

CHAPTER 8

CONCLUSIONS

In this work, five polymer electrolyte systems have been prepared. The first objective was to optimize the polymer blend–salt composition in PEMA/PVdF–HFP–LiTf system. The 70 wt.% [PEMA/PVdF–HFP]–30 wt.% LiTf was chosen as the optimized composition due to its sufficient ionic conductivity of $2.87 \times 10^{-7} \text{ S cm}^{-1}$ and mechanical stability at room temperature. This objective has been achieved.

The second objective was to improve the ionic conductivity of the optimized PEMA/PVdF–HFP–LiTf composition. With addition of EC, PC, BMII and BMITf, the ionic conductivity was improved; the best conducting sample in each respective system is EC–6 ($\sigma = 1.05 \times 10^{-4} \text{ S cm}^{-1}$), PC–6 ($\sigma = 1.46 \times 10^{-6} \text{ S cm}^{-1}$), BI–12.5 ($\sigma = 4.86 \times 10^{-5} \text{ S cm}^{-1}$) and BT–60 ($\sigma = 8.59 \times 10^{-5} \text{ S cm}^{-1}$). The PEMA/PVdF–HFP–LiTf and the two ionic liquid containing polymer electrolyte systems (PEMA/PVdF–HFP–LiTf–BMII and PEMA/PVdF–HFP–LiTf–BMITf) obeyed the Arrhenius model which suggests that the ionic conduction occurs mainly through the hopping of Li^+ ions from one coordination site to another. In each of the systems mentioned above, the lowest activation energy was exhibited by S–40 ($E_{a2} = 0.11 \text{ eV}$), BI–12.5 ($E_{a2} = 0.16 \text{ eV}$) and BT–60 ($E_a = 0.15 \text{ eV}$) samples which were also the best conducting sample in the respective system as the lowest amount of energy is required to transport Li^+ ions in the electrolyte. On the other hand, the two plasticizer–containing samples, namely the PEMA/PVdF–HFP–EC and PEMA/PVdF–HFP–PC were found to obey the VTF model. This model suggests that the ionic conduction is assisted by the creation of free

volume which allows the transport of ions and polymer segmental motion. The best conducting sample EC-6 and PC-6 exhibit the lowest T_0 value of 244 K and 264 K respectively. This proves that the second objective has been achieved.

The third objective was to investigate the interactions that occur in each polymer electrolyte system by vibrational spectroscopy. Miscibility between PEMA and PVdF-HFP to form PEMA:PVdF-HFP blend in the weight ratio 70:30 was evidenced by the formation of intermolecular interactions between the carbon atom in the C=O group of PEMA and the fluorine atoms in the CF₃ group of PVdF-HFP, and between the carbon atom in the CF₃ group of PVdF-HFP and the oxygen atom in the C-O-C group of PEMA. In PEMA/PVdF-HFP-LiTf system, the coordination of Li⁺ ions from LiTf was shown to occur on the oxygen atoms in the C=O and C-O-C groups of PEMA and on the fluorine atoms in the CF₂ group of PVdF-HFP. For the plasticized PEMA/PVdF-HFP-LiTf-EC and PEMA/PVdF-HFP-LiTf-PC systems, Li⁺ ions coordinate to both the oxygen atom of the C=O groups of PEMA and the plasticizer while the carbon atom of the plasticizer is shown to interact with the C-O-C group of PEMA and the CF₂ group of PVdF-HFP. For the PEMA/PVdF-HFP-LiTf-BMII and PEMA/PVdF-HFP-LiTf-BMITf systems, each respective ionic liquid has coordinated through the imidazolium cation (BMI⁺) onto the O atoms in the C=O and C-O-C groups of PEMA and the CF₂ group in PVdF-HFP. The interactions between the polymers and BMII were shown to decrease above 12.5 wt.% while for the BMITf system, the interactions decreased with increasing BMITf content. The occurrence of interactions through FTIR studies shows that the third objective has been achieved.

The fourth objective involves the investigation of the thermal stability of all polymer electrolyte systems. The increased decomposition temperature of PEMA upon

blending with PVdF–HFP to form PEMA/PVdF–HFP (70:30) shows that the presence of PVdF–HFP improved the thermal stability of PEMA from 229 °C to 268 °C. Additions of various LiTf contents into PEMA/PVdF–HFP blend lowered the decomposition temperature due to the breaking of the strong intra– and inter– dipole–dipole interactions involving the fluorine atoms in PVdF–HFP to around 256–260 °C. The electrolytes of PEMA/PVdF–HFP–LiTf–EC and PEMA/PVdF–HFP–LiTf–PC systems are thermally stable up to around 255–271 °C and 256–269 °C. BMII–added electrolytes exhibit the lowest decomposition temperature while the BMITf–containing samples are the most thermally stable polymer electrolytes. The fourth objective has been achieved.

In this work, the highest conductivity achieved is 10^{-4} S cm⁻¹. As the ionic conductivity comes from both anions (i.e. Tf⁻) and cations (i.e. Li⁺), the concentration of anions can be reduced to allow higher ionic conductivity due to Li⁺ ions. High conductivity due to cations is favourable especially in the application of rechargeable lithium batteries. One way to reduce the concentration of anions is by introducing anion receptors such as calix molecules which has been reported to hold the anions, hence restricting their mobility, and consequently enhancing the transport of Li⁺ ions in the polymer electrolytes.

Another suggestion for future work is to incorporate an iodide (I⁻) based inorganic salt (i.e. lithium iodide (LiI)) or ionic liquid and iodine into the polymer electrolytes to fabricate a solar cell. This is because the preparation of solar cells is increasingly more popular due to it being a renewable energy.