sought for to produce polymer electrolytes.

In the present work, a water soluble polymer, viz., methyl cellulose (MC) was chosen as host for ionic conduction due to advantageous properties such as biodegradability, high mechanical strength, high water retention, cheap and non-toxic. Excellent film forming ability is another important property in preparing polymer electrolytes and MC has this property. MC has lone pair electrons in their structure which play an important role in polymer–salt complexation. MC is also compatible for use in electrodes as a binder since it can help reduce internal resistance in electrodes [Pichon *et al.*, 2002]

Ammonium nitrate (NH_4NO_3) is a hygroscopic salt and was used as the source of protons. It is colorless, soluble in water and crystalline [Oommen and Jain, 1999]. Polymer electrolytes obtained by the complexation of NH_4NO_3 with MC have not been reported elsewhere by other researchers. There are several studies however, about the use of other polymers and ammonium salts. Kadir *et al.* (2010), for example, reported that the addition of 40 wt.% NH_4NO_3 to a polymer blend of 36 wt.% PVA and 24 wt.% chitosan, gives a conductivity of 2.07×10^{-5} S cm^{-1}. Conductivity of polymer electrolyte with composition 55 wt.% chitosan - 45 wt.% NH_4I is 3.7×10^{-7} S cm^{-1} at the room temperature [Buraidah *et al.*, 2009]. Many studies on polymer-ammonium salt complexes indicate that hydrogen bonding plays an important role in interactions involving NH_4^+ with short chain polyethers [Chintapalli *et al.*, 1996]. There are two possible ionic species in polymer electrolytes, which are cations and anions. In this work, the possible cation mobility may be due to NH_4^+, NH_3^+ or H^+ and the anion mobility is due to NO_3^-. Srivastava and Chandra (2000) and Hashmi *et al.* (1990) have reported that H^+ is the charge carrier or conducting ion in poly (ethylene succinate) and poly (ethylene oxide) doped with NH_4ClO_4 polymer electrolytes respectively. The conductivity enhanced up to 1.10×10^{-4} S cm^{-1} when 15 wt.% PEG was added. The conductivity value of the plasticized system in the present work is comparable with that obtained by other researchers. Subban *et al.* (2005) obtained the highest conductivity of 1.03×10^{-4} S cm^{-1} for the sample with composition 58 wt.% PVC-32 wt.% $LiCF_3SO_3$-10 wt.% PEG. Srivastava and Chandra (2000) obtained conductivity approaching 10^{-4} S cm^{-1} for the sample 55 wt.% PESc-30 wt.% NH_4ClO_4-15 wt.% PEG.

The increase in conductivity with increasing concentration of NH_4NO_3 and PEG as shown in Figures 4.15 and 5.8 is attributed to the increase in number density and/or possibly ionic mobility and diffusivity of the charge carriers.

Ionic conduction only takes place in the amorphous phase of the polymer electrolyte. X-ray diffraction (XRD) was carried out to investigate the nature of MC based polymer electrolytes. From Figure 4.1, amorphousness of the samples was observed to increase with salt concentration and conductivity is optimized at 25 wt.% NH_4NO_3. The sample containing 30 wt.% salt is a two-phase system since salt peaks can be observed at $2\theta = 22$ and 28° in the diffractogram of the sample. Using Hodge *et al*. (1996) criterion, the crystalline fraction was calculated. From calculation, it was found that, the degree of crystallinity decreases with salt concentration up to 25 wt.%. The increase in amorphousness will be reflected by conductivity enhancement [Kumar and Sekhon, 2002]. Similar behavior was observed when PEG was added to MC-NH_4NO_3 system. PEG with low glass transition temperature (-74 °C) and moderate dielectric constant (19.95 at 293 K) was used as a plasticizer in this work. From XRD patterns of plasticized MC-NH_4NO_3 system, it can be observed that sample containing 15 wt.% PEG is more amorphous compared to other samples. This has been proven by calculating the degree of crystallinity and the sample containing 15 wt.% PEG has the lowest crystalline fraction. Although the crystalline fraction of 63.75MC21.25AN15PEG is higher compared to that of 75MC25AN, it still exhibits a higher conductivity than 75MC25AN because the presence of PEG will dissociate more salt into free ions and ion pairs or aggregates into free ions thus enabling conductivity enhancement.

In order to establish how the amount of NH_4NO_3 added affects conductivity of MC based polymer electrolytes, FTIR studies were carried out. The increase in intensity of the peak at 827 cm^{-1}, which can be assigned to $\delta(NO_2)$ vibration of 'free' nitrate ions of pure NH_4NO_3, shows the increase of charge carriers with addition of NH_4NO_3 as shown in Figures 4.5 and 4.10. The results of FTIR correlate well with the variation of conductivity as shown in Figure 4.15. The conductivity of pure MC is 3.08×10^{-11} S cm^{-1} and was increased by two orders of magnitudes when 25 wt.% NH_4NO_3 was added. Beyond 25 wt.% NH_4NO_3, conductivity dropped to 6.40×10^{-8} S cm^{-1} and is attributed to recrystallization of salt out of the polymer. Recrystallization can be detected from FTIR studies as shown in Figure 4.5 and Figure 4.12 when the peak attributed to $\delta(NO_2)$ vibration of NO_3^- ions of pure NH_4NO_3 was observed at 715 cm^{-1} and a peak due to $\upsilon(NH_4^+)$ detected at 1754 cm^{-1} for 30 wt.% NH_4NO_3. For lower concentrations of NH_4NO_3 (5 to 25 wt.%), no such peaks were observed implying that NH_4NO_3 has fully dissociated in the polymer. From FTIR studies, the interaction between MC and NH_4NO_3 could be inferred. Figures 4.7 and 4.10, obviously revealed complexation between MC and NH_4NO_3 when the 1053 and 1314 cm^{-1} peaks shifted to 1051 and 1318 cm^{-1} respectively. The 1053 cm^{-1} band is a C-O stretching of pure MC. The 1314 cm^{-1} band is an infrared spectral characterization for MC as reported by Filho *et al*. (2007). Cation from the salt is expected to form a "soft" bond with the oxygen atom. The effect of PEG on MC-NH_4NO_3 (AN) system was also investigated using FTIR. To that, a comparative FTIR study involving pure MC, pure AN, pure PEG, MC-PEG, PEG-AN, 75MC25AN and MC-AN-PEG have been done to examine the interactions within the systems. In MC-PEG system, it was observed that the change of wavenumber is dependent on concentration of the components. The ring stretching (894 cm^{-1}), 944 cm^{-1}, C-O stretching (1053 cm^{-1}), C-H stretching (2902 cm^{-1}) and O-H stretching (3440 cm^{-1}) of pure MC and the C-O-C stretching (885, 936, 1061 cm^{-1}),

CH_2 stretching (2867 cm^{-1}) and O-H stretching (3403 cm^{-1}) of pure PEG were noted to change when different amounts of MC were dissolved in different concentrations of PEG. This indicates that some interactions have occurred in the MC-PEG system. The interaction between PEG and AN is also inferred when the wavenumber of C-O-C stretching of pure PEG at 1098 cm^{-1} shifted to lower wavenumber (1093 cm^{-1}) when 5 wt.% AN was dissolved in 95 wt.% PEG. The CH_2 stretching band of pure PEG at 2867 cm^{-1} was observed to shift to 2875 cm^{-1} with addition of 5 wt.% AN. From FTIR studies of MC-NH_4NO_3 system, evidence of interaction between MC and AN occurred at 1053 cm^{-1} for 75MC25AN sample. When PEG was added to this matrix, the wavenumber was observed to increase with PEG concentration increment (1058 cm^{-1} for sample containing 25 wt.% PEG).

TGA studies show that the thermal degradation for pure MC occurs in two stages and for MC-NH_4NO_3 system, thermal degradation take place in three stages. The early minor weight loss is attributed to moisture or water loss on heating and hence confirms that all samples contain free water since MC is very sensitive to water and tends to absorb moisture easily. According to Hatakeyama and Hatakeyama (1998), there are three types of thermodynamic water. Type I is free water which does not interact with polymer and behaves as normal water. Type II is “unbound” water which loosely bound to the polymer and type III is water, which is tightly bound to the polymer. In powder form, the water in MC will be bound to the polymer surface. There will be more bound water content if the moisture content in the environment increases [Ford, 1999]. The second stage weight loss for pure MC in temperature range from 125 to 425 °C and is attributed to degradation of MC. On addition of NH_4NO_3 from 5 to 25 weight percent, the second stage weight loss corresponds to the decomposition of NH_4NO_3 since the decomposition temperature of

NH_4NO_3 is 170 °C [Gunawan and Zhang, 2009]. The decomposition temperature of MC is around 325 °C [Filho *et al*., 2007; Zohuriaan and Shokrolahi, 2004]. When PEG was added in 75MC25AN, the thermal degradation still occurred in 3 stages. It can be observed that, PEG did not affect thermal stability of the samples.

Using electrochemical impedance spectroscopy (EIS), impedance, dielectric and transport properties of MC-NH_4NO_3 system was investigated. Impedance plot in this system shows the spike tilts at an angle less than 90 º. Wu *et al*. (2000) stated that the low frequency spike is due to the effect of blocking electrodes. The effect of blocking electrodes indicates the formation of double layer at the electrode/electrolyte interface or capacitance [Karthikeyan *et al*., 2000]. Normally, the ideal capacitance shows a 90 º low frequency vertical spike in impedance plot. Following Karthikeyan *et al*. (2000), the intersection of a low frequency straight line with real axis at less than 90° is attributed to the irregularities in the electrode/electrolyte interface geometry. From impedance plot also, it was found that the bulk resistance decreased with increasing salt concentration and hence, leads to the increase in conductivity. The addition of more salt has led to the increase in amorphousness of the samples [Ali *et al*., 1998; Rajendran *et al*., 2006] allowing more ions to conduct charge as the salt concentration increases. Same features were observed with addition of PEG. The bulk resistance was observed to increase after 15 wt.% PEG and hence decreased the conductivity due to increase in degree of crystallinity of the samples having 20 and 25 wt.% PEG as verified by XRD studies.

Dielectric behavior studies show that dielectric constant, ε_r and dielectric loss, ε_i decreases with increasing frequencies. At high frequencies, the periodic reversal of the electric field occurs so fast at the interface that the contribution of mobile ions towards ε_r

decreases with increasing frequency. Baskaran *et al*. (2004) explained that, due to the formation of space charge regions at the electrode-electrolyte interfaces at low frequencies, the ions have different relaxation time. Thus the sample exhibits a non-Debye behavior and the ions have a distribution of relaxation time. The occurrence of relaxation time is the result of the efforts carried out by ionic charge carriers within the polymer material to obey the change in the direction of applied field [Winie and Arof, 2004]. It was found that the increase and decrease of relaxation time with salt concentration is opposite with conductivity. The highest conducting sample has lowest relaxation time. On addition of PEG in the MC-NH_4NO_3 the dielectric constant can exhibit the increase in number density of mobile ions in polymer electrolyte [Khiar *et al*., 2006]. In this work, it can be observed that, with addition of PEG in MC-NH_4NO_3 system, the value of dielectric constant and dielectric loss increased. The increase in dielectric constant and dielectric loss implies that there are more free ions and this maybe an explanation to the reduction in impedance [Khiar *et al*., 2006]. Plasticizer helps to dissociate the salt into free ions by increasing the distance between the cation and anion of the salt and thereby weakening the force of attraction between the opposite ions. This leads to dissociation of the salt and increases the number density of mobile ions leading to conductivity increment for plasticized polymer electrolyte system. Not only that, the plasticizer can also dissociate neutral ion agglomerates into free conducting ions.

The samples are ionic conductors when the plot of imaginary modulus, M_i versus log frequencies exhibits a peak [Mellander and Albinsson, 1996]. The capacitances of MC-NH_4NO_3 samples can only be evaluated for samples, the M_i versus frequency plots contain relaxation peaks as shown in Figure 4.19. Only capacitance for samples containing 5, 10, 15 and 30 wt.% NH_4NO_3 can be determined. The capacitance was in the range of 0.25 to

0.43 pF and indicates that the dispersion peaks observed correspond to the bulk effect of the material [Khiar *et al*., 2006]. For plasticized MC-NH_4NO_3 system, no peaks were observed in the M_i versus frequency plot.

Generally, conductivity increases when temperature increased. From the Figure 4.23, it can be observed that the conductivity increases with temperature up to 60 °C, after which conductivity increases at a decreasing rate or remains almost constant. According to Sarkar and Walker (1995), at low temperatures and in the solution state, MC molecules can be easily hydrated. Hence, when the MC-salt solution forms film at room temperature, it may contain water. Although samples in this investigation have been kept in desiccators for purpose of continuous drying, there is still possibility that the film contains water as explained in section 4.4. As the temperature is increased during conductivity-temperature measurements, the water molecules are gradually removed and hence the number density of hydroxonium ions is reduced leading to a drop in the rate of increase in conductivity between 25 °C and 60 °C. Above 60 °C, conductivity did not increase significantly and is attributed to the increase in the rate of water loss that could also contain dissolved NH_4NO_3 in it. However, when PEG was added to 75MC25AN with different concentrations from 5 to 25 wt.%, it can be observed that, the conductivity rise with temperature up to 100 °C. This is because PEG can retain moderate moisture in the sample (Park and Ruckestein, 2001).

From the log σ versus $1000/T$ in Figure 4.23, the conductivity-temperature relationship is not linear and could be ascribed to the concept of free volume [Karan *et al*., 2008]. The increase in free volume facilitates the motion of ionic charge or in other words; the migration of ions through the amorphous region [Reddy and Chu, 2002]. Uma *et al*.

(2003) pointed that the non-Arrhenius behavior implies that the ion transport in polymer electrolytes is dependent on polymer segmental motion. The segmental motion either creates space for ions to move or allows the ions to hop from one site to another site with ease. The polymer chain acquires faster internal modes with increasing temperature that includes bond rotations, hence producing faster segmental motion [Reddy and Chu, 2002]. On the contrary, the log σ versus 1000/T plot for plasticized system is linear and could be considered to follow Arrhernius rule. This allows calculation of activation energy for each sample.

The effect of glass transition temperature, T_g was also investigated in this work using conductivity-temperature relationship. T_g is observed to change with salt concentration. The increase in T_g with salt concentration has been reported by Bandara *et al.* (1998) and Idris *et al*. (2001). The increase in T_g with salt concentration has been attributed to the transient crosslinking of the dissolved ions [Forsyth *et al.*, 2000]. In this work, increase in T_g is possibly due to interaction between the salt and the oxygen atoms of the C–O groups in MC. Kim *et al*. (2000) have also reported similar relationship for PEO-$LiClO_4$ complexes. Li^+ ion coordination to the polymer backbone decreases chain flexibility and increased T_g.

Using the Rice and Roth model, the number density, mobility and diffusion coefficient of charge carriers were estimated. The increase in conductivity with temperature is due to the dissociation of more salt into ions when the sample was heated as represented in Figures 4.34 and 4.35 for the unplasticized system and Figures 5.18, 5.19 and 5.20 for the plasticized system. From the calculations, for the unplasticized system, the number density of charge carriers increases with temperature indicating that conductivity is thermally assisted up to 323 K. For the plasticized system, conductivity increased up to 373 K. Due to the changes in number density, mobility and diffusion coefficient of mobile ions of the unplasticized system, it may be inferred that conductivity is contributed by number of free mobile ions and their mobility and diffusivity up to 333 K after which conductivity is controlled by mobility and diffusion coefficient only. For the plasticized system, mobility and diffusion coefficient of mobile ions increased with temperature but their values are lower than that for the unplasticized system. Although the number density of mobile ions for plasticized system is quite independent of temperature, but the larger value of number density for plasticized system (~ 10^{23} cm^{-3}) compared to unplasticized system (10^{12} to 10^{17} cm^{-3}) indicate that PEG has dissociated NH_4NO_3 into more ions and possibly prevents formation of ion pairs and aggregates. The higher number density of mobile ions helped to enhance the conductivity of MC-NH_4NO_3-PEG system.

The electrochemical stability of the polymer electrolyte was carried out for the highest conducting sample of both systems (unplasticized and plasticized). From the linear sweep voltammogram, the current onsets of the unplasticized and plasticized sample were detected at about 2.20 V and 2.40 V respectively. The differences on the current onset and current output for both samples indicated that the plasticized sample which has higher conductivity is more stable and can be applied on high current output compared to the unplasticized sample.

The electrode slurry was prepared using dip-coating method onto the aluminum mesh as current collector. The electrode was cut on different size 0.8 × 0.9, 1.3 × 1.4 and 1.5 × 3.0 cm^2. The electrolyte, 63.75MC21.25AN15PEG was sandwiched between two identical electrodes and was clamped between rectangular Perspex plates. A layer of PEG was coated on the electrode surface and dried to improve electrode-electrolyte contact and hence reduce the internal resistance in EDLC.

From CV test, good capacitive behavior was observed when all of the voltammograms show near to rectangular shape indicating that the prepared sample could work as membrane in EDLC. The power loss for cathodic and anodic part showed some differences. For EDLC using uncoated electrode with size 0.8 × 0.9 cm^2, power loss for anodic part is 25 % higher than the cathodic part. For EDLC using uncoated electrode with size 1.5 × 3.0 cm^2, power loss for cathodic part is larger than anodic part. For EDLC using coated electrode with size 1.5 × 3.0 cm^2, the value of power loss is the same. An ideal capacitor does not show differences in power loss if it has a perfect rectangular voltammogram. The voltammogram of EDLC using coated electrode with size 1.5 × 3.0 cm^2 is more rectangular and almost reaches the plateau region at anodic part, so no differences on power loss for cathodic and anodic part was observed. When compared to the results of other researchers, i.e. Matsuda *et al*. (1999), Lewandowski *et al*. (2003) and Staiti *et al*. (2002), the present results show better EDLC performance since the power loss is smaller.

The capacitance of EDLC is higher for low current density. According to Yang *et al*. (2005), this is due to the diffusion-limiting process of carbon material used in the electrode. This has been reported by Morita *et al*. (2004). Mitra *et al*. (2001) also reported similar performance from EDLCs using PAN based gel-polymer electrolytes. At high current density, 0.22 mA cm^{-2}, charge and discharge capacitance is 41.94 and 38.45 F g^{-1} respectively.

The effect of PEG on EDLC performance was also investigated when a layer of PEG was coated on the electrode surface. From Figure 6.4, it can be observed that the EDLC using coated electrodes has more rectangular voltammogram compared to voltammogram of EDLC using uncoated electrode. From charge-discharge characteristics, it can be seen that the charge-discharge curves of EDLC using coated electrodes exhibit almost perfect inverse V shape compared to EDLC using uncoated electrode. Self-discharge characteristics shows that EDLC using coated electrodes give higher voltage retention than uncoated electrodes. All this is due to internal resistance which must be minimized.