

CHAPTER 9

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

9.1 Conclusions

Polymer electrolytes with optimum ionic conductivity of at least 10^{-4} S cm⁻¹ for the fabrication of solid state dye sensitized solar cells were successfully prepared with solution casting technique. In fact we have managed to achieve conductivity as high as 10^{-3} S cm⁻¹. Different iodide salts (NaI and KI) has been chosen as doping salts with PVDF-HFP as polymer host and EC/PC mixture as plasticizer. Plasticization has been recognized as one of the effective methods for reducing the crystallinity and enhancing the amorphous nature in polymer electrolytes. The electrolytes were characterized by FTIR, XRD and EIS.

The shifting and elimination of some FTIR peaks have proven the formation of polymer-salt complexes and miscibility between polymer, salt and plasticizer. PVDF-HFP vibrational bands has undergone changes in the (PVDF-HFP)-NaI and (PVDF-HFP)-KI infrared spectra, where the intensity of CH₂ rocking band at 851 cm⁻¹ has been reduced in all salt concentrations. The C-C skeleton band at 1062 cm⁻¹ has shifted to 1069 cm⁻¹, CF₂ stretching band at 1145 cm⁻¹ to 1131 cm⁻¹, CF₃ symmetrical stretching band at 1179 cm⁻¹ to 1166 cm⁻¹ and the CF₂ assymmetric stretching band at 1197 cm⁻¹ to 1228 cm⁻¹. CF₂ stretching band at 1381 cm⁻¹ has merged with another CF₂ stretching at 1401 cm⁻¹ and has peaked at new position, 1398 cm⁻¹. Besides the changes in the vibrational bands, PVDF-HFP crystalline peaks at 761, 795, 972 and 1381 cm⁻¹ have disappeared. The shifting of the amorphous peak at 870 cm⁻¹ and the difference in area and intensity of the amorphous band also implied that the addition of salts reduced the crystallinity and hence increased

amorphousness in both NaI and KI based electrolytes. From analysis on the area under the amorphous band determined by Origin 8.0 software, the sample having 60 wt.% (PVDF-HFP)-40 wt.% NaI and 80 wt.% (PVDF-HFP)-20 wt.% KI displayed the largest amorphous band area. It can therefore be inferred that these two samples are the most amorphous in the unplasticized electrolyte system. The shifting of wave number in the FTIR spectra of NaI-(EC/PC), KI-(EC/PC) and (PVDF-HFP)-(EC/PC) electrolytes has confirmed the miscibility and interaction between polymer, salt and plasticizer in the plasticized electrolytes. Area under amorphous band showed that the sample having 20 wt.% (EC/PC) in NaI based electrolyte and 50 wt.% (EC/PC) in KI based electrolyte inferred that these two samples are the most amorphous samples in the plasticized electrolyte system. These results were justified by XRD studies.

The degree of crystallinity for each samples were confirmed by XRD studies. From XRD deconvolution analysis with Origin 8.0 software, the lowest degree of crystallinity was found in sample having 40 wt.% NaI in the (PVDF-HFP)-NaI electrolyte system and 20 wt.% KI in the (PVDF-HFP) – KI electrolyte system. The result proved that these samples are the most amorphous samples in each electrolyte. Upon addition of (EC/PC) plasticizer mixture, both samples have shown further reduction in the degree of crystallinity. For (PVDF-HFP) – NaI – (EC/PC), the lowest degree of crystallinity found in sample with 20 wt.% (EC/PC) and in sample with 50 wt.% (EC/PC) in KI based plasticized electrolyte. The results also inferred that the use of plasticizers in polymer electrolytes have increased the amorphousness of the systems which are also favourable for high conductivity.

From EIS studies, the conductivity of the electrolytes was observed to increase with increasing salts concentration up to a certain limit. It is also proven that the incorporation of plasticizer into polymer-salt electrolytes has enhanced the conductivity in both NaI and KI salt containing polymer electrolytes. The highest conductivity value obtained for

(PVDF-HFP)-NaI electrolyte was $5.21 \times 10^{-5} \text{ S cm}^{-1}$ in 60 wt.% (PVDF-HFP)-40 wt.% NaI sample and for unplasticized (PVDF-HFP)-KI electrolyte was $1.20 \times 10^{-4} \text{ S cm}^{-1}$ in the 80 wt.% (PVDF-HFP)-20 wt.% NaI sample. These two samples were also the most amorphous samples as confirmed from FTIR and XRD studies. The plasticized film for (PVDF-HFP) – NaI with 20 wt. % (EC/PC) showed the highest conductivity value of $1.53 \times 10^{-4} \text{ S cm}^{-1}$ and the plasticized (PVDF-HFP) – KI, showed highest conductivity value of $1.10 \times 10^{-3} \text{ S cm}^{-1}$ in the electrolytes with 50 wt. % (EC/PC). The conductivity results have justified the FTIR and XRD results where samples with highest degree of amorphousness in polymer electrolytes showed the highest conductivity value. Since conductivity is the product of charge carrier density, mobility and ionic charge, the values of charge carrier density (n), ion mobility (μ) and diffusion coefficient (D) obtained from Nyquist plot using the proposed method called the equivalent circuit model approach were used to describe the conductivity behavior. It has been proven that the value of n, μ and D variation against salt content followed the trend of conductivity variation against salts content. These results indicate that the three parameters determined the conductivity simultaneously.

Dye-sensitized solar cells have been fabricated using the highest conducting samples of the plasticized NaI and KI based electrolytes that have been added with small quantity of iodine to produce the redox mediator. Synthetic Ruthenium dye and natural dyes were used as the sensitizer. It is well known that the highest conductivity of the electrolyte influences short circuit current (I_{SC}) density and efficiency of the solar cells. From EIS studies, 40 wt.% (PVDF-HFP)–10 wt.% KI–50 wt.% (EC/PC) electrolyte had showed better conductivity value than 48 wt.% (PVDF-HFP)–32 wt.% NaI–20 wt.% (EC/PC) electrolyte. DSSCs fabricated with the [40 wt.% (PVDF-HFP)–10 wt.% KI–50 wt.% (EC/PC)]-1 wt.% I_2 electrolyte with both Ruthenizer 535 N3 and natural dyes showed better performance than DSSC fabricated with [47 wt.% (PVDF-HFP)–31 wt.% NaI–19 wt.% (EC/PC)]-3

wt.% I₂. DSSCs fabricated with the [40 wt.% (PVDF-HFP)–10 wt.% KI–50 wt.% (EC/PC)]–1 wt.% I₂ electrolyte with Ruthenizer 535 N3 exhibited open-circuit voltage (V_{OC}) = 0.65 V, short-circuit current density (J_{SC}) = 7.54 mA cm⁻², fill factor (FF) = 0.51, and conversion efficiency (η) = 2.49% compared to DSSC having [47 wt.% (PVDF-HFP)–31 wt.% NaI–19 wt.% (EC/PC)]–3 wt.% I₂ electrolyte and Ruthenizer 535 N3 dye with performance of V_{OC} = 0.58 V, J_{SC} = 6.40 mA cm⁻², FF = 0.48 and efficiency = 1.78 %. DSSC with the same KI containing electrolyte and N3 dye had showed efficiency of 4.13% and 3.68% respectively under illumination of 30 mW cm⁻² and 60 mW cm⁻² light intensities compared to 2.76% and 2.48% respectively for DSSC having the same NaI containing electrolytes and N3 dye. It is also proven from this work that the efficiency of the DSSC can further improved on addition of a second salt. On replacing part of the KI salt electrolyte with tetrabutyl ammonium iodide (TBAI) the efficiency of the DSSC improved further from 2.49% to 2.69% due to mixed cation effect.

9.2 Suggestions for Further Work

Work should be continued to improve the efficiency of the dye sensitized solar cell in future. All aspect of DSSC components includes TiO₂ working electrode, Pt counter electrode, electrolytes and the dye materials should be studied. Suggestions for future works are:

- (i) Using an alternative oxide semiconductor for the working electrode
- (ii) Improve the conductivity of polymer electrolyte to the order of 10⁻² or 10⁻¹ S cm⁻¹