

CHAPTER 3

EXPERIMENTAL METHODS

3.1 INTRODUCTION

In the present work, chitosan was used as polymer host for the electrolyte. PVA and PEO were used as co-hosts. Four systems were prepared i.e. chitosan-salt, chitosan-PVA-salt, chitosan-PEO-salt and chitosan-salt-IL systems. All polymer electrolytes have been prepared by the solution cast technique. Ammonium iodide (NH_4I) was used as the doping salt and 1-butyl-3-methylimidazolium iodide (BMII) ionic liquid (IL) was prepared to provide the extra charge carriers as well as to act as a plasticizer. The polymer electrolytes were characterized using several techniques including fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS) and transference number measurements. The highest conducting electrolyte from the four systems was used as polymer electrolyte in the fabrication of TiO_2 dye-sensitized solar cells (DSSC).

3.2 ELECTROLYTE PREPARATION

3.2.1 Polymer-salt electrolytes

To prepare polymer-salt electrolyte, 0.5 g chitosan (Fluka) was dissolved in 50 ml 1% acetic acid solution. To this solution, 5 to 50 wt.% ammonium iodide (NH_4I) were added separately and the mixtures continuously stirred until complete dissolution. The solutions were cast into different Petri dish and left to dry (room condition) for films to form. The films were kept in a dessicator for further drying before

characterization. Table 3.1 summarizes the compositions of the prepared polymer-salt systems.

Table 3.1: The ratio content of chitosan-salt electrolytes

Designation	Chitosan		Ammonium Iodide (NH ₄ I)	
	(g)	(wt.%)	(g)	(wt.%)
Ch0	0.5	100	0	0
Ch1	0.5	95	0.026	5
Ch2	0.5	90	0.053	10
Ch3	0.5	85	0.088	15
Ch4	0.5	80	0.125	20
Ch5	0.5	75	0.166	25
Ch6	0.5	70	0.214	30
Ch7	0.5	65	0.269	35
Ch8	0.5	60	0.333	40
Ch9	0.5	55	0.409	45
Ch10	0.5	50	0.500	50

3.2.2 Polymer blend-salt electrolytes

To prepare the polymer blend-salt system, poly(vinyl alcohol) (PVA) and poly(ethylene oxide) (PEO) were blended with chitosan. Chitosan:PVA and chitosan:PEO weight ratios of 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70 and 20:80, respectively were blended in 50 ml dilute acetic acid. The mixture was stirred for 24 h at room temperature. After the polymers have dissolved in the dilute acetic acid, 45 wt.% of ammonium iodide (NH₄I) were added to the solution and the mixtures were again continuously stirred until complete dissolution. The total mass of chitosan and

PVA was 0.5 g and that of salt was 0.409 g. Tables 3.2 and 3.3 summarize the contents of the prepared polymer blend-salt systems.

Table 3.2: The compositions of chitosan-PVA blend electrolytes

Designation	Polymer				Ammonium Iodide (NH ₄ I)	
	Chitosan		PVA		(g)	(wt.%)
	(g)	(wt.%)	(g)	(wt.%)		
CV1	0.45	49.5	0.05	5.5	0.409	45
CV2	0.40	44.0	0.10	11.0	0.409	45
CV3	0.35	38.5	0.15	16.5	0.409	45
CV4	0.30	33.0	0.20	22.0	0.409	45
CV5	0.25	27.5	0.25	27.5	0.409	45
CV6	0.20	22.0	0.30	33.0	0.409	45
CV7	0.15	16.5	0.35	38.5	0.409	45
CV8	0.10	11.0	0.40	44.0	0.409	45

Table 3.3: The compositions of chitosan-PEO blend electrolytes

Designation	Polymer				Ammonium Iodide (NH ₄ I)	
	Chitosan		PEO		(g)	(wt.%)
	(g)	(wt.%)	(g)	(wt.%)		
CEO1	0.45	49.5	0.05	5.5	0.409	45
CEO2	0.40	44.0	0.10	11.0	0.409	45
CEO3	0.35	38.5	0.15	16.5	0.409	45
CEO4	0.30	33.0	0.20	22.0	0.409	45
CEO5	0.25	27.5	0.25	27.5	0.409	45
CEO6	0.20	22.0	0.30	33.0	0.409	45
CEO7	0.15	16.5	0.35	38.5	0.409	45

3.2.3 Preparation of BMII

13.96 g 1-Methylimidazolium was added in 45 ml cyclohexane. 31.28 g butyliodide was added drop wise at 333 K to 343 K during 1 hour. The solution was stirred vigorously for 24 hour. Cyclohexane was distilled off using rotary evaporator. The 1-butyl-3-methylimidazolium iodide (BMII) was washed using n-hexane for 3 times and dried under vacuum at 318 K for 5 hour.

3.2.4 Polymer-salt-IL electrolytes

To prepare the polymer-salt-IL electrolyte, 0.5 g chitosan (Fluka) was dissolved in 50 ml 1% acetic acid solution. To this solution, 0.409 g NH_4I was added and the mixtures were continuously stirred until complete dissolution. Different amounts of 1-Butyl-3-methylimidazolium iodide (BMII) ionic liquid (IL) were added separately to the solutions. The solutions were cast in different Petri dish and left to dry for films to form. Table 3.4 summarizes the ratio content of the prepared polymer-salt-IL systems. Only up to 50 wt.% IL has been incorporated into the polymer electrolyte in order that the material prepared is not a polymer-salt complex in an IL system.

Table 3.4: The compositions of chitosan- NH_4I -BMII electrolytes

Designation	Chitosan		Ammonium Iodide (NH_4I)		BMII	
	(g)	(wt.%)	(g)	(wt.%)	(g)	(wt.%)
CIL1	0.5	49.5	0.409	40.5	0.101	10
CIL2	0.5	44.0	0.409	36.0	0.227	20
CIL3	0.5	38.5	0.409	31.5	0.39	30
CIL4	0.5	33.0	0.409	27.0	0.606	40
CIL5	0.5	27.5	0.409	22.5	0.909	50

3.3 X-RAY DIFFRACTION (XRD)

XRD analysis was used to identify the nature of the polymer electrolytes whether crystalline or amorphous. This experiment was carried out by applying an X-ray beam with wavelength λ at different θ angles on the sample. The diffraction only occurs when the distance traveled by the rays are reflected from successive planes.

Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material. The peaks in an X-ray diffraction pattern are directly related to the atomic distances. The condition for diffraction to occur can be simply written as

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

which is known as Bragg's law. Here, d is the interplanar spacing, θ is the Bragg angle, n is the order of reflection and λ is the wavelength of x-rays. In this study, the crystallinity/amorphousness of the polymer electrolytes was determined using an X-ray diffractometer (Siemens D5000) with operating voltage and current of 40 kV and 40 mA, respectively. The X-ray wavelength is 1.5406 Å.

An example of x-ray diffractogram for polymer-salt system is depicted in Figure 3.1. Selvasekarapandian *et al.* (2010) reported that 80PVA:20NH₄NO₃ electrolyte in the PVA:NH₄NO₃ system that they studied is the most amorphous film and exhibits the highest conductivity. Figures 3.2 and 3.3 shows the XRD patterns for polymer blend-salt and polymer blend-salt-plasticizer systems, respectively.

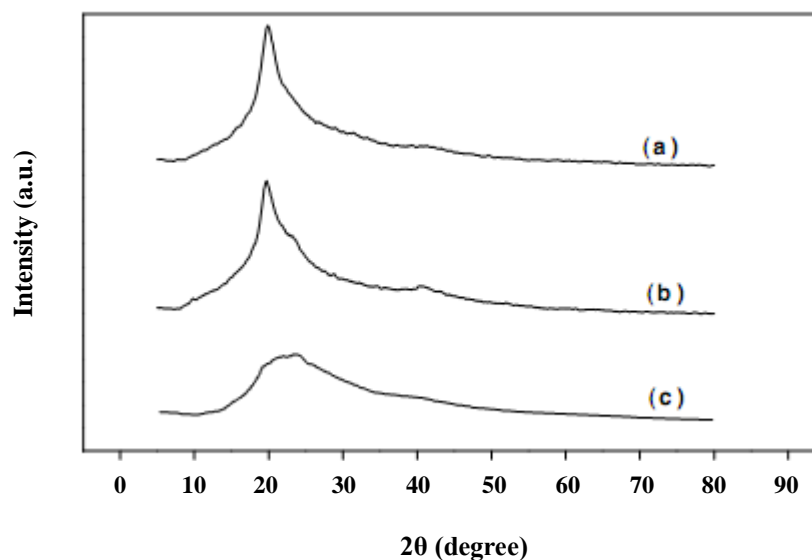


Figure 3.1: XRD patterns of (a) pure PVA (b) 90 PVA:10 NH₄NO₃ and (c) 80 PVA:20 NH₄NO₃ [Selvasekarapandian *et al.*, 2010]

From Shuhaimi and co-workers' work (2008), chitosan- κ -carrageenan-ammonium nitrate (CCPAAN) system is the most amorphous sample. Rajendran and Bama (2010) observed that all plasticized PVAc-PMMA-LiClO₄ electrolytes are amorphous in nature as shown in Figure 3.3 (d-g) but EC plasticized system is the most amorphous with highest conductivity value.

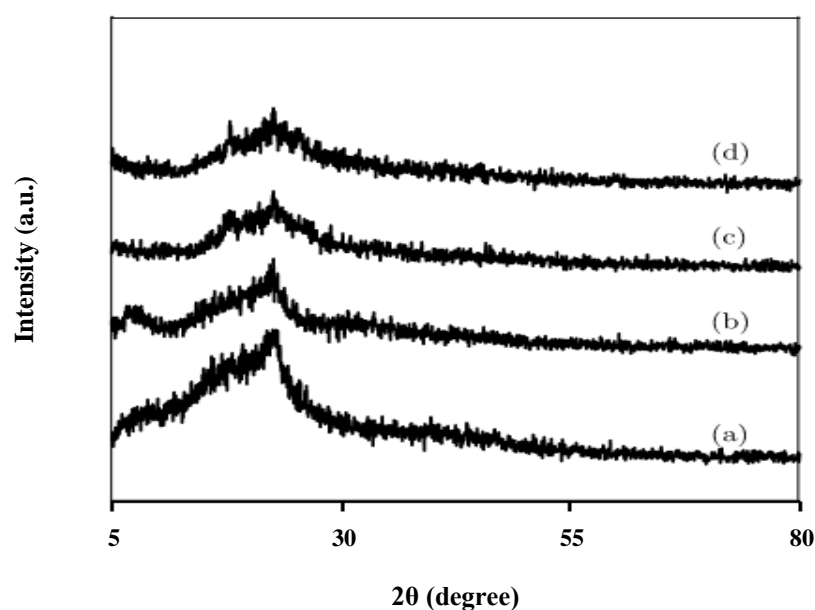


Figure 3.2: XRD patterns of (a) pure chitosan, (b) pure carrageenan, (c) 0.5 g chitosan+0.5 g κ -carrageenan (CCPA) film and (d) 0.5 g chitosan+0.5 g κ -carrageenan + 0.1765 g ammonium nitrate (CCPAAN) [Shuhaimi *et al.*, 2008]

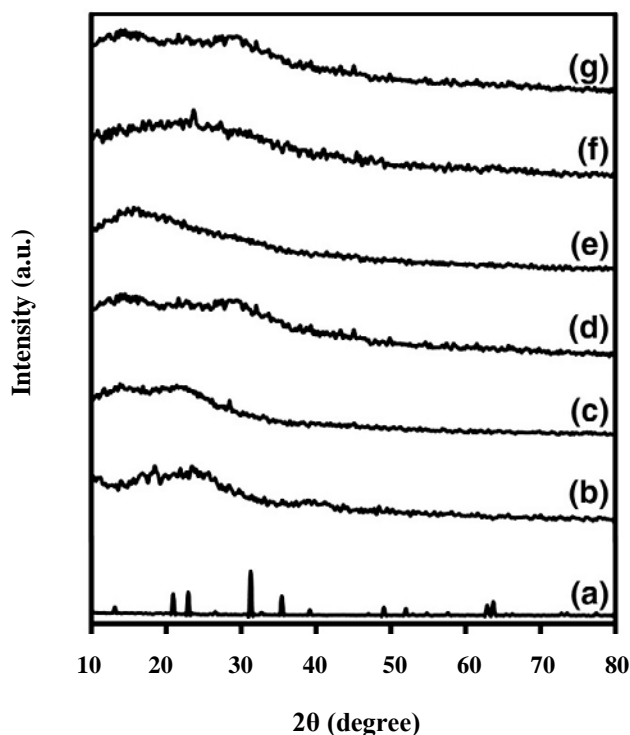


Figure 3.3: X-ray diffraction patterns of (a) LiClO_4 , (b) pure PMMA, (c) pure PVAc, (d) PVAc(6.5)–PMMA(18.5)– LiClO_4 (8)–PC(67), (e) PVAc(6.5)–PMMA(18.5)– LiClO_4 (8)–EC(67), (f) PVAc(6.5)–PMMA(18.5)– LiClO_4 (8)–MC(67), (g) PVAc(6.5)–PMMA(18.5)– LiClO_4 (8)–DEC(67)
[Rajendran and Bama, 2010]

3.4 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

FTIR spectroscopy is an analytical technique that provides information about the functional groups and chemical bonds in materials through the vibrational state of the functional group. The technique is based on the fact that different bonds and groups of bonds vibrate at characteristic frequencies.

In this work, FTIR characterization was done to investigate the polymer-salt interaction, polymer-polymer interaction and polymer-salt-IL interaction. Infrared (IR) spectra exhibited in this work were obtained using FTIR-Spectrophotometer (Thermo Scientific/Nicolet iS10) in the wavenumber region between 4000 and 650 cm^{-1} . The resolution is 2 cm^{-1} .

Figures 3.4 and 3.5 show two sets of FTIR spectra for polymer electrolyte systems. According to Arof *et al.* [2010], complexation between iota-carrageenan and doping salt is expected to occur at wavenumbers between 1240 to 1260 cm^{-1} for O=S of sulfate esters band and at wavenumbers 1070 and 930 cm^{-1} for C–O of 3,6-anhydrogalactose band. Yahya and co-authors [2002] observed that the amine band shifts to lower wavenumbers and thus indicates that complexation has taken place between the cation of lithium acetate salt and the nitrogen atom of the amine group in chitosan.

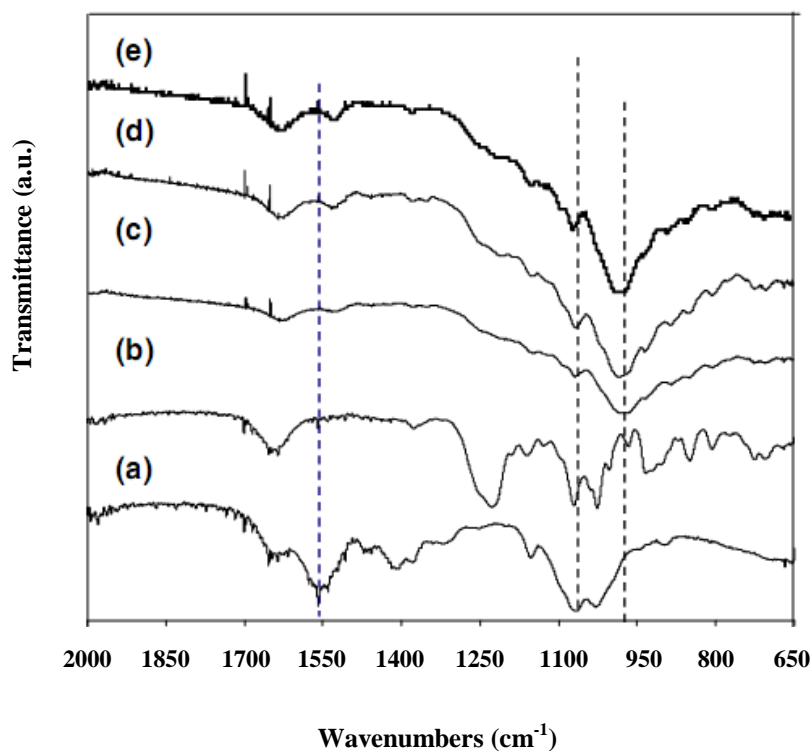


Figure 3.4: FTIR spectra of (a) chitosan, (b) iota-carrageenan, (c) 37.50 wt.% chitosan–37.50 wt.% iota-carrageenan–12.50 wt.% H_3PO_4 –12.50 wt.% PEG, (d) 37.50 wt.% chitosan–37.50 wt.% iota-carrageenan–6.25 wt.% H_3PO_4 –18.75 wt.% PEG, and (e) 37.50 wt.% chitosan–37.50 wt.% iota-carrageenan–18.75 wt.% H_3PO_4 –6.25 wt.% PEG in wavenumber range of 2000–650 cm^{-1} [Arof *et al.*, 2010]

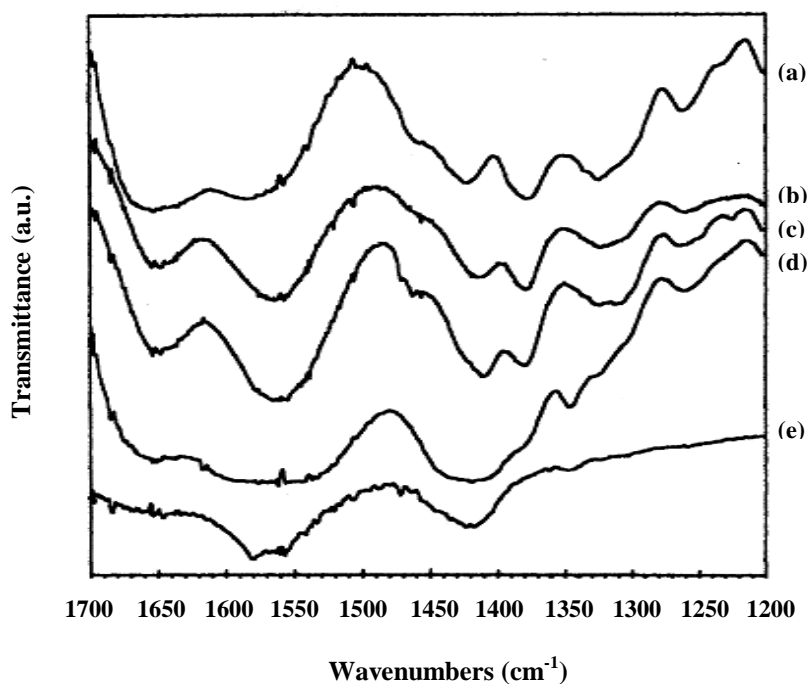


Figure 3.5: FTIR spectra of (a) pure chitosan (b) chitosan acetate (c) chitosan acetate+palmitic acid (d) chitosan acetate+lithium acetate (e) chitosan acetate+lithium acetate+palmitic acid [Yahya *et al.*, 2002]

3.5 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Polymer electrolyte films were cut into small discs of 2 cm diameter and were sandwiched between two stainless steel electrodes of a conductivity cell. The electrodes and electrolyte were held under spring pressure. The impedance of the polymer electrolyte was measured by complex impedance technique in the frequency range between 50 Hz to 1 MHz using the Hioki 3531 Z Hi Tester that was interfaced to a computer. The conductivity of the electrolyte can be calculated from the equation.

$$\sigma = \frac{t}{R_b A} \quad (3.2)$$

Here, A is the electrode-electrolyte contact area and t is thickness of the film. R_b is the bulk resistance of the material which can be obtained from the intersection of complex impedance plot with the real impedance axis.

In impedance spectroscopy measurements were carried out by applying an alternating voltage, in a wide range of frequencies across to the samples. The applied voltage (V) is defined as

$$V(t) = V_0 \sin(\omega t) \quad (3.3)$$

where V_0 is the voltage amplitude and $\omega = 2\pi f$, where f is frequency. The resulting electric current (I) through the sample is given by:

$$I(t) = I_0 \sin(\omega t + \varphi) \quad (3.4)$$

where I_0 is the current amplitude and φ is the phase angle between the applied voltage and the resultant current. The electrical impedance, $Z(\omega)$ is defined as

$$Z(\omega) = \frac{V(t)}{I(t)} \quad (3.5)$$

and can be expressed as

$$Z(\omega) = Z' + jZ'' \quad (3.6)$$

where Z' is the real part of the electrical impedance and Z'' is its imaginary part. The real and imaginary parts of the complex impedance can be defined as

$$Z' = Z \cos \theta \quad (3.7)$$

$$Z'' = Z \sin \theta \quad (3.8)$$

Analysis of the impedance experimental data can be carried out by plotting the impedance imaginary part ($-Z''$) against the real part (Z') in a diagram called a Nyquist plot or Cole-Cole plot. Figure 3.6 shows the Cole-Cole plot of PCL-NH₄SCN

electrolyte. The semi-circle at high frequency is related to relaxation process in bulk polymer electrolyte and the spike at low frequency is due to polarization effect.

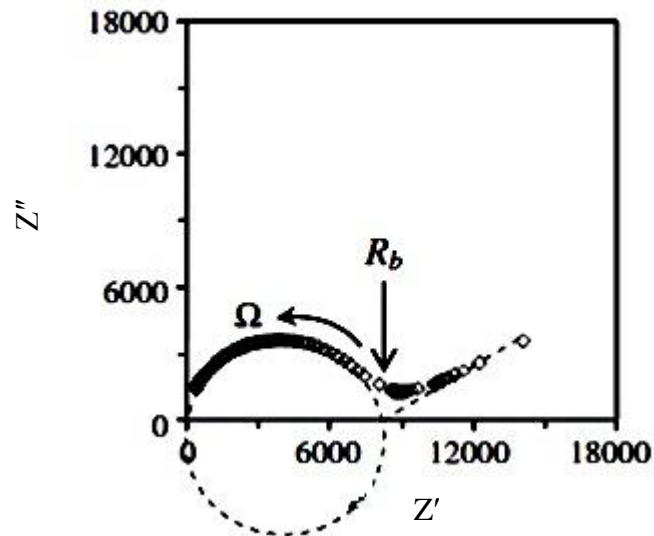


Figure 3.6: Cole-Cole plot of poly(ϵ -caprolactone) (PCL) incorporated with 5 wt.% ammonium thiocyanate (NH_4SCN) at room temperature [Woo *et al.*, 2011]

The Cole-Cole plot can be representing by the equivalent circuit as shown in Figure 3.7. The depression of semi-circle can be modeled as a parallel resistor and constant phase elements (CPE) and the spike also can be represented by another CPE.

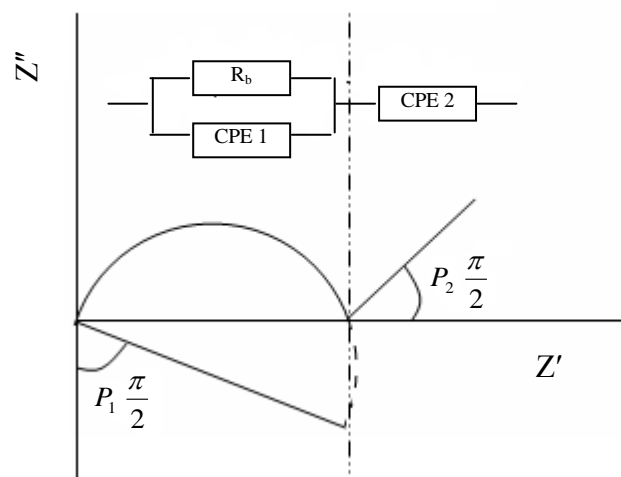


Figure 3.7: Impedance plot and its equivalent circuit

The impedance of CPE is given by [Linford, 1988]:

$$Z_{CPE} = 1/k(j\omega)^p \quad \text{where } 0 \leq p \leq 1 \quad (3.9)$$

Or

$$Z_{CPE} = k[\cos(p\pi/2) - j\sin(p\pi/2)]/\omega^p \quad (3.10)$$

Here k^{-1} corresponds to the capacitance value of the CPE element, ω is angular frequency ($\omega = 2\pi f$ where f is frequency) and p is related to the deviation from the vertical axis in the Z'' versus Z' plot.

Other related functions such as complex permittivity $\varepsilon(\omega)$ can be expressed by

$$\varepsilon(\omega) = \varepsilon' + j\varepsilon'' \quad (3.11)$$

Here ε' is the real part of complex permittivity and ε'' is the imaginary part.

The real and imaginary parts of the complex permittivity is given by

$$\varepsilon' = \frac{Z''}{\omega C_0(Z'^2 + Z''^2)} \quad (3.12)$$

$$\varepsilon'' = \frac{Z'}{\omega C_0(Z'^2 + Z''^2)} \quad (3.13)$$

Here, $C_0 = \varepsilon_0 A/t$ where ε_0 , A and t is permittivity of space, area and thickness of the electrolyte, respectively.

3.6 TRANSFERENCE NUMBER MEASUREMENTS

The materials prepared in this research are polymer electrolytes. Therefore, they must be ionic conductors. To prove this, several techniques can be used and amongst them is the measurement of transference number. Transference number was performed using Wagner's polarization technique [Mohan *et al.*, 2005]. This technique has been carried out by supplying a fixed dc voltage (1 V) and the polarization current generated was recorded as a function of time. Hence, transference numbers (t_{ion} and t_e) were evaluated. To determine t_{ion} and t_e an electrochemical cell with the configuration SS/polymer electrolyte/SS was fabricated. Stainless steel (SS) was used as blocking electrodes. The transference number can be calculated from the equation below:

$$t_{ion} + t_e = 1 \quad (3.14)$$

$$t_e = \frac{I_s}{I_0} \quad (3.15)$$

where t_{ion} and t_e are ionic and electronic transference number, respectively. I_0 is the initial current due to the movement of ions and electrons in the applied electric field whereas I_s is steady state electron current. Figure 3.8 shows the polarization current as a function of time for PEO+NaBiF₄ electrolyte system. It has been reported that the ionic and electronic transference numbers estimated from the polarization curves for the three systems are $t_{ion} = \sim 0.9$ and $t_e = \sim 0.1$, respectively [Mohan *et al.*, 2005]. This suggests that charge transport in the polymer electrolyte is dominated by ions.

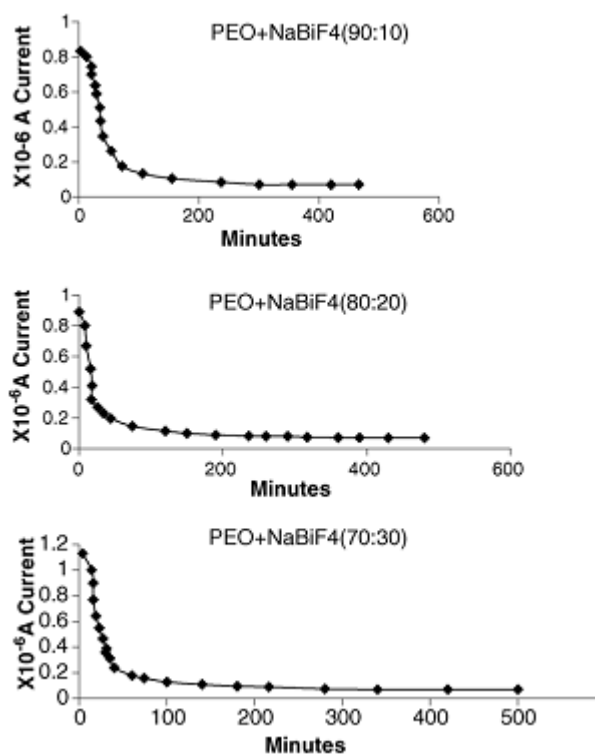


Figure 3.8: Polarization current versus time graph of PEO+NaBiF₄ (90:10), PEO+NaBiF₄ (80:20) and PEO+NaBiF₄ (70:30) [Mohan *et al.*, 2005]

3.7 DYE PREPARATION

The natural colorant containing anthocyanin was extracted from black rice, blueberry fruits and red cabbage, respectively. The black rice, blueberries and red cabbage were immersed in 95 % ethanol solution and kept at room temperature without exposing to direct sunlight for 24 hours. The residues were removed by filtration and the pH of the dye was adjusted accordingly. The absorption characteristics of the anthocyanin containing natural colorant in the range 400 to 800 nm were determined using a Shimadzu PC3101 UV-Vis NIR spectrophotometer.

3.8 PREPARATION OF THE TiO₂/DYE ELECTRODE

An indium tin-oxide (ITO) glass ($2.5 \times 2.5 \text{ cm}^2$) with sheet resistance of $5 \Omega \text{ cm}^{-2}$ was cleaned with distilled water and acetone. A part of the ITO layer was covered and the active area of the ITO layer is about 0.16 cm^2 . Diisopropoxytitanium bis(acetylacetonate) (0.38 M) was coated on indium tin-oxide (ITO) glass as a blocking layer and heated at 723 K for 30 minutes. After that, TiO₂ paste (JGC Catalysts & Chemicals Ltd) was coated on the blocking layer using the doctor-blade method and the thickness of the layer was controlled using adhesive tape of thickness 100 μm . The TiO₂ layer was then heated at 773 K for 1 hour. When the temperature of the TiO₂ electrodes reached 373 K on cooling, they were immersed in the anthocyanin dye solution for 24 hours and the ITO sheet resistance is now $11 \Omega \text{ cm}^{-2}$. The white TiO₂ paste will change color when the dye is absorbed. The TiO₂ paste was then washed with water to remove impurities and then with ethanol to remove trapped water from the initial washing.

3.9 PREPARATION OF PLATINUM (Pt) ELECTRODE

To prepare platinum catalyst coated on ITO glass substrate, 5 mmol L^{-1} hexachloroplatinic acid solution in isopropanol was spread on the ITO conducting surface. The Pt coated ITO counter electrode was then heated in furnace at 723 K for 30 minutes.

3.10 FABRICATION OF NATURAL COLORANT SENSITIZED SOLAR CELLS (NCSSC)

Natural colorant sensitized solar cells (NCSSCs) with active area are about 0.16 cm^2 were fabricated by sandwiching the prepared electrolyte between the TiO₂/dye photoelectrode and Pt counter electrode. The schematic diagram of DSSC is displayed

in Figure 3.9. For redox couple formation in the NCSSC, 0.04 g of iodine crystals were added into the electrolyte.

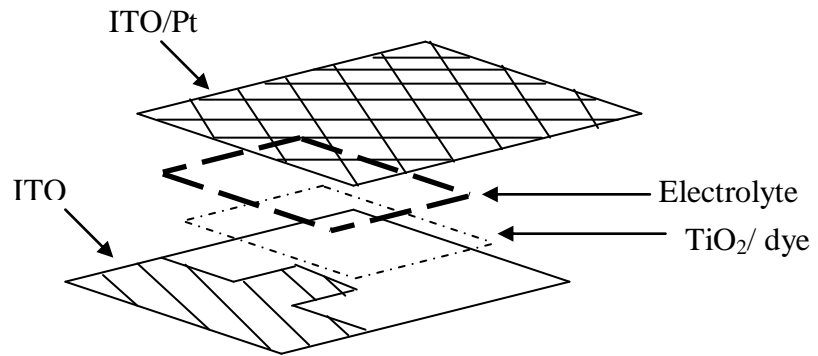


Figure 3.9: Diagram of DSSC cell

The J - V characteristics of the dye-sensitized solar cells were obtained under white light illumination (100 mW cm^{-2}) using the Keithley 2400 electrometer. The fill factor (ff) was calculated using the following equation:

$$ff = \frac{V_{\max} \times J_{\max}}{V_{oc} \times J_{sc}} \quad (3.16)$$

where J_{sc} is the short-circuit current density (mA cm^{-2}), V_{oc} is the open-circuit voltage (V), and J_{\max} (mA cm^{-2}) and V_{\max} (V) are the current density and voltage in the J - V curves, respectively, at the point of maximum power output. The external light to electricity conversion efficiency, η was obtained from the following relationship:

$$\eta (\%) = \frac{V_{oc} \cdot J_{sc} \cdot ff}{P_{in}} \times 100 \% \quad (3.17)$$

Here P_{in} is the incident light power.

3.11 SUMMARY

Although the ultimate aim is to fabricate and study solar cells, one of the important components that need to be prepared is the electrolyte. Preparation of the electrolyte should be accompanied by characterization. This chapter has presented the characterization methods employed in this study.