CHAPTER 7

FABRICATION AND CHARACTERIZATION OF DYE SENSITIZED SOLAR CELLS

7.1 Introduction

Plasticized PVDF-HFP based polymer electrolytes containing two different salts NaI and KI have been prepared and characterized in the previous chapters. The highest conducting compositions for (PVDF-HFP)-NaI-(EC/PC) and (PVDF-HFP)-KI-(EC/PC) systems have been determined as described in Chapter 6. These electrolytes have been used to fabricate dye-sensitized solar cells with synthetic and natural dye sensitizers. A small amount of iodine (10% weight of salt) was added to the electrolytes to make them redox active. The polymer electrolyte systems for DSSC fabrication composed of :

(i) [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]-3 wt.% I_2

(ii) [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2

Other main components prepared for the DSSCs are photoanode, counter electrode and dye materials. The dyes used are commercial synthetic Ruthenium (II) polypyridyl complexes or Ruthenizer 535 N3 dye and natural dyes which are anthocyanin, chlorophyll and anthocyanin-chlorophyll mixture. According to Yuliarto et. al, (2010), anthocyanin was used in DSSCs since it has good chemical bonding with titanium dioxide. Chlorophyll is chosen as dye sensitizer because it is a natural photosensitizer for photosynthesis in green plants hence has attractive potential as photosensitizer in the visible region for DSSCs (Amao et. al, 2004; Sima et. al, 2010 and Zhou et. al, 2011). The commercial synthetic dyes are widely used in DSSCs due to the satisfactory photoelectric conversion efficiency up to 12.4% (Yella et. al, 2011). These synthetic dyes however, use metal compound complexes, which are expensive and produce environmental pollution (Asano et. al, 2004; Kim et. al, 2005) while natural dyes are environmentally friendly, non-toxic, biodegradable and cheaper. A disadvantage of natural sensitizing dyes which are anthocyanin extracted from black rice, chlorophyll extracted from *pandan* leaves and the mixture of anthocyanin and chlorophyll in the present study is the instability of the dyes. In this work, the dyes were mixed with tartaric acid and the pH adjusted to 1 since it has been shown that at this pH the absorbance of the dye is highest compared to other pH values (Buraidah et al., 2011). DSSCs with different electrolytes and dyes were fabricated in this work and their performance is presented in this chapter. The DSSCs fabricated in this work contain the following electrolytes and dyes.

(i) [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]- 3 wt.% I_2 and anthocyanin or chlorophyll or the mixture of anthocyanin and chlorophyll. Investigated under different light intensites.

(ii) [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]-3 wt.% I_2 and Ruthenizer 535 N3. Investiagted under different light intensites

(iii) [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]- 1 wt.% I_2 and anthocyanin or chlorophyll or the mixture of anthocyanin and chlorophyll. Investigated under different light intensites.

(iv) [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]- 1 wt.% I_2 and Ruthenizer 535 N3. Investiagted under different light intensites

(v) [40 wt.% (PVDF-HFP)-10 wt.% (KI/TBAI)-50 wt.% (EC/PC)]-1 wt.% I_2 and Ruthenizer 535 N3 with electrolytes having KI:TBAI weight ratios of 2:8, 4:6, 6:4, 8:2 and 10:0.

7.2 Visible Absorption Spectra of Dye Materials

Fig. 7.1 shows the UV-vis absorption spectra of Ruthenizer 535 (N3), anthocyanin, chlorophyll and a mixture of anthocyanin and chlorophyll sensitizers at 1:1 volume ratio.

Fig. 7.1: Absorption spectra of different dye materials (a) Ruthenizer 535 (N3), (b) anthocyanin/chlorophyll mixture, (c) anthocyanin and (d) chlorophyll

The N3 dye exhibits maximum absorption at 535 nm, anthocyanin from black rice extraction at 532 nm, chlorophyll at 413 and 665 nm and the mixture of anthocyanin and chlorophyll with equal volume ratio shows maximum peaks at 413, 536, 612 and 665 nm. Since, the sun's spectrum peaks at 550 nm, N3 and anthocyanin dyes should be able to absorb maximum sunlight and yield higher possibility of light harvesting (Yuliarto et. al, 2010). Chlorophylls, which act as effective photosensitizers in photosynthesis of green plants, has absorption maximum at 670 nm thus, it is an attractive compound as a photosensitizer in the visible region (Amao et. al, 2004). It is also found that more absorption peaks are found when the two natural dyes are mixed showing that the absorption range is enhanced. This indicates the possibility of increasing the photoelectric conversion efficiency of a dye-sensitized solar cell with mixed dyes (Chang et. al, 2010).

7.3 Characterizations of DSSCs Containing NaI based Electrolytes

7.3.1 DSSCs with [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]-3 wt.% I_2 and anthocyanin, chlorophyll and the anthocyanin and chlorophyll mixed dyes

The photocurrent density – voltage graphs for the DSSCs fabricated with the optimized electrolyte having different natural dye sensitizers are shown in Fig. 7.2. The DSSCs were illuminated with 100 mW cm^{-2} light intensity. The values of open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and conversion efficiency (η) obtained from the curves in Fig. 7.2 are summarized in Table 7.1. Compared to the DSSCs with individual natural dye sensitizers, the DSSC with mixed anthocyanin-chlorophyll dyes shows the best overall performance with the short-circuit current density of 2.63 mA cm^{-2}, open-circuit voltage of 0.47 V, fill factor of 0.58 and photo conversion efficiency of 0.72 %.

The results illustrate the possibility of utilizing a mixed natural dye mixture for the production of better sensitizer dyes for use in DSSCs. The DSSC with mixed dyes was also tested under lower light intensities of 30 and 60 mW cm^{-2} and the results are presented in the next section.

Fig. 7.2: Photocurrent density – voltage graphs for DSSCs fabricted with [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]- 3 wt.% I_2 electrolyte and different natural dyes

Table 7.1: Performance parameters of DSSCs utilizing [47 wt.% (PVDF-HFP)-31 wt.% NaI-19 wt.% (EC/PC)]-3 wt.% I_2 electrolyte and different natural dyes

	anthocyanin	chlorophyll	(anthocyanin + chlorophyll) at 1/1 volume ratio
J_{sc} (mA cm^{-2})	2.09	1.91	2.63
V_{oc} (V)	0.47	0.48	0.47
FF	0.57	0.56	0.58
Efficiency (η) (%)	0.56	0.51	0.72

7.3.2 Perfomance of DSSCs with anthocyanin-chlorophyll mixed dye and [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]- 3 wt.% I_2 electrolye at different light source intensities

From the previous sub-section, it has been noted that the DSSC with mixed anthocyanin-chlorophyll dyes shows the best overall performance than the DSSCs with the individual natural dye sensitizers. This DSSC was further tested under different light source intensities by reducing the irradiance condition to 30 and 60 mW cm^{-2}.

The J-V curves obtained are shown in Fig. 7.3 and the performance parameters derived from these curves are summarized in Table 7.2. The results show that the lower 30 mW cm^{-2} light intensity gives the best performance with 1.85 % efficiency. Under high light intensity the number of excited electrons is expected to be large and therefore the current produced must be large. However due to the possibility of larger recombination loss the current produced can be less than the amount expected. Under low light intensity the number of excited electrons will be less and so is the recombination loss and therefore the current observed will be comparatively larger than that is produced under high light intensity.

Since the current density produced under 100 mW cm^{-2} light intensity is 2.63 mA cm^{-2}, 30 mW cm^{-2} light intensity can be expected to produce 0.79 mA cm^{-2}. However the observed current density with 30 mW cm^{-2} light is higher with a value of 1.94 mA cm^{-2}. The *fill factor* under 30 mW cm^{-2} light also has improved slightly to 0.61 while the open circuit voltage remains same. The comparatively the larger current density and *fill factor* under 30 mW cm^{-2} light intensity led to the highest observed efficiency of 1.85%.

Fig. 7.3: Photocurrent density – voltage graph for DSSC with mixed anthocyanin-chlorophyll dyes and [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19wt.% (EC/PC)]-3 wt.% I_2 electrolyte under 30, 60 and 100 mW cm^{-2} light intensities

Table 7.2: Performance parameters for DSSCs with mixed anthocyanin-chlorophyll dyes and [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]-3 wt.% I_2 electrolyte at 30, 60 and 100 mW cm^{-2} light intensities

Light intensity (mW cm^{-2})	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF*	Efficiency (%)
100	2.63	0.47	0.58	0.72
60	2.41	0.47	0.59	1.11
30	1.94	0.47	0.61	1.85

7.3.3 DSSC with [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]-3 wt.% I_2 and Rhutenizer 535 N3 dye

Fig. 7.4 shows the photocurrent density – voltage graph for the DSSC fabricated with [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]- 3 wt.% I_2 and Ruthenizer 535 N3 dye. The open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF), and conversion efficiency (η) are shown in the figure.

Fig. 7.4: Photocurrent density – voltage graph for the DSSC with N3 dye and [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]-3 wt.% I_2 electrolyte 7.3.4 Performance of the DSSC with [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]-3 wt.% I_2 and Rhutenizer 535 N3 dye at different light intensities

The same DSSC fabricated with [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]- 3 wt.% I_2 and Ruthenizer 535 N3 dye shown in Fig. 7.4 was tested under different light source intensities by reducing the irradiance condition to 30 mW cm^{-2} and 60 mW cm^{-2}. The *J-V* curves for the DSSC obtained under different light intensities are shown in Fig. 7.5 and the performance parameters calculated are summarized in Table 7.3. From the results, it can be seen that the efficiency increases when the light intensity was reduced. The DSSC under illumination of 30 mW cm^{-2} intensity shows highest efficiency of 2.76 %.

Fig. 7.5 Photocurrent density – voltage graphs for the DSSC with [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]-3 wt.% I_2 electrolyte and Ruthenizer 535 N3 dye under 30, 60 and 100 mW cm^{-2} light intensities

Table 7.3: Performance parameters of DSSCs with [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]-3 wt.% I_2 electrolyte and Ruthenizer 535 (N3) dye under 30, 60 and 100 mW cm^{-2} light intensities

Light Intensity (mW cm^{-2})	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF*	*Efficiency* (%)
100	6.40	0.58	0.48	1.78
60	5.74	0.54	0.48	2.48
30	3.45	0.50	0.48	2.76

7.4. Characterization of DSSCs Containing KI Based Electrolytes

7.4.1 DSSCs with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 and anthocyanin, chlorophyll and the anthocyanin and chlorophyll mixed dyes

The photocurrent density–voltage graphs for DSSCs fabricated with highest conducting plasticized [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]/ 1 wt.% I_2 electrolyte having different natural dyes as sensitizer are shown in Fig. 7.6. The open-circuit voltage *(V_{OC})*, short-circuit current density *(J_{SC})*, fill factor *(FF)* and conversion efficiency *(η)* obtained from the graphs are summarized in Table 7.4. Similar to the results with (PVDF-HFP)-NaI-(EC/PC)/I_2 electrolyte, the DSSC with mixed anthocyanin-chlorophyll dyes shows the best overall performance with the short-circuit current density of 2.62 mA cm^{-2}, open-circuit voltage of 0.67 V, fill factor of 0.47 and photo conversion efficiency of 0.83%. However, the DSSC with the (PVDF-HFP)-NaI-(EC/PC)/I_2 electrolyte showed a lower efficiency of 0.72%.

Fig. 7.6: Photocurrent density – voltage graphs for DSSCs fabricated with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 electrolyte and different natural dyes.

Table 7.4: Performance parameters of DSSCs with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 electrolyte and different natural dyes.

	anthocyanin	chlorophyll	anthocyanin + chlorophyll
J_{sc} (mA cm^{-2})	2.22	1.83	2.62
V_{oc} (V)	0.63	0.62	0.67
FF	0.46	0.45	0.47
Efficiency (%)	0.64	0.51	0.83

7.4.2 Performance of the DSSC with anthocyanin-chlorophyll mixed dye and [40wt.% (PVDF-HFP) -10 wt.% KI - 50 wt.% (EC/PC)]- 1 wt.% I_2 electrolye at different light source intensities

In section ***7.4.1***, it was observed that the DSSC with mixed anthocyanin-chlorophyll dyes shows the best overall performance than the DSSCs with individual natural dye sensitizers which are anthocyanin and chlorophyll dyes. This DSSC was further tested under different light source intensities by reducing the irradiance condition to 30 mW cm^{-2} and 60 mW cm^{-2}. The *J-V* curves for the DSSCs obtained under different light intensities are shown in Fig. 7.7 and the performance parameters calculated are summarized in Table 7.5. From the results, it can be seen that the efficiency and fill factor, *FF* were increased when the light intensity was reduced. The DSSC under illumination of 30 mW cm^{-2} intensity shows highest efficiency of 1.7 % and *FF* value of 0.50**.**

Fig. 7.7: Photocurrent density – voltage graph for the DSSC with mixed anthocyanin-chlorophyll dyes and [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 electrolyte at 30, 60 and 100 mW cm^{-2} light intensities

Table 7.5: Performance parameters for the DSSC with mixed anthocyanin-chlorophyll dyes and [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 electrolyte at 30, 60 and 100 mW cm^{-2} light intensities

Light Intensity (mW cm^{-2})	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF*	*Efficiency* (%)
100	2.62	0.67	0.47	0.83
60	1.83	0.65	0.49	0.95
30	1.37	0.65	0.50	1.47

7.4.3 DSSC with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 and Rhutenizer 535 N3 dye

Fig. 7.8 shows the photocurrent density – voltage graph for the DSSC fabricated with the [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]/ 1 wt.% I_2 electrolyte and Ruthenizer 535 N3 dye. The values of 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% are all higher than the corresponding values for the DSSC having [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]/ 1 wt.% I_2 electrolyte and Ruthenizer 535 N3 dye; V_{OC}= 0.58 V, J_{SC} = 6.40 mA cm^{-2}, FF = 0.48 and efficiency = 1.78 %.

Fig. 7.8: Photocurrent density – voltage graph for the DSSCs with N3 dye and [40 wt.% (PVDF-HFP) -10 wt.% KI- 50 wt.% (EC/PC)]- 1 wt.% I_2 electrolyte

7.4.4 Performance of the DSSC with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]- 1 wt.% I_2 and Rhutenizer 535 N3 dye at different light intensities

The same DSSC fabricated with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]/ 1 wt.% I_2 with Ruthenizer 535 N3 was used to get the results shown in Fig. 7.8 was tested under different light source intensities by reducing the irradiance condition to 30 mW cm^{-2} and 60 mW cm^{-2}. The *J-V* curves for the DSSC obtained under different light intensities are shown in Fig. 7.9 and the performance parameters calculated are summarized in Table 7.6. From the results, it can be seen that the efficiency increases when the light intensity was reduced. The DSSC under illumination of 30 mW cm^{-2} intensity shows highest efficiency of 4.13 %.

Fig. 7.9: Photocurrent density – voltage graphs for the DSSC with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 electrolyte and Ruthenizer 535 (N3) dye under 30, 60 and 100 mW cm^{-2} light intensities

Table 7.6: Performance parameters of the DSSC with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 electrolyte and Ruthenizer 535 N3 dye under 30, 60 and 100 mW cm^{-2} light intensities

Light intensity (mW cm^{-2})	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF*	*Efficiency* (%)
100	7.54	0.65	0.51	2.49
60	7.16	0.67	0.46	3.68
30	5.73	0.54	0.40	4.13

7.4.5 Performance of DSSC With Electrolytes Having Double Iodide Salts KI and TBAI

The fabrication and characterization of DSSCs with two types of plasticized PVDF-HFP based polymer electrolytes having different salts such as sodium iodide, NaI and potassium iodide, KI and natural and synthetic dyes have been described in the earlier sections. The DSSCs for both electrolyte systems have been fabricated using the highest conducting electrolytes.

The performance parameters of all DSSCs studied have also been discussed in the earlier sections in this chapter. Of all the DSSCs investigated, the DSSC with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]/1 wt.% I_2 electrolytes and Ruthenizer 535 N3 has shown the best overall performances under one sun illumination and at lower light intensities. It is believed that the efficiency of the DSSC still can be improved further with improved electrolyte systems. One of the suggestions is to mix the KI with another iodide salt having bigger sized cation as reported by Bandara et al., (2013) and

Dissanayake et al., (2012). In their work, they have fabricated DSSCs using binary salt with polyacrylonitrile (PAN) as polymer host and EC/PC as the plasticizer. Bandara and co-workers used lithium iodide as salt with small cation and tetrahexylammonium iodide (Hex_4NI) as larger cation salt while Dissanayake and co-workers used KI (small cation) and tetra propyl ammonium iodide, Pr4NI (larger cation) as binary salt. They have found that an electrolyte system containing mixed cations gives better solar cell performance.

To check this possibility with PVDF-HFP based electrolytes, DSSCs were fabricated with electrolytes having double salts using the highest conducting [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 electrolyte mixed with tetrabutyl ammonium iodide (TBAI). In [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 electrolyte system, the polymer-salt-plasticizer ratio was 40:10:50. For double salt electrolytes, the 10 wt.% of KI was replaced with a mixture of KI and TBAI in the weight ratio of KI:TBAI at 2:8, 4:6, 6:4, 8:2 and 10:0. The DSSCs were fabricated with Ruthenizer dye and these double-salt electrolytes and were characterized. The photocurrent density – voltage graphs for the DSSCs containing double salts for different ratios of KI:TBAI are shown in Fig. 7.8 and the performance parameters obtained are summarized in Table 7.7. It can be seen that the DSSC with electrolytes having KI:TBAI ratio of 4 : 6 and 2 : 8 have efficiencies of 2.53 and 2.69% respectively which are higher than the efficiency of 2.49% obtained for the DSSC with electrolyte having 100% KI. This result is in close agreement with the findings of Bandara and co-workers, (2013).

Fig. 7.10: Photocurrent density – voltage graphs for DSSCs with N3 dye and [40 wt.% (PVDF-HFP)-10wt.% (KI/TBAI)-50 wt.% (EC/PC)]- 1 wt.% I_2 electrolyes having different KI:TBAI weight ratio of 2:8, 4:6, 6:4, 8:2 and 10:0

Table 7.7: Performance parameters of DSSCs with with N3 dye and [40 wt.% (PVDF-HFP)-10wt.% (KI/TBAI)-50 wt.% (EC/PC)]- 1 wt.% I_2 electrolytes having different KI:TBAI weight ratio of 2:8, 4:6, 6:4, 8:2 and 10:0.

KI: TBAI weight ratio	J_{SC} (mA cm^{-2})	V_{OC} (V)	*FF*	Efficiency (%)
100 : 0	7.54	0.65	0.51	2.49
80 : 20	7.11	0.56	0.48	1.91
60 : 40	7.43	0.57	0.50	2.12
40 : 60	7.28	0.74	0.47	2.53
20 : 80	7.98	0.66	0.51	2.69

7.5. Summary

The performance of DSSCs with (PVDF-HFP) based electrolytes with different iodide salts NaI and KI have been presented in this chapter. Highest conducting electrolytes from both systems were chosen for DSSCs fabrication using natural and synthetic dyes. DSSCs with [40 wt.% (PVDF-HFP) - 10 wt.% KI - 50 wt.% (EC/PC)]/ 1 wt.% I_2 electrolytes show better performance than the DSSCs with [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]/ 3 wt.% I_2 electrolytes with both natural and synthetic dyes. On replacing part of the KI electrolyte with TBAI electrolyte the efficiency of the DSSC improves further due to mixed cation effect.