Ionic Liquid Electrolytes for Dye-Sensitized Solar Cells

by

Siti Munirah Bt Mhd Yusof

15625

Dissertation submitted in partial fulfilment of

the requirements for the

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32610, Bandar Seri Iskandar,

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr Wan Zaireen Nisa Yahya)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SITI MUNIRAH BT MHD YUSOF

ABSTRACT

This thesis studied the effect of mixing two ionic liquids at different ratios to form binary ionic liquid solvent in the electrolyte on the efficiency of the Dye-Sensitized Solar Cells (DSSCs). 1-Propyl-3-Methylimidazolium Iodide (PMImI) is mixed with 1-Butyl-3-Methylimidazolium Thiocynate(BMmISCN) at four different ratios and the efficiency of the DSSCs is measured. The addition of BMImSCN in PMImI is to overcome the problems faced by pure ionic liquid which are high viscosity and low ion mobility that limits the transportation of iodide/triiodide and the restoration of the oxidized dye. Adding the BMImSCN to the imidazolium iodide ionic liquid can lower the viscosity of the solution and improve the iodide/triiodide diffusion in the electrolyte. The effect of mixing different ratios of these ionic liquids on the viscosity and iodide/triiodide diffusion in the solution is studied. Based on the result obtained from the experimental work, the addition of low viscosity ionic liquid which is BMImSCN into the high viscosity PMImI reduced the mass transport limitation of triiodide in the electrolyte by lowering the viscosity of the ionic liquid. The ratio 1:0.75 has been identified as the best ratio of binary ionic liquid of PMImI:BMImSCN as it has the highest efficiency among all the electrolyte. This work has provided useful insight for further improvement of binary ionic liquid electrolyte for DSSCs.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Increase in population and rising demand from developing countries are causing the increase of energy requirement worldwide. To meet the requirements, alternative energy resources have been explored such as carbon-fuel based sources, nuclear power and renewable sources such as solar. For carbon-fuel energy sources such as the coal and crude oil, the main criticism against them is the impact on the environment as its use will lead to a substantial increase in atmospheric Carbon Dioxide levels, thus provoking catastrophic climate changes. On the nuclear front, hundreds of gigawatt (GW)- level nuclear power stations required to be built in order to generate power and the viable method to dispose the dangerous radioactive waste is yet to be found (Kalyanasundaram, 2010). The third option which is the solar energy is viewed as very attractive and promising option for several reasons which one of them is the abundant energy source which is the sunlight.

Dye-sensitized solar cells (DSSCs) have been getting the attention from researchers and industry as the potential energy generator. In the beginning, the organic solvents were frequently used as the electrolyte for DSSCs due to its high efficiency in producing energy. However, the high volatility of some organic solvents has raised an issue and people start to focus on the use of ionic liquid as it has good chemical and thermal stability, tuneable viscosity, non-flammable, high ionic conductivity and also low volatility (Wu et al., 2015).

Pure ionic liquids have relatively high viscosity and low ion mobility that limits the transportation of iodide/triiodide and also the restoration of oxidized dye. Therefore, in order to reduce the mass transport limitation in pure ionic liquid, a low-viscosity ionic liquid such as thiocyanate-based IL is mixed together to form binary ionic liquid that has higher efficiency (Wu et al., 2015). However, so far there is no study that indicates the best ratio of the binary ionic liquids that can optimise the DSSCs efficiency.

1.2 Problem Statement

For the past several years, considerable research and industry have been focused on the ionic liquids as the electrolyte for dye-sensitized solar cells to replace the organic solvent that frequently used before. This is because ionic liquids have been identified as a promising alternative stable electrolyte solvent due to their features such as chemical and thermal stability, tuneable viscosity; non-flammable, high ionic conductivity and low vapour pressure (Wu et al., 2015) which suit the DSSCs the best.

However, pure ionic liquid has relatively high viscosity and low ion mobility that limits the transportation of iodide/triiodide and the restoration of oxidized dye. Therefore, binary ionic liquid electrolyte has been introduced to overcome the problem. Low-viscosity ionic liquid is mixed with imidazolium iodide to achieve higher efficiency of DSSCs. In most study, Thiocyanate (SCN)-based ionic liquids is mixed with imidazolium iodide in ratio of 13:7 (Wang et al., 2004) and 12:8 (Cao et al., 2008). There is no study that indicates the best ratio of these ionic liquid that could give high DSSCs efficiency. Therefore, in this project, the ratio of 1-Propyl-3-Methylimidazolium Iodide (PMImI) to 1-Butyl-3-Methylimidazolium Thiocyanate (BMImSCN) that gives the highest DSSCs efficiency is determined.

1.3 Objectives

The main objectives of this project are:

i. To synthesize and characterize the ionic liquid used as the solvent for the electrolyte which is 1-Propyl-3-Methylimidazolium Iodide (PMImI).
ii. To study the effect of mixing PMImI with 1-Butyl-3-Methylimidazolium Thiocyanate (BMImSCN) at different ratios on the DSSCs efficiency.

1.4 Scope of Study

This project focuses on mixing the ionic liquid electrolyte for DSSCs which is 1-Propyl-3-Methylimidazolium Iodide (PMImI) and 1-Butyl-3-Methylimidazolium Thiocyanate(BMImSCN) at four different ratios. PMImI will be synthesized and characterized according to the literature (Kim, Shin, & Lee, 2004) while BMImSCN is readily available in the laboratory. The viscosity and iodide/triiodide diffusion of individual and binary ionic liquid will be measured to study the effect of mixing these ionic liquids on the improvement of iodide/triiodide diffusion. The efficiency of DSSCs that used binary ionic liquid electrolyte at different ratios will be measured and the ratio that gives the best efficiency will be determined.

CHAPTER 2

LITERATURE REVIEW AND THEORIES

2.1 Dye-Sensitized Solar Cells

Solar cells or photovoltaic cells are electrical devices that directly convert sunlight into electricity. As stated by Yu (2012), the solar industry has been the fastest growing renewable energy technology in recent years which supports the chart of World Energy Production produced by Innovative Clean Energy. Therefore, considerable research and industry attention have been paid to dye-sensitized solar cells (DSSCs) with a nanostructured TiO_2 film. DSSCs have become a potential low-cost with reasonably high efficiency compared to the conventional Si and GaAs cell (Satoh et al.).

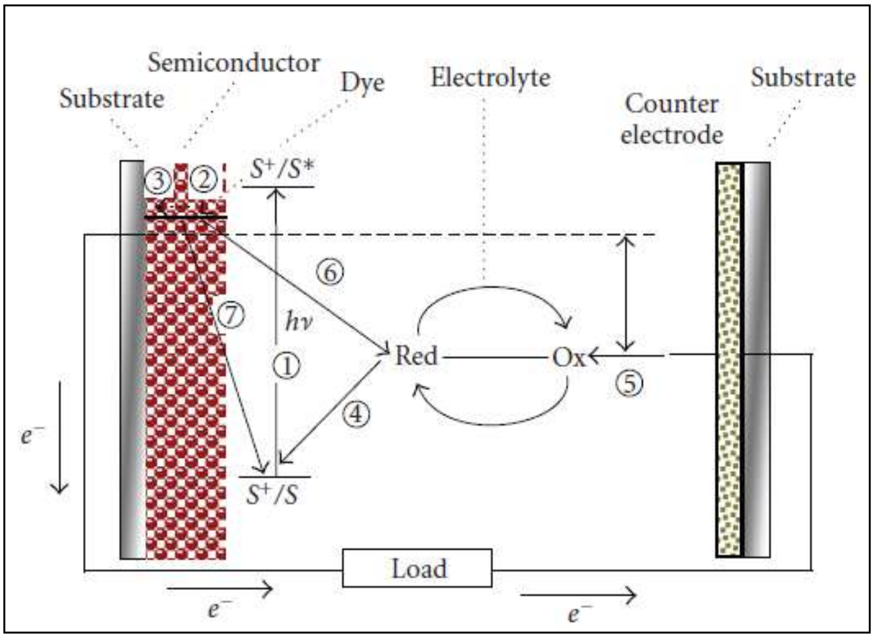


FIGURE 2.1 Principle Operation of DSSCs

Figure 2.1 shows the principle operation of DSSCs. The main components of DSSCs consist of the following:

i. A transparent glass sheet covered with a conductive indium-doped tin oxide (ITO) or fluorine-doped tin oxide (FTO) layer which is used as the anode substrate to allow light to pass through and electron transport.
ii. A mesoporous oxide layer which is TiO_2 deposited on the substrate for electron transportation.
iii. A monomolecular layer of dye adsorbed on the surface of the mesoporous oxide layer to harvest incident sunlight.
iv. An electrolyte containing a redox mediator such as iodide/triiodide couple for the recovery of dye and regeneration of electrolyte itself during operation.
v. A counter electrode (cathode) made of ITO or FTO conductive glass sheet coated with a catalyst such as platinum to catalyze the redox couple regeneration reaction and collect electrons from the external.

In DSSCs, the electricity conversion is based on the injection of electron from the photoexcited state of the sensitized dye into the conduction band of TiO2. The electron from the iodide in the electrolyte is used to regenerate the dye. The iodide is restored by the reduction of triiodide at the cathode. Then, the circuit will then completed via the electron migration through the external load.

2.2 Electrolyte for DSSCs

Liquid electrolyte consists of a redox couple and/or additives dissolved in solvent. It is responsible for the inner charge carrier transport between electrodes (Yu, 2012). It provides the I^- / I_3^-(iodide/triiodide) ions to continuously regenerate the dye and itself during DSSCs operation. The regeneration of dye is as follows:

$$D^+ + I^- \rightarrow [D..I] + I^- \rightarrow D + \mathrm{I}_2^{-\cdot} \rightarrow D + I_3^- + I^- \tag{1}$$

$$I_3^- + e^- \rightarrow I^- + I_2^- \rightarrow 3I^- \tag{2}$$

Equation 1 shows the excited dye (D^+) is reduced by iodide in the electrolyte after the electron injection into TiO_2 under the formation of a complex (D..I). Then the complex dissociates when a second iodide ion comes in. The diiodide radicals react to form triiodide and iodide. Then, the regeneration cycle of electrolytes is completed by the conversion of $I_3{}^-$ to I^- ions on the counter electrode shown by Equation 2.

Good electrolytes must have long-term stabilities, including chemical, thermal, optical, electrochemical and interfacial stability and not cause degradation to the sensitized dye. Other than that, it is essential for the electrolytes to guarantee fast diffusion of charge carriers (high conductivity) for the DSSCs to have high efficiency. For liquid electrolyte, it is important to ensure the solvent of the electrolyte has small leakage and/or evaporation to prevent loss of the liquid electrolyte (Yu, 2012).

2.2.1 Organic Solvent in Electrolytes

Organic solvent is typically used in DSSCs electrolyte. The highest efficiency of using organic solvent electrolytes is about 12 %(Yu, 2012). Various organic solvents have been subsequently been tested such as alcohols, tetrahydrofuran, N-dimethylformamide, propylene carbonate, acetonitrile, water and also glutaronitile. Among these organic solvents, acetonitrile has been shown to be the most efficient organic solvents for DSSCs electrolyte mainly due to its low viscosity (0.34 cp, 25°C) and good solubility to dissolve the organic components and salts in the electrolyte (Yu, 2012) . However, the sealing of volatile organic-solvents based electrolytes in large scale remains an issue in the view of practical application due to their high vapour pressure. The solvent vaporise causing loss of the electrolyte and problem of leakage in the DSSCs.

2.2.2 Ionic Liquid Solvent in Electrolytes

Many studies are conducted to study the use of ionic liquids as electrolytes for DSSCs as replacement of organic solvents. This is due to the concern raised of the high volatility of the organic solvent electrolyte despite of its high efficiency of 12%. Therefore, ionic liquids possessing good chemical and thermal stability, negligible vapour pressure, non-flammability and high ionic conductivity have been intensively pursued as alternative electrolytes for DSSCs (Cao et al., 2008).

Ionic liquid is the combination of anion-cation pairs leading to salts with phase transition at or below room temperature. In DSSCs, it functions as the solvent and/or redox ion source depending on the anion used in the ionic liquid. Figure 2.2 and Figure 2.3 show the common cations and anions used for DSSCs respectively.

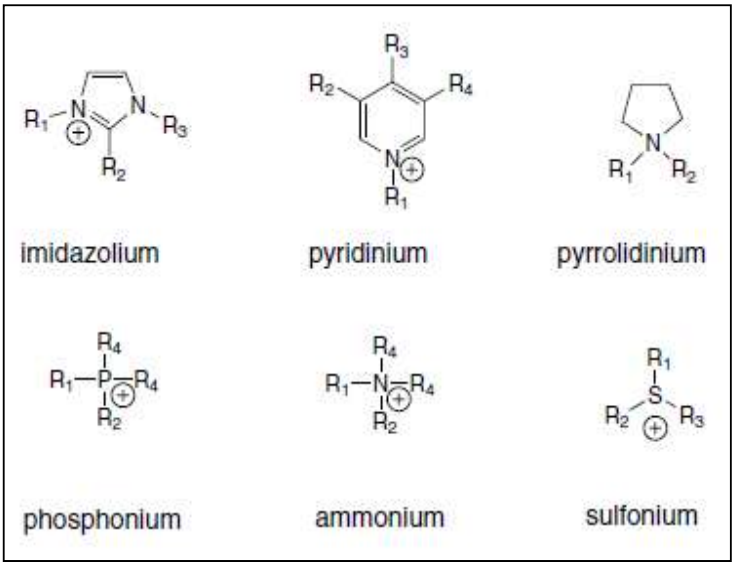


FIGURE 2.2 Common Cations Used for DSSCs

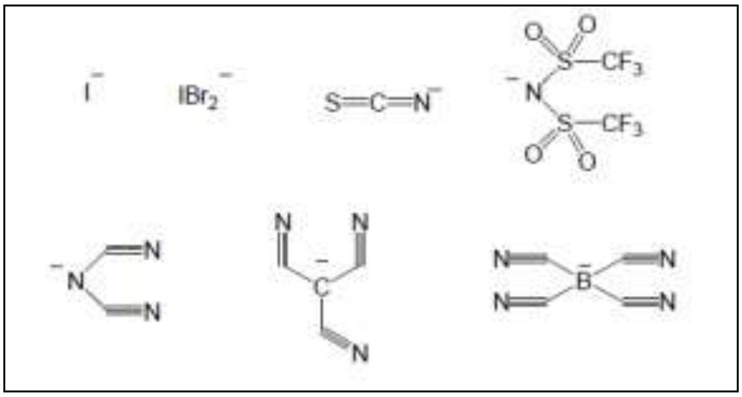


FIGURE 2.3 Common Anions Used for DSSCs

Typical ionic liquids used for DSSCs are composed of nitrogen-containing cations coupled with halides or polyatomic anions (Min et al., 2006). Some commonly used cations are imidazoliums, pyridiniums and quaternary ammonium. The anions are usually halides such as I^- , thiocyanate, dicyanamide, tricyanomethide and tetracyanoborate. Among the cations mentioned, the ionic liquids with imidazolium cations exhibit higher ionic conductivities and lower viscosity as stated by Min et al. (2006) which in subsequent is frequently used as the solvent for DSSCs. Studies show that imidazolium iodide-based ionic liquids have high conductivity and serve not only as the solvent but also as redox ion source due to presence of iodide ions in the solvent.

2.2.3 Binary Ionic Liquid Solvent in Electrolytes

Pure ionic liquid has relatively high viscosity and low ion mobility that limits the transportation of iodide/triiodide and the restoration of oxidized dye. This is because the diffusion coefficient of the triiodide in ionic liquid are about 1-2 orders of magnitude lower than those in volatile organic solvents, especially at high illumination intensities (Wu et al., 2015). The transport of triiodide to the counter electrode does affect the performance of the DSSCs. As mentioned by Boschloo & Hagfeldt (2009), the transportation of triiodide to the counter electrode can be a rate-limiting step in the DSSCs if the solvent is viscous or the concentration of triiodide is low. Therefore, in order to solve the mass-transport limitation of pure ionic liquids, the imidazolium iodide is mixed with low-viscosity ionic liquids such as thiocyanate-based ionic liquids to reduce its viscosity. Table 2.1 shows the viscosity of ionic liquids at room temperature.

TABLE 2.1 Viscosity of Ionic Liquids at Room Temperature

Chemical	Viscosity (cp)	Source
1-Propyl-3-Methylimidazolium Iodide	865	Lee, Chen, & Ho, Ionic Liquid Based Electrolytes for Dye-Sensitized Solar Cells, 2011
1-Butyl-3-Methylimidazolium Thiocyanate	51	Urszula & Malgorzata, 2012

Few researches have been made to study the effect of mixing low-viscosity ionic liquids with imidazolium iodide electrolyte on the DSSCs efficiency. For example, an ionic liquid composed of 1-Ethyl-3-Methylimidazolium Thiocyanate(EMISCN) and 1-Propyl-3-Methylimidazolium Iodide (PMImI) had a triiodide diffusion coefficient of 2.95 x $10^{-7} cm^2 s^{-1}$ which is 1.6 higher than in pure PMImI electrolye (Wu et al., 2015). This is supported by Wang et al.(2004) in their study that ionic liquids electrolyte composed of PMImI and EMISCN(volume ratio 13:7) obtain 6.4% efficiency under simulated air mass (AM) 1.5 full sunlight. Meanwhile, in a study conducted by Cao, et al. (2008) binary ionic liquid composed of imidazolium iodide is mixed with 1-Ethyl-3-Methylimidazolium Thiocyanate at a ratio of 12:8. Table 2.2 shows the comparison of the study conducted by (Wu et al., 2015) and (Cao et al., 2008).

TABLE 2.2 Comparison of Composition of Electrolyte and Its Photovoltaic Characteristics

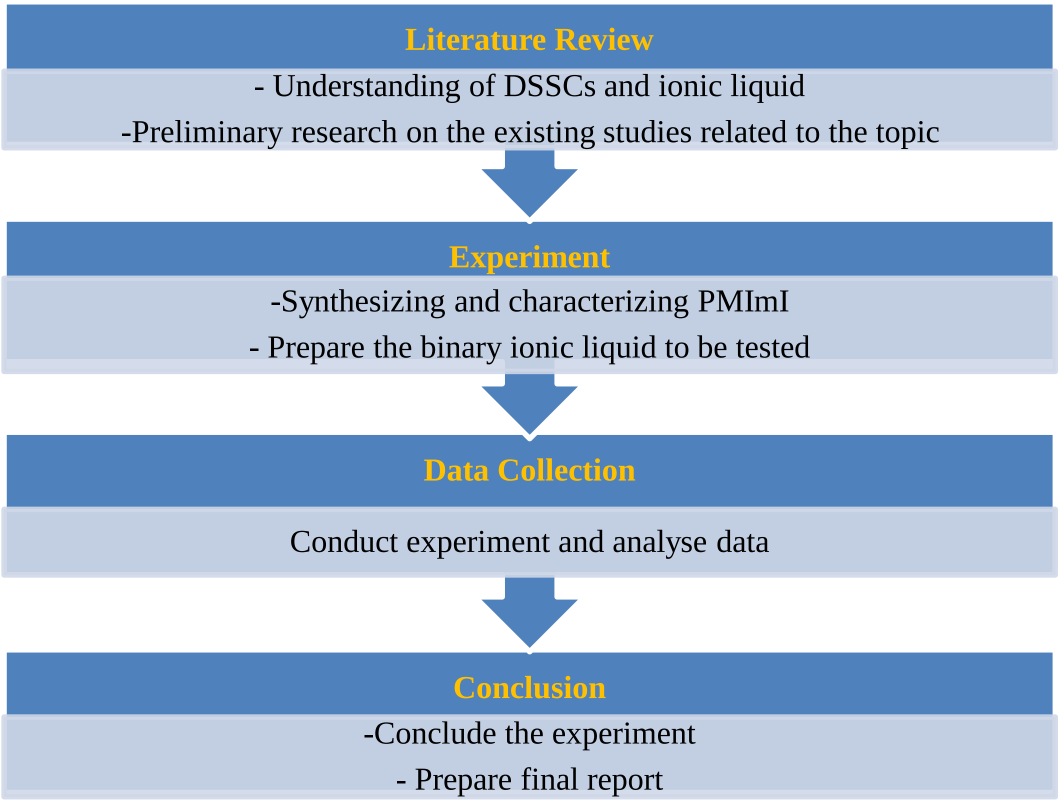
Composition of electrolyte	Jsc (mA)	Voc(mV)	Fill Factor	Efficiency (%)
PMImI:EMImSCN (13:7) + Additives (Wu et al.,2015)	13.3	0.746	0.72	7
PMImI:EMImSCN (12:8) + Additives (Cao et al., 2008)	11.37	0.718	0.749	6.11

Therefore, it is shown that different ratios of imidazolium iodide and imidazolium thiocyanate are mixed to form the binary ionic liquid electrolyte for DSSCs. However, the best ratio of the binary ionic liquid that gives the highest efficiency of DSSCs is yet to be studied.

CHAPTER 3

METHODOLOGY

3.1 Project Flow Chart



3.2 Gantt Chart and Key Milestones

Beside the project activities, one of the important aspects that must be monitored is the key milestone. The key milestone is an indication of the project completion and provides guideline of work process and the due date. It is a helpful tool to ensure that the project runs effectively.

The milestone of this projects are divided into two parts; FYP1 and FYP2. For FYP1, the key milestones are the extended proposal submission, proposal defence and the progress report. The laboratory works started during FYP2 semester due to the availability of the chemicals. The submission of technical paper and dissertation are FYP2 key milestone.

Gantt Chart FYP1

No	Detail Work	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Selection of project topics	🟩	🟩												
2	Preliminary Research Work		🟩	🟩	🟩	🟩									
3	Submission of Extended Proposal							🟨							
4	Project Defence									🟨					
5	Project work continue								🟩	🟩	🟩	🟩	🟩		
6	Submission of Interim Draft Report												🟨		
7	Submission of Final Draft Report													🟨	

🟩 Process

🟨 Milestone

Gantt Chart FYP2

	Detail Work	Week													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Project Work Continues	🟩	🟩	🟩	🟩	🟩	🟩	🟩							
2	Submission of Progress Report (9 Nov 2015)								🟧						
3	Project Work Continues								🟩	🟩	🟩	🟩	🟩		
4	Pre-SEDEX (30 Nov 2015)											🟧			
5	Submission of Draft Report (1 Dec 2015)											🟧			
6	Submission of Dissertation (7 Dec 2015)												🟧		
7	Submission of Technical Paper (9 Dec 2015)												🟧		
8	Viva Oral Presentation													🟧	
9	Submission of Project Dissertation														🟩

🟩 Process

🟧 Milestone

3.3 Experiment Methodology

3.3.1 Preparation of 1-Propyl-3-Methylimidazolium Iodide (PMImI)

PMImI was synthesized according to the literature by Kim, Shin, & Lee (2004). 0.1 mol (8 ml) of 1-Methylimidazole was dissolved in 80 ml of Tetrahydrofuran (THF) and 0.1065 mol (10.4 ml) of Iodopropane was added to the solution in a round bottomed three-necked flask by using 5 ml syringe. The flask was greased to ensure close circulation.The mixture was refluxed with vigorous stirring at 50 °C for 20 hours. The stirring speed was maintained at 200 rpm. At the beginning of the experiment, continuous monitoring was done until a stable temperature of 50 °C was achieved. Figure 3.1 shows the reflux boiler equipment set up for the experiment and Figure 3.2 shows the ionic liquid formed after 20 hours of reflux.

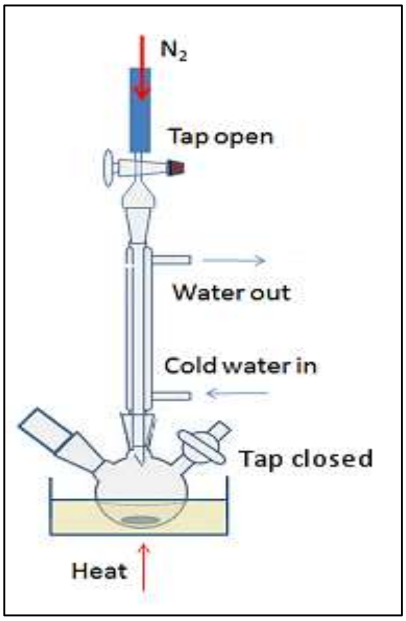


FIGURE 3.1 Reflux Boiler Equipment Set Up

FIGURE 3.2 Synthesizing of PMImI

After 20 hours of reflux, the reaction mixture was cooled down to room temperature. Then, decantation was carried out to remove the unreacted reactant and also THF. The decantation apparatus was set upped in a fume hood. The yellow colour liquid was isolated and washed with 30 ml of THF. The salt was dried in Rotary Evaporator and under vacuum for 10 hours at temperature and pressure of 70°C and 357 mbar respectively.

FIGURE 3.3 The Ionic Liquid was Dried by Using Rotary Evaporator

The dried product was analysed using NMR Spectroscopy to confirm the chemical structure of PMImI. The solvent used for the test is D_2O since the salt was soluble in the solution.

3.3.2 Mixture of PMII and BMImSCN

From literature Wang et al.(2004) made the binary ionic liquids of PMImI and 1-Ethyl-3- Methylimidazolium Thiocyanate in a volume ratio of 13:7 which is around 1:0.5. Therefore, this project will mix PMImI and BMImSCN at different ratios as follows:

i. 1 : 1
ii. 1 : 0.75
iii. 1 : 0.5
iv. 1 : 0.25

The binary ionic liquid of PMImI and BMImSCN was prepared according to Table 3.1. The mixture was stirred using magnetic stirrer for 20-30 minutes until no more layers were visible in the solution.

TABLE 3.1 Binary Ionic Liquid Preparation

Ratio (PMImI: BMImSCN)	PMImI (mL)	BMImSCN (mL)
1 : 1	1	1
1 : 0.75	1	0.75
1 : 0.5	1	0.5
1: 0.25	1	0.25

FIGURE 3.4 Ionic Liquid Mixture

3.3.3 Ionic Liquid Characterization

The measurement of viscosity is done following the literature by Wachter et al. (2008). The measurement of triiodide diffusion coefficient is conducted following the method by Adachi et al. (2006).

3.3.3.1 Measurement of Viscosity

A Brookfield Viscometer was used to measure the viscosity of the ionic liquid. It is a rotational viscometer based on torque measurement. When the spindle rotates, the torque is measured by the resistance of the fluid against the torque. This type of viscometer is suitable for measuring the viscosity of the ionic liquid because it requires only small amount of the sample and can be used for a wide range of temperatures. The range of viscosity that can be measured by using this viscometer is from 0.0005 to 2 Pa.s. (Fendt et al., 2011). The measurement were made at low shear rates to ensure that ILs are Newtonian fluids. The uncertainties are within ± 2%. The measurement was carried out at room temperature and speed of the rotating spindles were maintained at 250 rpm for all ionic liquids. The viscosity of each ionic liquid was measured using spindle 1 until spindle 6. The viscosity reading recorded by the highest percentage of accuracy was taken as the viscosity of the measured ionic liquid.

FIGURE 3.5 Brookfield Viscometer to Measure Viscosity

3.3.3.2 Diffusion Coefficients of Triiodide Measurement

Electrochemical Impedance Spectroscopy was used to measure the diffusion coefficient of triiodide. The measurement was analysed by using Echem Analyst Software to get the Nyquist and Bode diagram. The method of measuring the triiodide diffusion coefficient was carried out by following the method stated by Adachi et al. (2006). The diffusion coefficient of triiodide in the electrolyte can be obtained from the low frequency arc. The peak frequency of low frequency arc, W_{max} was identified from Nyquist plot and Bode diagram. The diffusion coefficient of triiodide, D was calculated by using Equation 3 where the thickness of the thermoplastic resin film, δ used is 50 μm.

$$D = \left(\frac{1}{2.5}\right)\delta^2 \mathrm{W}_{max} \qquad (3)$$

3.3.4 Photovoltaic Measurement of Solar Cells as Cited by Sun et al.(2012)

The electrolyte was prepared by adding the mixture of PMImI and BMmISCN with 2.0 M I_2 and 2.0 M LiI. For the fabrication of DSSCs, a fluorine-tin-oxide (FTO) conductive glass with a sheet resistance of 30 Ω was used as the substrate. 20 nm-sized TiO_2 nanoscale materials was printed on the glass by repetitive coating and calcination. Then the film was immersed in an ethanol solution of the ruthenium butylammonium carboxylate)-ruthenium(II)(N719, Solaronix) for 12 hours. The concentration of the dye is 3 x 10^{-4} M. For the counter electrode, thin layer of platinum was deposited on the glass and injecting hole was made by sand-blasting drill. Both electrodes were assembled and sealed with thermoplastic sealent(Surlyn) with thickness of 50μm as the spacer by heating. The electrolyte was filled into the cells using a vacuum back filling system.

FIGURE 3.6 TiO2 Printing

A Newport M-66907 450W xenon light source through an infrared blocking filter with a Keithley 2400 digital source meter linked to a computerized control and data acquisition system is used to measure the photovoltaic reading of the solar cells. The light intensity used is 1000 W/m2 under an AM 1.5 light source. The cell temperatures were kept at 25°C during the illumination. Light intensity is calibrated using a mono-Si reference solar cell. A 300W xenon arc lamp solar simulator with an AM 1.5 Globe filter is used to measure the I-V characteristics of the DSSCs.

FIGURE 3.7 I-V Measurement

CHAPTER 4

RESULT AND DISCUSSION

4.1 Synthesis of PMImI

During synthesis, a continuous monitoring was done until a stable temperature of 50 °C was achieved in order to monitor any changes occurs such as condensation and colour changes. The observation was recorded in Table 4.1 and Table 4.2.

TABLE 4.1 Observation of synthesizing PMImI Batch 1

Time	Temperature (°C)	Colour	Remarks
1600	25.9	Colourless	
1617	30.5	Transparent yellow	
1641	61.5	Cloudy Yellow	2 phases were formed
1651	56.3	Cloudy Yellow	Condensation started
1655	54.4	Cloudy Yellow	
1704	50.0	Cloudy Yellow	
1717	51.0	Cloudy Yellow	
1720	50.08	Cloudy Yellow	

TABLE 4.2 Observation of synthesizing PMImI Batch 2

Time	Temperature (°C)	Colour	Remarks
1625	25.9	Colourless	
1630	40.7	Transparent yellow	
1635	60.5	Cloudy Yellow	2 phases were formed
1655	50.8	Cloudy Yellow	Condensation started
1700	50.4	Cloudy Yellow	
1705	50.2	Cloudy Yellow	

From the observation, the reaction has started at temperature of 30.5 °C. It is indicated by the changing of the mixture from colourless to transparent yellow. PMImI was formed at temperature greater than 50 °C. It is indicated by the formation of the cloudy yellow solution which is the desired product. At this point of time, there was 2 immiscible solutions in the flask, which is cloudy yellow solution (PMImI) and colourless solution (unreacted reactants and THF). This is because the ionic liquid, which is PMImI is immiscible in the solvent used which is THF whereas the reactants which are 1-Methylimidazole and Propyl Iodide are miscible in THF.

In the decantation process, the yellow liquid was isolated, and the remaining mixture was washed with THF for few times to further isolate any PMImI in the mixture since the ionic liquid is immiscible in THF. After that, the isolated yellow liquid which is the ionic liquid was dried using the Rotary Evaporator to completely remove the solvent from the ionic liquid. The percentage of yield of PMImI was tabulated in Table 4.3.

TABLE 4.3 Percentage of Yield of PMImI

Batch	Product	Number of Moles	Theoretical Mass (g)	Experimental Mass (g)	Yield (%)
Batch 1	PMImI	0.05	12.61	10.28	81.52
Batch 2	PMImI	0.1	25.21	21.51	85.32

4.1.1 NMR Spectroscopy Analysis

NMR Spectroscopy analysis was conducted to confirm the chemical structure of PMImI. The results are shown in Table 4.4. Both results show that the ionic liquid that were synthesized are PMImI since the results had confirmed the IUPAC nomenclature of PMImI.

TABLE 4.4 NMR Spectroscopy Result

Batch	Result
Batch 1	^{1}H NMR spectrum (ppm, D_2O) contains peak: δ 8.6 [s, 1H, H(2)], 7.38 [s, 1H, H(4)], 7.3 [s, 1H, H(5)], 4.05[t,2H,NCH_2], 3.75[s,3H, NCH_3], 1.8[m, 2H, NCH_2CH_2], 0.8[t, 3H, CH_3].
Batch 2	^{1}H NMR spectrum (ppm, D_2O) contains peak: δ 8.8 [s, 1H, H(2)], 7.5 [s, 1H, H(4)], 7.4 [s, 1H, H(5)], 4.1[t,2H,NCH_2], 3.9[s,3H, NCH_3], 1.8[m, 2H, NCH_2CH_2], 0.8[t, 3H, CH_3].

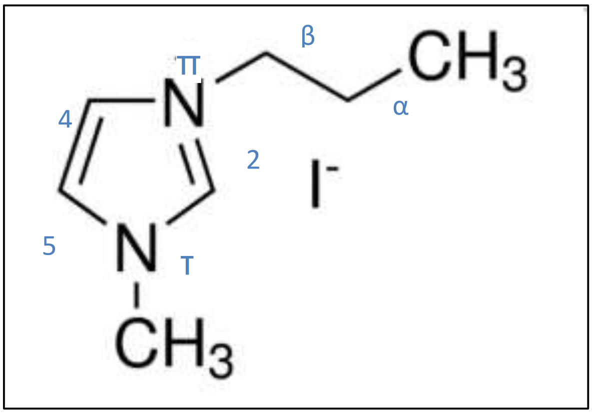


FIGURE 4.1 IUPAC nomenclature of PMImI

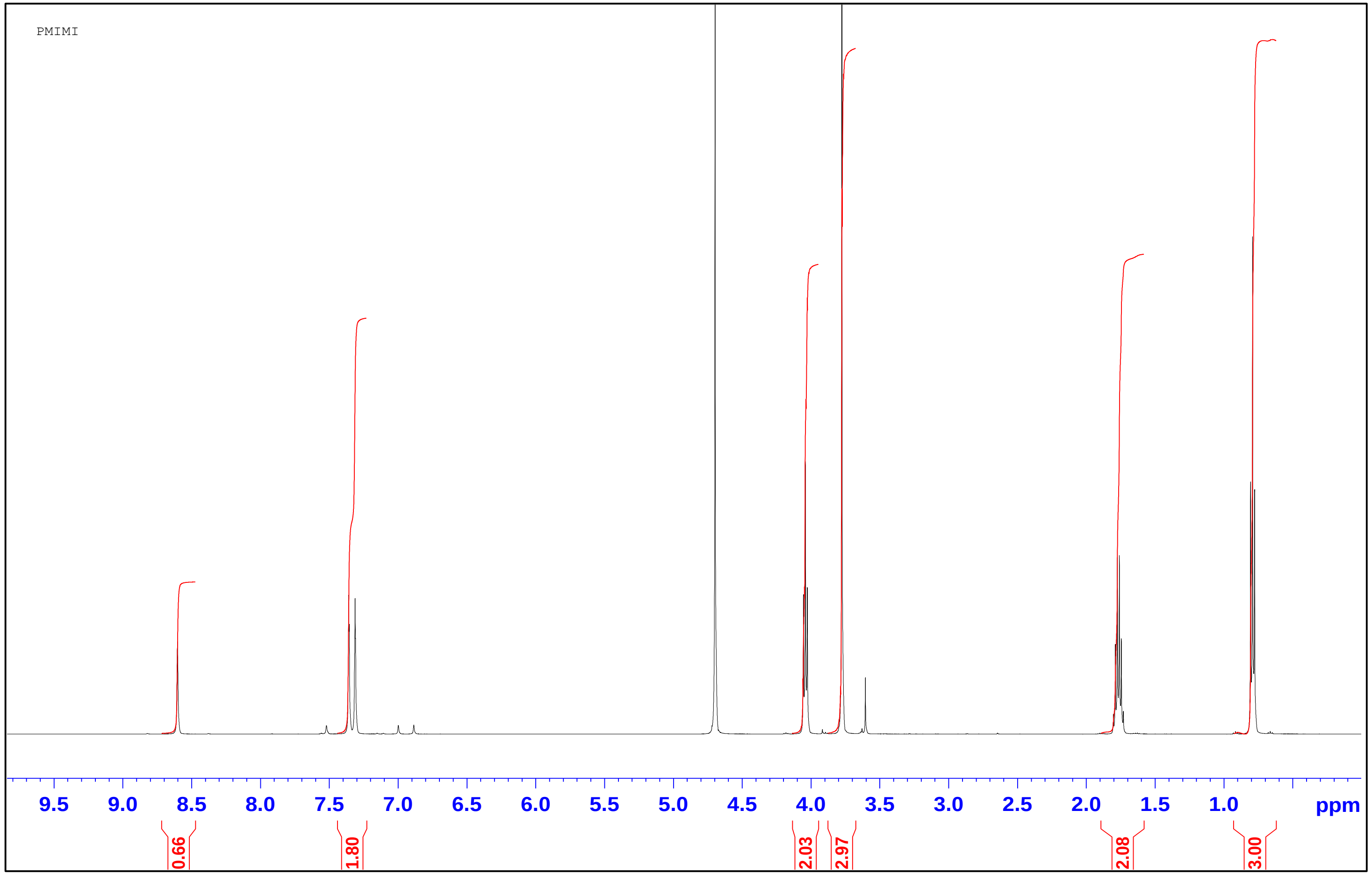


FIGURE 4.2 NMR Spectrum for PMImI Batch 1

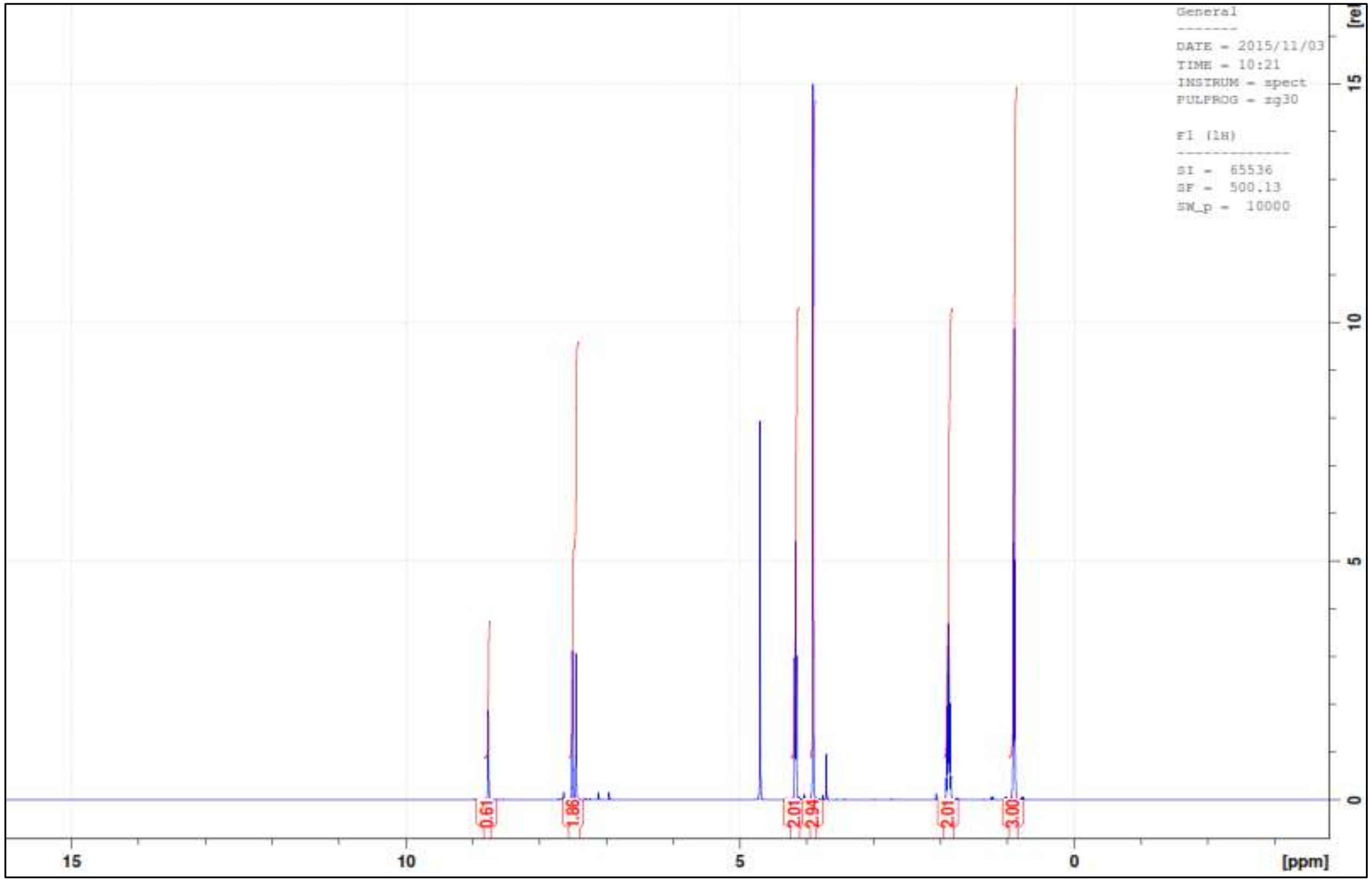


FIGURE 4.3 NMR Spectrum for PMImI Batch 2

4.2 Viscosity measurement

The viscosity measurement for all spindles was tabulated in Appendix B. Based on the highest percentage of accuracy for each sample, the viscosity of the ILs is as shown in Table 4.5.

TABLE 4.5 Viscosity of the Ionic Liquid

Sample Label	Ionic Liquid	Viscosity (cP)
A	PMImI	336
B	PMImI:BMImSCN (1:0.25)	300
C	PMImI:BMImSCN (1:0.5)	241
D	PMImI:BMImSCN (1:0.75)	168
E	PMImI:BMImSCN (1:1)	68
F	BMImSCN	56

Table 4.5 shows the viscosities of ILs measured at room temperature. The viscosity of BMImSCN measured agreed well with the study conducted by Urszula & Malgorzata (2012) with 9.8% of error. However, the viscosity of PMImI measured is different from the viscosity mentioned in the literature which is 865 cP. This is due to the rotational speed of the spindle. For comparison purposed, the speed of the spindle was maintained at 250 rpm to ensure the value of viscosity measured for all samples are comparable as mentioned in Brookfield Viscometer Manual that when the viscosity data must be compared, the test parameters such as spindle, speed, temperature and test time must be maintained. From the viscosity measured, it is shown that the viscosity of PMImI is 336 cP which is six times higher than the viscosity of BMImSCN. Therefore by mixing PMImI and BMImSCN from ratio 1:0.25 to 1: 1 which is in decreasing order of PMImI concentration, the viscosity of the mixture is decreasing as shown in Figure 4.4.

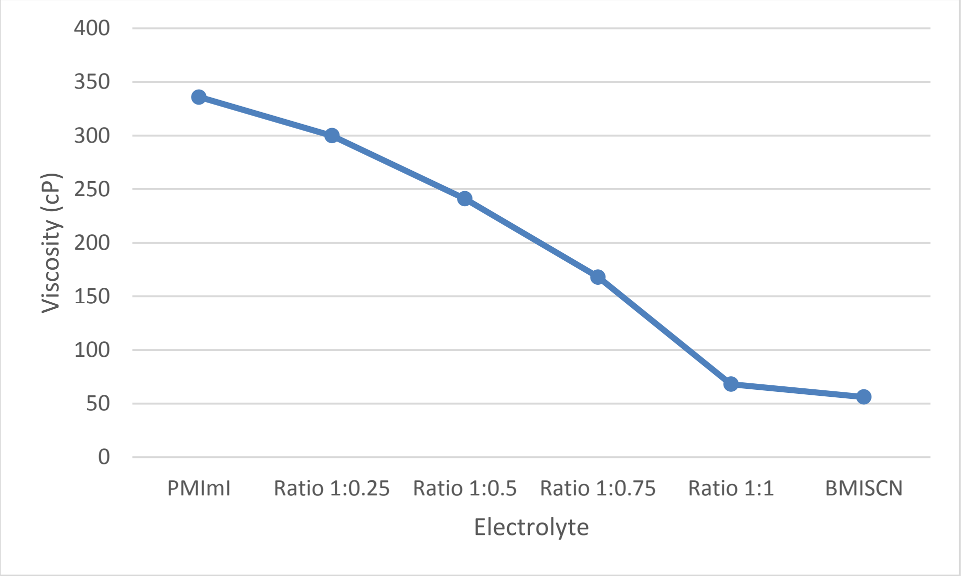


FIGURE 4.4 Graph of Viscosity of Different Electrolytes

4.3 Electrochemical Impedance Spectroscopy (EIS)

TABLE 4.6 Triiodide Diffusion Coefficient of Electrolyte

Electrolyte	ω_{max}, Bode	D (cm^2/s)
DYESOL EL-HSE	0.134	1.34×10^{-6}
BMISCN	0.05798	5.80×10^{-7}
PMImI	0.05983	5.98×10^{-7}
PMImI:BMImSCN (1:0.25)	0.0701	7.01×10^{-7}
PMImI:BMImSCN (1:0.5)	0.08373	8.37×10^{-7}
PMImI:BMImSCN (1:0.75)	0.08465	8.47×10^{-7}
PMImI:BMImSCN (1:1)	0.09852	9.85×10^{-7}

Table 4.6 shows the triiodide diffusion coefficient measured for all the electrolytes. For this project, high stability of Dyesol’s EL-HSE electrolyte is used as reference cells for EIS and photovoltaic measurement. The electrolyte contains iodide/triiodide redox couple with organic iodide salt, inorganic iodide salt, imidazole compound and Guanidine Thiocyanate as the additive. The solvent used for this electrolyte is 3-Methoxypropionitrile.

From the EIS measurement, it is shown that the reference cells has the highest triiodide diffusion coefficient. It is due to the low viscosity of the organic solvent used which is 3-methoxypropionitrile. For the binary ionic liquid electrolyte, as the concentration of PMImI in the electrolyte decreases, which caused the viscosity to decrease, the triiodide diffusion coefficient increases. This relationship is clearly shown in Figure 4.5. This is because low viscosity of the electrolyte enables the triiodide ions to diffuse easily to the counter electrode to be reduced back to iodide. This result is in agreement with the study conducted by Wachter et al.(2008) which stated that the triiodide diffusion coefficient shows strong increase with decreasing viscosity.

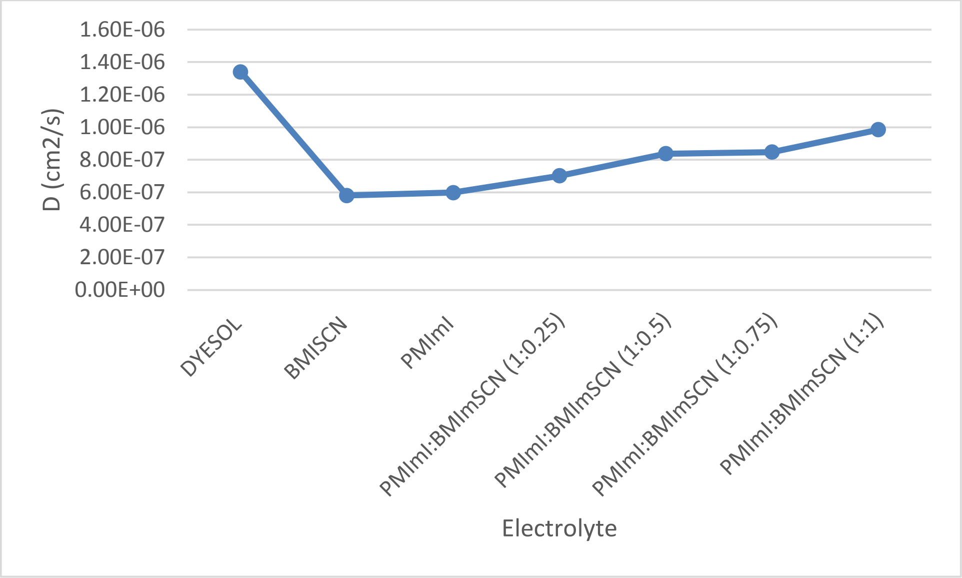


FIGURE 4.5 Graph Triiodide Diffusion Coefficient of Different Electrolyte

4.4 Photovoltaic Measurement

Table 4.7 shows the photovoltaic parameters measured for all cells. The efficiency of pure PMImI is 1.19% and it is higher than BMImSCN due to the presence of iodide ions in the ionic liquid.

TABLE 4.7 Photovoltaic Parameters measured under the illumination of AM 1.5 G full sunlight

Electrolyte	D (cm^2/s)	FF	Voc (V)	Jsc (mA/cm2)	Efficiency (%)
DYESOL	1.34 x 10^{-6}	0.463	0.668	9.062	2.807
BMISCN	5.80 x 10^{-7}	0.57	0.543	2.633	0.814
PMImI	5.98 x 10^{-7}	0.517	0.549	4.189	1.19
PMImI:BMImSCN (1:0.25)	7.01 x 10^{-7}	0.471	0.585	5.527	1.523
PMImI:BMImSCN (1:0.5)	8.37 x 10^{-7}	0.485	0.592	5.498	1.578
PMImI:BMImSCN (1:0.75)	8.47 x 10^{-7}	0.469	0.617	6.517	1.886
PMImI:BMImSCN (1:1)	9.85 x 10^{-7}	0.476	0.588	5.425	1.519

For the binary ionic liquid, the ratio of PMImI to BMImSCN does affect the efficiency of the cells. The ratio gives a big impact to the photocurrent of the DSSCs. As shown in Figure 4.6, initially the photocurrent of the DSSCs increases from electrolyte PMImI until it reaches the maximum at electrolyte PMImI:BMImSCN(1:0.75) and then it decreases. It is shown that as the triiodide diffusion coefficient increases, the photocurrent is also increased. This is because high diffusion rate enables the triiodide to diffuse easily to the counter electrode. For PMImI electrolyte, its high viscosity caused it to has low diffusion rate thus hindering its ability to diffuse towards the counter electrode after being oxidized after donating electrons to the dye molecules. This would in turn increases the rate of electrolytes capturing electrons that is diffusing through the TiO_2 nanoparticles in the photoelectrode of the DSSCs which results in back-recombination and contributes to photocurrent losses and impacts performance of DSSCs.

For electrolyte consist of PMImI:BMImSCN (1:1), even though it has the highest triiodide diffusion coefficient, the J_{SC} decreased. The decreased of the current density, J_{SC} could be explained by assuming that in that cell, different limiting processes are dominant. Based on Wachter et al. (2008), there are four major processes that limits the efficiency of DSSCs which are light harvesting, recombination of dye-cation or reduction of triiodide with previously injected electrons at the TiO_2 electrode, diffusion of triiodide to the counter eletrode and its reduction at the counter electrode. Therefore, for DSSCs with ratio of PMImI:BMImSCN 1:1, the triiodide diffusion coefficient no longer becomes the limiting process dominant in the cell.

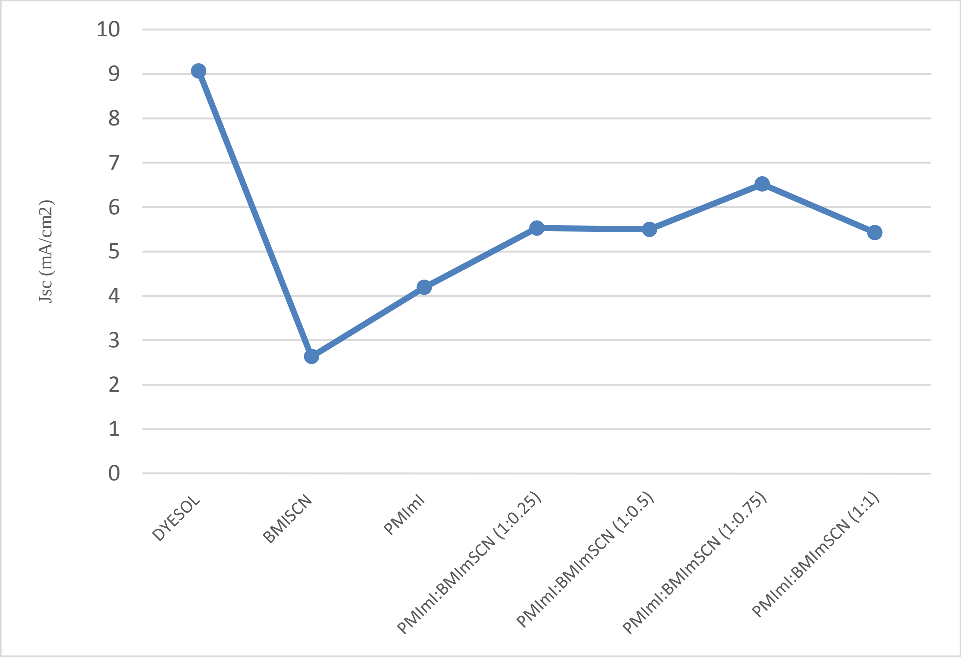


FIGURE 4.6 Graph of Current Density, Jsc of DSSCs with Different Electrolytes

Figure 4.7 shows the I-V Characteristics Curve for all electrolyte. Dyesol EL-HSE has the highest efficiency followed by electrolyte of PMImI/BMImSCN(1:0.75) which is 2.8% and 1.9% respectively. The efficiency of the DSSCs is directly proportional to the current density, J_{SC} provided that the voltage of the cells is not strongly affected by the ratio of the binary ionic liquid.

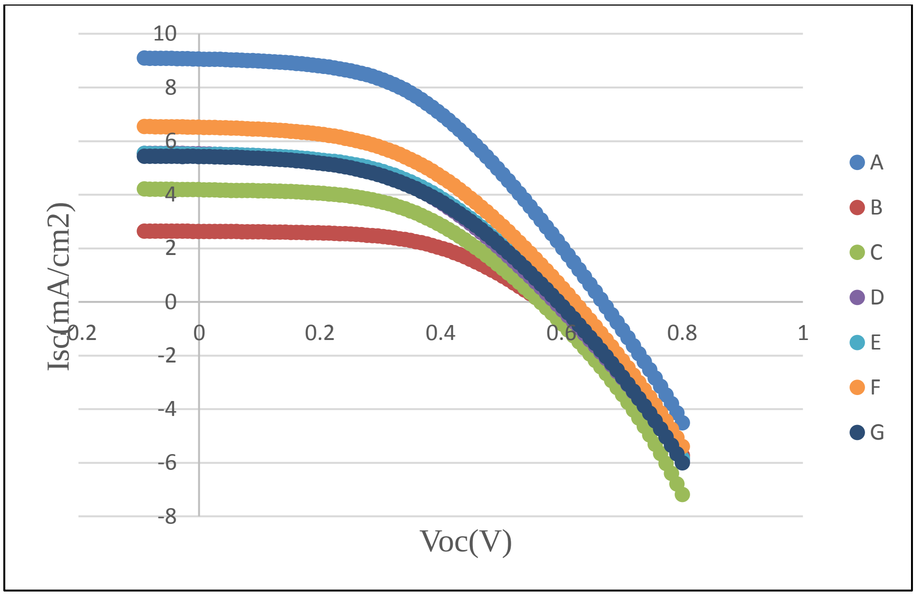


FIGURE 4.7 I-V Characteristics Curve

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Based on the result obtained from the experimental work, the addition of low viscosity ionic liquid which is BMImSCN into the high viscosity PMImI reduces the mass transport limitation of triiodide in the electrolyte by lowering the viscosity of the ionic liquid. This result is in agreement with the study conducted by Wu et al.(2015). The EIS characterisation and analysis have proven that the electrolyte system of PMImI/BMImSCN with 2M I_2 and 2M LiI showing increasing of triiodide diffusion coefficient with decreasing of the PMImI concentration which related to the decreasing of the electrolyte viscosity. Electrolyte of PMImI:BMImSCN with ratio of 1:0.75 has a triiodide diffusion coefficient of 8.47 x 10^{-7} cm^2/s which is higher than the triiodide diffusion coefficient of pure PMImI which is 5.98 x 10^{-7} cm^2/s. Based on I-V measurement, it is shown that increasing the triiodide diffusion does increases the efficiency of DSSCs. However, further increase in triiodide diffusion coefficient after it has reached its optimum value leads to decreasing the DSSCs performance due to the changes of the limiting process dominant to the cells. The ratio 1:0.75 has been identified as the best ratio of binary ionic liquid of PMImI/BMImSCN as it has the highest power conversion efficiency among all the electrolytes. Therefore, for electrolyte system of binary ionic PMImI/BMImSCN, it is highly recommended to use this ratio to optimize the efficiency of DSSCs.

There is an avenue for future work to study other dominant factors that would affect the electrolyte behaviour as a hole mediator in DSSCs such as light harvesting, recombination of dye-cation, back recombination of injected electrons to the electrolyte and reduction at the counter electrode. This would further improve the performance of DSSCs.

This project has provided useful insight for further improvement of binary ionic liquid electrolyte for DSSCs. The best ratio of binary ionic electrolyte system is successfully identified which enables us to optimized the ionic liquid electrolyte thus improve the DSSCs performance.

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APPENDICES

Appendix A

Appendix A: Calculation of Percentage of Yield And Triiodide Diffusion Coefficient

1. Calculation of percentage of yield of PMImI

$$Yield\ (\%) = \frac{Experimental\ Weight}{Theoritical\ Weight}\ x\ 100$$

For example, the percentage of yield for PMImI Batch 1:

$$Yield\ (\%) = \frac{10.28\ g}{12.61\ g}\ x\ 100 = 81.52$$

2. Calculation of Triiodide Diffusion Coefficient, D

$$D = (\frac{1}{2.5})\delta^2 \mathrm{W}_{max}$$

For example, the triiodide diffusion coefficient of Dyesol EL-HSE,

$\delta = 0.005$ cm;

From Bode Diagram, the W_{max} is 0.134 s^{-1};

$$D = \left(\frac{1}{2.5}\right)(0.005\ \mathrm{cm})^2(0.134\ s^{-1}) = 1.34\mathrm{E} - 06\ cm^2$$

Appendix B

Appendix B: Viscosity Measurement for All Spindles

Sample	Spindle No.	Viscosity (cP)	Percentage of accuracy (%)
BMImSCN	1	9.8	1.3
	2	56	3.7
	3	12	0.4
	4	54	0.9
	5	N/A	N/A
	6	60	0.2
PMImI	1	33.8	4.5
	2	71	4.7
	3	N/A	N/A
	4	336	5.6
	5	24	0.2
	6	90	0.3
PMImI:BMImSCN (1:1)	1	21.7	2.9
	2	68	4.5
	3	N/A	N/A
	4	168	2.8
	5	12	0.1
	6	60	0.2
PMImI:BMImSCN (1:0.75)	1	48	6.4
	2	168	11.2
	3	N/A	N/A
	4	252	4.2
	5	36	0.3
	6	N/A	N/A
PMImI:BMImSCN (1:0.5)	1	27	3.6
	2	56	3.7
	3	N/A	N/A
	4	360	6
	5	12	0.1
	6	30	0.1
PMImI/BMImSCN (1:0.25)	1	31.5	4.2
	2	66	4.4
	3	N/A	N/A
	4	241	5
	5	36	0.3
	6	60	0.2