CHAPTER 9

DISCUSSION

Research on solid polymer electrolytes (SPEs) have been actively carried out in view of their application in electrochemical devices such as EDLC, electrochromic display devices, fuel cells, solid-state batteries and sensors. Problems associated with liquid electrolytes such as solvent vaporization, leakage and corrosion can be avoided while the mechanical stability and flexibility of packaging design can be improved (Dias, Plomp, & Veldhuis, 2000; Fujishima & Zhang, 2005). The development of SPEs has seen the emergence of natural biopolymers such as starch (Khiar & Arof, 2010), methyl cellulose (Shuhami et al., 2012) and chitosan (Buraidah et al., 2009; Majid & Arof, 2005, 2007, 2008) as the polymer host.

In the present work, corn starch is of interest. Starch is composed of amylose and amylopectin where amylose resides mainly in amorphous region of starch (Sajilata et al., 2006; Ochubiojo & Rodrigues, 2012). Since starch is sourced from various foods, the choice of corn starch is based on its higher amylose content than other types of starch as shown in Table 2.3. Corn starch has been used as polymer host in SPE as reported by Khiar and Arof (2010), Liew et al. (2012) and Teoh et al. (2012). Using acetic acid as the solvent is an approach to improve the mechanical properties and hydrophobicity of starch (Gonzalez & Perez, 2002; Song & Cheng, 2014; Xu & Hanna, 2005). In Chapter 5, the shift of the peak at hydroxyl and glycosidic linkage bands as well as changes in intensity of the peak at C-O bond stretching and C-H stretching mode.
bands proved the interaction between starch and acetic acid. The interaction has occurred since the oxygen atoms in the functional groups of starch contain lone pair electrons which can form dative bond with H$^+$ ions from the acetic acid.

The problems possessed by starch based products such as brittle, hydrophilic and low mechanical strength has led towards idea to blend starch with other polymers (Mathew et al., 2006; Miyamoto et al., 2009; Wu & Zhang, 2001; Xu et al., 2005). The reasons to blend starch with chitosan are:

- Good miscibility between both polymers through interactions between amino groups of chitosan and hydroxyl groups of starch (Salleh et al., 2009). Good miscibility indicates strong interaction between the polymers and tends to suppress the crystalline phase, which in turn enhances the amorphous phase.
- Improved the formation condition and ductility of starch-based films (Zhai et al., 2004).
- Able to provide transparent and mechanically strong films (Salleh et al., 2009).
- Both polymers are at low cost (Jiang, Quan, Liao, & Wang, 2006; Lu et al., 2009).

Commonly, the interaction between the polymer components of a polymer blend occurs through hydrogen bonding (Guo, Sato, Hashimoto, & Ozaki, 2010; He, Zhu, & Inoue, 2004). The hydrogen bond is an attractive interaction involving a hydrogen atom bound to a highly electronegative atom and other highly electronegative atom (Arunan et al., 2011). From the FTIR analysis on starch-chitosan blend in Chapter 5, the interaction between the polymers has occurred through hydrogen bonding formation between the functional groups of both polymers as listed below:

- Hydroxyl groups of starch and hydroxyl groups of chitosan,
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- hydroxyl groups of starch and amine groups of chitosan,
- hydroxyl groups of starch and glycosidic linkages of chitosan,
- hydroxyl groups of starch and C-O-C groups in chitosan, and
- hydroxyl groups of chitosan and glycosidic linkages of starch.

The results of various characterizations for determination of best ratio of starch-chitosan blend to serve as the polymer host were presented in Chapter 4. From the XRD results, crystalline peaks of starch and chitosan have been suppressed by a broad amorphous hump in the diffractogram of 80 wt.% starch-20 wt.% chitosan blend (S8C2). This result demonstrates the good miscibility and interaction between starch and chitosan in the blend. The calculation of the degree of crystallinity ($\chi_c$) has been done by using two different methods i.e. Nara-Komiya method and deconvolution method. From the deconvolution method, the crystalline and amorphous peaks have been separated via Gaussian fitting. It is noticed that there are three crystalline peaks at $2\theta = 14.4^\circ$, $18.5^\circ$ and $22.8^\circ$ superimposed on the broad amorphous hump centered at $2\theta = 20.5^\circ$ in the XRD diffractogram of S8C2 film, proving that this blend film is not fully amorphous. Although different values of degree of crystallinity have been obtained from the two methods, it is confirmed that the amorphous content in S8C2 film is higher than other blend ratio. According to Kadir (2010), the miscibility between two polymers in a blend can be implied from the smooth and homogenous surface of the blend film. The scanning electron micrograph of S8C2 film shows a homogenous surface without phase separation suggesting the good miscibility between starch and chitosan in the blend. Similar result has been reported by Jayaprakash et al. (2013) on potato starch-chitosan blend.
DSC analysis on pure starch film (S10C0) and pure chitosan film (S0C10) has revealed that the glass transition temperature ($T_g$) of the films are 67.21 °C and 97.41 °C, respectively. As discussed by He, Xue, Yang, Liu and Song (2009), the $T_g$ of chitosan is still a subject of controversy since no consistent results were reported in the literature. The same thing goes to starch (Liew et al., 2012; Liu et al., 2009). This phenomenon could be due to the fact that natural polymers are originated from different sources or method of extraction which can reflect to the variation in their properties including the $T_g$ value (He et al., 2009). However, the $T_g$ values obtained in this work are comparable to the values reported by Liu et al. (2009) and Cheung et al. (as cited in Correia et al., 2014). DSC thermogram of S8C2 film consists only single $T_g$ at 82.33 °C which is in between the $T_g$ values of S10C0 and S0C10 films. This result has confirmed the miscibility between starch and chitosan in S8C2 film. From TGA analysis, the water content of S8C2 film is lower than that of S0C10 and S10C0 films indicating that the water content of a starch based film can be reduced by blending it with chitosan. According to Xu et al. (2005), the interaction between chitosan and starch molecules has prevented water molecules from diffusing through the film. This phenomenon decreases the water content of starch based film. The decomposition temperature does not change on blending starch with chitosan, as S8C2 film decomposes at 270 °C.

Proton conducting electrolytes have long been recognized as an initiative to lithium ion conductors in electrochemical device applications (Nasef et al., 2007; Panero et al., 2003). Ammonium salts are usually used as proton donor for polymer electrolyte as inorganic acids are problematic choices (Hema et al., 2008). The choice of ammonium chloride (NH$_4$Cl) as the doping salt is due to its lower lattice energy of 663.0 kJ mol$^{-1}$ compared to other ammonium salts like ammonium acetate, NH$_4$C$_2$H$_3$O$_2$ (703.1 kJ mol$^{-1}$), ammonium sulfate, (NH$_4$)$_2$SO$_4$ (1754.7 kJ mol$^{-1}$) and ammonium
phosphate, \((\text{NH}_4)_3\text{PO}_4\) (3443.0 kJ mol\(^{-1}\)) (Buraidah & Arof, 2011; Kadir, 2010). Lattice energy of an ammonium salt depends on the size of anion. The radius of Cl\(^-\) is \(~1.68\) Å (Roobottom, Jenkins, Passmore, & Glasser, 1999). Larger anion of salt indicates lower lattice energy. Low lattice energy of a salt indicates that less energy is required to break the bond between anion and cation which is favourable for coordination of ions at the functional groups of polymer host (Buraidah, 2012).

From the FTIR results in Chapter 5, the addition of NH\(_4\)Cl up to 25 wt.% has shifted the hydroxyl band to lower wavenumbers of 3264 cm\(^{-1}\). Hence it has been proven that interaction has occurred involving the oxygen atom of hydroxyl groups and the cations of salt. The occurrence of salt recrystallization has been detected in S8 electrolyte with the appearance of \(v_{as}(\text{NH}_4^+)\) and \(v_s(\text{NH}_4^+)\) modes in its FTIR spectrum. The interaction also occurred at the carboxamide, amine, C-O-C groups and glycosidic linkages as the bands’ peak has shifted with the addition of NH\(_4\)Cl. Based on these FTIR results, the interaction between the cations and the oxygen and nitrogen atoms of the polymer blend host has been illustrated in Figure 5.18. As mentioned earlier, the oxygen and nitrogen atoms of the functional groups contain lone pair electrons, which provide the coordination site for cations, thus are able to form dative bond with the cations.

In the salted system, the highest conductivity value of \((6.47 \pm 1.30) \times 10^{-7}\) S cm\(^{-1}\) has been achieved on addition of 25 wt.% NH\(_4\)Cl (S5 electrolyte). The increase in conductivity can be attributed to the increase in the number density \((n_d)\) and mobility \((\mu)\) of ions which have been calculated using the Rice and Roth model (as cited in Kadir et al., 2010; Samsudin et al., 2012). This model relates the conductivity with \(n_d\), activation energy \((E_a)\) and time travelling of ion \((\tau)\). The \(E_a\) values were determined
from the Arrhenius plots while $\tau$ values were determined using the value of $l$, which is the distance between two complexation sites. As shown in Tables 6.11, 6.13, 6.15 and 6.17, the $n_d$ and $\mu$ values increase as the NH$_4$Cl concentration increases from 5 to 25 wt.%. This phenomenon perfectly follows the following relation:

$$\sigma = n_d e \mu \quad (9.1)$$

Here, the increase in $n_d$ and $\mu$ values will obviously increases the conductivity. A decrease in conductivity was resulted when more than 25 wt.% NH$_4$Cl was added to the electrolyte. According to Kadir et al. (2010), high salt concentration in an electrolyte causes the distance between dissociated ions become closer that they are able to recombine and form neutral ion pairs. This phenomenon reduces the number density of ions and eventually decreases the conductivity of electrolyte.

Further investigation on conductivity trend in the salted system has been carried out by XRD, SEM and DSC. The addition of salt up to 25 wt.% to the polymer host has decreased the degree of crystallinity as shown in Tables 6.5 and 6.6. From Tables 6.11, 6.13, 6.15 and 6.17, the addition of salt up to 25 wt.% increases the number density of ions. According to Aji et al. (2012), the increase in ion concentration increases both the fraction of amorphous phase and charge carriers simultaneously. The increase in amorphousness of electrolyte assists the mobility of ions, thus provide answer for the increasing conductivity with increasing NH$_4$Cl content up to 25 wt.%. When more than 25 wt.% NH$_4$Cl was added to the polymer, a number of crystalline peaks appear in the XRD patterns in Figure 6.19. These crystalline peaks can be attributed to the crystalline nature of the salt. This result indicates the occurrence of recrystallization of salt within
the electrolytes with more than 25 wt.% NH₄Cl. This phenomenon leads to an increase in the degree of crystallinity as shown in Table 6.6, hence decreases the conductivity.

Comparing the SEM micrographs of S8C2 and S4 electrolytes, several particles can be observed on the electrolyte’s surface when 20 wt.% of NH₄Cl was added to the polymer host. This type of particles has also been observed in other polymer electrolyte systems by Ahmad et al. (2010) and Bhad & Sangawar (2013). The latter authors inferred that these particles act as the channels for ion conduction through the electrolyte. More particles can be observed in the micrograph of S5 electrolyte, indicating more ions are available for conduction thus further strengthens the conductivity result. Too many particles can be observed in the micrograph of S8 electrolyte, where some of these particles agglomerate. From Figure 6.19, it is inferred that the recrystallization of salt has become dominant in S8 electrolyte as crystalline peaks appear in the X-ray diffractogram of S8 electrolyte. From the micrograph of S8 electrolyte, the agglomeration of the particles may lead towards ion pairs formation.

Plasticization technique is one of the most practical ways to optimize the conductivity of electrolyte. Plasticizer possesses a high value of dielectric constant which can ease the dissociation of salt by weakening the Coulombic force between cation and anion. From a report by Ping, Wang, Sun, Feng, and Chen (2011), although ethylene carbonate (EC) has a high value of dielectric constant of 89.6, its high melting point of 39 °C may lead to poor low temperature performance of devices. In this work, glycerol has been chosen as the plasticizer. As stated in Chapter 2, the choice of glycerol is based on the following facts:

- Dielectric constant of 42.5, which is higher than other plasticizers such as dimethylacetamide, DMA \( (\varepsilon_{DMA} = 37.8) \) (Kumar & Sekhon, 2002),
\(\gamma\)-Butyrolactone, GBL \((\varepsilon_{\text{GBL}} = 39.1)\) (Ping et al., 2011) and ethylene sulfite, ES \((\varepsilon_{\text{ES}} = 39.6)\) (Azli, Manan, & Kadir, 2015).

- Melting and boiling points of 18 °C and 290 °C, respectively (Speight, 2002). These values of melting and boiling points ensure that glycerol will not solidify or boil in the present temperature range study.

- Most compatible plasticizer for starch based film (Curvelo, de Carvalho, & Agneli, 2001; Marcondes et al., 2010).

According to Liang et al. (2009), glycerol possesses the strong ability to interact with the polysaccharide matrix through hydrogen bonding interactions. From the FTIR analysis on starch-chitosan-glycerol in Chapter 5, the increase in glycerol content shifts the peak at hydroxyl, C-O-C, glycosidic linkage, carboxamide and amine bands indicating that there are formation of hydrogen bonding between the polymers and glycerol. As shown in Figure 2.4, the glycerol molecule has three hydroxyl groups that can provide the coordination sites for cations of salt. This is proven by the shifting of the hydroxyl band peak of pure glycerol to lower wavenumbers on addition of \(\text{NH}_4\text{Cl}\) up to 7 wt.% as shown in Figure 5.24. This result hypothesizes that apart from assists the salt dissociation, the presence of glycerol in the SPE may provide the additional sites and conducting pathways for ion conduction (Gondaliya et al., 2013). From Figure 5.26, the hydroxyl band peak of S5 electrolyte has shifted to lower wavenumbers of 3254 cm\(^{-1}\) in the spectrum of electrolyte with 30 wt.% glycerol (P6 electrolyte) and further shifted to 3247 cm\(^{-1}\) in the spectrum of electrolyte with 35 wt.% glycerol (P7 electrolyte). Another peak shifting was observed at carboxamide, amine, glycosidic linkage and C-O-C bands which further proves the interaction between glycerol and other electrolyte’s components.
In the plasticized system, the conductivity has been increased with the addition of glycerol up to 35 wt. % concentration with the value of \((5.11 \pm 1.60) \times 10^{-4}\) S cm\(^{-1}\).

From Tables 6.12, 6.14, 6.16 and 6.18, the increase in conductivity can be attributed to the increase in the number density and mobility of ions. In the plasticized system, P7 electrolyte has the highest \(n_d\) and \(\mu\) values, confirming its highest conductivity value. However, when more than 35 wt.% glycerol was added to the electrolyte, the conductivity decreases as well as the number density and mobility of ions. To get into a bigger picture about this matter, SEM and XRD analysis were carried out.

From the SEM analysis, the addition of plasticizer has altered the morphology of the electrolyte. On addition of 10 wt.% glycerol (P2 electrolyte), the number of particle observed on the electrolyte’s surface has been reduced whereas the dark areas start to appear. On addition of 20 wt.% glycerol (P4 electrolyte), the dark region starts to dominate accompanied by the appearance of linkage like structures. The maximum dominancy of the dark region as well as increasing number of link can be seen in the micrograph of P7 electrolyte. From the literature, the dark region in surface micrograph represents the amorphous phase of the electrolyte (Ahmad et al., 2010; Su’ait et al., 2011). Thus, it can be inferred that the addition of glycerol increases the amorphous phase of the electrolyte. From the XRD analysis, the degree of crystallinity of P7 electrolyte is found to be lower than S5 electrolyte as shown in Tables 6.7 and 6.8. The presence of plasticizer in the electrolyte assists salt dissociation which in turn decreases the occurrence of salt recrystallization. Alternative pathways provided by the plasticizer for ion conduction helps the polymer host to accommodate the salt, as evidenced by the appearance of linkage like structure on plasticizer electrolyte’s surface. The plasticizer is believed to act as a spacer between molecules of polymer by forming links with them (Pandey et al., 2013). From the FTIR studies, glycerol has formed hydrogen bond with
the polymer. These phenomena enhance the amorphousness of the electrolytes which in
turn increases the number density and mobility of ions. The degree of crystallinity of P8
electrolyte is higher than P7 electrolyte, inferring that P8 is less amorphous than P7
electrolyte. As shown in the SEM micrograph of P8 electrolyte, too much links appear
on the electrolyte’s surface when 40 wt.% glycerol was added. The linkages may be
formed between the plasticizer itself causing the salt to recrystallize thus decreases the
conductivity (Johan & Ting, 2011).

In the amorphous region, ionic migration is associated with the polymer
segmental motion (Money et al., 2012). The polymer segmental mobility can be
enhanced by lowering the \( T_g \) (Woo et al., 2013). Since the conductivity is attributable to
the increase in segmental motion (Aravindan & Vickraman, 2007), determination of \( T_g \)
can further enhance the understanding in conductivity trend. On addition of 5 wt.%
\( \text{NH}_4\text{Cl} \), the \( T_g \) decreases from 82.33 °C to 55.08 °C. Further decrease in \( T_g \) is observed
when 25 wt.% \( \text{NH}_4\text{Cl} \) was added to the electrolyte. The decrease in \( T_g \) with increasing
salt content is also been observed by Vijaya et al. (2013) on PVP-\( \text{NH}_4\text{Cl} \) electrolytes.
The presence of salt has weakened the dipole-dipole interactions between the polymer
chains thus provides the plasticizing effect on the polymer (Malathi et al., 2010). This
phenomenon stimulates the flexibility of polymer backbone thus enables the ions to
move easily through the polymer chain network when an electric field is applied (Liew
et al., 2014; Malathi et al., 2010). It can be concluded that by lowering the \( T_g \), the
conductivity can be increased. The addition of glycerol up to 35 wt.% decreases the \( T_g \),
thus satisfies the conductivity result. The addition of glycerol to the electrolyte increases
the chain flexibility which results in a decrease in \( T_g \) (Kumar & Sekhon, 2002). On
addition of 45 wt.% glycerol, the \( T_g \) is observed to increase. From the transport analysis,
the number density of ion is decreased with the addition of more than 35 wt.% glycerol
due to the recrystallization of salt. This phenomenon increases the rigidity of electrolyte thus impedes the segmental mobility as well as the ionic migration (Liew et al., 2014; Noor et al., 2013; Silva et al., 2004).

TGA analysis of selected electrolytes has been carried out to check the stability of the electrolytes within the temperature range of the present studies. S1 and S5 electrolytes decompose at 198 °C and 185 °C, respectively. According to Ramesh et al. (2012), the decrease in thermal stability with the addition of salt reveals the decline in capability of the polymer chain to sustain its original form upon subject to heating. On addition of 35 wt.% glycerol, there is an additional stage of weight loss at 136-177 °C due to the degradation of glycerol in the electrolyte (Ayala et al., 2012). The major decomposition of P7 electrolyte occurs at 180 °C. The first weight loss of S1, S5 and P7 electrolytes is higher (~ 7-10%) than that of S8C2 film due to the hydrophilic nature of NH₄Cl salt and glycerol (Halim et al., 2012; Noor et al., 2012). These results show higher water content within S1, S5 and P7 electrolytes compare to S8C2 electrolyte. To study the effect of water on conductivity, variation of conductivity of P7 electrolyte with temperature under one heating-cooling cycle has been carried out. The conductivity is found to be lower on cooling cycle than the heating cycle by ~ 3%. This is attributed to the loss of water from the electrolyte during the heating cycle.

Ionic and electronic transference numbers of an electrolyte are crucial in explaining the conductivity of the electrolyte (Sekhar et al., 2012a). For an ionic conductor, ionic transference number \( t_{ion} \) should be higher than the electronic transference number \( t_e \) (Aziz et al., 2012; Shukur & Kadir, 2015; Woo et al., 2011b). From Figures 6.44 to 6.46, the current is observed to decrease rapidly at the initial before being saturated at 0.2 µA. Before reaching the saturation level, the current is
carried by both ions and electrons. However, the ions cannot pass through the ion blocking stainless steel electrodes leaving only electrons to carry the current through the electrodes (Woo et al., 2011b). This phenomenon results in saturation of current at 0.2 µA. Generally, ions are mobile in the amorphous phase while crystalline phase favours electron transport (Gadjourova et al., 2001). From the XRD analysis in Chapter 6, the degree of crystallinity of P7 electrolyte is the lowest, followed by P5 and S5. Due to its higher amorphous content than the other two electrolytes, P7 electrolyte has the highest $t_{ion}$ value of 0.98 and the lowest $t_e$ of 0.02.

The contribution of cation to the total conductivity is important to be known due to its major role during the charge-discharge process of a battery. Manganese (IV) oxide (MnO$_2$) was used as the electrodes for cation transference number ($t_+$) measurements since it is proton transparent. It is found that the value of $t_+$ of P7 electrolyte is 0.56. As for comparison, the values of $t_+$ for other P3 and S5 electrolytes were also determined and found to be 0.33 and 0.26, respectively. According to Suthanthiraraj and Vadivel (2012), the increase in $t_+$ value with increasing amount of plasticizer in polymer electrolyte could be due to favourable cation migration within the electrolyte. As shown in Chapter 5, the addition of glycerol has provided the alternative pathways for the cations for migration, thus leading to the increase in $t_+$.

The dielectric constant ($\varepsilon_r$) and dielectric loss ($\varepsilon_i$) as a function of NH$_4$Cl and glycerol concentration at selected frequencies were presented in Chapter 7. The objective of the presentation of $\varepsilon_r$ and $\varepsilon_i$ is to correlate the conductivity with those parameters. As NH$_4$Cl content increases to 25 wt.%, the charge stored in the electrolyte increases indicating an increase in the number density of mobile ions hence increases the conductivity (Buraidah et al., 2009). The decreasing $\varepsilon_r$ and $\varepsilon_i$ values for electrolytes
containing more than 25 wt.% \( \text{NH}_4\text{Cl} \) can be attributed to ion reassociation, leading to a decrease in conductivity (Woo et al., 2011a). A higher glycerol content up to 35 wt.% increases the value of \( \varepsilon_r \) and \( \varepsilon_i \). As glycerol was added, more undissociated salt become ions, hence the stored charge in the electrolyte increases. The \( \varepsilon_r \) and \( \varepsilon_i \) values are observed to decrease with the increase in frequency. As frequency increases, the periodic reversal of the electric field occurs so rapidly which disable the charge carriers from orienting themselves in the field direction, resulting in the decrease of \( \varepsilon_r \) and \( \varepsilon_i \) (Ali et al., 2011; Mishra & Rao, 1998).

The \( \varepsilon_r \) and \( \varepsilon_i \) values are observed to be affected by temperature as depicted in Figures 7.5 to 7.8. Temperature assists the dissociation of ions by increasing the vibration of the anions and cations which leads towards the break up of the salt and increase the number of ions (Kadir, 2010). This result is in agreement with the transport parameters as shown in Tables 6.21 and 6.22, where the number density of ion increases with the increase in temperature.

The frequency dependent of loss tangent (\( \tan \delta \)) for the electrolytes indicates that the loss peaks (\( \tan \delta_{\text{max}} \)) are shifted to high frequency side with increasing conductivity. The shift of \( \tan \delta_{\text{max}} \) to high frequencies indicates the decrease in relaxation time (\( t_{\tan \delta} \)) (Hashim & Khiar, 2011; Ramly et al., 2011; Subban & Arof, 2003a). The \( \tan \delta_{\text{max}} \) are also observed to shift to high frequencies with increasing temperature, meaning that the value of \( t_{\tan \delta} \) decreases as shown in Tables 7.6 and 7.7. The height of \( \tan \delta_{\text{max}} \) also increases which attributed to the decrease in resistivity of the electrolytes (Idris et al., 2007). The activation energy of the frequency at \( \tan \delta_{\text{max}} \) (\( f_{\text{max}} \)) is very close to those obtained from the plots of \( \log \sigma \) vs 1000/\( T \) in Chapter 6. Thus it can be indicated that
the ion transport mechanism has the same potential energy barrier upon conducting and relaxing (Ali et al., 2009).

Debye relaxation denotes a system with a single relaxation time (Macdonald, 1999). In polymer electrolytes, under an alternating external electric field, different polarization mechanism such as electronic, dipolar and ionic polarization occur. Thus a distribution of relaxation times will occur in polymer electrolytes, which deviates from Debye type relaxation (Aziz, 2012). To prove this matter, scaling of \( \tan \delta \) has been done by plotting the normalized of \( \tan \delta / (\tan \delta_{\text{max}}) \) against \( f/f_{\text{max}} \) for selected electrolytes. For a typical Debye peak, the value of full width at half maximum (FWHM) of the plot is 1.14 decades, which gives the Kohlrausch exponent (\( \beta_{\text{KWW}} \)) = 1 (Dutta et al., 2002; Idris et al., 2007). The value of \( \beta_{\text{KWW}} \) for S5 electrolyte at 298-343 K is 0.57-0.60. For P1 electrolyte, the value of \( \beta_{\text{KWW}} \) is found to be 0.42-0.47 at 298-343 K. The small value of \( \beta_{\text{KWW}} \) in the present system shows the deviation of relaxation from Debye relaxation.

Jonscher’s universal power law (Buraidah et al., 2009; Winie & Arof, 2004) has been used to predict the ac conduction mechanism of the highest conducting electrolyte in salted and plasticized systems. The conduction mechanism was predicted from the variation of power law exponent \( s \) with temperature. For S5 electrolyte, the exponent \( s \) is almost temperature independent which follows quantum mechanical tunneling (QMT) model (Kadir et al., 2009). In QMT model, the polarons are able to tunnel through the potential barrier that exists between two complexation sites (Majid & Arof, 2007). In S5 electrolyte, the polarons are resembled by the \( \text{H}^+ \) ions and their stress fields. For P7 electrolyte, the exponent \( s \) decreases with the increase in temperature, thus follows correlated barrier hopping (CBH) model. In CBH model, the ions are surrounded by several potentials. The ions can only hop from one site to another after acquiring
enough energy (Buraidah, et al, 2009). The difference in conduction mechanism of S5 and P7 electrolytes can be attributed to the difference in $E_a$ value. Due to the higher $E_a$ (0.31 eV), the ions in S5 electrolyte are able to tunnel through the potential barrier. The $E_a$ of P7 electrolyte is lower (0.19 eV). The addition of plasticizer decreases $T_g$ and increases the segmental motion. Hence, the ions can easily hop across the potential barrier (Kufian et al., 2007).

The electrochemical stability of the highest conducting electrolyte (P7) was carried out using LSV measurement with stainless steel foils as working, counter and reference electrodes. As for comparison, LSV measurements for other selected electrolytes were also been carried out using the same type of electrodes. P7 electrolyte was found to be electrochemically more stable than S5, P3 and P5 electrolytes due to its higher conductivity value than the other electrolytes. The current onset of P7 electrolyte was detected at 1.65 V which is suitable for EDLC and proton batteries application.

In an EDLC, the charge storage mechanism is based on the formation of Helmholtz double-layers (Lim et al., 2014a). Since electrodes of the same type (i.e symmetry) were used, the EDLC needed to be charged first to provide the potential difference between the electrodes. During the charging process, electrons from the positive electrodes move towards the negative electrode through the outer circuit. This movement of electrons provides holes at the positive electrode. At the same time, the cations in the electrolyte migrate to the negative electrode while the anions move to the positive electrode. The accumulation of cations and anions at the surface of electrodes to compensate the opposite electronic charges at the electrode surfaces provide the potential difference between the two electrodes. No chemical reactions are involved in this energy storage mechanism. The energy storage mechanism of the EDLC is based on
the physical movement of electrons and ions. During the discharge, these electrons move back from the negative electrode to the positive electrode, and ions are released from the electrode surface into the electrolyte, so the cathode and anode come back to the same potential (Chen, 2011; Ho, Khiew, Isa, & Tan, 2014).

In the present work, the EDLC was fabricated by sandwiching P7 electrolyte with two carbon based electrodes using perspex plates. The EDLC was charged and discharged at a constant current density of 0.063 mA cm\(^{-2}\) between 0 to 0.85 V for 500 cycles. The specific capacitance (\(C_s\)) is observed to decrease to 3915 mF g\(^{-1}\) during the first 70 cycles before remains constant at ~ 3444 mF g\(^{-1}\) until 500\(^{th}\) cycle. The strong relation between conductivity and mobility of charge carriers means that the EDLC’s performance affected by the mobility of charge carriers. The ionic mobility of P7 electrolyte is \((4.42 \pm 1.23) \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\). Comparing the present result with reports from literature (Arof, Amirudin, et al., 2014; Arof, Shuhaimi, et al., 2014; Majid, 2007), it can be concluded that the higher the ionic mobility, the greater the \(C_s\) value. The Coulombic efficiency (\(\eta\)) of the EDLC increases from 69\% to 91\% towards the 50\(^{th}\) cycle before remains constant at ~ 90-95\%. Efficiency of ~ 90\% indicates the intimate electrode-electrolyte contact (Lim et al., 2014a). This result shows that the present EDLC exhibits good cycling stability for 500 cycles.

The value of \(C_s\) is also obtained using the result from cyclic voltammetry (CV) measurements before and after galvanostatic charge-discharge measurement. The \(C_s\) value decreases as the scan rate increases. According to Nasibi et al. (2012), when the scan rate was increased, energy loss increases and the stored charge on the electrode surface decreases leading to a decrease in \(C_s\). At low scan rates, ions can utilize all the vacant sites in the active electrode material since they have enough time to diffuse into
the vacant sites leading to the higher $C_s$ value (Lim et al., 2014b). The enclosed area of the CV curve becomes smaller after 500 charge-discharge measurement, indicating smaller $C_s$ value. This phenomenon is due to the effect of internal resistance. From the literature (Arof et al., 2010; Liew et al., 2015; Pendashteh et al., 2014), internal resistance increases with increasing charge-discharge cycle. At higher resistance, less charges flow causes less current flow which result a decrease in $C_s$ value (see Table 8.2).

In a primary battery, the energy storage mechanism is based on the chemical reactions occur at the electrodes. During the discharge of proton battery, zinc at the anode is oxidized and releases Zn$^{2+}$ and electrons. The reaction involving the ZnSO$_4$·7H$_2$O releases H$^+$ ions. Electrons from the anode will then move to the cathode through the outer circuit, while the H$^+$ ions (from the anode and the electrolyte) move to the cathode through the electrolyte. At the cathode, the reaction between MnO$_2$, electrons and H$^+$ ions causes MnO$_2$ to undergo reduction. All these reactions will provide the battery with the potential as shown in Table 8.4. However, as stated in Chapter 8, the difference between the theoretical and experimental result of potential of battery could be due to the concentration and transport of ions (Botte & Muthuvel, 2012).

Primary proton batteries were fabricated by sandwiching P7 electrolyte with zinc based anode and MnO$_2$ based cathode in coin cells. Result of 48 h open circuit potential (OCP) shows that the potential of the batteries is (1.54 ± 0.02) V, which is 20.31% higher than the expected potential (see Table 8.4). Botte and Muthuvel (2012) stated that the difference between the theoretical and experimental values of OCP is due to several factors e.g. concentration and transport of ions. Similar result has been reported
in the literature (Alias et al., 2014; Samsudin et al., 2014). The batteries were then
discharged at different constant currents (0.10, 0.25, 0.40 and 0.60 mA) at room
temperature. During the discharge process, the zinc was oxidized while MnO$_2$ was
reduced thus forming Mn$_2$O$_3$-ZnO (McComsey, 2001; Rahman et al., 2013). As the
discharge time increases, more Mn$_2$O$_3$-ZnO particles are formed causing the increase in
charge transfer resistance. This phenomenon has resulted to the abrupt decrease in
potential after ~ 1.0 V. The discharge capacity ($Q$) was found to be higher at lower
discharge current ($Q = 9.36$ mA h at 0.10 mA). According to Roscher et al. (2011), at
high discharge current, the variation of ion concentration along the pores depth of an
electrode increases, forcing a non-uniform proton insertion process. From the current-
potential ($I$-$V$) and current density-power density ($J$-$P$) characteristics measurement, the
internal resistance ($r$) of the batteries is found to be 36.74 Ω. The maximum power
density is (7.90 ± 0.50) mW cm$^{-2}$ while the short circuit current of the batteries is 35
mA. The characteristics of the present primary proton batteries are comparable with
other reported works (Kadir et al., 2010; Ng & Mohamad, 2006; Shukur, Ithnin, et al.,
2013).

In a secondary proton battery, the battery is able to charge to its initial potential.
During the charging process, the process of discharge is reversed where the electrons
move back to the anode through the outer circuit while the H$^+$ ions move to the
electrolyte towards the anode. In the present work, P7 electrolyte was also been used in
the fabrication of secondary proton battery. Before the fabrication, the highest
conducting electrolyte solution has been added to the cathode to enable the
deintercalation of proton from the cathode active material and enter the anode through
the electrolyte for rechargeable process (Kadir et al., 2010). The OCP of the secondary
proton battery for 48 h is lasted at (1.58 ± 0.01) V. The secondary proton battery was
subjected to discharge and charge at a constant current of 0.35 mA. This charge-discharge process was performed for 40 times and lasted for ~ 440 h. At the first cycle, the battery is discharged to 1.00 V before being recharged to 1.58 V. A decrease in specific discharge capacity ($Q_s$) at 2nd cycle can be attributed to the electrode-electrolyte contact, which is not always perfect at the first charge (Guinot et al., 1998; Mohamad et al., 2003). The $Q_s$ value increases thereafter and reaches 7.83 mA h g$^{-1}$ after 6th cycle. The $Q_s$ value is almost stable until 15th cycle before decreases until the 40th cycle. This phenomenon may be caused by the poor interfacial stability of the electrode thus develop the large interfacial resistance between the electrode and the electrolyte as reported for other proton batteries (Mishra et al., 2014; Samsudin et al., 2014; Selvasekarapandian et al., 2010).