

## CHAPTER 9

### CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The first objective of this work is to develop polymer electrolyte systems based on PCL, an eco-friendly material in the effort to lower environmental impact. Films of PCL-NH<sub>4</sub>SCN polymer electrolyte were firstly prepared by solution cast technique. The ionic conductivity of pure PCL film was obtained as  $1.86 \times 10^{-10} \text{ S cm}^{-1}$ . Upon addition of 26 wt.% NH<sub>4</sub>SCN, the ionic conductivity was increased to  $3.94 \times 10^{-7} \text{ S cm}^{-1}$ . EC was then added (from 10 to 50 wt.%) to the highest conducting PCL-NH<sub>4</sub>SCN sample to further improve the ionic conductivity. The highest room temperature conductivity of PCL-NH<sub>4</sub>SCN-EC system was  $3.82 \times 10^{-5} \text{ S cm}^{-1}$  at 50 wt.% EC, two orders of magnitude higher than PCL-NH<sub>4</sub>SCN system. To the author's knowledge, this is the first time that PCL has been incorporated with an ammonium salt.

The role of ion dissociation on ionic conductivity enhancement was studied. The room temperature conductivity enhancement for PCL-NH<sub>4</sub>SCN system up to 26 wt.% NH<sub>4</sub>SCN was mainly due to the increase in number density of free ions. This was deduced from FTIR result where the percentage of free ions at  $2040 \text{ cm}^{-1}$  keeps increasing until 26 wt.% salt. From the relative permittivity studies, the variation of  $\epsilon'$  with the addition of salt content reflected the increase in number density of salt ions. The good linear fit with high regression value using VTF equation on the temperature dependence conductivity also verified this conclusion. The increasing trend of parameter  $A$  in the VTF equation revealed the growing number density of ions in PCL matrix.

On the other hand, the improvement in conductivity for PCL-NH<sub>4</sub>SCN-EC system was contributed by the increase in number density of ions and ion mobility. From the deconvolution of FTIR spectra, the number density of free ions was proven to increase with increasing EC content. From the dielectric studies,  $\epsilon'$  value was amplified with the addition of EC showing the enhancement of number density of ions. The high dielectric constant value (89.8) of EC had made EC an effective ion dissociation agent. Ion pairs and aggregates were dissociated contributing to more free ions. Similar as PCL-NH<sub>4</sub>SCN system, temperature dependence conductivity investigation showed that parameter  $A$  increased with increasing EC content.

The enhancement of ion mobility in PCL-NH<sub>4</sub>SCN-EC system was supported by FTIR analysis. The new EC-NH<sub>4</sub><sup>+</sup> complex sites at 1773 cm<sup>-1</sup> acted as new pathways for ions to migrate with possible shorter jump distance. The incorporation of EC had made the polymer chains more flexible. This was proven by DSC analysis that showed a lower  $T_g$  and lower degree of crystallinity. From the fact that ionic motion was coupled with polymer segmental motion, more flexible polymer segment in expanding amorphous domain meant easier ion migration.

The increase of  $T_g$  for PCL-NH<sub>4</sub>SCN system was due to the interaction between PCL and NH<sub>4</sub><sup>+</sup> at 1623 cm<sup>-1</sup>. On the other hand, the decreasing  $T_g$  for PCL-NH<sub>4</sub>SCN-EC system was attributed to the more competitive EC-NH<sub>4</sub><sup>+</sup> complex sites at 1773 cm<sup>-1</sup> which reduced the PCL-NH<sub>4</sub><sup>+</sup> interaction. Both systems demonstrated a reduced  $\chi_c$ . From XRD analysis, the degree of crystallinity reduced from 43.8 % of pure PCL film to a minimum 32.7 % upon addition of 26 wt.% salt in PCL-NH<sub>4</sub>SCN system. This  $\chi_c$  value continues to decrease from 32.7 % to 16.0 % when 50 wt.% of EC was

incorporated to the highest conducting PCL-NH<sub>4</sub>SCN sample. This concludes that the highest conducting samples possess the highest amorphous content for both PCL-NH<sub>4</sub>SCN and PCL-NH<sub>4</sub>SCN-EC systems.

From morphology investigation, spherulites with definite boundary were observed in PCL-NH<sub>4</sub>SCN system. When more NH<sub>4</sub>SCN was added up to 26 wt.%, the number of spherulites increased tremendously with corresponding reduction in spherulite size and surface roughness. For PCL-NH<sub>4</sub>SCN-EC system, the clear spherulite boundaries fade away with increasing EC content. The surface morphology becomes smooth.

The coupling effect between ionic motion and polymer segmental motion was analyzed in both PCL-NH<sub>4</sub>SCN and PCL-NH<sub>4</sub>SCN-EC systems. From EIS analysis, the two PE systems exhibited a VTF type conducting behavior, showing that the ionic motion was coupled with polymer segmental motion. This coupling effect was also manifested as a single and asymmetric peak in the  $M''$  versus  $\log f$  plot and a depressed semicircle arc in the argand plot of  $M''$  versus  $M'$ . The addition of EC has improved the flexibility of polymer chains and lowered the activation energy for coupling to occur. Loss tangent studies showed that the variation of relaxation time was the inverse of dc conductivity. It meant the  $\tan \delta$  peak was observed to shift to higher frequency with increasing NH<sub>4</sub>SCN or EC content, in the respective system. The estimated  $\sigma_{dc}$  from real part of complex conductivity also matches well the experimental value for both respective systems.

Further investigation should be carried out to improve the room temperature conductivity of the PCL-based polymer electrolyte. This can be done in two ways.

- (i) Add electrochemically inert nano-scale ceramic fillers with appropriate chemical and morphological properties such as  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  to the highest conducting PCL-based sample. This may enhance the conductivity by decreasing the degree of crystallinity, introducing surface group interactions and thus new pathways for ion conduction [Croce *et al.*, 2001].
- (ii) Add ionic liquid to the highest conducting sample. Ionic liquid is room temperature molten salt that is known for non-flammability, high volatility, high chemical and thermal stability. The ionic motion was reported [Ueki and Watanabe, 2008] to decouple from polymer segmental motion which mark the potential to achieve room temperature conductivity  $> 10^{-2} \text{ Scm}^{-1}$  [Angell *et al.*, 1996].

Further work should also be extended to apply this PCL-based polymer electrolyte to the electrochemical double layer capacitor (EDLC), proton battery and fuel cell applications.