

## CHAPTER 8

### DISCUSSION

The discovery of polymer-alkali metal complexes to conduct ions has led towards the development of polymeric thin films that can be a good candidate as a solid polymer electrolyte (SPE) in electrochemical device applications. As ability to perform as an electrolyte conductivity has become an issue, lots of work have been carried out in order to enhance the conductivity of SPE and various approaches [Rajendran and Mahendran, 2001] have been made that include;

- Identification of a new polymer host
- Polymer electrolyte composite
- Cross linking of polymers
- Blending of two different types of polymers
- Plasticized polymer electrolytes

Solid electrolytes prepared from the above mentioned approaches, have been used in the fabrication of electrochemical devices. Proton batteries are one of the applications for solid state electrolytes.

In the present work, polymer blend based proton conducting electrolyte has been prepared and has been tested to satisfy requirements that have been mentioned by Mukoma *et al.*, (2004) and Kumar and Sekhon (2002a). These requirements are;

- High ionic conductivity at room temperature. Conductivity of the order  $10^{-3} \text{ S cm}^{-1}$  has been achieved.
- Low cost
- No electronic-conductivity
- Good mechanical properties
- Chemically, electrochemically, thermally and photochemically stable
- Ease of processing

It is important to know the reasons for the choice of PVA and chitosan that were used to form the blends. The reasons for choosing PVA and chitosan to form the blend are:

- Chitosan and PVA blend membrane exhibits good mechanical properties [Mucha *et al.*, 1998]
- Chitosan and PVA form a homogenous blend [Miya *et al.*, 1984].
- Chitosan and PVA are compatible [Bel'nikovich *et al.*, 2003].
- Good ionic conductivity and flexibility [Razak *et al.*, 2009].
- Both PVA, [Yang *et al.*, 2009] and chitosan [Mukoma *et al.*, 2004] are low cost polymers.

Due to the above reasons, the blend between chitosan and PVA should be able to serve as a good polymer host for ionic conduction.

The choice of ammonium nitrate,  $\text{NH}_4\text{NO}_3$  as the doping salt is due to its low lattice energy of  $648.9 \text{ kJ mol}^{-1}$  compared to other ammonium salt such as ammonium acetate, ( $\text{CH}_3\text{COONH}_4 = 703.1 \text{ kJ mol}^{-1}$ ), ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4 = 1754.7 \text{ kJ mol}^{-1}$ ), ammonium phosphate ( $(\text{NH}_4)_3\text{PO}_4 = 3443.0 \text{ kJ mol}^{-1}$ ). Hema *et al.*, (2009a) pointed out that salt with lower lattice energy gives a higher conductivity value.

One of the four hydrogen atoms in  $\text{NH}_4^+$  ions can dissociate easily under the influence of an electric field as it is most weakly bound. The  $\text{H}^+$  ion movements from one site to another result in a vacancy that will be filled by another  $\text{H}^+$  ion from a nearer neighboring site [Buraidah *et al.*, 2009]. Solution casting method has been employed to prepare the polymer blend-salt and polymer blend-salt-plasticizer system which consist of chitosan-PVA- $\text{NH}_4\text{NO}_3$  and chitosan-PVA- $\text{NH}_4\text{NO}_3$ -ethylene carbonate respectively. A blend with the composition of [40 wt. % chitosan + 60 wt. % PVA] (C4P6) exhibits the most homogenous blend therefore C4P6 was chosen to become as a polymer host in the salted system. The conductivity value of the pure chitosan/PVA blend film (C4P6) was obtained to be  $4.48 \times 10^{-11} \text{ S cm}^{-1}$ . With the addition of 40 wt. %  $\text{NH}_4\text{NO}_3$ , the conductivity value has increased to a maximum value of  $2.07 \times 10^{-5} \text{ S cm}^{-1}$ . The increased in conductivity is believed to be influenced by the increased in number of charge carriers supplied by  $\text{NH}_4\text{NO}_3$  salt and its mobility.

From the FTIR results as studied in Chapter Five, the addition of  $\text{NH}_4\text{NO}_3$  has shifted the amine band to a lower wave numbers up to  $1518 \text{ cm}^{-1}$  hence it has proven that complexation has occurred and as more than 40 wt. %  $\text{NH}_4\text{NO}_3$  added, the wave numbers shifted back to lower value at  $1516 \text{ cm}^{-1}$ . The decreased of conductivity in the salted system could be attributed to the formation of salt aggregates prior to the film formation leading to the decrease in the number of charge carriers and this has been proven by the SEM micrographs of the 50[C4P6]-50AN and 40[C4P6]-60AN samples where the surface morphology exhibited some crystalline structures. In Chapter Six, results from XRD diffractograms are in good agreement with the SEM micrographs where it can clearly be observed that the XRD patterns for the 50[C4P6]-50AN and 40[C4P6]-60AN samples exhibited peaks that are attributed to  $\text{NH}_4\text{NO}_3$  at  $2\theta = 17.9^\circ$ ,  $22.4^\circ$ ,  $28.9^\circ$ ,  $32.8^\circ$  and  $39.8^\circ$  and  $2\theta = 17.9^\circ$ ,  $22.4^\circ$ ,  $28.9^\circ$ ,  $31.1^\circ$ ,  $32.8^\circ$ ,  $39.8^\circ$  respectively.

From the electrochemical impedance studies in Chapter Six, transport parameters of the salted system have been calculated employing the Rice and Roth model (1972). 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. The increase in number density of ions will increase the conductivity and vice versa on condition the mobility of ions does not change significantly. In the salted system the mobility increases from  $3.27 \times 10^{-7}$  to  $1.97 \times 10^{-6}$   $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$ , as the  $\text{NH}_4\text{NO}_3$  concentration increases from 10 to 40 wt. %. Conductivity can be related to the dielectric constant  $\epsilon_r$  of the samples and from Figure 6.10 the  $\epsilon_r$  versus frequency plot shows that the dielectric constant increases in accordance with the increase in conductivity. It can be clearly observed that when the conductivity decreases the value of  $\epsilon_r$  behaved as such.

The conductivity has increased with the addition of ethylene carbonate (EC) up to 70 wt. % of EC concentration with the value of  $1.60 \times 10^{-3} \text{ S cm}^{-1}$ . The conductivity at room temperature for plasticized system is shown in Figure 6.21. Ethylene carbonate with (donor number = 16.4) [Kim *et al.*, 2000] a relatively low viscosity and high dielectric constant (89.7) [Xu, 2004] has been added to enhance the conductivity. The addition of low molecular weight and high dielectric constant plasticizers results in increment of the amorphous phase, increase flexibility of the polymer and increase the number density of mobile charge carriers [Pitawala *et al.*, 2008].

The use of EC can weaken the coulombic forces between the cation and anion of the salt and results in salt dissociation [Wintersgill, 1987] hence more undissociated salt and ion aggregates can break away to form conducting ions that contribute to conductivity. The interaction between EC and  $\text{NH}_4\text{NO}_3$  can be observed in the FTIR

spectra where the C=O stretching band of EC has shifted to lower wave numbers with the addition of  $\text{NH}_4\text{NO}_3$  from 1771 and  $1797\text{ cm}^{-1}$  to 1773 and  $1803\text{ cm}^{-1}$  respectively. The C=O bending band of EC has also shifted from 715 to  $719\text{ cm}^{-1}$ . Interaction between EC and lithium salt has been studied by Osman and Arof, (2003), and from the literature it can be inferred that EC has helped to create a new pathway for the transport of charge carriers.

The SEM micrograph for 30[60C4P6-40AN]-70EC sample (Figure 6.28) shows that the surface morphology of the sample is denser and more amorphous as compared to other samples. The XRD pattern for sample 30[60C4P6-40AN]-70EC has also proved that the sample is amorphous. After the addition of more than 70 wt.% EC, the conductivity of the plasticized system decreased. The explanation that can be given to clarify this situation is that the “overdose” of EC has made the sample more crystalline that ion transport is hindered. Increase in crystallinity of the sample is supported by the XRD pattern and SEM micrograph in Figure 6.30 and Figure 6.31 respectively.

Using the Rice and Roth model (1972) it has been shown that the addition of EC has increased the number density of mobile ions and resulted in conductivity enhancement. The addition of 70 wt.% EC has optimized the conductivity value with number density of ions value of  $2.20 \times 10^{21}\text{ cm}^{-3}$ . In the plasticized system, the mobility of the charge carriers has not that significantly since the increase is  $2.09 \times 10^{-6}$  to  $4.54 \times 10^{-6}\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ , as the EC concentration increases from 10 to 70 wt.%. In the polymer-salt system increase in mobility does reach about one order of magnitude. Thus it can be inferred that the factors influencing the conductivity in the plasticized and unplasticized systems are not the same.

From the plots of  $\log \sigma$  versus  $1000/T$  for both salted and plasticized system as depicted in Figure 6.12 and 6.35 respectively, it is observed that the conductivity is thermally assisted. The linear behavior in both Figure 6.12 and 6.35 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 in both salted and plasticized sample possessed the lowest  $E_a$  value of 0.30 and 0.14 eV respectively. The decrease in activation energy supports the ion conduction mechanism shown in Chapter Five where the plasticizer has created alternative pathways that requires a lower energy for conduction.

The dielectric constant  $\epsilon_r$  of the polymer electrolyte is also affected by temperature. Temperature help to increase the dissociation of ions by increasing vibration of the anions and cations which leads towards the break up of the salt and increase the number of ions. From the plot of  $\epsilon_r$  versus frequency for 60[C4P6]-40AN and 30[60C4P6-40AN]-70EC sample as depicted in Figure 6.11 and 6.34 respectively at various temperature (298K-343 K), it is observed that as the temperature increases the  $\epsilon_r$  also increases.

Both primary and secondary proton batteries in this work could acquire a voltage of around 1.60 to 1.70 V implying that the suggested battery chemistry  $Zn + MnO_2 + 4H^+ \rightarrow Zn^{2+} + Mn^{2+} + 2H_2O$  is acceptable. Further more from the linear sweep voltammogram (Figure 7.1), it can be observed that the electrolyte has a breakdown voltages detected at 1.70 V hence supported the proposed battery chemistry. The primary proton batteries were subjected to discharge at 2 mA constant current with  $(38.86 \pm 4.12)$  mAh discharge capacity. At different current of 1 and 3.5 mA, the battery

can deliver almost similar capacity of the value between 30 to 40 mAh. From the voltage-current-power characteristic in Figure 7.4, it was found that the maximum power density was  $(9.47 \pm 0.26)$  mW cm<sup>-2</sup>. Current applied, discharge capacity and power density of the primary proton batteries was found to be higher as compared to other reports elsewhere [Ng and Mohamad, 2006; Saaid *et al.*, 2009]. For the secondary proton battery or well known as rechargeable proton battery was performed for nine cycles and no significant loss of the potential value was observed. However, after the ninth cycle, the potential of the rechargeable battery has dropped to lower than 20 % of the initial potential value. The charge and discharge processes of the secondary proton battery lasted for almost ninety hours at 0.3 mA discharged-charged current. Discharge-charge current for secondary proton battery in this work was observed to be higher than that reported in the literature [Pandey *et al.*, 1998; Lakshmi and Chandra, 2002; Pratap *et al.*, 2006].

EDLC fabricated in the present work could acquire a working voltage of 0.95 V. The EDLCs was charged and discharge with two different current density of 0.095 and 0.381 mA cm<sup>-2</sup> respectively. Both EDLCs have performed for 100 cycles and the capacitance of the EDLC at charge-discharge current density of 0.095 and 0.381 mA cm<sup>-2</sup> was 27.1 and 16.7 F g<sup>-1</sup> respectively.