CHAPTER 10

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

10.1 Conclusions

Solid polymer electrolyte systems of starch-chitosan, starch-chitosan-NH$_4$Cl (salted system) and starch-chitosan-NH$_4$Cl-glycerol (plasticized system) were successfully prepared via solution cast technique. From XRD analysis, the blend of 80 wt.% starch and 20 wt.% chitosan (S8C2) was found to be the most amorphous blend and was chosen to serve as the polymer host. SEM studies have revealed the miscibility between starch and chitosan. Starch-chitosan miscibility in S8C2 film was further confirmed by the appearance of only one $T_g$ value in the DSC thermogram, which is found to fall in between the $T_g$ values of pure starch (S10C0) and pure chitosan (S0C10) films. TGA analysis shows that the water content of the film has been decreased upon blending starch with chitosan.

From FTIR analysis, the shifting of bands’ peak as well as changes in intensity has proved the occurrence of interaction among the materials. Hydrogen bonding interaction between starch and chitosan has been proposed. Interaction between NH$_4$Cl and the polymer blend host was observed by the shifting of the peak at hydroxyl, carboxamide and amine bands as well as glycosidic linkage and C-O-C group bands. The addition of glycerol has further shift those peaks indicating more ions have interacted with the polymer host.
In the salted system, the addition of 25 wt.% NH₄Cl has optimized the conductivity to \((6.47 \pm 1.30) \times 10^{-7}\) S cm\(^{-1}\). The increase in conductivity was due to the following reasons:

- Increase in the number density of ions with the increase in NH₄Cl concentration up to 25 wt.%.
- Amorphousness of the electrolyte.
- Increase in the mobility of ions since ions are more mobile in the highly amorphous electrolyte.
- Low value of \(T_g\) increases the segmental motion of the polymer chains, thus assists the ion mobility.

In the plasticized system, the addition of 35 wt.% glycerol enhanced the conductivity to \((5.11 \pm 1.60) \times 10^{-4}\) S cm\(^{-1}\). The plasticizer has assisted the conductivity enhancement by the ways stated below:

- Its high dielectric constant value helps to weaken the Coulombic force between cation and anion, thus ease the salt dissociation.
- Provides the alternative pathways for ionic conduction.
- Reduces the crystallinity as well as the \(T_g\) of electrolytes.

The conductivity-temperature relationship in the temperature range of 298-343 K for all electrolytes was found to follow Arrhenius rule. The increase in conductivity with increasing temperature was contributed by the increase in mobility of ions. Higher conducting electrolyte obtained lower activation energy implying that lower energy is required for ionic conduction in higher conducting electrolyte. From transference number measurements, ion has been found as the dominant conducting species. Transference number of cation for P7 electrolyte was 0.56. The relaxation time
of the electrolytes was found to decrease with increasing conductivity and temperature. Scaling of \( \tan \delta \) confirmed that electrolyte systems in this study obey non-Debye behaviour. The ac conduction mechanism for S5 and P7 electrolytes was best explained by QMT and CBH models, respectively.

LSV results revealed that P7 electrolyte decomposed at 1.65 V, confirming the suitability of P7 electrolyte for EDLC and proton batteries application. The EDLC was charged and discharged for 500 cycles, where the specific capacitance was lasted at \( \sim 3444 \ \text{mF g}^{-1} \). The EDLC’s performance has been related to ionic mobility, with comparison to other works. From CV, the specific capacitance was scan rate dependent, and decreases after 500 charge-discharge cycles due to the increasing internal resistance. The OCP of the primary and secondary proton batteries after 48 h was \((1.54 \pm 0.02) \ \text{V}\) and \((1.58 \pm 0.01) \ \text{V}\), respectively. The discharge capacity of the primary batteries was enhanced by lowering the discharge current. The internal resistance and short circuit current of the primary proton batteries were 36.74 \(\Omega\) and 35 mA, respectively. Charge-discharge of the secondary battery was able to perform up to 40 cycles for \(\sim 440 \ \text{h}\).

### 10.2 Suggestions for Future Work

Since the maximum conductivity of the electrolyte in the present work is in the order of \(10^{-4} \ \text{S cm}^{-1}\), the conductivity of the electrolyte should be further enhanced by using the following methods:

- Modify the structure of polymer host by inserting an additional functional group using processes such as carboxymethylation (Mobarak, Ramli, Ahmad, &
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Rahman, 2012), phthaloylation (Aziz et al., 2012), hydroxyalkylation (Lawal, 2009) and acylation (Zong, Kimura, Takahashi, & Yamane, 2000). This method provides additional complexation site for the ions, thus more salt can be solvated which can increase the conductivity.

- Addition of inorganic filler like aluminum oxide (Al₂O₃) (Aziz, Majid, Yahya, & Arof, 2011), silicon dioxide (SiO₂) (Subban & Arof, 2003b) and titanium dioxide (TiO₂) (Rosli, Chan, Subban, & Winie, 2012) into the electrolyte. The presence of filler can create favourable pathways for ionic conduction, increase the amorphousness and immobilize the anions (Hassan et al., 2013).

- Double salt system (Ramesh & Arof, 2000; Yap, 2012). Mixed salts in an electrolyte can encourage more ion dissociation by anion-anion dipole interactions (Yap, 2012).

- Gamma irradiation treatment on the electrolytes. Irradiation with gamma rays of the electrolytes can cause more ions to dissociate (Rahaman et al., 2014).

The performance of EDLC and proton batteries could be further studies by the following ways:

- The performance of the devices at different temperatures.
- Alteration of the electrodes by addition of suitable additives.
- Increases the surface area of activated carbon.
- Synthesizes the carbon material from natural materials such as fruit shells (Arof et al., 2012) and woods (Abdullah et al., 2001).