CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

A dye-sensitized solar cell (DSSC) is an electrochemical device which consists of a transparent conducting oxide (TCO) glass, semiconductor as photoelectrode, dye-sensitizer agent, electrolyte containing redox mediator and counter electrode. Figure 2.1 illustrates the structure of DSSC. Each of these components plays an important role in making a DSSC with good performance. The operating principle of DSSC, function of every component, the requirements and properties of the selected materials will be discussed in this chapter.

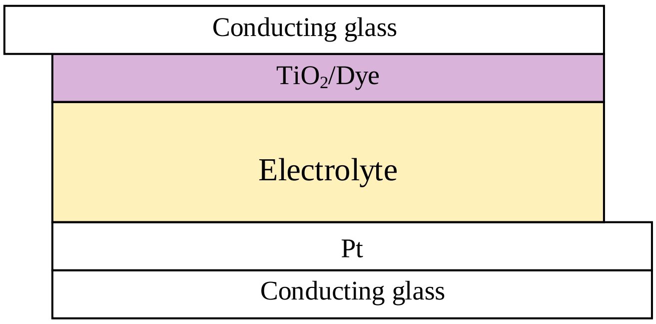


Figure 2.1: Schematic diagram of the DSSC structure

2.2 WORKING PRINCIPLE OF DSSC

In this study, the semiconductor photoanode is TiO_2, the dye is anthocyanin extracted from blueberry fruit and red cabbage, the polymer electrolyte consists of a polymer or polymer blend doped with NH_4I, the mediator is the I^-/I_3^- redox couple and the counter electrode is platinum (Pt).

On illumination, the anthocyanin dye (D) will be excited and injects electrons into the conduction band.

$$hv + D \rightarrow D^* \tag{2.1}$$

where hv is the incoming photon and D^* is the excited anthocyanin dye. The excited dye will inject electron(s) into the conduction band of TiO_2 according to the equation below:

$$D^* + TiO_2 \rightarrow D^+ + e_{cb}^-(TiO_2) \tag{2.2}$$

and the excited dye will be oxidized. The oxidized dye molecules will be reduced by an iodide ion which in turn becomes a triiodide ion following the equation below:

$$2D^+ + 3I^- \rightarrow I_3^- + 2D \tag{2.3}$$

The electron in the conduction band of TiO_2 flows through the external circuit while at the counter electrode

$$I_3^- + 2e^- \rightarrow 3I^- \tag{2.4}$$

The iodide ion is restored and the difference between the Fermi level of the electron in the semiconductor photoanode and the redox potential of the electrolyte gives the voltage generated under illumination.

According to Calogero and Di Marco (2008), in order to generate high current, the reactions from equation (2.3) and equation (2.4) must effectively compete with the recombination reactions

$$D^{+} + e_{cb}^{-}\left(TiO_2\right) \rightarrow D + TiO_2 \qquad (2.5)$$

and

$$I_3^{-} + 2e_{cb}^{-}\left(TiO_2\right) \rightarrow 3I^{-} + TiO_2 \qquad (2.6)$$

The schematic diagram of a DSSC structure and its working principle is also illustrated in Figure 2.2.

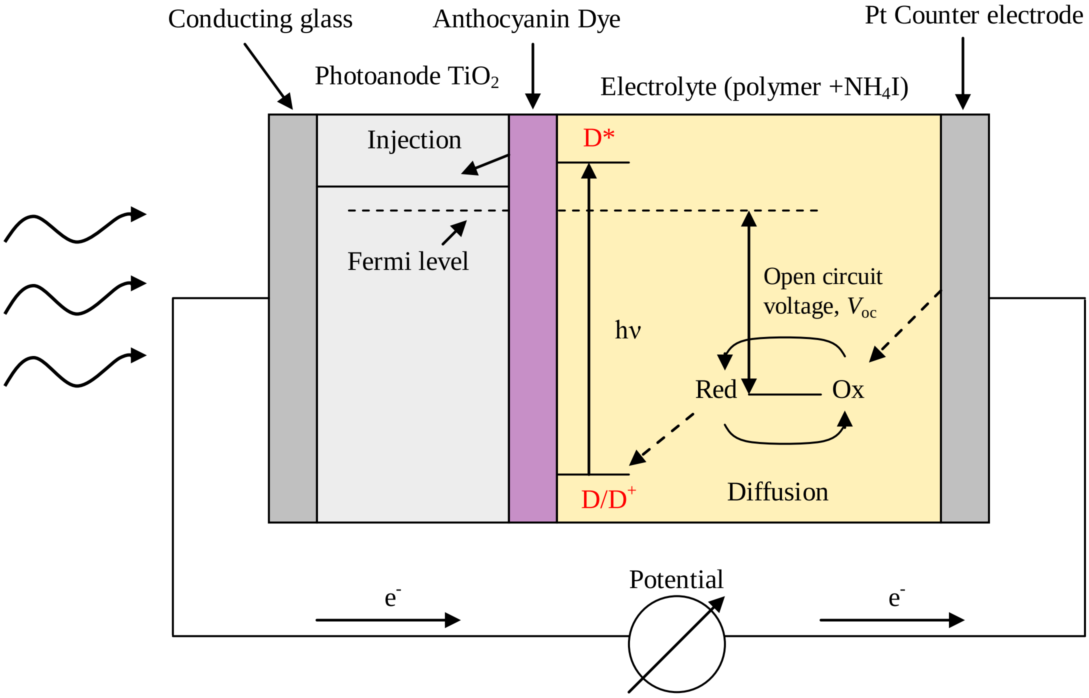


Figure 2.2: Schematic diagram of the DSSC structure and operating principle [adapted from Grätzel, 2003]

2.3 INDIUM-TIN-OXIDE (ITO) SUBSTRATE

Transparent conducting oxide (TCO) glass substrate is used to deposit the TiO_2 photoanode and the Pt counter electrode, repectively. Fluorine-doped tin oxide (FTO) and indium-tin-oxide (ITO) glasses are two substrates commonly used in DSSC. Other applications include flat panel displays [Lee *et al.*, 1997], electroluminescent devices [Meng *et al.*, 1987] and sensors [Luff *et al.*, 1997]. In DSSC, TCO glass substrate works both as a current collector and as a support for the electrodes [Ngamsinlapasathian *et al.*, 2006]. The transparent conducting substrates must have low sheet resistance, highly transparent, high transmittance and high heat stability to ensure good cell performance [Hara and Arakawa, 2003]. In the present study, ITO glass substrate is used.

2.4 TITANIUM DIOXIDE (TiO_2) PHOTOELECTRODE

Titanium dioxide (TiO_2) is the most popular choice of photoanode in DSSC application since it has a large energy bandgap, E_g of ~3 eV and can be efficiently sensitized by a dye [Vlachopoulos *et al.*, 1988]. TiO_2 is cheap, non-toxic, inert, biocompatible, has strong oxidizing ability, long-term stability and good optical and electrical properties [Karruppuchamy *et al.*, 2006; Hoffmann *et al.*, 1995].

TiO_2 has been used as electrodes in photoelectrochemical (PEC) devices for hydrogen production [Hamnett, 1982], as catalysts for photocleavage of water [Linsebigler, 1995], in photocatalytic decomposition of water [Kiwi and Gratzel, 1986] and as electrodes in solar cells [Matsumoto *et al.*, 1996; Deb, 2005; Flores *et al.*, 2007].

TiO_2 can exists in two crystalline structures i.e. rutile and anatase. Rutile TiO_2 has energy bandgap, E_g of 3.0 eV while the E_g of anatase TiO_2 is 3.2 eV [Kalyanasundaram and Grätzel, 1998]. Although rutile TiO_2 structure is more stable, anatase structure of TiO_2 is more suitable for DSSC application [Deb, 2005; Singh *et al.*, 2008b]. The use of anatase nanocrystalline TiO_2 as photoelectrode in DSSC results in higher short-circuit current compared to that of rutile nanocrystalline TiO_2 [Chen *et al.,* 2008].

The use of nanosized TiO_2 particles with higher surface area will enable TiO_2 to absorb the dye efficiently [Kalyanasundaram and Grätzel, 1998]. Nanocrystalline TiO_2 electrodes can be prepared using the sol-gel method [Li *et al.,* 1999], spray pyrolysis [Okuya *et al.,* 2002], sputter deposition [Gómez *et al.,* 2000] and doctor-blade method [Singh *et al.*, 2008b]. In the present work, nanocrystalline TiO_2 electrodes were applied on indium tin-oxide (ITO) glass by the doctor-blade method using commercially available TiO_2 paste. The doctor-blade method is a simple and inexpensive technique to prepare a crack free TiO_2 film with controllable thickness [Chen *et al.,* 2007; Singh *et al.*, 2008b].

2.5 UNDERLAYER

Although nanocrystalline TiO_2 is able to absorb a large amount of dye efficiently and thereby leads to better DSSC performance, it has one drawback i.e. the large surface area will increase recombination of electrons in the TiO_2 conduction band and electrolyte [Kong *et al.,* 2007]. Electron recombination will cause the occurrence of dark current at the electrode-electrolyte interface and deteriorate the performance of DSSC.

To overcome this, an extra layer has been coated on the ITO substrate before depositing TiO_2. The underlayer, Ti(IV)bis(ethyl acetoacetato)-diisopropoxide serves as blocking layer and minimizes electron recombination losses to the oxidized electrolyte [Kim *et al.*, 2005; Singh *et al.*, 2008b]. In this work, the blocking layer used is diisopropoxytitanium bis(acetylacetonate).

2.6 DYE

The function of dye is to absorb light, inject electrons into the semiconductor conduction band and then accept electrons from the redox mediator in the electrolyte. The cycle continues. An ideal dye-sensitized agent should possess unique characteristics as listed below [Grätzel, 2003; Longo and De Paoli, 2003]:

- Absorb light below minimum wavelength of 920 nm.
- Good attachment at the surface of photoelectrode to ensure fast electron transfer.
- Good interfacial properties and high stability to enable good absorption to TiO_2.
- Easily accepting replacement electron from electrolyte.
- Excited state of dye must be slightly above the conduction band of TiO_2 whereas its ground state level is slightly below the redox potential of electrolyte.
- Lifetime of the dye must be consistent with device life.
- Stable enough to sustain at least 10^8 redox turnovers under illumination corresponding to about 20 years of exposure to natural light.

In general, dyes are divided into two groups i.e. synthetic and natural dyes.

2.6.1 Synthetic dyes

Ruthenium(II) polypyridyl complexes are most commonly used as sensitizer in DSSC [Kalyanasundaram and Grätzel, 1998; Nazeeruddin *et al.*, 2004; Klein *et al.*, 2005; Wang *et al.*, 2005a] due to its high stability, excellent redox properties, broad absorption spectrum in the visible light region [Kong *et al.*, 2007; Longo and De Paoli, 2003]. *cis*-Ru(II) bis(2,2'-bipyridyl-4,4'-dicarboxylate)-$(NCS)_2$ or also known as red dye or N3 is one of the popular photosensitizer and its structure is displayed in Figure 2.3. Osmium polypyridyl complexes are other examples of effective photosensitizers [Kuciauskas *et al.*, 2001; Argazzi *et al.*, 2004].

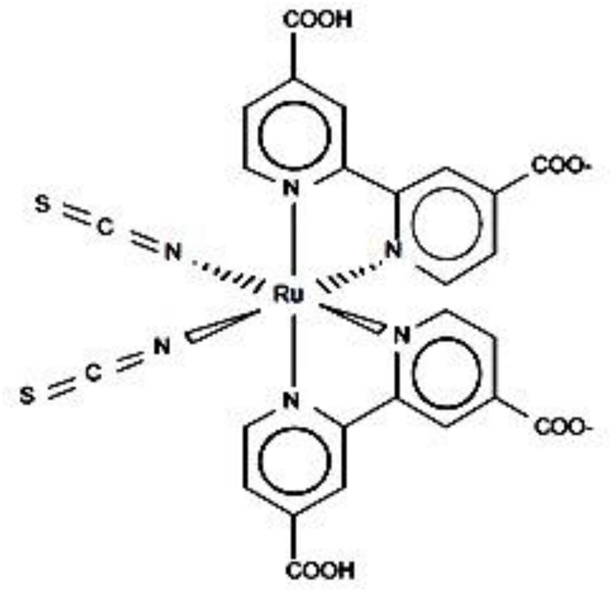


Figure 2.3: N3 ruthenium complex structure [Grätzel, 2003]

Table 2.1 shows some examples of DSSCs employing various polypyridyl ruthenium(II) complexes as sensitizers which exhibit high efficiency compared to DSSCs with other photosensitizers. Other sensitizers used are copper(II) co-proporphyrin-I [Alibabaei *et al.*, 2010], phthalocyanines [Giribabu *et al.*, 2007], coumarin [Hara *et al.*, 2003] and indoline [Chen *et al.*, 2010] to name a few. Although the ruthenium (II) polypyridyl complexes are good candidate as sensitizers, it has several disadvantages including high cost, long term unavailability, complex process of synthesis and is hazardous to the environment due to the heavy metal it contains [Amao and Komori, 2004; Wongcharee *et al.*, 2007]. Hence, this does not meet the requirement of this study i.e. to fabricate a low cost, environmentally friendly and reasonably good performance DSSC with natural dye. Further work, beyond the scope of this thesis, can improve the DSSC performance. To date, Singh *et al.* (2010a) have reported an efficiency of 1% from chitosan-based DSSC using synthetic dye.

Table 2.1: The photovoltaic performance of DSSC using different polypyridyl ruthenium(II) complexes as sensitizers

Dyes	DSSC Performance	References
cis-Ru(II) bis(2,2'-bipyridyl-4,4'-dicarboxylate)-$(NCS)_2$ (also known as red dye or N3)	J_{sc} 18.2 mA cm^{-2} V_{oc} 720 mV η 10 %	Nazeeruddin *et al.*, 1993
cis-diisothiocyanato-bis(2,2’-bipyridyl-4,4’-dicarboxylato)-Ru(II) bis(tetrabutylammonium) (also known as N719)	J_{sc} 17.73 mA cm^{-2} V_{oc} 846 mV η 11.2 %	Nazeeruddin *et al.*, 2005
Ru(II) tri(cyanato)-2,2’,2”-terpyridyl-4,4’,4”-tricarboxylate) (also known as black dye or N749)	J_{sc} 20.53 mA cm^{-2} V_{oc} 720 mV η 10.4 %	Nazeeruddin *et al.*, 2001
cis-diisothiocyanato-(2,2’-bipyridyl-4,4’-dicarboxylic acid)-(2,2’-bipyridyl-4,4’-dinonyl) Ru(II) (also known as Z907)	J_{sc} 12.8 mA cm^{-2} V_{oc} 707 mV η 6.6 %	Wang *et al.*, 2003
Ru(4,4-dicarboxylicacid-2,2′-bipyridine)(4,4′-bis(2-(4-(1,4,7,10-tetraoxyundecyl) phenyl)ethenyl)-2,2′-bipyridine)-$(NCS)_2$ (also known as K60)	J_{sc} 16.85 mA cm^{-2} V_{oc} 730 mV η 8.44 %	Kuang *et al.*, 2007a

Table 2.1 continued …

Ru(2,2'–bipyridine-4,4'-dicarboxylic acid)(4,4'-bis(2-(4-*tert*-butyloxyphenyl) ethenyl)-2,2'–bipyridine)-(NCS)$_2$ (also known as K77)	J_{sc} 17.5 mA cm^{-2} V_{oc} 737 mV η 9.0 %	Kuang *et al.,* 2007b
cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)-Ru(II) bis(tetrabutylammonium) (also known as N719)	J_{sc} 16.12 mA cm^{-2} V_{oc} 732 mV η 6.5 %	Mathew *et al.*, 2011
cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato)-Ru(II) bis(tetrabutylammonium) (also known as N719)	J_{sc} 18.20 mA cm^{-2} V_{oc} 638 mV η 7.1 %	Bandara *et al.*, 2011

2.6.2 Natural dyes

Natural dyes can be a very economical alternative to the synthetic dyes as sensitizing agents for DSSC since they are cheap and readily available. They are also non-toxic, environmentally friendly, biodegradable, can be extracted using simple methods and used without any purification [Fernando and Senadeera, 2008]. Natural dye colorants from chlorophyll, betalain, carotenoid and anthocyanin have been employed as photosensitizers in DSSC. These can be found in flowers, fruits and vegetables.

2.6.2.1 Chlorophyll

It is well known that chlorophyll plays an important role in photosynthesis process. However, there are very scanty reports on the utilization of chlorophyll as sensitizer in DSSC. This maybe attributed to the alkyl group in the structure of chlorophyll that makes it unable to bind with the TiO$_2$ photoelectrode [Hao *et al.,* 2006]. The structure of chlorophyll is illustrated in Figure 2.4. The poor absorption of chlorophyll dye on the TiO_2 surface is due to the weak interaction between the ester keto and carbonyl functional groups with TiO_2 [Calogero *et al.,* 2009]. Nonetheless, dye obtained from chlorophyll extracted from shiso leaf [Kumara *et al.,* 2006], spinach leaves [Calogero *et al.,* 2009], kelp [Hao *et al.,* 2006], Chinar leaf (*Platanus orientalis L.*) [Liu *et al*., 2008], papaya leaf [Yuliarto *et al.,* 2010a] and pomegranate leaf [Chang and Lo, 2010] have been studied as possible photosensitizers for DSSC.

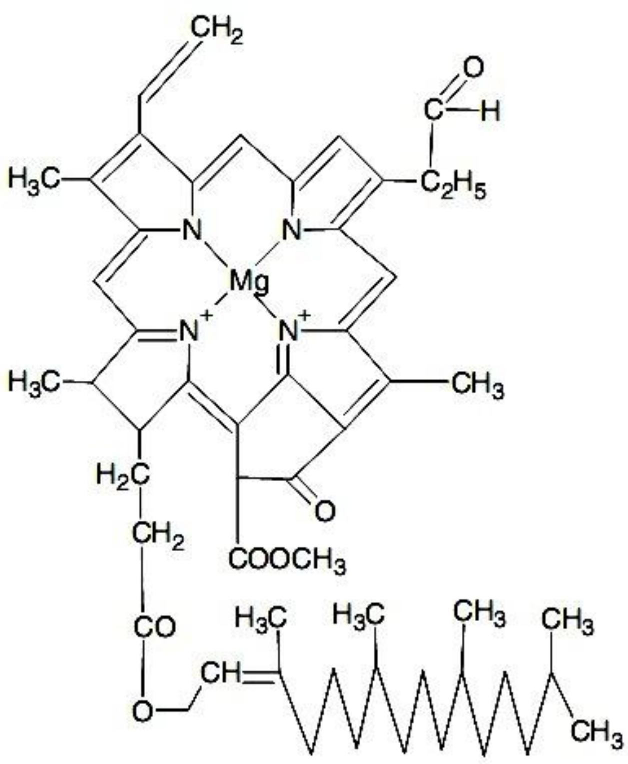


Figure 2.4: Chlorophyll structure [Hao *et al.,* 2006]

2.6.2.2 Carotenoids

Carotenoids are natural fat soluble pigments responsible for the orange-red color of many living things [Pfander, 1992; Bartley and Scolnik, 1995]. Carotenoid helps in photosynthesis [Bartley and Scolnik, 1995], provides the main dietary source of vitamin A [Ong and Tee, 1992] and serves as antioxidants [Rao and Agarwal, 1999; Mayne, 2003]. Figure 2.5 depicts the structure of β,β-carotene which is an example of carotenoid. The presence of the carboxylic groups in the structure of carotenoid is favorable for attachment at the semiconductor photoelectrode surface and electron injection into the semiconductor conduction band [Ruiz-Anchondo *et al.,* 2010]. Some sources of carotenoids that have been used in DSSC applications include capsicum [Hao *et al.,* 2006], erythrina variegata flower [Hao *et al.,* 2006], gardenia fruit [Yamazaki *et al.,* 2007] and the pericarp of achiote seeds [Gómez-Ortíz *et al.,* 2010].

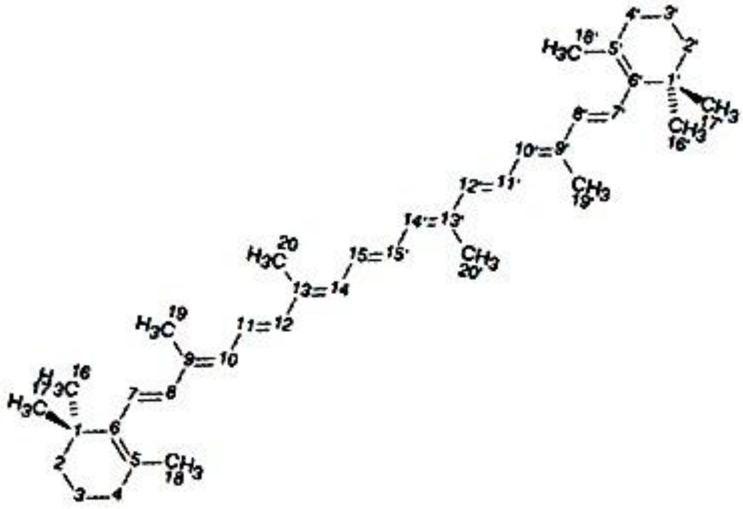
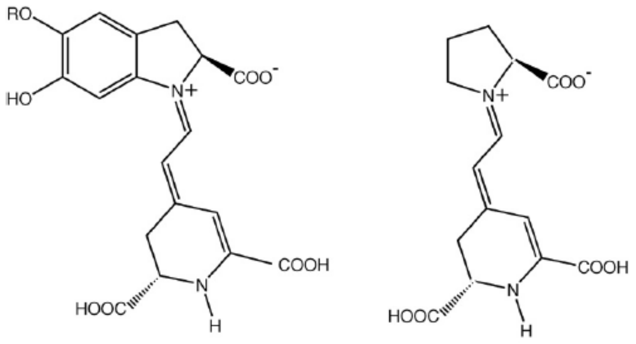


Figure 2.5: β,β-carotene structure [Hao *et al.,* 2006]

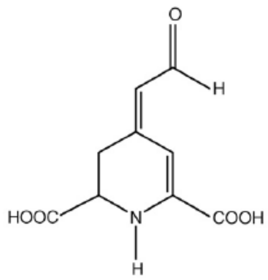
2.6.2.3 Betalains

Betalain pigments can be found in *Caryophyllales* plants [Han *et al.,* 2009]. Almost every part of the plant i.e. flowers, petals, fruits, leaves, stems and roots contain betalain [Calogero *et al.,* 2009]. Betalains have good light absorption properties, carboxyl functional group to attach to the TiO_2 semiconductor electrode, high molar extinction coefficients in the visible region of the electromagnetic spectrum and pH dependent redox properties which makes them potential photosensitizers [Zhang *et al.*, 2008a; Calogero *et al.*, 2010]. Betalains which are soluble in water consist of red-violet betacyanins and the yellow betaxanthins [Han *et al.*, 2009]. Some structures of betalain dyes are illustrated in Figure 2.6. Betalains extracted from red beet roots [Zhang *et al.*, 2008a], callus of *Celosia plumosa* [Buraidah *et al.*, 2010a], red turnip (*Beta vulgaris rubra, Kogel*), wild purple Silician prickly pear (*Opuntia engelmannii var. Lindhemeir*), Silician indian fig (*Opuntia ficus indica, [L] Mill.*) and bougainvillea flowers [Calogero *et al.*, 2010] have been tested as sensitizers for DSSC applications.



I. Betanin R = β-D-glucose
II. Betanidin R = H

III. Indicaxanthin



IV. Betalamic Acid

Figure 2.6: Betalain structures [Zhang *et al.*, 2008a]

2.6.2.4 Anthocyanins

Unlike betalains, anthocyanins are mostly found in flowers, fruits, leaves of plants and vegetables [Wongcharee *et al.*, 2007; Fernando and Senadeera, 2008]. Anthocyanins have been reported to exhibit anti-oxidant and anti-cancer properties [Andersen *et al.,* 2004]. The presence of the carbonyl and hydroxyl functional groups in the structure of anthocyanins helps the dye to bind with the photoelectrode making them excellent dye-sensitizers [Hao *et al.,* 2006; Wongcharee *et al.*, 2007]. Furthermore, due to their interaction with metal ions, anthocyanins can display colors in the visible region from red to blue [Cherepy *et al.,* 1997] that makes them efficient photosensitizers. Anthocyanins are the most popular natural sensitizer among chlorophylls, carotenoids and betalains for DSSC applications. Anthocyanins have been extracted from various sources such as blackberries [Cherepy *et al.,* 1997; Olea *et al.*, 1999; Zhu *et al.*, 2008], mulberries [Faria *et al.*, 2007; Chang and Lo, 2010], pomegranate fruits [Dai and Rabani, 2002; Sirimanne *et al.*, 2006], jaboticaba (*Myrtus cauliflora* Mart) [Polo and Iha, 2006], red Silician orange (*Citrus Sinensis*) [Calogero and Marco, 2008], calafate fruit (*Berberies buxifolia* Lam) [Polo and Iha, 2006], black rice [Hao *et al.,* 2006; Buraidah *et al.,* 2010a; Yuliarto *et al.,* 2010b], eggplant (*Solanum melongena L.*) [Calogero and Marco, 2008], rosella (*Hibiscus sabdariffa L.*) and blue pea (*Clitoria ternatea*) flowers [Wongcharee *et al.*, 2007] and canary bird flower (*rosa xanthina*) [Hao *et al.,* 2006] have been used as natural sensitizers.

In the present study, anthocyanin pigments from red cabbage (*Brassica oleracea var. capitata "f. rubra"*), black rice (*Oryza sativa*) and blueberry (*Vaccinium myrtillus*) have been employed as dye-sensitizer. The structures of anthocyanin pigments from red cabbage, black rice and blueberry are depicted in Figure 2.7, Figure 2.8 and Figure 2.9 respectively. Red cabbage containing anthocyanin is used mainly in food coloring and beverage industries as well as in making sweets and chewing gum [Chigurupati *et al.*, 2002]. To date, only Furukawa's group employed anthocyanin dye from red cabbage as sensitizer in DSSC [Furukawa *et al.*, 2009; 2010]. Black rice has a number of nutritional advantages over common rice, such as a higher content of protein, vitamins and minerals [Sompong et al., 2011]. According to Kong and Lee (2010), the antioxidant compounds found in black rice can eliminate reactive oxygen species (ROS) such as lipid peroxide and superoxide anion radicals and lower cholesterol content. Blueberries have excellent anti-oxidant properties compared to other berry fruits [Castrejón *et al*., 2008] and are good for health against diseases such as diabetes, cancer and heart diseases [Khanal *et al.*, 2010]. Blueberry is chosen because they are rich in anthocyanin content [Khanal *et al.*, 2010] and there are only a few reports available in the literature on DSSC utilizing blueberry as photosensitizer [Patrocínio *et al.*, 2009; Patrocínio and Iha, 2010].

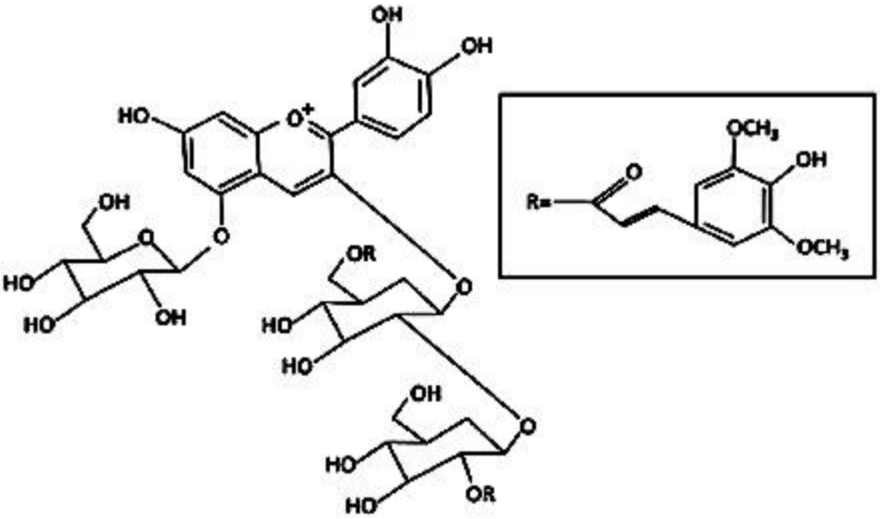
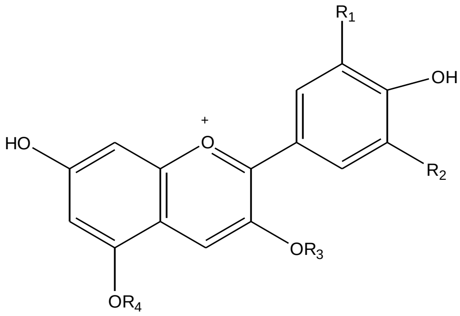
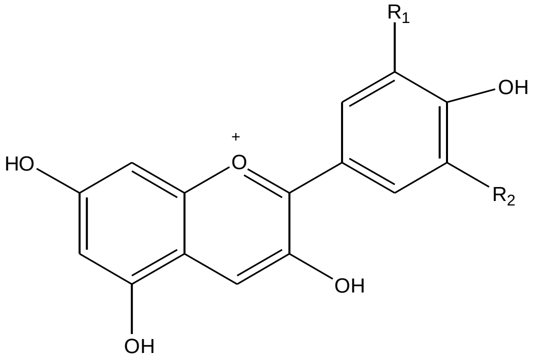


Figure 2.7: Anthocyanin structure from red cabbage [Furukawa *et al.*, 2009]



Anthocyanin	R_1	R_2	R_3	R_4
Cyanidin 3-glucoside	OH	H	Glu	H
Peonidin 3-glucoside	OCH_3	H	Glu	H

Figure 2.8: Structure of two major anthocyanin in black rice [Ryu *et al.*, 1998]



Anthocyanin	R_1	R_2
Cyanidin	OH	H
Delphinidin	OH	OH
Malvidin	OCH_3	OCH_3
Pelargonidin	H	H
Peonidin	OCH_3	H
Petunidin	OCH_3	OH

Figure 2.9: Structure of six most common anthocyanins in blueberry [Lohachoompol *et al.*, 2008]

2.7 ELECTROLYTE

Electrolyte is one of the key components for photoelectrochemical cells. In fact, all electrochemical devices require an electrolyte. Electrolyte conducts electricity resulting from dissociation of ions. Electrolytes generally consist of salt and solvent and for DSSCs include charge mediators.

Hence, the properties of the electrolyte should meet the requirements as given below [Wu *et al.*, 2008]:

- Excellent interfacial properties with both photoelectrode and counter electrode.
- Good chemical, thermal, optical, interfacial and electrochemical stability to prevent degradation of the dye.
- Compatible with dye – the redox potential and regeneration of the dye must be taken into consideration.
- High conductivity to ensure fast charge transfer.
- Do not show any significant absorption in visible light region.

In general, electrolytes can be divided into two categories: liquid and solid (Ito and Nohira, 2000).

2.7.1 Liquid Electrolyte (LE)

Liquid electrolyte usually contains a redox mediator dissolved in an organic solvent. Liquid electrolytes exhibit high ionic conductivity which is an important parameter in obtaining good DSSC performance. Table 2.2 lists the photovoltaic parameters of some DSSCs utilizing liquid electrolyte and natural dye. The conversion efficiency for DSSCs based on liquid electrolytes and synthetic dyes as photosensitizer has reached 10 % under irradiation of AM 1.5 [Nazeeruddin *et al.*, 1993]. Although the conversion efficiencies are quite high for DSSCs based on liquid electrolytes, there are problems arising from leakage and electrochemical corrosion. Some of these problems can be solved using a "solid electrolyte" containing the redox couple instead of liquid electrolyte [Matsumoto *et al.*, 1996; Bhattacharya *et al.*, 1996]. A lot of research on DSSCs have been carried out using polymer electrolytes [Ileperuma *et al.*, 2004; Bandara *et al.*, 2008 and Ileperuma *et al.*, 2011] due to their advantages over liquid electrolytes in electrochemical devices applications [Shuhaimi *et al.*, 2008; Kadir *et al.*, 2010; Mohan *et al.*, 2005].

Table 2.2: The photovoltaic performance of some DSSCs using liquid electrolyte and natural dye as sensitizer

Liquid Electrolyte (LE)	DSSC Performance	References
KI-I_2 Solvent: ethylene glycol or propylene carbonate	J_{sc} 2.2 mA cm^{-2} V_{oc} 0.45 V η 0.56 %	Cherepy *et al.*, 1997
LiI-I_2-DMPImI-TBP-PC	J_{sc} 0.81 mA cm^{-2} V_{oc} 0.53 V η 0.6 %	Furukawa *et al.*, 2009
KI-I_2 Solvent: ethylene glycol+ acetonitrile	J_{sc} 1.14 mA cm^{-2} V_{oc} 0.55 V	Hao *et al.*, 2006
LiI-I_2 Solvent: 3-methoxyproprionitrile	J_{sc} 9.5 mA cm^{-2} V_{oc} 0.43 V η 1.7 %	Calogero *et al.*, 2010

2.7.2 Polymer Electrolyte (PE)

Solid polymer electrolytes are solid films which consist of a dissolved salt in a high molecular weight polymer solvent [Andreev and Bruce, 2000]. Polymer electrolytes can also be prepared in semi-solid or gel form [Ileperuma *et al.*, 1999]. As already mentioned, solid polymer electrolytes (SPEs) have emerged as important ion conducting materials with potential applications in electrochemical devices due to some special properties such as fast ionic transport, electrochemical stability, good electrode-electrolyte contact, simple preparation in different forms, good mechanical and adhesive properties [MacCallum and Vincent, 1987, 1989; Linford, 1987].

The ionic conductivity of a polymer electrolyte has positive effect on the solar cell's performance [Ileperuma *et al.*, 2004; Rahman *et al.*, 2004]. The choice of polymer as a host in an electrolyte system [Ratner, 1987; Gray, 1991] is governed by two main characteristics which are the ability of the polymer to solvate salts and low glass transition temperature, T_g. In order to solvate salts, the polymer must consists of polar groups (i.e. atoms that possess lone pair electrons) to serve as electron donors and form dative bond with the cation of the doping salt. The low T_g makes the segmental motion occur easily and thereby helps in conduction process.

Polymers such as poly(ethylene oxide) (PEO) [Fenton *et al.*, 1973; Hashmi *et al.*, 1990], poly(propylene oxide) (PPO) [Acosta and Morales, 1996; Pas *et al.*, 2006], poly(vinyledene fluoride) (PVDF) [Sekhon and Singh, 2002; Shen *et al.*, 2004], polyvinyl chloride (PVC) [Stephen *et al.*, 2000; Ramesh *et al.*, 2002], poly(N-vinylpyrrolidone) (PVP) [Ramya *et al.*, 2008a; 2008b] and poly(vinyl alcohol) (PVA) [Every *et al.*, 1998; Hirankumar *et al.*, 2005] have been reported as host in polymer electrolyte systems. For DSSC applications, in particular, various polymers have been used including polyacrylonitrile (PAN) [Dissanayake *et al.*, 2002; Ileperuma *et al.*, 2002], poly(acrylonitrile-co-styrene) [Lan *et al.*, 2006], poly(butyl acrylate) (PBA) [Kim *et al.*, 2005], poly(methyl methacrylate) (PMMA) [Yang *et al.*, 2008], poly(epichlorohydrin-co-ethylene oxide) P(EPI-EO) [Nogueira and Paoli, 2000; Nogueira *et al*., 2006; De Freitas *et al*., 2006] and poly(acrylic acid)-poly(ethylene glycol) [Lan *et al*., 2008].

2.7.2.1 Chitosan

Other than those mentioned above, chitosan has been used as polymer host in electrolyte systems [Velazquez-Morales *et al*., 1998; Morni and Arof, 1999; Fuentes *et al*., 2003; Ng and Mohamad, 2006]. Chitosan is a biopolymer that can be obtained by extensive deacetylation of chitin [Molinaro *et al*., 2002; Wang *et al*., 2004; Gorochovceva *et al*., 2004]. Chitin is a polysaccharide of β-(1,4)-linked 2-amino-deoxy-D-glucopyranose that exists in crustaceans such as shrimps, lobsters and crabs [Okuyama *et al*., 2000]. Chitosan is usually dissolved in 1% acetic acid and the product is known as chitosan acetate. Other dilute acids such as hydrochloric, butyric and formic acid can also be used [Demarger-Andre and Domard, 1994].

Chitosan is non-toxic [Jumaa and Muller, 1999] and thus environmental friendly [Muzzarelli, 1973]. It is odorless, biocompatible [Mi *et al*., 2002], biodegradable [Zong *et al*., 2000] and has high mechanical strength [Muzzarelli, 1973]. Chitosan is an amorphous (partially crystalline) polymer exhibiting high T_g of around 480 K [Lewandowska, 2009].

Chitosan is used in food packaging industry [Butler *et al*., 1996], pharmaceutical and biomedical engineering [Aiba *et al*., 1986; Furda *et al*., 1990], paper production, textile finishes, cosmetics, photographic products, cements, filters for heavy metal and waste water treatment [Kawamura, 1995]. Figure 2.10 and 2.11 show the structures of chitin and chitosan, respectively. The oxygen atom in the hydroxyl functional group and the nitrogen atom in the amine group of chitosan can serve as electron donors and form dative bonding with cations giving the biopolymer the ability to host ionic conduction [Arof *et al.*, 1998; Osman *et al.*, 2001; Idris *et al.*, 2005]. Literature review of polymer electrolytes based on chitosan and their application in various electrochemical devices have been tabulated in Table 2.3.

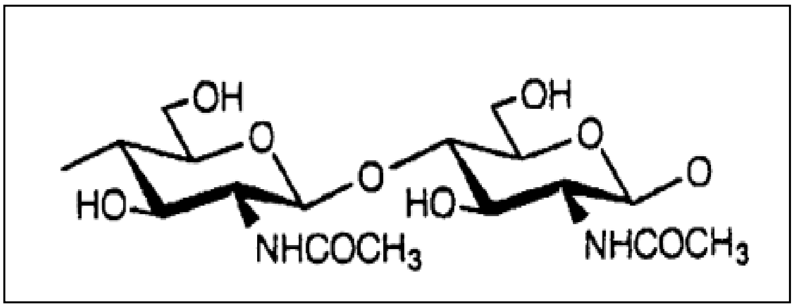


Figure 2.10: Chitin structure [Yahya and Arof, 2003]

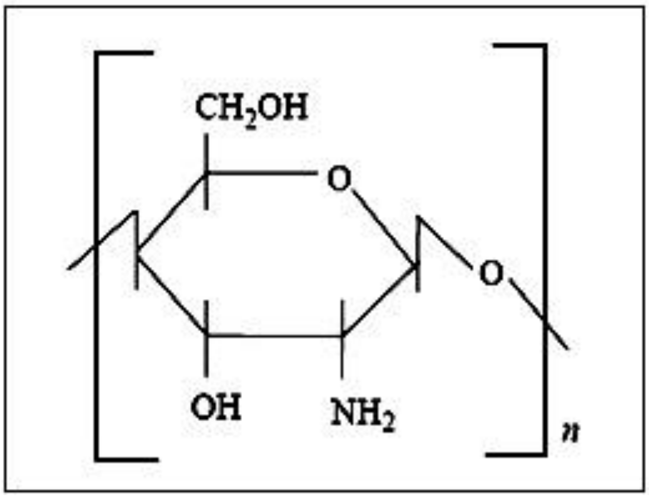


Figure 2.11: Chitosan structure [Majid and Arof, 2005]

Table 2.3: Review of earlier works on chitosan-based polymer electrolytes and their application in various electrochemical devices

Polymer Electrolytes (PE)	Conductivity, σ (S cm^{-1})	Devices	References
chitosan-NH_4I-BMII	3.43 x 10^{-5}	ITO/TiO_2/dye/chitosan-$NH_4I(+I_2)$-BMII/ITO J_{sc} 0.029 mA cm^{-2} V_{oc} 0.14 V	Buraidah *et al.*, 2010a
chitosan-IL	2.60 x 10^{-4}	ITO/TiO_2/dye/chitosan-$NaI(+I_2)$-IL/Pt J_{sc} 2.62 mA cm^{-2} V_{oc} 0.53 V	Singh *et al.*, 2010a
chitosan-$LiCF_3SO_3$-EC	1.30 x 10^{-5}	$LiMn_2O_4$/PE/C	Kamarulzaman *et al.*, 2001
Chitosan-$NaClO_4$	4.60 x 10^{-5}	Zn+$ZnSO_4$/PE/PbO_2+ V_2O_5 V_{oc} 1.121 V Zn+$ZnSO_4$/PE/ MnO_2+ V_2O_5 V_{oc} 1.116 V	Subban *et al.*, 1996
chitosan-LiOAc-PA	5.50 × 10^{-6}	$LiCoO_2$/PE/Graphite Optimum voltage 2.5 V	Yahya and Arof, 2002
chitosan-NH_4NO_3-EC	9.93 x 10^{-3}	Zn+$ZnSO_4.7H_2O$/PE/MnO_2 discharge capacity 17 mAh	Ng and Mohamad, 2006
chitosan-$AgNO_3$	2.6 x 10^{-5}	Ag/PE/I_2 V_{oc} 0.672 V	Morni *et al.*, 1997
chitosan-LiCAC	2.70 x 10^{-4}	Zn+$ZnSO_4.7H_2O$/PE/I_2+C V_{oc} 1.113 V Zn+$ZnSO_4.7H_2O$/PE/ MnO_2+C V_{oc} 0.765 V	Mohamed *et al.*, 1995
chitosan-$LiCF_3SO_3$-EC	3.00 x 10^{-4}	Li/PE/V_2O_5 discharge capacity 6.6 nAh	Morni and Arof, 1999

2.7.2.2 Poly(vinyl alcohol) (PVA)

Unlike chitosan, PVA is a synthetic polymer that exhibits similar properties such as non-toxic, biocompatible, biodegradable, simple to prepare, has excellent mechanical strength and is chemically and thermally stable [Jia *et al.*, 2007; Yang and Wu, 2009]. PVA is a partially crystalline polymer with T_g of 363 K [Agrawal and Awadhia; 2004]. Applications of PVA are mainly found in the biomedical field [Koyano *et al.*, 2000], packaging industry [Alexy *et al.*, 2002] and as host in electrolyte systems [Kufian *et al.*, 2007; Awadhia *et al.*, 2006; Hema *et al.*, 2010].

In this work, PVA with 88.7 % degree of hydrolysis is used since Mac Farlane *et al.* [1998] reported that 88 % hydrolyzed PVA exhibits higher conductivity compared to PVA with 99 % degree of hydrolysis. The PVA structure is depicted in Figure 2.12. The oxygen atom in the hydroxyl group has a lone pair electron that is expected to form coordinate bonds with doping salts; hence complexation can take place.

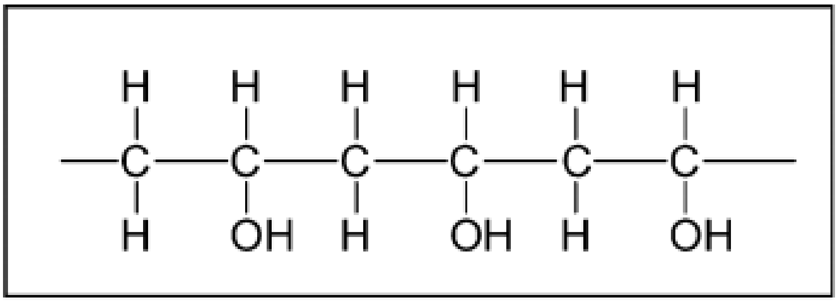


Figure 2.12: PVA structure [Praptowidodo, 2005]

Table 2.4 lists the works done by other researchers on PVA-based electrolyte in electrochemical devices. PVA is chosen since to the author's knowledge there is no report on PVA-based polymer electrolyte in photoelectrochemical applications.

Table 2.4: Review of earlier work on PVA-based polymer electrolytes and their application in electrochemical devices

Polymer Electrolytes (PE)	Conductivity, σ (S cm^{-1})	Electrochemical Devices	References
PVA-NaI-H_2SO_4	1.70 x 10^{-3}	Na/PE/MnO_2 battery Power density 0.25 mW cm^{-2} V_{oc} 3.34 V	Badr *et al.*, 2010
PVA-NMP-$LiCF_3SO_3$	1.60 x 10^{-3}	Capacitor with PE Capacitance 62 F g^{-1}	Chatterjee *et al.*, 2010
PVA-KOH-$ZnCF_3SO_3$	2.54 x 10^{-2}	Zn/PE/AgO battery Capacity 25 mAh g^{-1}	Vatsalarani *et al.*, 2009
PVA-KOH	10^{-2}	EDLC with PE Specific capacitance 110 F g^{-1}	Yang *et al.*, 2005

2.7.2.3 Poly(ethylene oxide) (PEO)

PEO is a synthetic semicrystalline polymer with monomer unit –CH_2CH_2O– in which oxygens are separated by hydrophobic ethylene unit [Ramesh *et al.*, 2006]. PEO has T_g at around 209 K [Stephan, 2006] and dielectric constant, ε of ~5 [Kumar and Sekhon, 2002]. Depicted in Figure 2.13 is the structure of PEO. It can be seen from the figure that the oxygen atoms have lone pair electrons where complexation with cation of the salt can occur. PEO is cheap, electrochemically stable [Zhang *et al.*, 2008b] and has the ability to solvate high concentration of various salts [Armand, 1987; Kuila *et al.*, 2007]. Hence, many works on polymer electrolytes used PEO as the host and applied in batteries, display devices, sensors and photoelectrochemical cells [Latham *et al.*, 2003;

Mohamed *et al*., 1997; Ohno, 1992; Bhattacharya *et al*., 1996; Kalaignan *et al*., 2006].

Table 2.5 summarizes previous works on PEO-based electrolyte in DSSC applications.

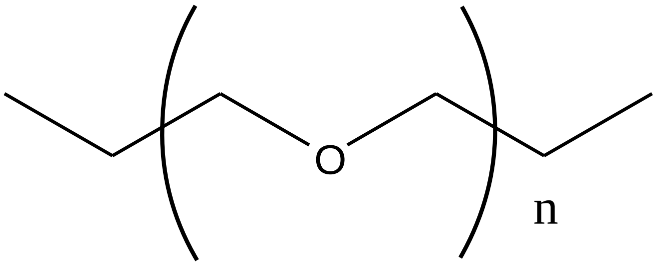


Figure 2.13: Structure of PEO

Table 2.5: Review of earlier works on PEO-based polymer electrolytes and their application in DSSC

Polymer Electrolytes (PE)	Conductivity, σ (S cm^{-1})	DSSC	References
PEO-Pr_4NI-EC-I_2	4.90 x 10^{-5}	FTO/TiO_2/dye/PE/Pt/FTO J_{sc} 0.051 mA cm^{-2} V_{oc} 0.44 V	Bandara *et al.*, 2008
PEO-NaI-I_2	2.02 x 10^{-6}	FTO/TiO_2/dye/ PE/Pt/FTO J_{sc} 1.51 mA cm^{-2} V_{oc} 0.83 V	Singh *et al.*, 2009a
PEO-KI	6.33 x 10^{-5}	ITO/ TiO_2/dye/ PE/Pt/ITO J_{sc} 5.04 mA cm^{-2} V_{oc} 0.62 V	Kalaignan *et al.*, 2006
PEO-NaI-I_2-DOP	~10^{-4}	ITO/ TiO_2/dye/ PE/Pt/ITO J_{sc} 5.50 mA cm^{-2} V_{oc} 0.71 V	Bang *et al.*, 2008

2.7.2.4 Polymer Blend

Conductivity of polymer electrolyte which plays an important role on the performance of solar cell has demanded researchers to find ways to improve the conductivity of polymer electrolyte. Blending of polymer is one feasible technique to increase the ionic conductivity and mechanical strength of the polymer electrolyte [Utracki, 2002]. It has been reported that electrolyte containing polymer blends will exhibit better properties compared to electrolytes using single polymer host [Sadoval *et al*., 2005]. There has been considerable interest in the utilization of chitosan in polymer blends since chitosan has many functional groups [Zong *et al*., 2000] and is able to form miscible and compatible blends [Sadoval *et al*., 2005].

In this work, PVA and PEO are chosen as co-host. The selection of chitosan and PEO as polymer blend hosts is due to their good film forming ability, compatibility and miscibility [Abdul Kadir *et al*., 2009; Idris *et al*., 2005; Mucha *et al*., 1998]. Blending chitosan with PVA also shows good compatible and miscible characteristics [Mucha, 1998]. Also, good mechanical properties have been exhibited in chitosan-PEO and chitosan-PVA systems, respectively [Alexeev *et al*., 2000; Mucha, 1998] due to the existence of strong hydrogen bonding between the hydroxyl groups in chitosan and the ether groups in PEO or between the amine groups in chitosan and hydroxyl groups in PVA. Some earlier works on polymer electrolytes based on chitosan blend are summarized in Table 2.6.

Table 2.6: Review of earlier work on chitosan polymer blend electrolytes and their application in electrochemical devices

Polymer Electrolytes (PE)	Conductivity, σ (S cm^{-1})	Electrochemical Devices	References
Chitosan-PEO-NH_4I	4.33 x 10^{-6}	ZnTe/PE(+I_2)/ITO I_{sc} 4.7 μA V_{oc} 345 mV	Mohamad *et al.*, 2007a
Chitosan-PVA-NH_4NO_3-EC	1.60 x 10^{-3}	Zn+$ZnSO_4.7H_2O$/PE/Mn_2O charge capacity 38 mAh I_{sc} 32 mA	Kadir *et al.*, 2010a
Chitosan-κ-carrageenan-NH_4NO_3	2.39 x 10^{-4}	EDLC with PE Discharge capacitance 18 F g^{-1}	Shuhaimi *et al.*, 2008
Chitosan-ι-carrageenan-H_3PO_4-PEG	6.29 x 10^{-4}	EDLC with PE Discharge capacitance 35 F g^{-1}	Arof *et al.*, 2010

2.7.2.5 Ammonium Iodide (NH_4I)

For effective complexation of salt in polymer, two parameters i.e. large anion and low lattice energy of the salt should be taken into consideration. There has been great interest on polymer electrolytes employing LiI, NaI, KI for DSSC applications [Chatzivasiloglou *et al.*, 2007; Shen *et al.*, 2008; Singh *et al.*, 2009a; Kalaignan *et al.*, 2006; Wu *et al.*, 2007]. However, little attention has been paid towards proton-conducting polymer electrolytes in DSSC. Proton-conducting polymer electrolytes which possess unique characteristics including reasonably good ionic conductivity, good mechanical and elastic properties, thermal and electrochemically stable, good electrode-electrolyte interfacial contact have been the subject of intense research for application in electrochemical devices such as fuel cells, sensors and electrochromic windows [Reiter *et al.*, 2008].

Among various ammonium salts, NH_4I is chosen as the doping salt in this work for proton conduction. Hema *et al.* [2009] reported that PVA-NH_4I electrolyte exhibits the highest conductivity compared to PVA-based electrolyte doped with NH_4Br and NH_4Cl, respectively. Lee *et al.* [2010a] investigated the effect of various iodide salts viz. LiI, NaI and NH_4I on the performance of DSSC utilizing phosphazene-based liquid electrolyte. Higher anionic conductivity is obtained for phosphazene-NH_4I electrolyte compared to that of phosphazene-NaI and phosphazene-LiI electrolytes. Results show that DSSC with phosphazene-NH_4I electrolyte exhibits highest J_{sc} of 1.28 mA cm^{-2}. For the three electrolytes, the anionic conductivity follows the order of σ (NH_4I) > σ (NaI) > σ (LiI) while the J_{sc} of DSSC with the corresponding salts decreases in the same order. Hence, the low lattice energy of NH_4I is favourable for providing high ionic conductivity.

2.7.2.6 Ionic Liquid (IL)

Besides blending, plasticization is another simple, low cost and effective way to improve the ionic conductivity of the polymer electrolyte [Zhang and Fang, 2000; Morita *et al.*, 2000; Binesh and Bhat, 1999]. Other than enhance the conductivity, plasticization also improves the electrolyte/electrode interfacial properties to ensure good performance in electrochemical devices [Mohamad and Arof, 2007]. A good plasticizer has high dielectric constant and low viscosity. High dielectric constant of plasticizer assists in salt dissociation [Osman *et al.*, 2001] while low viscosity helps to increase the ion mobility [Kadir *et al.*, 2010a] and thus results in conductivity enhancement.

Plasticizers incorporated in polymer electrolytes for DSSC applications include ethylene carbonate (EC) [Bandara *et al.*, 2008], propylene carbonate (PC)

[Chatzivasiloglou *et al.*, 2007], poly(ethylene glycol)methyl ether [Nogueira *et al.*, 2006], poly(ethylene glycol) dibenzoate [Flores *et al.*, 2007] and ionic liquid (IL) [Singh *et al.*, 2009a]. However, it has been reported that the addition of plasticizer reduces the mechanical stability of polymer electrolyte [Srivastava and Chandra, 2000].

On the contrary, IL with low viscosity can act as plasticizer and increase the ionic conductivity of polymer electrolyte with no effect on its mechanical stability [Bhattacharya *et al.*, 2007; Singh *et al.*, 2008a]. An ionic liquid is a liquid that contains essentially ions. Ionic liquids are also known as room temperature molten salts and are non-volatile, non-flammable, thermally and chemically stable, have high ionic conductivity, high solvating capability and wide electrochemical windows [Wang *et al.*, 2003; Wang *et al.*, 2007; Ueki and Watanabe, 2008]. ILs have dual roles as charge carrier and plasticizer [Noda and Watanabe, 2000; Rahman and Brazel, 2006; Singh *et al.*, 2007].

Due to its special properties, IL is used in various electrochemical devices such as batteries [Chew *et al.*, 2008; Taggougui *et al.*, 2008], fuel cells [Sekhon *et al.*, 2006], electrochromic devices [Brazier *et al.*, 2007], capacitors [Lewandowski and Świderska, 2004; Galiński *et al.*, 2006] and DSSCs [Singh *et al.*, 2006; Buraidah *et al.*, 2010a]. Some examples of IL incorporated polymer electrolyte for DSSC applications are 1-ethyl 3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI) [Singh *et al.*, 2008a], 1-methyl 3-propyl imidazolium iodide (PMII) [Singh *et al.*, 2008b], 1-ethyl 3-methylimidazolium trifluoromethanesulfonate (EMImTFO) [Singh *et al.*, 2009a], 1-ethyl 3-methylimidazolium thiocyanate (EMImSCN) [Bhattacharya *et al.*, 2007; Singh *et al.*, 2010a], 1-ethyl 3-methylimidazolium dicyanamide (EMImDCN) [Singh *et al.*, 2010b]. The ionic liquid 1-butyl-3-methylimidazolium iodide (BMII) is chosen in this work. BMII in this work is self-prepared.

2.7.2.7 Redox Couple

Redox couple or redox mediator in electrolyte plays a crucial role in photovoltaic applications. Below are the essential properties that a redox couple must possess [Wolfbauer *et al.*, 2001]:

- Redox potential.
- Highly soluble.
- Good diffusion coefficient to ensure efficient diffusional transport.
- Low extinction coefficient.
- The reduced and oxidized forms of the couple must be highly stable.
- Electrochemically and chemically reversible to enable fast electron transfer.
- Chemically inert towards other DSSC components.

In the present study, iodine crystals (I_2) were used to provide the redox couple I^-/I_3^-. I^-/I_3^- redox couple is most commonly used in DSSC [Kang *et al.*, 2004; Santa-Noki *et al.*, 2007; Sergawie *et al.*, 2007; Lan *et al.*, 2008]. Other redox couple such as Br^-/Br_2 [Wang *et al.*, 2005a], $SCN^-/(SCN)_2$ [Bergeron *et al.*, 2005], $SeCN^-/(SeCN)_2$ [Oskam *et al.*, 2001], 5-mercapto-1-methyltetrazolecesium salt (CsT)/di-5-(1-methyltetrazole) (T_2) [Philias and Marsan, 1999], Fe^{3+}/Fe^{2+} [Butler and Ginley, 1980], Co(II/III) [Sapp *et al.*, 2002], OH^-/O_2^- and S/S^{2-} [Deb, 2005] have been used. Oskam and co-workers [Oskam *et al.*, 2001] have examined the effect of $(SeCN)_2/SeCN^-$, $(SCN)_2/SCN^-$ and I^-/I_3^- couples on the performance of TiO_2 DSSC. The outcome of their findings shows that $(SeCN)_2/SeCN^-$ and $(SCN)_2/SCN^-$ exhibits slower dye regeneration rate compared to I^-/I_3^- thus resulting in lower efficiency of DSSC. The amount of redox couple added in the electrolyte must be taken into consideration [Wu *et al.*, 2008]. For example, too much of iodine content turns the electrolyte into dark color and thus reduces the visible light absorption by the dye. Also, electron recombination is most likely to occur due to the increase in dark current from the reaction between the increasing I_3^- ion and the injected electron.

2.8 COUNTER ELECTRODE

As previously mentioned, the reaction of triiodide reduction occurs at the counter electrode. It has been reported that the rate of reaction is very slow for transparent conducting oxide (TCO) glass substrate without a catalyst coating [Hauch and Georg, 2001; Yen *et al.*, 2009]. Hence, a catalytic material must be coated on the TCO counter electrode to ensure fast reduction. In this work, platinum is chosen as the catalyst coated on ITO glass substrate. Below are the desirable properties of the material to be selected as catalyst for counter electrode [Longo and De Paoli, 2003; Denaro *et al.*, 2009]:

- Low charge-transfer resistance i.e. low electrical resistance.
- High catalytic activity – high exchange current density for the reduction of triiodide.
- Chemically and electrochemically stable in the electrolyte medium when in contact. In particular, high corrosion stability against iodine in the electrolyte.

According to Caramori and co-workers [2010], platinum coating is very compatible to I^-/I_3^- redox couple but not the best choice for Co(II/III) mediator. The utilization of platinum coating for counter electrode together with I^-/I_3^- redox mediator has been reported in the literature [Koo *et al*., 2006; Singh *et al*., 2009b; Furukawa *et al*., 2009]. Other counter electrodes that have been used include graphite [Denaro *et al*., 2009], carbon [Smestad, 1998], carbon nanotube [Zhu *et al*., 2008] and conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) [Lee *et al*., 2010b].

2.9 SUMMARY

In this chapter, DSSC's background and its operating principle as well as the function and choice of all its components have been discussed in detail. The next chapter presents the materials used, sample preparation and explains why the various experimental technique are employed.