CHAPTER 8

DISCUSSION

Dye-sensitized solar cells (DSSCs), pioneered by Gratzel and co-workers in 1991 still attract growing interest due to their appealing properties such as easy fabrication and low fabrication cost. The long standing record of 11.1% photoconversion efficiency has been reported for DSSC utilizing ruthenium-based dye and the iodide/triiodide redox couple (Anta et al., 2012). Recently it has been reported that DSSC with porphyrin dye and a cobalt-based redox couple in the (0.165 M $[Co^{II}(bpy)_3](B(CN)_4)_2$, 0.045 M $[Co^{III}(bpy)_3](B(CN)_4)_3$ - 0.8 M *tert*-butyl pyridine (TBP)-0.1 M $LiClO_4$) liquid electrolyte exhibited a photocoversion efficiency of 12.3% (Yella et al., 2011). In the present work, DSSCs were fabricated using PVDF-HFP based plasticized polymer electrolyte with synthetic and natural dyes. NaI and KI were chosen as cation and anion providers. Furthermore, the reaction of iodide anion from the salts with the iodine crystals will provide iodide/triiodide (I^-/I_3^-) redox couple for the DSSCs to work. A binary mixture containing equal weights of EC and PC was used as the plasticizer. According to Lee et al (2010) plasticizers can promote ion dissociation with respect to dielectric constant and can increase mobility and promote ion transfer better the lower their viscosity. In this work, plasticizers can be considered to further increase the amorphousness of the electrolytes and to increase ion dissociation from salt and/or ion pair and ion aggregate dissociation.

PVDF-HFP was chosen as polymer host for the fabrication of plasticized polymer electrolyte due to its high dielectric constant of 8.4 (Choi et al., 2006) compared to other polymer hosts, e.g. poly (ethylene oxide) (PEO) with $\varepsilon \sim 5$ (Kumar and Sekhon, 2002) and poly-ε-caprolactone (PCL), $\varepsilon = 2.9$ (Lince et al., 2008). The high dielectric constant of the polymer host is important to facilitate the dissolution of salts (Stephan, 2006) to promote ion dissociation and increase the conductivity of the polymer electrolyte. Another attractive property of PVDF-HFP is the semi-crystalline structure. The highly crystalline PVDF phase acts as a mechanical support (Song et al.,2013) while the amorphous phase helps ionic conduction in the polymer electrolyte (Hwang et al., 2008). The incorporation of a HFP amorphous phase into the VDF blocks reduces the degree of crystallinity. The HFP units provide plasticity to the co-polymer. However, the remaining crystallinity retains sufficient mechanical stability for the PVDF-HFP co-polymer (Abbrent et al., 2001).

FTIR results have proven that the salt have interacted with the host co-polymer and form polymer-salt complexes. This is obvious from the shifting of PVDF-HFP characteristics and vibrational bands. The fluorine atom in PVDF-HFP has lone pair electrons through which electrostatic interaction can occur with the Na^+ and K^+ cations of the salts. The complexation is confirmed by the shifting of C-F_2 bands from CF_2 at 1145 cm^{-1} to 1131 cm^{-1}, CF_3 symmetrical stretching from 1179 cm^{-1} to 1166 cm^{-1}, asymmetric stretching vibrations of CF_2 at 1197 cm^{-1} to 1228 $cm^{-1}$and CF_2 stretching at 1381 cm^{-1} to 1398 cm^{-1}. Nogueira et al., (2001) have reported similar interaction between Na^+ with oxygen lone pair electrons in the ethylene oxide repeating units in their studies on PEO-NaI complexes. Similar behaviors have also been observed in other NaI concentrations.

For the (PVDF-KI) samples, CF_2 stretching at 1381 cm^{-1} merged with another CF_2 stretching mode at 1401 cm^{-1} and peaked at 1397 cm^{-1} after the addition of of KI. C-C skeleton band at 1062 cm^{-1} has become less broad and sharp in the polymer – salt spectrum and had shifted to between 1067 and 1069 cm^{-1} respectively for different KI contents. CF_2 stretching peak at 1145 cm^{-1} has merged with that at 1179 cm^{-1}, becomes broader and less intense, and peaked at 1167 cm^{-1}. The 1197 cm^{-1} peak, which is a CF_3 symmetrical stretching has also broadened and shifted to higher wavenumber of 1227 cm^{-1}. These bands are also observed to shift in the plasticized PVDF-NaI and PVDF-KI samples, proving the formation of polymer-salt complexes and interaction between salt and polymer.

The variation in amorphousness was also indicated from FTIR studies. This was implied from the change in area of the amorphous band which was located at 871 cm^{-1} in the pure PVDF-HFP spectrum. This band shifts to 876 cm^{-1} and 877 cm^{-1} in (PVDF-HFP)-NaI samples, and to between 876 cm^{-1} and 878 cm^{-1} in (PVDF-HFP)-NaI-(EC/PC), to 876 cm^{-1} and 877 cm^{-1} in (PVDF-HFP)-KI samples and peaks at 877 cm^{-1} in all (PVDF-HFP)-KI-(EC/PC) samples. It is to be noted that the area of the band increases with NaI and KI content indicating the increase in amorphous content of the material up to a certain optimum salt concentration after which the area decreased indicating the crystalline peak has begun to increase again. A more quantitative analysis on the amorphousness or d.o.c. of the samples is obtainable from XRD. From XRD studies in chapter 5, it can be inferred that addition of NaI has partially disrupted the d.o.c. of 78.4% obtained for pure PVDF-HFP to 34.9% for the most amorphous sample of 60 wt.% (PVDF-HFP)- 40 wt.% NaI.

XRD of NaI reported by Tripathi et al., (2012) shows sharp and high intense peaks at $2\theta \cong 17^o$, 18^o, 21^o, 22^o, 25^o, 26^o, 27^o, 30^o, 33^o, 35^o, 38^o, 40^o, 42^o and 45^o. Some of these peaks are comparable with XRD JCPDS-00-001-0715 data for NaI peaks at $2\theta=23.772\ ^o$, 27.507^o, 39.312^o, 46.535^o and 48.930^o. From XRD JCPDS-00-004-0471, X-ray diffraction of KI shows sharp and intense peaks at 2θ=27.765°, 35.992°, 42.381°, 44.393° and 51.690°. The absence of such peaks in the X-ray diffractogram of (PVDF-HFP)-NaI and (PVDF-HFP)-KI complexes indicate complete salt dissolution in the polymer matrix (Hema et al., 2009). According to Fonseca et al. (2007), the decrease in d.o.c implied that the interaction has caused disorder in the oriented PVDF crystalline-rich phase and expanded the amorphous phase. XRD studies on plasticized (PVDF-HFP)-NaI-(EC/PC) presented in section 5.2.3 also showed that the d.o.c. further decreased to 6.6% at 20 wt.% EC/PC. The results implied that the (EC/PC) binary plasticizer has increased the amorphousness of the electrolytes. The d.o.c. increased again on further addition of EC/PC i.e. above 20 wt.% EC/PC. The same explanation as for the NaI system can be given for the observation in the KI system. The absence of such peaks in the X-ray diffractogram of (PVDF-HFP)-KI complexes indicate complete salt dissociation in the polymer matrix. The d.o.c. value decreased to the lowest value of 27.9 % for the sample with 20 wt.% KI and increased with further KI concentration.

The addition of (EC/PC) plasticizer further improved the amorphousness of the KI based electrolyte. With the addition of EC/PC binary plasticizer the d.o.c. value decreased to the lowest d.o.c. of 13.6% in the electrolyte having 40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC). It may be inferred that KI can easily disrupt the crystalline phase of PVDF-HFP compared to NaI since a lesser amount of KI (1.51×10^{-3} mole) can reduce the d.o.c. to a lower level compared to NaI (4.45×10^{-3} mole). This could be an explanation for the higher conductivity of the highest conducting sample in the (PVDF-HFP)-KI system compared to highest conducting (PVDF-HFP)-NaI electrolyte.

On addition of EC/PC plasticizer, the d.o.c. of the NaI containing polymer electrolyte was reduced to 6.6% making it more amorphous than the KI containing plasticized electrolyte. This implies that the amorphousness was increased with the help of plasticizer. For the case of electrolyte containing KI, (EC/PC) was only able to reduce the crystallinity up to 13.6% which indicates that the reduction in crystallinity has almost saturated with addition of KI. The variation in amorphousness was also confirmed by FTIR studies. The addition of plasticizer is also known to improve the electrical conductivity of polymer electrolyte by increasing the amorphous content and dissociating ion aggregates present in polymer electrolytes (Sekhar et al., 2012). It can be inferred that the addition of plasticizer has increased the amorphous phase of the electrolyte and increased number density and mobility of charge carriers up to a certain concentration.

From the diffractogram of (PVDF-HFP)-NaI having 10 wt.% NaI shown in Fig. 5.3(a), the peaks at $2\theta = 20.1^o$ and 38.3^o have shifted to $2\theta = 20.28^o$ and 38.99^o. Further addition of salt until 50 wt.% NaI has also shown the shifting of these two peaks. For the plasticized (PVDF-HFP)-NaI system in Fig. 5.5(a)-(e) the peaks at $2\theta = 20.1^o$ and 38.3^o have shifted to $2\theta = 20.27^o$ and 40.12^o for 60 wt.% EC/PC concentration. From Fig. 5.5(a), it can be seen that for 10wt.% EC/PC concentration, the crystalline peak at $2\theta = 18.2^o$ has merged with that at $2\theta = 20.1^o$ and shifted to $2\theta = 20.27^o$. The crystalline peak at $2\theta = 26.5^o$ has disappeared and the peak at $2\theta = 38.3^o$ has shifted to 40.12^o.

For all samples in (PVDF-HFP)-KI system shown in Fig. 5.7 and (PVDF-HFP)-KI-(EC/PC) system shown in Fig. 5.9, the $2\theta = 20.1^o$ and 38.3^o peaks have also shifted to new positions between 39^o and 42^o. The changes in peak position implied the interaction between polymer, salt and plasticizer. Similar observations are noted for the (PVDF-HFP)-KI and (PVDF-HFP)-KI-(EC/PC) samples. These results support inference from FTIR spectroscopy that the cation of the salt interact with the polymer and specifically indicates that the K^+ cation can weakly interact with the F atom in PVDF-HFP.

The variations of d.o.c. and area of the amorphous band in PVDF-HFP co-polymer as a function of salt and plasticizer concentrations are expected to affect conductivity variations with the two variables. This has been confirmed in the EIS chapter. The same trend is observed in all other samples where the d.o.c. increases again after an optimum salt and plasticizer concentration. This is also accompanied by a decrease in conductivity. The increase in d.o.c. and decrease in conductivity above the optimum salt concentration in all samples are accompanied by the decrease in n, μ and D from calculations performed using the ECM approach. The amorphous band also showed a decrease in area for NaI salt concentration of 50 wt.% for the (PVDF-HFP)-NaI system. For the plasticized (PVDF-HFP)-NaI system the amorphous band showed a decrease in area when more than 20 wt.% EC/PC has been added. The variation in area of the amorphous band was also observed in the (PVDF-HFP)-KI and (PVDF-HFP)-KI-(EC/PC) systems where the area decrease when more than 20 wt.% KI and 50 wt.% (EC/PC) plasticizer have been added.

The increase in conductivity for all the samples studied has been attributed to the increase in amorphousness and the decrease in conductivity is due to the increase in crystallinity. The highest conducting sample in the (PVDF-HFP)-NaI system has the composition of 60 wt.% (PVDF-HFP) - 40 wt.% NaI. Its conductivity at room temperature (RT) is 5.21×10^{-5} S cm^{-1}. This result is comparable with the value reported by Nogueira et al. (2001) who obtained a RT conductivity of 1.5×10^{-5} S cm^{-1} in poly(ethylene oxide-co-epichlorohydrin)-NaI system.The highest conducting sample in the plasticized (PVDF-HFP) - NaI system with a conductivity of 1.53×10^{-4} S cm^{-1} has composition of 48 wt.% (PVDF-HFP) - 32 wt.% NaI -20 wt.% (EC/PC). Kim et al. (2006) obtained the highest RT conductivity of 0.23×10^{-4} S cm^{-1} for plasticized (PVDF-HFP)-NaI-PC-I_2 at weight ratio (1:3:1.07:0.07) which is lower but still comparable than the conductivity obtained in this work. This is probably due to the addition of I_2. The highest conducting sample for (PVDF-HFP)-KI system has the composition of 80 wt.% (PVDF-HFP) - 20 wt.% KI with a conductivity of 1.24×10^{-4} S cm^{-1}. This conductivity value is comparable with the value reported by Kalaignan et al. (2006) who obtained a RT conductivity of 0.84×10^{-4} S cm^{-1} for the electrolyte having (PEO: KI: I_2) at (12:1:0.1) mole ratio. The plasticized (PVDF-HFP)–KI system has the highest RT conductivity is 1.10×10^{-3} S cm^{-1}. The composition for the plasticized system is 40 wt.% (PVDF-HFP) - 50 wt.% NaI -10 wt.% (EC/PC).

Since there are many factors affecting conductivity, the increase and decrease in conductivity, the changes cannot be attributed to d.o.c. or amorphousness alone. Conductivity is the product of number density of ionic (cationic and anionic) charge carriers (n), electron charge for a monovalent ion (e) and ionic mobility (μ). Hence, the increase in conductivity with increase in salt concentration up to 40 wt.% NaI in the (PVDF-HFP) - NaI system, for example, can be attributed to the increase in number density of charge carriers resulting from the dissociation of Na^+ and I^- and the ionic mobility. The conductivity decreases on further addition (> 40 wt.%) of salt can also be attributed to the decrease in number density and mobility of the charge carriers due to formation ion aggregates. Some workers have attributed the decrease in conductivity to the increase in viscosity of the electrolyte (Kufian et al., 2012).

The decrease in number density at high salt concentration can be attributed to ion association (Forsyth et al., 1997; Choi and Bae, 2003) which is more effective at high salt concentrations. Ion association can lead to neutral ion pairs and ion aggregates which do not contribute to conductivity.

Since we have mentioned that the variation of conductivity, σ can be attributed to the variation in number density, n and mobility, μ of the charge carriers it will be useful if n and μ can be quantified. The number density and mobility of charge carriers can be evaluated using the broadband dielectric response (BDR) or the Bandara-Mellander (B-M) approach. The BDR or B-M approach is thoroughly explained in the literature (Bandara and Mellander, 2011). We will briefly discuss the B-M approach and in doing so discuss the equivalent circuit model (ECM) approach. Derivation of the equations used to calculate n, μ and D via the ECM approach are shown in Appendix A.

The B-M approach considers that a polymer electrolyte sandwiched between two blocking electrodes for impedance measurement can be represented by an equivalent circuit which consists of a parallel resistor and capacitor combination and connected to two capacitors each on both sides of the parallel combination as shown in Fig. 8.1.

Fig.8.1: Equivalent circuit of a polymer electrolyte sandwiched between two blocking electrodes.

Here C_e is the capacitance due to the electrical double layer (EDL) and C is the geometrical capacitance of the polymer electrolyte. C_e is much larger than C for a sample with thickness ~1 mm. $C_e = \varepsilon\varepsilon_o A/\lambda$ and $C = \varepsilon\varepsilon_o A/2d$, ε_o is the vacuum permittivity, ε is the dielectric permittivity of the polymer electrolyte, λ is the mean thickness of the EDL, A is the electrolyte/electrode contact area and $2d$ is thickness of the sample. The real and imaginary parts of the complex impedance of the above circuit is given by the equations:

$$Z' = \frac{R}{1+(\omega RC)^2} \qquad (8.1)$$

and

$$Z'' = \frac{\omega CR^2}{1+(\omega RC)^2} + \frac{2}{\omega C_e} \qquad (8.2)$$

Hence the dissipative loss equation can be written as

$$\tan\phi = \frac{\omega RC_o}{2+\omega^2 R^2 C\left(C_e + 2C\right)} \qquad (8.3)$$

Dissipative loss normally increases with frequency, reaches a maximum and then decreases as frequency continues to increase. At the peak the differential of equation (8.3) with respect to ω is zero. This occurs when

$$\omega = \frac{1}{RC}\sqrt{\frac{2C}{C_e}} \qquad (8.4)$$

The peak value of the dissipative lost curve will then be given by

$$\left(\tan\phi\right)_m = \frac{\sqrt{\delta}}{2} \qquad (8.5)$$

Hence, in terms of δ and τ_2,

$$\tan\phi = \frac{2\pi f\left(\sqrt{\delta}\right)\tau_2}{1+\left(2\pi f\tau_2\right)^2} \tag{8.6}$$

The mobility (μ), number density (n), and diffusion coefficient (D) of mobile ions can be calculated using equations proposed in the B-M approach (Bandara and Mellander, 2011):

$$\mu = \frac{ed^2}{kT(\delta)^2\tau_2} \tag{8.7}$$

$$n = \frac{\sigma kT\tau_2\delta^2}{d^2e^2} \tag{8.8}$$

$$D = \frac{d^2}{\delta^2\tau_2} \tag{8.9}$$

where k is the Boltzmann constant, T is the absolute temperature and d is half sample thickness. It can be observed from equations (8.7) to (8.9), that in order to calculate μ, n and D, the values of δ and τ_2 are extremely important. This is the significant contribution of the B-M approach in evaluating the chosen set of parameters to study the conducting behavior of the polymer electrolyte. Besides, the ratio between half sample thicknesses to the EDL thickness can be considered normalizing the results with respect to different cell geometries.

In the case of the ECM approach introduced in this thesis, analysis begins with the use of the actual Nyquist plot of the samples. This is more realistic compared to the B-M approach as from equation (8.1) and (8.2) it can be realized that the Nyquist plot assumed in the B-M approach should be a perfect semicircle with a vertical line at the low frequency side. In other words, it may be implied that the B-M approach assumes that the samples are Debye type and the dipoles align themselves at the same time or the dipoles have a single relaxation time. This is usually not the case as in most samples, the dipoles have a distribution of relaxation times. In the ECM approach, the equivalent circuit that represents the Nyquist plot and the derivation of its impedance follows the description given by Linfard (1981). By determining and substituting the bulk resistance and all the necessary parameters required in the impedance equation of the equivalent circuit, the capacitance values can be obtained by trial and error so that the calculated *Z"* and *Z'* values can be satisfactorily matched to the experimental *Z"* and *Z'* data. The mean percentage difference between calculated and experimental Z' and Z" are presented in Appendix B. The lowest mean percentage difference (M.P.D.) observed between the calculated and experimental *Z'* is 1.46% and the highest M.P.D. is 18.00%. For *Z"*, the lowest M.P.D. is 2.10% and the highest M.P.D. is 11.00%. The percentage difference is the difference between the calculated impedance value and the experimental impedance value divided by experimental impedance value multiply by 100% for a particular frequency. The M.P.D. is the average of percentage difference for all frequencies in the range studied. The low M.P.D. values obtained indicate that the fittings done on the Nyquist plots are reasonably accurate. The capacitance of the EDL layer which can be obtained from the spike is of utmost importance in the ECM approach. This is because its value is required to obtain the three parameters *n*, μ and *D* via the equations:

$$n = \frac{\sigma k_b T \tau_2}{\left(e k_2 \varepsilon_r \varepsilon_o A\right)^2} \tag{8.10}$$

$$\mu = \frac{e\left(k_2 \varepsilon_r \varepsilon_o A\right)^2}{k_b T \tau_2} \tag{8.11}$$

$$D = \frac{\left(k_2 \varepsilon_r \varepsilon_o A\right)^2}{\tau_2} \qquad (8.12)$$

The behavior of the conductivity can be justified from the results obtained for the charge carrier number density *n*, ion mobility μ and diffusion coefficient *D* variation with NaI in Fig. 6.8. where the plot for all the three parameters has shown the same trend with the plot of conductivity variation with salt concentration. The maximum value of *n,* μ and *D* occurred at 40 wt.% NaI and decreased after further addition of NaI. However, for μ and *D* it can be seen that only small increments occurred from 20 to 30 wt.% NaI. This may imply that the addition of NaI after 20wt.% increased the charge carrier number density but did not influence the mobility and diffusivity of the ion.

According to Cha et al. (2004) the addition of plasticizer (EC/PC) enhances the conductivity due to oxygen atoms in the carbonyl group of EC and PC that may act as transit sites for the mobile ions. This may not be the case in the present study. In this work the number density of mobile ions, *n* for (PVDF-HFP)-NaI system is between 0.6×10^{21} and 3.0×10^{21} cm^{-3}. In the plasticized system *n* varies between 1.0×10^{22} to 4.2×10^{22} cm^{-3}. In this work n for (PVDF-HFP) –KI system n is between 3.9×10^{19} to 374.8×10^{19} cm^{-3} and in the plasticized system the value of n lies between 2.5×10^{21} and 55×10^{21} cm^{-3}. It can therefore be inferred that the plasticizer has increased the number density of mobile ions through the process of ion dissociation.

For the highest conducting sample of 60 wt.% (PVDF-HFP) -40 wt.% NaI, *n* is 2.96 x 10^{21} cm^{-3}. On addition of 20 wt.% EC/PC *n* increase ~14 times its initial value. μ decrease by a factor of ~0.8 of the initial value (for the unplasticized system). However, the diffusion coefficient, *D* decrease by ~30% of the value in the unplasticized state.This shows that in the highest conducting plasticized (PVDF-HFP)-NaI the enhancement in conductivity is due to increase in *n* and *D*. In the 80 wt. % (PVDF-HFP)-20 wt.% KI *n* is 3.75×10^{21} cm^{-3}. On addition of 50 wt.% EC/PC to this composition *n* increases ~15 times its value in the unplasticized state. μ has increase ~5% of its plasticized value and *D* increase by ~6% upon plasticization. Hence for the highest conducting (PVDF-HFP)-KI) electrolyte the increase in conductivity upon plasticization is attributed to *n*, μ and *D*. It may therefore be inferred that in the KI containing electrolyte the mechanism of conductivity is different from that of the NaI containing electrolyte.

The characterization of DSSCs was reported in Chapter 7. The characterization of the DSSC was based on the photocurrent density (*J*) *vs* voltage (*V*) characteristics from which the performance parameters: short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), fill factor *(FF)* and photo-conversion efficiency (η) or PCE were obtained.

J_{sc}, V_{oc}, *FF* and *PCE* for DSSCs fabricated with the highest conducting plasticized electrolytes i.e. [47 wt.% (PVDF-HFP)-31 wt.% NaI- 19 wt.% (EC/PC)]- 3 wt.% I_2 and [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]- 1 wt.% I_2 were obtained. The DSSCs have configuration FTO/TiO_2/dye/electrolyte/Pt/FTO and the dyes were anthocyanin, chlorophyll, a mixture of anthocyanin and chlorophyll (at 1 : 1 volume ratio) and Ruthenizer 535 N3. These DSSCs were illuminated with 1 sun (100 mW cm^{-2}) light.

(i) With anthocyanin dye sensitizer, the DSSC with [47 wt.% (PVDF-HFP)-31 wt.% NaI-19 wt.% (EC/PC)]-3 wt.% I_2 electrolyte has *Jsc, Voc, FF* and *PCE* of **2.09 mA cm^{-2}, 0.47 V, 0.57 and 0.56%** respectively while the DSSC with [40 wt.% (PVDF-HFP)-10 wt.% KI-50 wt.% (EC/PC)]-1 wt.% I_2 has *Jsc, Voc, FF* and *PCE* of **2.22 mA cm^{-2}, 0.63V, 0.46 and 0.64%** respectively. DSSC of KI based electrolyte has shown higher *PCE*, J_{SC} and V_{OC} but lower *FF* than DSSC with NaI based electrolyte. The higher performance of KI based DSSC might be due to the higher conductivity of KI based electrolyte. Although conductivity is contributed by cations and anions of the salt in the polymer electrolyte, only the anionic contribution is important for good solar cell performance. According to Wang et al (2009), to pursue high conversion efficiency of the DSSCs, it is necessary and pivotal to enhance ionic conductivity of the electrolyte. Enhancement in ionic conductivity, results in an increase of the I^-/I_3^- mobility and in the increase of the open-circuit voltage, short-circuit current density and energy conversion efficiency of the DSSCs. These are also reflected from our results. The low *FF* in the KI based DSSCs implies that the recombination of electrons at the TiO_2/dye interface is significant (Li et al., 2006). The higher V_{OC} in the KI based DSSC implies the larger difference between the Fermi level of TiO_2 and the redox potential compared to the difference in Fermi level and the redox potential in the NaI based DSSC.

(ii) With chlorophyll dye sensitizer, DSSC with [47 wt.% (PVDF-HFP)-31 wt.% NaI-19 wt.% (EC/PC)]-3 wt.% I_2 electrolyte has *Jsc, Voc, FF* and *PCE* of **1.91 mA cm^{-2}, 0.48V, 0.56 and 0.51% respectively** while DSSC with [40 wt.% (PVDF-HFP)-10 wt.% KI-50 wt.% (EC/PC)]-1 wt.% I_2 has *Jsc, Voc, FF* and *PCE* of **1.83 mA cm^{-2}, 0.62V, 0.45 and 0.51%** respectively. DSSC of NaI based electrolyte has shown higher J_{SC} and *FF* but lower *Voc* compared to the DSSC with KI based electrolyte. Both DSSCs have the same *PEC*. The higher efficiency obtained from the DSSC with anthocyanin dye can be attributed to the absorbance peak at 532 nm which is comparable to the sun's absorbance peak of 535 nm (Yuliarto et al., 2010).

(iii) With anthocyanin-chlorophyll dye mixture sensitizer, DSSC with [47 wt.% (PVDF-HFP)-31 wt.% NaI-19 wt.% (EC/PC)]-3 wt.% I_2 electrolyte has *Jsc, Voc, FF* and *PCE* of **2.63 mA cm^{-2}, 0.47V, 0.58 and 0.72%** respectively while DSSC with [40 wt.% (PVDF-HFP)-10 wt.% KI- 50 wt.% (EC/PC)]-1 wt.% I_2 has *Jsc, Voc, FF* and *PCE* of **2.62 mA cm^{-2}, 0.67 V, 0.47 and 0.83%** respectively. Although DSSC with KI based electrolyte has shown the higher PEC of 0.83% compared to 0.72% for DSSC with NaI based electrolyte, DSSC of NaI based electrolyte has shown higher J_{SC} and *FF* but lower V_{OC} and PEC than DSSC of KI based electrolyte. The DSSC using the mixed dye exhibits the better performance compared to DSSC using individual dye for both NaI and KI based electrolytes. In all three cases it may be inferred that the use of KI in the electrolyte has widened the difference between the Fermi level of TiO_2 and the redox potential more than the NaI based electrolyte.

It can be seen that DSSC with anthocyanin exhibits higher efficiency than DSSC with chlorophyll in both NaI and KI based electrolyte. This is due to the better interaction between the carbonyl and hydroxyl groups of anthocyanin molecule in the dye extract and the surface of TiO_2 (Hao et al., 2006). The above results also showed that DSSC using the dye mixture as sensitizers with both KI and NaI based electrolytes exhibit higher performance than both the DSSCs utilizing the individual natural dye. This might due to higher range of light absorption by the dye mixture as shown in the UV-vis absorption spectroscopy result.

(iv) With N3 dye mixture sensitizer, DSSC with [47 wt.% (PVDF-HFP)-31 wt.% NaI-19 wt.% (EC/PC)]-3 wt.% I_2 electrolyte has *Jsc, Voc, FF* and *PCE* of **6.40 mA cm^{-2}, 0.58 V, 0.48 and 1.78%** respectively while DSSC with [40 wt.% (PVDF-HFP)-10 wt.% KI-50 wt.% (EC/PC)]-1 wt.% I_2 has *Jsc, Voc, FF* and *PCE* of **7.54 mA cm^{-2}, 0.65V, 0.51 and 2.49%** respectively. DSSC of KI based electrolyte has shown higher *PCE,* J_{SC} and V_{OC} and *FF* than DSSC of NaI based electrolyte. Again it may be implied that the difference between the Fermi level and redox potential in the KI based DSSC is larger compared to that for the NaI based DSSC. The better efficiency maybe be attributed to the peak of the N3 dye which is the same as that of the sun (Yuliarto et al., 2010). Hence the possibility of absorbing more photons.

For the DSSCs that was further tested under different light intensities, the *J-V* curves obtained are shown in Fig. 7.3, 7.5, 7.7 and 7.9 for NaI based DSSC with mixed dyes, NaI based DSSC with N3 dye, KI based DSSC with mixed dyes and KI based DSSC with N3 dye respectively. The results show that for all the four DSSC systems, the lower 30 mW cm^{-2} light intensity gives the best photo-conversion efficiency. Under high light intensity the number of excited electrons due to the higher number of oxidized and excited dye molecules are 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 higher light intensity. For example, in NaI based DSSC with mixed-dye system, the current density produced under 100 mW cm^{-2} light intensity is 2.63 mA cm^{-2}. It is expected that at 30 mW cm^{-2} light intensity the current density is only 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 is also higher being to 0.61 while the open circuit voltage remains same. The larger current density and fill factor under 30 mW cm^{-2} light intensity led to the highest observed efficiency of 1.85%.

In the attempt of further improve the efficiency of the DSSC, double salt electrolytes were used. The amount of salt was still maintained at 10 wt.% but the ratio between the two salts were varied. For double-salt based DSSCs, DSSC having [40 wt.% (PVDF-HFP)-10 wt.% (KI+TBAI) -50 wt.% (EC/PC)]-1 wt.% I_2 at (KI:TBAI) = 2:8 weight ratio exhibits the highest performance with J_{sc}, V_{oc}, *FF* and *PCE* of 7.98 mA cm^{-2}, 0.66V, 0.51 and 2.69% compared to DSSC with 100% KI which exhibits J_{sc}, V_{oc}, *FF* and *PCE* of 7.54 mA cm^{-2}, 0.65V, 0.51 and 2.49%. The best performance for the DSSC utilizing of (PVDF-HFP)-(KI+TBAI)-(EC/PC) system was obtained with 20 wt.% KI + 80 wt.% TBAI salt composition. This is in close agreement with the results of Dissanayake et al, (2012) where the DSSC with the highest efficiency had double salt composition of 16.6% (w/w) KI + 83.4% (w/w) Pr_4NI salt in the PAN-(KI+ Pr_4NI)-EC/PC electrolyte. The mixed-cation iodide salts (KI+TBAI) in the electrolyte give better efficiency than the single-cation iodide salt (KI) system. This is because the TBA^+ cation is bulky and therefore is less mobile. Hence the addition of TBAI helps to increase the iodide ion contribution to the conductivity which is more important than the cation contribution for good DSSC performance.