CHAPTER 8

DISCUSSION

Research and development for dye-sensitized solar cell (DSSC) began in 1991 when Grätzel and co-workers reported an efficiency of 7 % in nanocrystalline TiO_2 DSSC. Since then, DSSC has been the subject of particular interest due to its potential as an alternative to conventional silicon-based solar cells. Advantages of DSSC include [Nogueira *et al.*, 2004]:

- Low energy production cost.
- Low cost of raw materials.
- High efficiency.

In DSSC, TiO_2/dye is used as photoelectrode instead of silicon semiconductor. The dye plays an important role in electron injection into the TiO_2 conduction band. Natural dye is chosen in this work due to its unique properties such as [Calogero and Di Marco, 2008]:

- Cheap.
- Non-toxic.
- Environmentally friendly.
- Biodegradable.
- Simple to prepare.

The injected electron passes through the external circuit and arrives at the platinum (Pt) counter electrode. The function of counter electrode is to transfer the electron back to the electrolyte and catalyze the reaction of triiodide reduction [Lee *et al.*, 2010c]. To ensure fast reduction of triiodide, the ITO conducting glass was coated with Pt and used as counter electrode in this study. Platinum is said to help in reducing the overpotential for the triiodide–iodide reduction and thereby minimizing the energy loss [Yoon *et al.*, 2008]. From literature, the selection of platinum as catalytic material for counter electrode in DSSC is attributed to its special characteristics [Saito *et al.*, 2004; Koo *et al.*, 2006; Yoon *et al.*, 2008]:

- High catalytic activity for I_3^- reduction.
- High surface area to increase the catalytic activity.
- High electrical conductivity.
- Light-reflecting properties.
- Good stability at the platinum-electrolyte interface.

In addition, Pt is reported to exhibit excellent resistance in corrosion against iodine which serves as a component in the redox couple [Denaro *et al.*, 2009]. This makes Pt well-suited to iodide/triiodide redox mediator as mentioned before in Chapter 2. Apart from that, it is also beneficial to employ solid electrolyte together with Pt coated counter electrode in order to minimize the corrosion risk [Bönnemann, *et al.,* 2007]. Hence, solid polymer electrolyte (SPE) containing redox mediator is used in this study instead of liquid electrolyte since they are also easy to handle and is not prone to leakage problem. Other criteria of SPE to be employed in electrochemical devices include [Suthanthiraraj *et al.*, 2009]:

- High ionic conductivity.
- High specific energy.
- Light weight.
- Wide electrochemical stability windows.
- Easy to process.

Besides redox mediator, solid polymer electrolyte basically consists of polymer and salt. In this work, chitosan which is a biopolymer was used as the polymer host and its properties have been discussed in Chapter 2. The characteristics of ammonium iodide (NH_4I) are [Damle *et al*., 2009]:

- Cation with radius of 1.4 Å.
- Large soft anion.
- Low lattice energy of 637 kJ mol^{-1}.
- Electrochemically stable.

As mentioned in Chapter 2, ionic conductivity of the polymer electrolytes depends on anion size and lattice energy of the salt used. NH_4I has ammonium cation with radius 1.4 Å and large I^- anion with radius 2.11 Å [Roobottom *et al*., 1999]. The difference in cation and anion sizes decreases the electrostatic attraction between them making easier separation. This is favorable for the polymer-salt complexation. Salts with lower lattice energy will require less energy in order to break the ionic bond to release the ions into the polymer-salt system. Thus, conductivity of the polymer electrolytes will be enhanced with the use of large anion and low lattice energy of the salt.

The interaction between chitosan and NH_4I salt has been investigated via FTIR spectroscopy. FTIR results presented in Chapter 4 show that complexation between chitosan as polymer host and cation of the salt has taken place at the amine, hydroxyl and carboxamide sites of chitosan. This is proven from the shifting of these bands to lower wavenumbers observed in the FTIR spectra as depicted in Figures 4.3 and 4.4. According to literature, the shifting of amine and carboxamide bands towards lower wavenumbers in FTIR spectrum indicates that complexation has occurred between chitosan and the cation [Muzarelli *et al*., 1977]. The coordination of the NH_4^+ cation with the oxygen atom from hydroxyl group, nitrogen atom from amine group and oxygen atom from carboxamide group has been illustrated in Figure 4.5. The results of FTIR correlates well with XRD patterns as displayed in Figures 5.1 and 5.2. In the XRD diffractograms of chitosan-NH_4I electrolyte systems, the shifting of peak at $2\theta = 19.7°$ which belongs to pure chitosan film indicates that the complexation of salt and polymer has occurred. XRD patterns in Figure 5.2 show the absence of chitosan crystalline peaks at $2\theta = 11.5°$, 13.2°, 18.8°and 22.7° with the incorporation of salt which explains the more amorphous state of the chitosan-NH_4I electrolytes. Sample designated as Ch9 that contains 55 wt.% chitosan-45 wt.% NH_4I is the most amorphous. The amorphous hump in the vicinity between 5° and 35° (Figure 5.1) was deconvoluted using Gaussian fitting as shown in Figure 5.2 and the observed peak positions and FWHM have been summarized in Table 5.1. It is noted that sample Ch9 which is the most amorphous exhibits the largest FWHM value. Praveen *et al.* (2010) explained that the large FWHM value obtained in lithium bromide incorporated into poly(ethylene glycol), PEG based solid polymer electrolyte is attributed to the increase in amorphous region in the polymer upon addition of salt. In Chapter 6, EIS studies show that ionic conductivity is increased with the addition of salt up to 45 wt.% as can be seen in Table 6.1. Highest conductivity of 3.73×10^{-7} S cm^{-1} was obtained in 55 wt.% chitosan-45 wt.% NH_4I (Ch9) electrolyte which can be predicted from XRD results. From Figure 6.6, the linear relationship exhibited by the points suggests that the chitosan-NH_4I electrolytes obey Arrhenius rule and the ionic conductivity is thermally assisted. The fact that dielectric constant, ε' increases with temperature (as shown in Figure 6.11) further confirm that ionic conduction of chitosan-NH_4I electrolytes is a thermally activated process. Dielectric constant is related to the number of mobile ions present in the electrolyte [Mohamad and Arof, 2007; Ramya *et al.*, 2008a]. High dielectric constant means that there is an increase in the number density of mobile charge carriers in the electrolyte due to ion dissociation which leads to increment in conductivity. From Figures 6.9 and 6.11, it can be observed that the dielectric constant shows frequency dependence at low frequencies. In the low frequency region, the occurrence of electrode polarization and space charge effect are responsible for the high dielectric constant [Basak *et al*., 2005]. Also, it can be seen in Figures 6.9 and 6.11 that the dielectric constant increases as temperature increases. The high values of ε_r at higher temperatures maybe attributed to the increase in mobility of the ions as temperature increases.

The effect of blending chitosan with other polymers has also been investigated in this work. Some advantages of polymer blending technique are [Subramania *et al*., 2006; Sivakumar *et al*., 2006]:

- Simple to prepare.
- Easy to control properties of the blended polymer electrolyte by simply varying its composition.
- High ionic conductivity.
- Good flexibility.
- Good mechanical strength.
- Blending increases amorphousness of the material.

Poly (vinyl alcohol), PVA was used to blend with chitosan. Besides the properties of PVA mentioned in Chapter 2 which include biocompatibility and good mechanical strength, PVA also exhibits other characteristics such as [Subramania *et al*., 2006; Kufian *et al*., 2007; Awadhia and Agrawal, 2007; Rajendran and Bama, 2010]:

- Good solvent holding capability.
- Good adhesive property.
- Good film-forming ability.

- Good abrasion resistance.
- Easy to blend with other polymers.
- Wide temperature window for application.

Apart from good miscibility and compatibility discussed in Chapter 2, it has also been reported that chitosan-PVA blend films exhibit a higher flexibility than films produced from single polymers [Lewandowska, 2009]. Furthermore, PVA is a semicrystalline polymer containing hydroxyl groups which contribute to hydrogen bonding and thereby help in the formation of polymer blends [Rajendran *et al.*, 2004].

The shift of hydroxyl band to lower wavenumber upon the blending of chitosan with PVA in the (chitosan-PVA) spectrum as shown in Figure 4.7 indicates hydrogen bonding between hydroxyl group in PVA and hydroxyl group in chitosan. Similar observation is reported by Zhang and co-workers [Zhang *et al.*, 2007]. It is said that hydrogen bonding results in good compatibility between chitosan and PVA [Sadoval *et al.*, 2005]. For systems containing chitosan blended with PVA and doped with NH_4I, shifts in the amine, hydroxyl, carboxamide and carbonyl bands are observed and thus imply that interactions have occurred between chitosan, PVA and NH_4I. Shifting in these four bands have also been reported by Kadir *et al.* (2011) in the (chitosan-PVA)-NH_4NO_3 system. It is observed from the chitosan-NH_4I spectrum that evidence of polymer-salt complexation can be observed from the shifting of the amine and carboxamide bands. Blending chitosan with PVA provides more complexation sites at e.g. the carbonyl C=O group as evident from the FTIR spectrum. Hence, there will be more sites at which exchange of ions can take place and thus implying the possibility of increment in conductivity. The XRD patterns in Figure 5.4 reveals the amorphous nature of samples designated as CV2 (44 wt.% chitosan-11 wt.% PVA), CV4 (33 wt.%

chitosan-22 wt.% PVA) and CV5 (27.5 wt.% chitosan-27.5 wt.% PVA) upon blending chitosan and PVA. Of course, the other 45 wt % is the salt content. No peaks corresponding to pure NH_4I appeared in the diffractogram of the complexes which indicate the complete dissolution of the salt in the polymer blend matrix of these samples. However, with further increase in PVA content, peaks belong to pure NH_4I reappeared in the diffractogram of samples designated as CV6 (22 wt.% chitosan-33 wt.% PVA) and CV8 (11 wt.% chitosan-44 wt.% PVA) as depicted in Figure 5.4. This indicates that the salt has recrystallized out of the membranes which may lead to conductivity decrease. The ionic conductivity presented in Table 6.2 shows the increase in conductivity for samples designated as CV1, CV2, CV3, CV4 and CV5, which could be attributed to additional complexation sites upon blending with PVA and also the amorphous nature as revealed from XRD patterns. Referring to Table 5.2, sample designated as CV5 exhibits the lowest FWHM value which implies that sample CV5 is less amorphous compared to CV2 and CV4. On the contrary, CV5 is the highest conducting sample with conductivity of 1.77×10^{-6} S cm^{-1}. Gopal *et al*. (1996) and Low *et al*. (2010) have also observed that the highest conducting electrolyte exhibits the lowest FWHM value in the diffractograms of poly(vinyl butyral)-lithium iodide and MG49-$LiBF_4$-TiO_2 electrolyte systems, respectively. Hence, it can be inferred that lowest FWHM value obtained in a sample does not necessarily result in lowest conductivity. Beyond 27.5 wt.% PVA (CV5) content, decrement in conductivity can be observed in the samples designated as CV6, CV7 and CV8 as tabulated in Table 6.2. This could be due to ion aggregates and recrystallization of salt present in the electrolyte which in turn reduces the number density of charge carriers and thereby decrease the conductivity [Yahya *et al*., 2006]. It is evident that recrystallization of salt occur in the samples CV6 and CV8 from XRD diffractograms in Figure 5.4.

In a comparative study, it can be observed that the dielectric constant of the highest conducting electrolyte (CV5) in Figure 6.18 is higher than that of the highest conducting chitosan-NH_4I electrolyte (Ch9) as can be seen from Figure 6.11. It is known that increment in conductivity is usually attributed to the increase in number of mobile ions and/or increase in mobility of ions present in the electrolyte [Aziz *et al*., 2010; Buraidah *et al*., 2010b]. However, in this case, the salt was fixed at 0.409 g for all electrolyte blends. Thus, this indicates that only the increase in mobility of charge carriers contribute to the conductivity enhancement in chitosan-PVA-NH_4I systems. The mobility of the ions is related to the viscosity and the nature of the electrolyte i.e. whether it is amorphous or crystalline. Other than that, the mobility of ions is also dependent on the film's flexibility [Zhang *et al*., 2005] and thus influences the ionic conductivity of the electrolyte. According to literature, it is said that the flexibility of the polymer host is related to glass transition temperature, T_g of the electrolyte [Bandara *et al*., 2010, Tominaga *et al*., 2005]. Increase in the flexibility of the polymer chain is observed with the decrease in T_g and thereby leads to increment in conductivity [Xi *et al*., 2005, Wang *et al*., 2005b, Pitawala *et al*., 2007]. As mentioned before in Chapter 2, T_g of pure chitosan is around 480 K [Lewandowska, 2009] and PVA is around 363 K [Agrawal and Awadhia; 2004]. Hence, blending of chitosan with PVA improves the flexibility of the chitosan electrolyte and decreases the value of T_g. Decrement in T_g is observed when incorporating PVA (T_g = 355 K) into chitosan electrolyte (T_g = 480 K) which has been reported by Lewandowska (2009). This indicates that the increase in ionic conductivity of chitosan-NH_4I electrolyte by blending with PVA can be attributed to the increase in flexibility of the electrolyte which in turn leads to increase in mobility of the charge carriers.

Poly (ethylene oxide), PEO is another polymer employed as co-host in this work. Bhide and Hariharan (2006) stated that PEO has interesting properties as listed below:

- Presence of polar group with strong electron donor power to form complexation with cation of salt.
- Low hindrance to bond rotations enabling segmental motion to occur easily.
- A suitable distance between coordinating sites where multiple intrapolymer ion bonds can take place.
- Capable to dissolve high concentrations of a wide variety of salts.
- Excellent electrochemical stability.

As mentioned earlier, blending of chitosan with PVA improves flexibility of the film. Therefore, it can be deduced that increase in flexibility will also be observed upon blending chitosan with PEO since T_g of PEO (~209 K) is much lower than that of PVA (355 K). Also, it has been reported that films containing chitosan blended with PEO offer additional functionality compared to the pure polymer films [Zivanovic *et al.*, 2007] apart from the aforementioned compatibility and miscibility.

From the FTIR results as studied in Chapter 4, no interaction can be observed between chitosan and PEO at the C-O-C stretching of PEO as can be seen from the unchanged vibrational band at 1107 cm^{-1} in the chitosan-PEO spectrum (Figure 4.12). There has been shifting at the carboxamide, amine (Figure 4.13) and hydroxyl bands of chitosan (Figure 4.14) which indicates interaction has taken place between chitosan and acetic acid solvent or hydrogen bonding between CH group of PEO with carboxamide, amine and hydroxyl group of chitosan. With the addition of NH_4I into the polymer hosts, the cation of the ammonium salt has formed coordinate bond with the oxygen atoms from the ether oxygen group of PEO and from carboxamide band of chitosan, respectively as well as with nitrogen atom from the amine band and oxygen atom from the hydroxyl band of chitosan resulting in the complexation. This can be seen from shifting of C-O-C band for PEO and bands of carboxamide, amine and hydroxyl for chitosan in the spectrum of (chitosan-PEO)-NH_4I electrolytes (Figures 4.15, 4.16 and 4.18).

It is interesting to note that the blending of 30 wt.% chitosan with 70 wt.% PEO reduces the intensity of peak ascribed to CH_2 wagging of pure PEO film as shown in Figure 4.17 (a) and (b). Upon the addition of 45 wt.% salt, further decrease in intensity and broadening of the peak is observed as depicted in Figure 4.17 (c). Sim and co-authors (2010) observed the same effect, decrease in intensity and broadening of peak in polyacrylate-PEO-$LiClO_4$ electrolyte. They attribute these behaviors to increase in amorphousness upon blending and addition of salt. Suthanthiraraj *et al*. (2009) and Hema *et al*. (2009) also agreed that broadening of band indicates decrease in crystallinity. Chitosan is quite amorphous whereas PEO is a semicrystalline polymer. Hence, a blend of both is expected to reduce the crystallinity in PEO. XRD diffractograms in Figure 5.7 shows evidence of the increase in amorphousness in (chitosan-PEO)-NH_4I electrolytes with only a very small peak observed at 2θ = ~13°. Baskaran *et al.* (2006) have studied a polymer electrolyte blend based on PVAc–PMMA. Their XRD patterns showed that the semicrystalline nature of PMMA is disturbed by the addition of amorphous PVAc. Similar observations have been reported by Ramesh *et al.* (2010) in a PMMA–PVC blend system. The presence of NH_4I salt in the blend can also help to reduce the crystallinity part of the electrolytes [Sreekanth *et al*., 1999; Ramya *et al*., 2006]. According to Sunderrajan *et al.* (2001), there is no change in the crystallinity part of PEO when interaction occurs between ether oxygen of PEO and salts with a small cationic radius such as Li^+ (0.60 Å) and Na^+ (0.95 Å). On the contrary, the crystallinity part of PEO is completely disrupted by the incorporation of salt with a large cationic radius of Ag^+ (1.26 Å). This means that Li^+ and Na^+ cations can fit easily into the PEO crystal lattice but Ag^+ cation cannot. Thus, it can be deduced that the loss in crystallinity of (chitosan-PEO)-NH_4I electrolytes is due to the incorporation of salt into the polymer electrolytes since NH_4^+ has larger cationic radius compared to that of Ag^+. Table 6.3 shows that sample designated as CEO7 with the composition (16.5 wt.% chitosan-38.5 wt.% PEO)-45 wt.% NH_4I is the highest conducting sample. Above 38.5 wt.% of PEO content, the films are difficult to form and exhibit poor mechanical strength [Li *et al*., 2010]. Similar to (chitosan-PVA)-NH_4I systems, the increment in conductivity of (chitosan-PEO)-NH_4I electrolytes is attributed to the increase in mobility of ions for a fixed salt content.

Besides polymer blending technique, ionic liquid has also been incorporated into chitosan-NH_4I electrolyte as an attempt to increase the ionic conductivity and also enhance the DSSC's performance. 1-butyl-3-methylimidazolium iodide (BMII) has the following properties [Kim *et al*., 2006; Bai *et al*., 2008; Gorlov and Kloo, 2008; Shukla *et al*., 2010]:

- Liquid state at room temperature.
- Pale yellow color.
- Melting point -72 °C or equivalent to 201 K.
- Viscosity of 400 mPa.s at 298 K.
- High conductivity of ~10^{-4} S cm^{-1} at 298 K.
- High ion conducting capability.
- Negligible vapor pressure.
- Large electrochemical windows.

Bai *et al*. (2008) reported that ionic liquid 1-butyl-3-methylimidazolium iodide exhibits higher conductivity at ambient temperature compared to that of 1-propyl-3-methylimidazolium iodide (PMII). Iodide anion based IL is chosen because it can provide extra charge carriers since iodine which serves as redox mediator is employed in DSSC of the present work.

Figure 4.20 reveals some insights of the interaction in chitosan-NH_4I-IL electrolyte where it can be deduced that the complexation occur between BMII and amine bands of chitosan only since no significant shift is observed at the wavenumber of carboxamide band. However, a new peak can be seen at wavenumber 1570 cm^{-1} with addition of 30 wt.% IL as displayed in Figure 4.20 (d). Intensity of this peak increases as IL content reaches 50 wt.% (Figure 4.20 (f)). This peak belongs to imidazole-ν (ring) of IL [Ranga Rao *et al*., 2009]. Complexation occurs between BMII and hydroxyl functional group of chitosan with shifting of hydroxyl band to lower wavenumber in the spectrum of 27.5 wt.% chitosan-22.5 wt.% NH_4I-50 wt.% IL electrolyte (Figure 4.21 (f)). XRD patterns in Figure 5.9 depict the amorphousness of the IL added chitosan-NH_4I electrolyte. It has been reported that the decrease in crystallinity is observed upon the addition of IL in the PEO-KI(+I_2) electrolyte [Singh *et al*., 2007]. IL is a non-volatile plasticizer. Electrolyte consisting of 50 wt.% IL is the highest conducting sample with ionic conductivity of 3.43×10^{-5} S cm^{-1} as shown in Figure 6.29 and Table 6.4. In this case, the increment in conductivity is attributed to the increase in number density of charge carriers. Singh and co-workers [2006; 2008b] reported that the incorporation of IL into solid polymer electrolyte increases the number of mobile ions and thereby leads to conductivity enhancement. The ionic liquid in this work consists of $[BMIm]^+$ and $[I]^-$. Hence, it can be inferred that the ionic conductivity in the chitosan-NH_4I-IL electrolyte is the combination of ionic mobility resulting from the dissociation of salt ($[NH_4]^+$ and $[I]^-$)

and ions from IL ($[BMIm]^+$ and $[I]^-$). In another work of Singh and co-authors [2009b], they examined the surface morphology on 40 wt.% IL added PEO-based electrolyte via atomic force microscopy (AFM) and found that the electrolyte added with IL exhibits smooth surface with decreased roughness which enables better contact at electrolyte-electrode interface and thus the performance of solar cell is improved.

The conductivity measurements will be insufficient without information on possible electronic and ionic transport numbers. Hence, transference numbers were evaluated in this study using Wagner's polarization technique. From Chapter 6, the ionic and electronic transference numbers are t_{ion} = 0.85 and t_{e} = 0.15 obtained for Ch9 electrolyte, t_{ion} = 0.91 and t_{e} = 0.09 for CV5 electrolyte, t_{ion} = 0.93 and t_{e} = 0.07 for CEO7 electrolyte and for CIL5 electrolyte, t_{ion} = 0.93 and t_{e} = 0.07. The high ionic transference numbers obtained in all electrolytes indicates that the charge transport is mainly due to ions. In other words, this implies that the electronic contribution to the total conduction process is negligible. Mohan *et al.* (2005) obtained the ionic transference number, t_{ion} for different PEO-$NaBiF_4$ electrolytes to be in the range of 0.91 to 0.94.

In Chapter 7, characterization of anthocyanin dyes extracted from black rice via UV-Vis studies showed a distinguished peak at λ = 535 nm as can be seen in Figure 7.1. According to Hao *et al.* (2006) and Yuliarto *et al.* (2010b), the absorbance peak of anthocyanin extracted from black rice is about 560 nm and 530 nm, respectively. This may be due to the different black rice origin and different methods of preparation. The shift of the absorption band of anthocyanin/TiO_2 towards lower energy can be attributed to complexation that has taken place between anthocyanin and metal ions, Ti^{4+} [Calogero and Marco, 2008]. Similar behavior has also been observed by Sirimanne and

Soga (2003). The hydroxyl group in anthocyanin molecule can be bound to the surface of TiO_2 film as proposed by Patrocínio and co-authors (2009). Chemical adsorption of the anthocyanin is the result of condensation of alcoholic-bound protons with the hydroxyl groups on the surface of nanostructured TiO_2. Adsorption of anthocyanin to the TiO_2 surface stabilizes the excited state of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the anthocyanin pigment, thus affect the energy gap and shift towards the lower energy or higher wavelength of the absorption spectrum [Polo *et al.*, 2004; Calogero and Di Marco, 2008]. From the figure, the absorption band of black rice anthocyanin is observed at wavelength below 920 nm and this meets the requirement of dye-sensitizer agent as mentioned before in Chapter 2.

Table 7.1 shows that DSSC with the highest conducting electrolyte with the composition of 27.5 wt. % chitosan-22.5 wt. % NH_4I-50 wt. % BMII exhibits highest short-circuit current density. The effect of electrolyte conductivity on the performance of DSSC has also been investigated by Rahman *et al.* (2004). They observed an increase in V_{oc} and J_{sc} of the ITO/TiO_2/PVC-$LiClO_4$/graphite solar cell with the increase in electrolyte conductivity. In this work, efficiency has been shown to increase with electrolyte conductivity.

The effects of anthocyanin pH on short-circuit current density and efficiency was also studied. Referring to Table 7.2, the DSSC utilizing anthocyanin black rice solution at pH 1 exhibits the highest short-circuit current density and efficiency which could be attributed to its ability of absorbing light compared to other solutions (pH = 2, 3 and 4) as evident in the absorbance spectra in Figure 7.2. The original color of anthocyanin extracted from black rice is brownish and the color turns to red upon acid treatment.

Anthocyanin usually occurs in quinonoidal form (purple color). Upon acid treatment, the quinonoidal form of anthocyanin is changed to flavylium form (red color) [Cherepy *et al.,* 1997]. Anthocyanin in flavylium form is more stable than that in quinonoidal form. The quinonoidal form of anthocyanin is likely to undergo changes and easily turn colorless [Wongcharee *et al.,* 2007]. From literature [Fernando and Senadeera, 2008], it is understood that the flavylium form which contains oxonium ion can assist in the absorption of photons in the visible light region. When the pH of anthocyanin decreases, the anthocyanin becomes deeper red in color which implies that flavylium form is dominant. This explains why the highest absorption intensity for anthocyanin black rice solution is observed at pH 1 (see Figure 7.2). Wongcharee *et al.* (2007) also reported that DSSC with TiO_2 photoelectrode soaked in anthocyanin solution extracted from roselle (*Hibiscus sabdariffa L.*) at pH 1 performed better compared to that of other pH values at 0.5, 2.0, 3.0 and 3.2. Hence, it can be concluded that upon more light absorption by the dye, more electrons can be driven into the conduction band of TiO_2 and thus increase J_{sc} of the cell.

The use of Pt as counter electrode for black rice anthocyanin DSSC exhibits higher J_{sc} and efficiency compared to DSSC utilizing ITO counter electrode (Tables 7.2 and 7.3). Better performance of DSSC with Pt counter electrode implies that platinum is more suitable to serve as counter electrode in solar cell application. According to literature, platinum is chosen for counter electrode due to its ability to help in the reduction of triiodide, I_3^- as previously mentioned in Chapter 2. From Table 7.3, J_{sc} of 0.29 mA cm^{-2} exhibited by DSSC with Pt counter electrode and blocking layer coated on ITO substrate before depositing TiO_2 is about four times lower compared to black rice anthocyanin DSSC reported by Hao *et al.* (2006) and Yuliarto *et al.* (2010b) with J_{sc} of

1.142 mA cm^{-2} and 1.287 mA cm^{-2}, respectively. This is attributable to liquid electrolyte used in their DSSC which has higher ionic conductivity.

For blueberry anthocyanin extract, the absorption peak in the spectra of anthocyanin and that of anthocyanin adsorbed onto TiO_2 electrode shifted to lower wavelength as observed in Figure 7.5. This confirmed the reaction between the TiO_2 and blueberry anthocyanin extract [Tennakone *et al*., 1997]. According to literature [Hao *et al*., 2006], the shifting trend is dependent on three factors i.e. solvent, arrangement of dye on the electrode's surface and the characteristic of the electrode to attract electron. Similar to black rice anthocyanin, solution of blueberry anthocyanin shows better absorbance at pH 1 as evident from Figure 7.6. It is worthy to mention that J_{sc} of 1.178 mA cm^{-2} obtained from blueberry anthocyanin DSSC in this work employing the electrolyte composition of 27.5 wt. % chitosan-22.5 wt. % NH_4I-50 wt. % BMII in gel form is comparable to blueberry DSSC employing liquid electrolyte fabricated by Patrocínio *et al*. (2009) which exhibits J_{sc} of 1.0 mA cm^{-2} under the same illumination of 100 mW cm^{-2}.

The absorption spectra in Figure 7.12 further confirmed that the optimum absorbance occurs when the anthocyanin dye solution is at pH 1 regardless of whether the anthocyanin was extracted from black rice, blueberry or red cabbage. Red cabbage DSSC using 27.5 wt. % chitosan-22.5 wt. % NH_4I-50 wt. % BMII electrolyte in gel form exhibits J_{sc} of 1.421 mA cm^{-2} which is higher than DSSC employing red cabbage dye and liquid electrolyte with J_{sc} of 0.68 mA cm^{-2} under illumination of 50 mW cm^{-2} [Furukawa *et al*., 2009]. Solar cells sensitized by red cabbage anthocyanin exhibit the best performance compared to anthocyanin extracts from other sources as presented in Chapter 7. This indicates that anthocyanin from red cabbage is able to inject electrons more efficiently into TiO_2 conduction band than the anthocyanin extracted from both blueberry and black rice. Dai and Rabani (2002b) pointed out that different absorption bands of various dyes have their own competency in electron injection into TiO_2 electrode. There are six common anthocyanin structures in blueberry (Cyanidin, Delphinidin, Malvidin, Pelargonidin, Peonidin and Petunidin) compared to two in black rice (Cyanidin and Peonidin) as shown in chapter 2. The diversity of the existing structure of anthocyanin in blueberry compared to that in black rice allows more sites for complexation to occur between TiO_2 and anthocyanin. Hence, blueberry anthocyanin DSSC showed better performance compared to DSSC using anthocyanin from black rice. The molecular structure of cyanidin-3-(sinapoyl)diglucoside-5-glucoside in red cabbage as shown in Figure 7.13, provides two binding sites with Ti^{4+} ions compared to cyanidin found in black rice (Figure 7.3) and blueberry (Figure 7.7). Therefore, it can be inferred that the strong electronic coupling for charge injection occurs in cyanidin-3-(sinapoyl)diglucoside-5-glucoside of red cabbage compared to cyanidin-3-glucose of black rice and cyanidin of blueberry which leads to better performance of DSSCs. The efficiency of DSSC is increased almost 4 times higher using N3 dye compared to the red cabbage dye. As shown in Figure 2.3, N3 dye is able to provides 4 binding sites with Ti^{4+} ions compared to two for cyaniding found in red cabbage hence gives the better performance of DSSC. The absorption peak of N3 (Figure 7.18) is also higher compared to red cabbage which means that N3 dye has better ability to absorb light. With incorporating 80 wt.% IL, the conductivity of the electrolyte increase to 3.04×10^{-4} S cm^{-1} thus improve the performance of DSSC with efficiency of 1.2 %. From this work, it can be understood that to get a better efficiency of DSSC, the conductivity should be improved.