# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

This chapter reviews research on polymer electrolytes (PEs), with emphasis on the types of polymer electrolytes that can be used in photoelectrochemical devices. Since the work done for this thesis focuses on the studies of plasticized PVDF-HFP based polymer electrolytes and their application in dye sensitized solar cell (DSSC) devices, this chapter contains information on previous studies of DSSCs utilizing PVDF-HFP based polymer electrolyte systems by other researchers. Finally, the construction, working principle of DSSCs and literature review of previous work done on them are given at the end of this chapter.

# 2.2 Polymer Electrolytes

A polymer electrolyte (PE) is an ionic conductor containing ionic salts dissolved in a polymer matrix. The salt provides free or mobile ions which take part in the conduction process while the polymer provides mechanical stability to host the conduction of ions. The solvent used to dissolve the polymer and salt will evaporate when the polymer-salt solution has been cast and left to dry for film formation. Polymer electrolytes were introduced during the 1970s, a period which saw considerable changes in the general climate of scientific research including the field of polymer science (Wright, 1998). The concept of polymer electrolytes was proposed and demonstrated by Fenton and co-workers in 1973. However, the research and development of PE started only when Wright

discovered ion conductivity in a PEO-alkaline metal ion complex in 1975 (Wright, 1975). The technological importance of these polymer electrolytes only became clear to the scientific community when Armand proposed the use of an ion conducting polymer in batteries in 1978 (Murata et al., 2000). The increasing interest on polymer electrolytes is related to the possibility of its use in solid state electrochemical devices such as batteries, capacitors, electrochromic displays, light emitting electrochemical cells, artificial muscles and photo-electrochemical cells (Nogueira et al., 2001). The high molecular weight poly(ethylene oxide) (PEO) receives much attention as the host for the polymer electrolytes because of its ability to dissolve alkali salts, electrochemically stable and it has a beneficial structure for supporting ion migration (Bhide and Hariharan, 2007). Other polymer-based electrolytes contain polymer matrix such as poly(propyleneoxide) (PPO), poly(acrylonitrile) (PAN), poly(methylmethacrylate) (PMMA), poly(vinylchloride)(PVC), poly (vinylidenefluoride)(PVdF) and poly (vinylidene fluoride-hexafluoro propylene) (PVDF-HFP) (Stephan, 2006).

#### **2.3 Ionic Conductivity in Polymer Electrolytes**

Ionic conductivity in a polymer electrolyte is due to the transport of cations and anions (Johansson et. al, 1996). Example of cation that has been widely discussed in polymer electrolytes is the Li<sup>+</sup> cation from lithium salt. Cations such as Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and Cu<sup>2+</sup> also have been studied. The anions include Cl<sup>-</sup> (chloride), ClO<sub>4</sub><sup>-</sup> ( perchlorate), CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> (triflate) and I<sup>-</sup> (iodide). According to Jayathilaka and co-workers (2003), ionic conductivity ( $\sigma$ ) of polymer electrolytes is given by equation

$$\sigma = \sum_{i} n_i \mu_i q_i \tag{2.1}$$

9

where  $n_i$  is the number density of ionic (cations and anions) charge carriers,  $\mu_i$  is the ionic mobility and  $q_i$  is the ionic charge which is equivalent to the electron charge for a monovalent ion. The increase in number density of ionic charge carriers and/or ionic mobility can increase the ionic conductivity of the polymer electrolyte.

### 2.4 Classifications of Polymer Electrolytes

Polymer electrolytes can be classified into three classes:

- (a) Solid Polymer Electrolytes (SPE)
- (b) Gel Polymer electrolytes (GPE)
- (c) Composite Polymer Electrolytes (CPE)

### (a) Solid Polymer Electrolytes

Solid polymer electrolytes (SPEs), formed by dissolving salts in a polymer matrix (Choi and Bae, 2003) have attracted much interest as they can be used in batteries and display devices (Sekhon et al., 1995). They are mostly based on polymers which can interact with cations. However, the ionic conductivity of these SPEs is below  $10^{-4}$  S cm<sup>-1</sup> at ambient temperature (Uchiyama et al., 2009). The research and development of solid polymer electrolyte began when Wright found ion conductivity in a PEO-alkaline metal ion complex in 1975 and the conductivity of PEO-based electrolytes studied during that period was ~ $10^{-7}$  S cm<sup>-1</sup> at room temperature (Murata, 2000). The ionic conductivity increases with temperature. The applications of PEs at low temperatures are limited (Ogata et al., 1995). Since then, various efforts have been made to improve the ionic conductivity of the SPE including the development of gelled SPE and porous SPE especially in consideration

of its practical application at low temperatures. Major applications of solid polymer electrolyte batteries are in the electronics devices, which have become smaller and lighter each year (Murata, 1995).

#### (b) Gel Polymer Electrolytes

Gel polymer electrolytes (GPEs) are also called plasticized polymer electrolytes. GPEs consist of a polymer, a salt and a plasticizer and possess both cohesive properties of solids and the diffusive properties of liquids (Stephan, 2006). Gel electrolytes can also be considered as liquid electrolytes entrapped in a polymer matrix, possess levels of ionic conductivity that are sufficient for application in lithium batteries (Andreev and Bruce, 2000). Although many methods have been proposed by previous researches to enhance ionic conductivity in polymer electrolytes, it is well-known that the ionic conductivity of a polymer electrolytes can be enhanced using plasticizers. A plasticizer can be defined as an agent which reduces the stiffness of polymer. It can interact with the polymer chains on the molecular level so as to speed up the viscoelastic response of the polymer and increase the ionic mobility in the electrolyte significantly (Lee et al., 2009). The choice of ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers is due to their high dielectric constant as compared with other plasticizers. A mixture of equal weights of EC and PC were chosen as the plasticizer for the polymer-salt electrolyte system in this work. EC which has dielectric constant,  $\varepsilon = 89$ , boiling point 248 °C and viscosity,  $\eta = 1.90$  cp at 25 °C and PC which has dielectric constant,  $\varepsilon = 64.4$ , boiling point 242 °C and viscosity,  $\eta =$ 2.53 cp at 25 °C are most promising and highly compatible with many polymers (Rajendran and Kumar, 2008; Deepa et al., 2004). Some of the reported EC and PC plasticized polymer electrolyte sytems and their conductivity values are tabulated in Table 2.1.

Polymer + Salts	Plasticizer	Conductivity (S cm <sup>-1</sup> )	References
(PMMA+PVC) + LiCF <sub>3</sub> SO <sub>3</sub>	(EC/PC)	$1.40 \times 10^{-3}$	Rhoo et al., 1997
Chitosan + LiCF <sub>3</sub> SO <sub>3</sub>	EC	$4.0  imes 10^{-5}$	Osman et al., 2001
PAN+LiTFSI	EC+PC	$2.50 \times 10^{-3}$	Jayathilaka et al., 2003
PMMA+ LiN(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub>	PC	$7.88 \times 10^{-3}$	Deepa et al., 2004
PMMA + LiTFSI	PC	$5.39 \times 10^{-4}$	Ali et al., 2007
PMMA+ LiTFSI	EC	$4.34 \times 10^{-4}$	
(PVDF+PVC) + LiClO <sub>4</sub>	(EC/PC)	$3.68 \times 10^{-3}$	Rajendran and Sivakumar, 2008
(PEO+PVDF-HFP)+ LiTFSi	PC	$1.35 \times 10^{-3}$	Cui et al., 2012

**Table 2.1:** Some reported plasticized PE systems and their room temperature conductivities

The plasticizers used in polymer electrolytes shown in Table 2.1 are EC and PC since they have high dielectric constants. The high dielectric constant helps in the dissociation of the ion providing salt (Rhoo et al., 1997). EC, being solid at room temperature is normaly mixed with a co-solvent or is melted first. From the table it can be seen that polymer electrolytes with EC/PC binary plasticizers exhibit RT conductivity of the order  $10^{-3}$  S cm<sup>-1</sup>.

## (c) Composite Polymer Electrolytes

A composite polymer electrolyte (CPE) is composed of three components: a polymer, salt and a filler (Ciosek et al., 2007). CPEs have recently attracted considerable attention due to the improvement in mechanical and temperature stabilities. The incorporation of a filler into the polymer matrices enhanced the ionic conductivity at low temperatures and improved the stability at the interface with electrodes. Fillers in general are classified into two categories active and passive fillers. The active type such as Li<sub>2</sub>N, LiAl<sub>2</sub>O<sub>3</sub> participate in the conduction process while passive fillers such as TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO are not involved in the lithium ion transport process (Kumar et al., 2000).

Some reported CPE systems and their conductivities are tabulated in Table 2.2. The conductivity value for each system is also included. The conductivity of the CPE ranges from  $10^{-7}$  to  $10^{-3}$  S cm<sup>-1</sup>. CPE with LiN(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and  $\alpha$ -LiAlO<sub>2</sub> or  $\gamma$ -LiAlO<sub>2</sub> fillers (Wen et al., 2000) showed better conductivity value of  $6.6 \times 10^{-5}$  S cm<sup>-1</sup> and  $6.4 \times 10^{-5}$  S cm<sup>-1</sup> respectively compared to the pristine PEO-LiN(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> SPE with conductivity 1.53 ×  $10^{-5}$  S cm<sup>-1</sup> at the same temperature.

The oxides provided additional pathways for ionic conduction in polymer electrolytes thereby increasing the conductivity and lowering the activation or pseudo-activation energy. Since fillers can also effectively enhance the mechanical properties (Itoh et al., 2003), various efforts have been made to improve ionic conductivity of polymer electrolytes by adding fillers. In their work, Ahmad and Agnihotry (2009) have obtained better conductivity for a CPE of  $3.79 \times 10^{-3}$  S cm<sup>-1</sup>.

Polymer + Salts	Fillers	Conductivity (Scm <sup>-1</sup> )	References	
$PEO + LiBF_4$	Al <sub>2</sub> O <sub>3</sub>	$1.60 \times 10^{-6}$	Krawiec et al., 1995	
PEO+ LiN(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	SiO <sub>2</sub>	$1.40  imes 10^{-4}$	Capiglia et al., 1999	
$PEO + LiClO_4$	TiO <sub>2</sub>	$10^{-3}$ and $10^{-5}$	Appetecchi et al., 2000	
PEO+ LiN(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	$\alpha$ -LiAlO <sub>2</sub> $\gamma$ -LiAlO <sub>2</sub> Without filler	$6.6  imes 10^{-5} \ 6.4  imes 10^{-5} \ 1.53  imes 10^{-5}$	Wen et al., 2000	
$PEO + LiBF_4$	$\gamma$ -LiAlO <sub>2</sub>	$3.0  imes 10^{-7}$	Croce et al., 2000	
$PEO + LiClO_4$	$Al_2O_3$	$1.0 \times 10^{-5} (30^{\circ}\text{C})$ $1.1 \times 10^{-4} (95^{\circ}\text{C})$	Chung et al., 2001	
P(EO+ PO) LiN(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	$\gamma$ -LiAlO <sub>2</sub> Without filler	$5.67 \times 10^{-5}$ $3.45 \times 10^{-5}$	Wen et al., 2003	
$PEO + LiCF_3SO_3$	$Al_2O_3$	$7.00 \times 10^{-5}$	Dissanayake et al., 2003	
PMMA+ LiClO <sub>4</sub>	SiO <sub>2</sub>	$3.8 \times 10^{-3}$	Ahmad et al., 2005	
PEO+ LiN(SO <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	$1.50 \times 10^{-4}$	Thokchom et al., 2005	
(PEO) <sub>9</sub> LiTf + EC	Al <sub>2</sub> O <sub>3</sub>	$8.20 \times 10^{-5}$	Pitawala et al., 2007	
PVC/PAN+ LiClO <sub>4</sub> + EC	TiO <sub>2</sub>	$4.46 \times 10^{-3}$	Rajendran et al., 2008	
PMMA+ LiClO <sub>4</sub>	$\gamma$ - Al <sub>2</sub> O <sub>3</sub>	$3.79 \times 10^{-3}$	Ahmad and Agnihotry 2009	
PAN+ LiClO <sub>4</sub>	Silica aerogel powder (SAP) Without filler	$6.0  imes 10^{-4}$ $4.8  imes 10^{-5}$	Chen et al., 2011	
PVAc+(PVDF- HFP))+LiBF <sub>4</sub> +EC +PC	BaTiO <sub>3</sub> Without filler	$5.53 \times 10^{-3}$ $2.08 \times 10^{-3}$	Ulaganathan et al., 2012	
PEO+ LiN(SO <sub>2</sub> CF <sub>3</sub> ) <sub>2</sub>	Zn <sub>4</sub> O	$3.16 \times 10^{-5}$	Yuan et al., 2013	

Table 2.2: Some reported CPE systems and their room temperature conductivities

### 2.5 PVDF-HFP

The use of poly (vinylidene fluoride-hexafluoro propylene) or PVDF-HFP as a polymer host in polymer electrolyte system has drawn the attention of many researchers (Stolarska et al.,2007; Ramesh and Lu, 2011). The structure of PVDF-HFP is as shown in Figure 2.1

## Fig. 2.1: The structure of PVDF-HFP

The PVDF crystalline phase acts as a mechanical support to provide sufficient mechanical strength for the processing of free-standing films. The HFP copolymer comprising an amorphous phase helps to entrap large amount of liquid electrolytes. PVDF-HFP also has a high dielectric constant of  $\varepsilon = 8.4$  (Choi et al., 2006). This enables the polymer to solvate more salts that can contribute towards higher electrical conductivity of the polymer electrolyte. Furthermore, there is a strong electron withdrawing functional group (-C-F-) that makes PVDF-HFP a favorable polymer matrix to host ionic conductivity (Gray, 1991). Due to these appealing properties of PVDF-HFP, it is chosen as a polymer host in the present work.

## 2.6 Dye Sensitized Solar Cells (DSSCs)

Dye-sensitized solar cells (DSSC) have attracted much attention of researches world wide after the pioneering work by O'Regan and Grätzel in 1991 (O'Regan and Grätzel, 1991). Although DSSCs have shown a relatively low conversion efficiency of about 12.3% (Yella et al., 2011) compared to conventional silicon solar cells, they have become the topic of interest due to their attractive features such as easy fabrication, low manufacturing cost and low environmental impact during fabrication (Smestad, 1998; Li et al., 2006; Chou et al., 2008). Recently, many polymer electrolytes have been used in DSSCs and have shown promising results in the photo-conversion efficiency of the cell (Qin and Peng, 2012). Many attempts have also been made to replace the conventional liquid electrolytes in DSSC with polymer electrolytes because devices using liquid electrolytes are prone to leakage and liquid electrolytes may also contain volatile materials (Mohan et al., 2013). The polymer electrolyte based cells have some advantages over DSSCs fabricated using liquid electrolytes as they show good mechanical stability and are leakproof, do not have volatile solvents and are therefore free from evaporation of the electrolyte component in the solar cell (Yang et al., 2008). In this work, DSSCs were fabricated using plasticized PVDF-HFP based polymer electrolytes. Many reports have shown that DSSCs assembled with plasticized polymer electrolytes exhibit much higher efficiencies when compared to those with unplasticized polymer electrolytes (Freitas et al., 2008).

## 2.7 DSSC Structure

Fig. 2.2 shows the structure assembly of main components of a dye sensitized solar cell. A typical DSSC consists of an electrolyte containing a redox couple ( $I^{-}/I_{3}^{-}$ ) sandwiched between a mesoporous TiO<sub>2</sub> semiconductor layer deposited on a transparent conducting oxide glass that has been coated with a compact layer and a Pt counter electrode. In this work FTO glass is used. This FTO/compact layer/TiO<sub>2</sub> assembly is soaked in a dye sensitizer to make it photoactive (Scully et al., 2004). Transparent conducting oxides (TCO) substrates commonly used are transparent tin-doped indium oxide (ITO) or fluorine-doped tin oxide (FTO) glass. The TiO<sub>2</sub> compact layer is obtained using di-

isopropoxytitanbis-(acetylacetonate) solution. Energy conversion in a DSSC is based on the injection of electrons from a photoexcited dye molecules into the conduction band of the nanocrystalline  $TiO_2$  semiconductor (Nogueira et al., 2004) that enters the external circuit and are returned to the de-excited ionized dye molecules through the redox mediator. The introduction of a compact layer at the FTO/TiO<sub>2</sub> interface has been proven theoretically and is practically effective in blocking electron recombination with the ionized dye molecules and to prevent the charge carriage leakage between electrolyte and the conducting electrode (Meng and Li, 2011).

The compact layer is much denser than the  $TiO_2$  layer therefore, it can reduce the contact surface area of bare FTO sites and the redox electrolyte (so-called blocking effect). The compact layer also improves adherence between the  $TiO_2$  layer and FTO surface resulting in larger  $TiO_2/FTO$  contact area. More electron pathways are provided from  $TiO_2$  to FTO for photo-generated electrons, which facilitates electron transfer and subsequently improves the electron transfer efficiency in the DSSC (Yu et al., 2009).

## Fig. 2.2 : The structure of a dye sensitized solar cell

# 2.8 The Working Principle of a DSSC

The working principle of a DSSC is illustrated in Fig. 2.3. Basically, a DSSC device comprises two facing electrodes which are the photoelectrode and the counter electrode in the configuration  $FTO/TiO_2/Dye/Electrolyte/Pt/FTO$  (Nazeeruddin et al., 2011).

Fig. 2.3: Working principle of a DSSC

To generate meaningful electrical power from the DSSC, the electrons need to pass four important interfaces of a DSSC; dye/TiO<sub>2</sub>, TiO<sub>2</sub>/FTO, electrolyte/counter electrode, and dye/electrolyte (Yu et al., 2009). The complete photoelectrochemical cycle of the device can be outlined as follows (Calogero et al., 2012):

(1) Upon illumination of light through the photoelectrode, dye molecules absorb photons (hv) forming excitons in the dye molecule (electron-hole pairs).

$$D + hv \rightarrow D^*$$
 (photoexcitation) (2.1)

(2) The excited dye molecules release electrons which are injected into the conduction band (*cb*) of  $TiO_2$  leaving a hole on each dye molecule.

$$D^* + TiO_2 \rightarrow D^+ + (e_{cb} TiO_2)$$
 (electron injection) (2.2)

- (3) The holes in the dye molecules are filled back with electrons from redox reaction. The dye is subsequently regenerated from its oxidized state by electron transfer from iodide ( $I^-$ ) ions in the electrolyte containing ( $I^-/I_3^-$ ) redox couple.  $2D^+ + 3I^- \rightarrow 2D + I_3^-$  (sensitizer generation) (2.3)
- (4) The triiodide  $(I_3^-)$  ions formed in this regeneration process diffuse to the platinum-coated electrode, where they are reduced rapidly to I<sup>-</sup>.

$$I_3^- + 2e^- \rightarrow 3I$$
 (electron donor regeneration) (2.4)

Provided that the dye is stable and the sequence of events takes place effectively, the cell is regenerative. The circuit being completed via electron migration through the external load. Photoinjected electrons should escape from any recombination process in order to have a unit charge collection efficiency at the photoelectrode back contact. The two major waste processes in a DSSC are due to back electron transfer, at the semiconductor-electrolyte interface, between electrons in the conduction band and the oxidized dye molecules.

#### 2.9 Dye Materials

Since the dye plays an important role in harvesting light and solar energy conversion to electricity, efforts have been focused on dye materials. The commercial synthetic ruthenium (II) polypyridyl complexes such as N719 and N3 are widely used in DSSCs due to the satisfactory photoelectric conversion efficiency up to 11% with  $I^{-}/I_{3}^{-}$  mediator

(Asano et al., 2004; Kim et al., 2005). However, these dyes use metal compound complexes, which are expensive and produce environmental pollution (Chang et al., 2010). Another approach is to use natural dyes, which are environmentally friendly, nontoxic, biodegradable, and cheaper compared to the synthetic dyes, but has yet to show good performance in terms of efficiency (Patroc'inio et al., 2009). Natural sensitizing dyes include anthocyanins (Wongcharee et al., 2007; Furukawa et al., 2009; Buraidah et al.,2011). In this study, the DSSCs were prepared with N3 dye or natural dyes. Anthocyanin from black rice extraction was used as the dye, since anthocyanin has good chemical bonding with titanium dioxide (Yuliarto et al., 2010). Chlorophyll extracted from natural sources also can be used as the dye. Basic molecular structures of anthocyanin and chlorophyll are shown in Fig. 2.5. The carbonyl and hydroxyl groups present in anthocyanin molecules help in binding the dye well to the surface of  $TiO_2$  porous film and help the photoelectric conversion effect in the DSSC (Jin et. al, 2010). Chlorophyll, a natural photosensitizer for photosynthesis in green plants, is another attractive potential compound as photosensitizer in the visible region for DSSCs (Amao et al., 2004; Zhou et al., 2011).



**Fig. 2.4:** Basic molecular structure of (a) anthocyanin (Hou et. al, 2006) and (b) chlorophyll dyes (Amao et al., 2004)

Some DSSCs fabricated using chlorophyll dyes and investigated by previous researchers are shown in Table 2.3 (a) and Table 2.3 (b) for anthocyanin dye. The photoconversion efficiency of the chlorophyll based DSSCs ranges from 0.1 to 0.9%. Chlorophyll extracted from wormwood shows the highest efficiency. From Table 2.3 (b), it can be seen that the photoconversion efficiency of the anthocyanin based DSSC ranges from 0.3 to 1.2%. The anthocyanin extracted from mangoesteen pericarp has the best efficiency of 1.17%. In the present work, chlorophyll extracted from *Pandanus amaryllifolius (pandan)* and anthocyanin extracted from black rice and a mixture of equal volumes of chlorophyll and anthocyanin were used as the dye sensitizers.

Table 2.3 (a): Some DSSCs with chlorophyll natural dye as sensitizers and their performance parameter

Natural dye	Electrolytes	$J_{SC}$	Voc	FF	Efficiency	References
source		$(mA/cm^2)$	(V)		(%)	
Chl-e <sub>6</sub>	KI/I <sub>2</sub> in ethylene	1.47	0.43	0.57	0.40	Amao et al.,
derivative	glycol/acetonitrile					2004
Bamboo	1,2-dimethyl-3-	1.9	0.67	0.56	0.7	Jin et al.,
wormwood	propylimidazolium	2.3	0.67	0.56	0.9	2010
	iodide-4-TBP					
pomegranate	LI/I <sub>2</sub> /4-TBP	2.05	0.52	0.56	0.60	Chang et al.,
leaf						2010
Perrila	1,2-dimethyl-3-	1.36	0.52	0.70	0.50	Zhou et al.,
	propylimidazolium					2011
	iodine-guanidinium					
	thiocyanate- I <sub>2</sub> - LiI-					
	(4-TBP)					

Natural dye	Electrolytes	$J_{SC}$	Voc	FF	Efficiency	References
sources		(mA/cm <sup>2</sup> )	(V)		(%)	
Rosella	KI/I <sub>2</sub> /ethylene	1.63	0.40	0.57	0.37	Wongcharee
	glycol solution					et al., 2007
Blue pea		0.37	0.37	0.30	0.50	
	1,2-dimethyl-3-					Jin et al.,
Maple	propylimidazoli	1.0	0.65	0.60	0.40	2010
	um iodide-4-					
	TBP					
Red Sicilian	KI/I <sub>2</sub> /ethylene					Calogero and
orange	glycol/	3.84	0.34	0.50	0.66	Di Marco,
	/acetonitrile					2008
Mangoesteen	1,2-dimethyl-3-					
-pericarp	propylimidazoli					
	um iodine-	2.69	0.69	0.63	1.17	Zhou et al.,
	guanidinium					2011
	thiocyanate- I <sub>2</sub> -					
	LiI- (4-TBP )					
Blackberry	BMII/LI/I <sub>2</sub>	6.52	0.32	0.55	1.13	Calogero et
						al., 2012

Table 2.3 (b): Some DSSCs with anthocyanin natural dye as sensitizers and their performance parameters

Some reported DSSCs utilizing (PVDF-HFP) based polymer electrolyte systems with synthetic dyes and their performance parameters are shown in Table 2.4. The best efficiency of 7.18% was reported by Huo et al. (2007) with N719 dye.

Polymer Electrolytes	DYE	Voc (V)	$J_{SC}$ (mA/cm <sup>2</sup> )	FF	η (%)	REFERENCES
System		0.44		0.47		
(PVDF-HFP)/	N3	0.61	9.95	0.65	3.95	
$ACN/L1I/I_2$	N710	0.60	11 49	0.64	4 4 1	Saikia et al., 2008
/FC/DEC/IBF	IN/19	0.00	11.40	0.04	4.41	
(PVDF-HFP)/ +(SiO <sub>2</sub> )/ acetone/ LiI/I <sub>2</sub> / EC/PC	N3	0.76	5.0	0.61	2.3	Scully et al., 2004
(PVDF-HFP)/ +SiO <sub>2</sub> / NMP/ LiI/I <sub>2</sub> / TBP	N719	0.79	3.93	0.48	1.47	Pasquier, 2007
(PVDF-HFP)/ /THF/water/ LiI/I <sub>2</sub> / PC/TBP	N3	0.72	11.86	0.51	6.0	Zhang et al., 2008
(PVDF-HFP)/ TiO <sub>2</sub> /DMPII/ LiI/I <sub>2</sub> /NMBI	N719	0.69	15.24	0.690	7.18	Huo et al., 2007
(PVDF-HFP)/ acetone/ NaI/I <sub>2</sub> /PC	PTCA	0.28	2.5	0.51	0.36	Kim et al., 2006
(PVDF-HFP)/ SiO <sub>2</sub> /MPN/TBAI /I <sub>2</sub> /TBP	N3	0.71	14.04	0.598	5.97	Lee et al., 2008
(PVDF-HFP)/ /AN/ TBAI/I <sub>2</sub>	N3	0.657	16.04	0.64	6.74	Lee et al.,2009
(PVDF-HFP)/ /NMP/ LiI/I <sub>2</sub>	N719	0.66	8.03	0.54	2.86	Kang et al.,2004
(PVDF-HFP)/ /PC/DME/ LiI/I <sub>2</sub> /0.1M APTS/EtOH	N3	0.59	7.2	0.627	5.08	Zhang et al.,2008
(PVDF-HFP)/ acetone/DMAc/I <sub>2</sub> /TBAI/PMII/EC/ PC/AN	N3	0.75	12.3	0.57	5.21	Kim et al.,2009

**Table 2.4:** Some PVDF-HFP polymer electrolyte based DSSCs with synthetic dyes as sensitizers and their performance parameters

\*N3: Ruthenizer 535

N719: Ruthenizer 535-bis TBA

PTCA: Perylenetetracarboxylic acid

## 2.10 Summary

In this chapter, polymer electrolytes and dye sensitized solar cells (DSSCs) have been introduced and their functions discussed. The discussion included the classification of polymer electrolytes, their basic properties and some previous work done on different types of polymer electrolytes and their conductivity values. DSSCs fabricated with PVDF-HFP based electrolytes have also been listed. The background of DSSCs, their components and working principles have also been discussed and some previous work on DSSCs were also reviewed. With information gathered, though inexhaustive, the research objectives are presented.