

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Introduction

Four different types of iodide based polymer electrolyte films were prepared by solution casting technique using poly (vinylidene fluoride-co-hexafluoropropylene) or PVDF-HFP as the polymer host. The salts used in each systems are sodium iodide (NaI) and potassium iodide (KI). Unplasticized and plasticized electrolytes were prepared for each NaI and KI system. A mixture of 1:1 weight ratio of ethylene carbonate (EC) and propylene carbonate (PC) was used as the plasticizer for both electrolyte systems. The polymer electrolyte systems prepared can be summarized as:

- (a) (PVDF-HFP) - NaI
- (b) (PVDF-HFP) - NaI - (EC/PC)
- (c) (PVDF-HFP) - KI
- (d) (PVDF-HFP) - KI - (EC/PC)

The electrolytes were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS). The highest conducting plasticized NaI and KI based polymer electrolytes together with other DSSC components such as platinum (Pt) counter electrode, titanium dioxide (TiO₂) working electrode and dye materials were used to fabricate dye sensitized solar cells (DSSCs). Fluorine-doped tin oxide (FTO) glass was used as the substrate for both working and counter electrodes. The DSSCs with electrolytes having two salts, KI and

tetrabutylammonium iodide (TBAI), at different weight ratios were also fabricated to study the effect of mixed-cations on the electrolyte to the performance of the DSSC.

3.2 Materials

Poly (vinylidene fluoride-co-hexafluoropropylene) denoted as PVDF-HFP of $M_w \sim 400,000 \text{ g mole}^{-1}$ was purchased from Sigma Aldrich in pellet form. Potassium iodide (KI), sodium iodide (NaI) and tetrabutylammonium iodide (TBAI) salts were also obtained from Sigma Aldrich. High purity (99%) acetone, ethylene carbonate (EC) and propylene carbonate (PC) were purchased from Fluka and TiO_2 paste PST-18NR from JGC Catalyst and Chemicals Ltd. Japan. All of the above materials were used as received. Di-isopropoxytitanbis -(acetylacetonate) solution, which was to be used to form a compact layer between the FTO glass and TiO_2 semiconductor layer was purchased from Aldrich and was diluted with ethanol to 0.38 M concentration. Rhutenizer 535 (N3) dye purchased from Solaronix, Switzerland was diluted to 0.003 M with ethanol. Chloroplatinic acid (Aldrich) that was spin coated to form the platinum (Pt) counter electrode was diluted to 0.005 M in 2-propanol.

3.3 Sample Preparation

The electrolyte systems prepared included plasticized polymer electrolytes with two different iodide salts. Other components needed for the DSSCs such as natural dye materials, photo- and counter electrodes were also prepared. Fig. 3.1 and 3.2 give the flow chart of the steps involved in the preparation and characterization of polymer electrolytes and DSSCs in the present work.

Fig. 3.1: Flow chart of preparation and characterization of polymer electrolytes

Fig. 3.2: Flow chart of preparation and characterization of dye sensitized solar cells

3.3.1 Preparation of NaI Based Polymer Electrolytes

Two types of NaI based polymer electrolytes were prepared:

- (i) (PVDF-HFP)-NaI electrolytes
- (ii) (PVDF-HFP)-NaI-(EC/PC) electrolytes

(i) (PVDF-HFP)-NaI Electrolytes

Different compositions of (PVDF-HFP)-NaI polymer-salt electrolyte films were prepared by solution casting. A fixed amount (1.00 g) of PVDF-HFP was continuously stirred in acetone under reflux for one hour at 60 °C to form a homogenous polymer solution and allowed to cool down. At room temperature, different amounts of NaI salt from 0 to 50 wt.% were added into the polymer solution and vigorously stirred for about 24 hours until the polymer-salt solution becomes homogenous. Polymer-salt solutions were cast onto separate clean glass petri dishes to allow the solvent to evaporate slowly until films are formed. The films were kept in a dessicator for further drying before characterization. Different weight percentage (wt.%) of salt were added to the fixed amount of polymer. The required weight of salt (in gram) was calculated using the equation $\frac{x}{(x+y)} \times 100\% = z\%$, where x is weight of salt in gram, y is weight of polymer in gram and z is weight percentage of salt. For example, for 10 wt.% NaI in 1.00 g (PVDF-HFP), NaI weight (in gram) is calculated as below:

$$\frac{x}{(x+1.00)} \times 100 = 10$$

$$x = 0.1111 \text{ g}$$

Hence, 0.1111 g of NaI was added to the mixture.

Table 3.1 lists the polymer–salt weight ratios used for preparing the (PVDF-HFP)-NaI electrolytes. The characterizations performed include room temperature electrical conductivity through impedance measurement by EIS technique, structural studies by X-ray diffraction (XRD) and fourier transform infrared (FTIR) spectroscopy.

Table 3.1: The weight ratio of (PVDF-HFP) – NaI electrolytes

(ii) (PVDF-HFP)-NaI- (EC/PC) Electrolytes

To prepare plasticized polymer electrolyte films, the composition of the highest conducting (PVDF-HFP)-NaI electrolyte was kept constant, but its weight percentage was varied to accommodate a mixture of equal weights of EC/PC binary plasticizers up to 50 wt.% in solution. Polymer-salt-plasticizer solutions were cast onto separate clean glass petri dishes to allow the solvent to evaporate slowly until plasticized polymer electrolyte films were formed. The films were kept in a dessicator for further drying before characterization. Table 3.2 lists the compositions of the (polymer+salt):plasticizer weight ratio. The interactions between PVDF-HFP, NaI and EC/PC were analyzed using the technique of fourier transform infrared (FTIR) spectroscopy. The amorphousness of the

films were investigated by FTIR and x-ray diffraction (XRD). Conductivity and dielectric properties were studied by electrochemical impedance spectroscopy (EIS).

Table 3.2: The weight ratio of (PVDF-HFP + NaI) – EC/PC electrolytes

3.3.2 Preparation of KI Based Polymer Electrolytes

Two types of KI based polymer electrolytes were prepared:

- (i) (PVDF-HFP)-KI electrolytes
- (ii) (PVDF-HFP)-KI-(EC/PC) electrolytes

(i) (PVDF-HFP)-KI Electrolytes

The same procedure described in section 3.3.1.(i) was used for (PVDF-HFP) – KI system preparation. Different amounts of KI salt from 0 to 30 wt. % were added into the polymer solution and vigorously stirred until the solutions become homogenous. Table 3.3 summarizes the compositions of the polymer – salt weight ratio.

Table 3.3: The weight ratio of (PVDF-HFP) – KI electrolytes**(ii) (PVDF-HFP)-KI-(EC/PC) Electrolytes**

To prepare a plasticized polymer electrolyte films, the composition of the highest conducting (PVDF-HFP)-KI electrolyte was kept constant, but its weight percentage was varied to accommodate up to 60 wt.% EC/PC (of equal weights) plasticizer mixture in solution. Table 3.4 summarizes the (polymer+salt): plasticizer weight ratios. Both polymer-salt and polymer-salt-plasticizer films were kept in a desiccator for further drying before characterization. The polymer-salt and plasticized polymer-salt films were characterized using FTIR, XRD and EIS.

Table 3.4 The weight ratio of (PVDF-HFP + KI) – EC/PC electrolytes

3.3.3 Preparation of (PVDF-HFP)-(KI+TBAI)-(EC/PC) Double Salt System

A double salt system containing KI and tetrabutylammonium iodide (TBAI) was also prepared for the fabrication of DSSC to study the mixed-cation effect on the DSSC efficiency. The highest conducting KI based system having composition of 40 wt.% (PVDF-HFP) - 10 wt.% KI - 50 wt.% (EC/PC) was chosen for modification. As seen from Table 3.4, this composition with designation PK5, contained 1.00 g (PVDF-HFP), 0.2500 g KI and 1.2500 g (EC/PC). For double salt electrolytes, the 10 wt.% of KI was replaced with a mixture of KI and TBAI in the weight ratio of KI:TBAI at 2:8, 4:6, 6:4, 8:2 and 10:0. Table 3.5 summarized compositions of the electrolytes containing double salt. For DSSC fabrication, the composition of electrolyte with iodine becomes 40 wt.% (PVDF-HFP) - 10 wt.% (KI+TBAI) - 50 wt.% (EC/PC) – 1 wt.% I₂.

Table 3.5: The compositions of (PVDF-HFP) – (KI+TBAI) – (EC/PC) electrolytes

3.4 Preparation of Dye Materials

Four type of dye systems were used in this study. These include one synthetic dye, chlorophyll, anthocyanin and an anthocyanin-chlorophyll dye mixture. Chlorophyll dye was extracted from fragrant screwpine (*Pandanus amaryllifolius*) or locally known as *pandan* leaves. Anthocyanin dye from black rice. The synthetic dye used was a Rhutenizer 535 N3 dye solution. Fig. 3.3 and 3.4 (a) to (c) show the *Pandanus Amaryllifolius* (*Pandan*) tree and the preparation steps for the extraction of chlorophyll dye from the *Pandan* leaves. 50 g fresh *pandan* leaves were cleaned with distilled water and rinsed with ethanol. The leaves were cut into small pieces and immersed in 50 ml ethanol. Black rice dye solution was prepared by immersing 100 g black rice immersed in 100 ml ethanol. The mixed dye was prepared by mixing equal volumes of anthocyanin and chlorophyll dyes. All solutions were kept for 24 hours in the dark before filtration to remove residues. To obtain a 0.003 M N3 dye, 10 mg Ruthenizer 535 N3 dye powder was diluted in 5 ml ethanol and kept for 24 hours in the dark before use.

Fig. 3.3: A *Pandanus amaryllifolius* (*pandan* leaves) tree

Fig. 3.4: Preparation steps of chlorophyll dye from *pandan* leaves

3.5 Preparation of Electrodes

Fluorine-doped tin oxide (FTO) glass was used as a substrate for both working and counter electrodes in this study. To prepare the working electrode or photoanode, TiO₂ paste was doctor bladed on the FTO surface (Ren et al., 2002; Saikia et al., 2008 and Sima et al., 2010). Prior to this, the FTO glass was thoroughly cleaned and spin-coated with diisopropoxytitanium bis(acetylacetonate) at 3000 rpm for 10 s and sintered at 450 °C for 30 min to form a good thin TiO₂ compact layer. The compact layer can improve adhesion of TiO₂ on the FTO glass and to provide a larger TiO₂/FTO contact area (Yu et al., 2009). This compact layer also minimizes contact between the redox electrolyte and the conductive FTO surface. This is necessary to prevent electron recombination in the DSSC and hence improve efficiency (Kovash et al., 2012). The TiO₂ layers were sintered at 450 °C for 30 min after each process. The prepared TiO₂ electrode was immersed in each dye solution and left for 24 hours in the dark to allow the dye to attach to the TiO₂ surface. The TiO₂/dye photoelectrode was washed in ethanol and dried before assembling the DSSC. The counter electrode was prepared by spin coating a platinum (Pt) solution (chloroplatinic acid diluted to 0.005 M in 2-propanol) on the conducting surface of a

cleaned FTO glass and sintered at 450 °C for 30 min to form a thin layer of Pt (Lee et al., 2010).

3.6 Preparation of DSSCs

The DSSCs were assembled by sandwiching the highest conducting electrolyte (with around 10 wt.% I₂ crystals added) between a photoelectrode with 0.16 cm² working area and a counter electrode of Pt-coated FTO glass. They were fixed with binder clips as shown in Fig. 3.5. I₂ was added so that an I⁻/I₃⁻ mediator will form in the electrolyte. The I⁻/I₃⁻ redox couple is needed for the operation of a DSSC as discussed in Chapter 2.

Fig. 3.5 Fabricated DSSC

3.7 Sample Characterization Techniques

3.7.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra for polymer electrolytes were obtained using the FTIR-Spectrophotometer (Thermo Scientific/ Nicolet iS10) over the range 650 – 4000 cm⁻¹. Spectrophotometer resolution was 4 cm⁻¹. The FTIR equipment used is shown in Fig. 3.6.

Fig. 3.6: FTIR machine

FTIR spectroscopy was carried out to investigate the interactions between polymer, salt and plasticizer and the complexation between these components in the polymer electrolytes (Huang et al., 2013). On addition of the salt into the polymer host, the cation of the metal is expected to coordinate with the polar groups in the host polymer matrix resulting in complex formation. This type of interaction will influence the local structure of the polymer backbone and certain infrared active modes of vibration will be affected. In this context, the infrared spectroscopic studies will give the evidence of the complexation (Hema et al., 2009).

FTIR can also be used to analyse the interactions among ions in the systems. These interactions can induce changes in the vibrational modes of the molecules in the polymer electrolyte (Selvasekarapandian et al., 2005). The presence of free ions, ion pairing and ion aggregates can also be studied by FTIR spectroscopy technique (Kumar et al., 2005).

3.7.2 X-ray Diffraction (XRD)

The Siemens D5000 X-ray diffractometer with operating voltage and current of 40 kV and 40 mA respectively was used to identify the crystallinity and amorphousness of the

samples. X-rays of 1.5406\AA wavelength were generated by a Cu $K\alpha$ source and the 2θ angle was varied from 5° to 55° . The XRD machine used is shown in Fig. 3.7. In this method, test samples were adhered onto microscope slides and placed in the chamber around which a detector is moved. An X-ray diffractometer illuminates the sample with X-rays ($\lambda=1.5406\text{\AA}$), and the sample and detector are moved in order to measure the intensity of the diffracted radiation as a function of beam and sample orientation.

Fig. 3.7: XRD machine

Interaction of X-rays with sample creates diffracted beams of X-rays related to interplanar spacings in the crystalline sample according to Bragg's Law:

$$2d \sin\theta = n\lambda \quad (3.1)$$

Here, n is the order of reflection, λ is the wavelength of the X-rays, d is the interplanar spacing generating the diffraction and θ is the Bragg angle. The plot of the intensities along the vertical axis against the angles (2θ) along the horizontal axis of diffractions recorded by the detector gives the XRD pattern of the sample. In order to quantify the amorphousness or crystallinity of the electrolytes, the diffractograms were deconvoluted using the Origin 8.0 software. The degree of crystallinity (X_C) was calculated using the equation (Hodge et. al, 1996)

$$X_C = (I_C/I_T) \times 100\% \quad (3.2)$$

Here, I_C is area of crystalline peak and I_T is total area of deconvoluted peaks.

3.7.3 Electrochemical Impedance Spectroscopy (EIS)

The impedance of the samples was measured using the HIOKI 3531-01 LCR Hi-Tester interfaced to a computer with frequency ranging from 50 Hz to 1 MHz at room temperature. Each sample was sandwiched between two stainless steel electrodes and clamped to ensure sufficient contact. The sample area was fixed at 2.0 cm². The sample thickness varies from 0.04 to 0.20 mm and is measured after assembling the cell. The conductivity was calculated using the equation:

$$\sigma = \frac{l}{R_B A} \quad (3.3)$$

R_B is the bulk resistance taken at the intersection of the Nyquist plot with the real impedance axis, A is the surface area of the electrode/electrolyte contact and l the thickness of the sample. To the polymer-salt composition giving the highest room temperature conductivity, equal amounts by weight of EC and PC were added to enhance

the conductivity and similar impedance measurements were carried out on the plasticized samples. The impedance analyzer was interfaced to a computer. The imaginary impedance (Z'') versus real impedance (Z') were plotted as a function of frequency with the vertical and horizontal axes having the same scales. This plot is known as the Nyquist plot. A typical plot for polymer electrolyte is as shown in Fig. 3.8. The bulk resistance (R_B) can be determined from this plot by taking the intercept value of the plot on the real axis.

Fig. 3.8 : A typical cole-cole or Nyquist plot for a polymer electrolyte and the R_B value

3.8 Dye Characterizations

The absorption spectra of four different dyes (N3, chlorophyll, anthocyanin and chlorophyll-anthocyanin mixture) were taken with Shimadzu UV-1650PC UV-vis spectrophotometer. The absorption spectra of solutions were recorded at room temperature for each dye sample in the range from 400 to 800 nm.

3.9 DSSCs Characterization

After the fabrication of the DSSCs using the highest conducting plasticized PVDF-HFP/NaI and PVDF-HFP/KI electrolytes with different dyes, the performance of each DSSC was tested under one sun illumination (AM1.5, 100 mW cm^{-2}). The performance parameters such as short-circuit current density (J_{SC}), open-circuit voltage (V_{OC}), field factor (FF) and the solar cell efficiency were evaluated. The solar cells were also tested under the lower light intensities varying between 30 mW cm^{-2} to 100 mW cm^{-2} . The photocurrent–voltage (I – V) characteristics of the DSSCs were measured using a Keithley 2400 source meter. The *fill factor* (FF) was calculated using the equation

$$FF = \frac{I_{\max} V_{\max}}{I_{SC} V_{OC}} \quad (3.4)$$

where I_{\max} and V_{\max} are the maximum output value of current and voltage respectively, and I_{SC} and V_{OC} are the short-circuit current and open-circuit voltage respectively. The total energy conversion efficiency was calculated using the equation:

$$\eta = \frac{I_{SC} V_{OC} \times FF}{P_{in}} \quad (3.5)$$

where P_{in} is the power of incident light. The I-V curve of a typical solar cell is shown in Fig. 3.9.

Fig. 3.9 I-V characteristic of a typical solar cell

In the I-V curve, V_{oc} is the open circuit voltage, I_{sc} is the short circuit current, I_m and V_m are the maximum cell current and voltage respectively. The maximum power point, P_m is

$$P_m = I_m \times V_m \quad (3.6)$$

Results obtained using these techniques are presented in the following chapters.

3.10 Summary

This chapter presents the preparation methods of (PVDF-HFP)-salt and plasticized (PVDF-HFP)-salt polymer electrolytes. The electrolytes were characterized using Fourier transform infrared (FTIR), X-ray diffraction (XRD) and electrochemical impedance spectroscopy (EIS). The highest conducting electrolyte from KI and NaI salt systems with added iodine were used as redox mediator in the dye sensitized solar cells (DSSCs). The preparation and characterization of the DSSCs have been described in this chapter.