EXPLORATION ON POLY(PROPYLENE) CARBONATE-BASED GEL POLYMER ELECTROLYTES FOR DYE-SENSITIZED SOLAR CELL

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FACULTY OF SCIENCE UNIVERSITY OF MALAYA KUALA LUMPUR

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ABSTRACT

Dye-sensitized solar cells (DSSCs) are devices that utilize solar energy by converting it into electrical energy. DSSCs are known to be an alternative to the conventional solar cells as well. Dye-sensitized solar cells (DSSCs) based on dye-coated mesoporous nanocrystalline TiO₂ photoelectrode have attracted a lot of attentions due to their simple fabrications, cheap and reasonable energy conversion efficiencies. Recent studies have demonstrated that DSSCs fabricated with liquid electrolytes show high energy conversion efficiency of more than 15%. However, there are a lot of drawbacks of using liquid electrolytes where they are widely known to have practical problems of leakage, volatilization, desorption, photo degradation of the dye, corrosion of the platinum secondary electrode and the ineffective sealing of cells for long term usage. Thus to overcome the drawbacks, gel type electrolytes have emerged as great alternative to replace the liquid electrolytes. Unfortunately, even with some advantages over the liquid electrolytes, GPEs are still facing serious problem on low energy conversion efficiencies and poor ionic conductivity. Thus, in order to overcome these problems, doping ionic liquid is one of the good ways to improve the performance of ionic conductivity as well as photovoltaic performance of these GPE-based DSSCs. In this study, we assembled dye-sensitized solar cells with Poly (Propylene) Carbonate based gel polymer electrolytes as host polymer and sodium iodide (NaI) as iodide salt. Then, various ionic liquids such as 1-butyl-3-methylimidazolium iodide (BmimI) and 1-methyl-3-propylimidazolium iodide (MPII) were added into the best polymer salt system sample. The gel polymer electrolytes were characterized for electrical and structural properties using electrochemical impedance studies (EIS), Fourier transform infrared (FTIR) and X-ray Diffraction (XRD). All GPE samples obeyed Arrhenius model which was observed from temperature dependent conductivity study. Furthermore, in structural study using XRD and FTIR, the complexation between polymers, salt and ionic liquids were confirmed for all GPE samples. Dye-sensitized solar cells (DSSCs) were fabricated using GPE systems. The

gel polymer electrolytes were sandwiched between working electrode and counter electrode with the configuration of glass/FTO/TiO₂/N719 dye/GPE/Pt/FTO/glass. The fabricated DSSCs were analysed for energy conversion using Sun simulator of 1000 (W m⁻²) as incident light power. In the salt system, samples were able to achieve highest ionic conductivity and energy conversion efficiency of 2.01 mS cm⁻¹ and 6.38% respectively. The highest ionic conductivity achieved upon the addition of MPII ionic liquid 4.98 mS cm⁻¹ and energy conversion efficiency 7.72% at its optimum concentration.

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ABSTRAK

Sel-sel solar dye-sensitif (DSSCs) adalah peranti yang menggunakan tenaga solar dengan menukar ia menjadi tenaga elektrik. DSSCs dikenali sebagai alternatif kepada sel-sel solar konvensional juga. Sel-sel solar Dye-sensitif (DSSCs) berdasarkan pewarna bersalut nanocrystalline mesoporous TiO₂ photoelectrode telah menarik minat kerana fabrikasi yang mudah, murah dan munasabah kecekapan penukaran tenaga. Kajian terbaru menunjukkan bahawa DSSCs direka dengan elektrolit cecair menunjukkan kecekapan penukaran tenaga tinggi lebih daripada 15%. Walau bagaimanapun, terdapat banyak kelemahan penggunaan elektrolit cecair iaitu masalah praktikal ketirisan, pemeruapan, desorption, foto degradasi pewarna, hakisan pada platinum elektrod dan kekurangan kesan kedap dalam sel untuk penggunaan jangka panjang .Oleh itu untuk mengatasi kelemahan, jenis gel elektrolit telah diperkenalkan sebagai alternatif yang baik untuk menggantikan elektrolit cecair. Malangnya, walaupun dengan beberapa kelebihan berbanding elektrolit cecair, GPEs masih menghadapi masalah yang serius pada kecekapan tenaga yang rendah dan kekonduksian ionic yang rendah. Oleh itu, untuk mengatasi masalah ini, dadah cecair ionik adalah salah satu cara yang baik untuk meningkatkan prestasi kekonduksian ionik serta prestasi photovoltaic ini DSSCs berasaskan GPE. Dalam kajian ini, kami memasang sel solar pewarna-peka dengan Poli (Propylene) Carbonate berdasarkan elektrolit gel polimer sebagai polimer dan natrium iodida (NAI) garam iodida. Kemudian, pelbagai cecair ionik seperti 1-butil-3-methylimidazolium iodida (BmimI) dan 1-metil-3-propylimidazolium iodida (MPII) telah ditambah ke dalam sistem garam polimer sampel yang terbaik. Gel polimer elektrolit telah dicirikan untuk elektrikal dan struktur dengan menggunakan kajian impedans electrokimia (EIS), Fourier mengubah inframerah (FTIR) dan X-ray diffraction (XRD). Semua GPEs mengikuti Arrhenius model haba diaktifkan untuk kajian kekonduksian pergantungan suhu. Tambahan pula, dalam kajian struktur yang menggunakan XRD dan FTIR, komplex antara polimer, garam dan cecair ionik telah disahkan untuk semua GPEs. Dye sel solar peka (DSSCs) telah direka dengan menggunakan sistem GPEs. Gel polimer elektrolit telah diapit di antara elektrod kerja dan kaunter elektrod dengan konfigurasi kaca/FTO/TiO₂/ N719 dye /GPEs/Pt/FTO/kaca. Rekaan DSSCs dianalisi untuk penukaran tenaga menggunakan simulasi cahaya matahari 1000 (W m⁻²) ditakrifkan sebagai kuasa cahaya jatuh. Di dalam sistem garam, sampel boleh di capai pada tahap kekonduksian ionik dan kecekapan penukaran tenaga masing-masing yang tertinggi kepada 2.01 mS cm⁻¹ dan 6.38% Kekonduksian ionik tertinggi yang dicapai atas penambahan MPII ionik cecair 4.98 mS cm⁻¹ dan kecekapan penukaran tenaga 7.72% pada kepekatan optimum.

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LIST OF SYMBOLS AND ABBREVIATIONS

BmimI	:	1-buty-3-methylimidazolium iodide		
С	:	Carbon		
DSSC	:	Dye sensitized solar cell		
Ea		Activation energy		
EIS	:	Electrochemical Impedance studies		
FF	:	Fill factor (%)		
FTIR	:	Fourier Transform Infrared		
GPE	:	Gel polymer electrolyte		
\mathbf{J}_{sc}	:	Short-circuit current density (mA cm ⁻²)		
MPII	:	1-propyl-3-methylimidazolium iodide		
NaI	:	Sodium iodide		
PPC	:	Poly(propylene) carbonate		
Pt	:	Platinum		
PV	:	Photovoltaic		
R_b	:	Bulk resistance (Ω)		
TiO ₂	÷	Titania		
V _{oc}	:	Open-circuit voltage (V)		
XRD	:	X-ray Diffraction		

 η : Photovoltaic conversion efficiency

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CHAPTER 1: INTRODUCTION

1.1 Introduction of Research

Energy is one of the main factors in the society progress. At the beginning of 20th century, the world population has become much larger, then the energy demand has increased and got so much attention from public. Subsequently, the usage of fossil fuel is getting huge. Fossil fuel have been formed by the organic remains of prehistoric plants and animals in which the most common forms are oil, gas and coal. The advantages of fossil fuels include the availability, cost, transportation and high energy production (Burschka et al., 2013). But, society finally realized that burning of the fossil fuels actually damages the environment terribly. The usage of fossil fuel can cause geopolitical tensions, catastrophe to the environment as well as global warming. The alternative renewable energy resource such as solar energy has been introduced and it is one of the good choices to encounter the growth of energy demand. Solar energy becomes more popular compared with the other renewable resource as its own major source is from the Sun. As we know, Sun is a primary source of energy and all types of energy on earth are derived from it.

Solar energy can be harvested directly from Sun. Examples of direct solar energy are photovoltaic conversion and solar hydrogen gas production technology. Solar energy also can be considered as environmental friendly as it does not pollute the environment like conventional burning of the fossil fuels. Thus, solar application could be considered as an alternative of energy resource without harnessing the environment.

Dye-sensitized solar cells (DSSCs) are devices that utilize solar energy by converting it into electrical energy. Nowadays, DSSCs are one of the potential solar technologies. It was firstly introduced by two researchers named as B.O'regan and M.Gratzel in 1991 (O'Regan & Grätzel, 1991). Over the years DSSCs are getting huge interest. There are several benefits of DSSCs such as low cost, simple and easy to fabricate, provide an acceptable promising conversion efficiencies (Zhou et al., 2013). As we know, DSSCs are made of different types of components and materials and this allowed the researchers to find the different direction of field for them to study the DSSCs. For the past decades, researchers with different fields of study have investigated different components to improve the photovoltaic performance of DSSCs. There are several examples of studies such as synthesizing and producing new inorganic dyes, different types of electrode materials, new counter electrode materials and various type of redox couple have been done since 1991. Among all studies, the performance of DSSCs based on liquid electrolytes has been achieved approximately 15% of power conversion efficiency (Tiautit et al., 2014).

Unfortunately, there are some shortcoming of using liquid electrolytes that limited the development of the DSSCs such as evaporation, leakage, desorption, degradation of dye and corrosion of the platinum on the counter electrode (Arof et al., 2014). In order to overcome these drawbacks, the replacement of liquid electrolytes has been introduced like solid and gel polymer electrolytes. There are several benefits of GPEs such as low vapor pressure, good contact, and pore filling properties with electrodes, high thermal stability, high ionic conductivity and excellent photovoltaic performances. However, there are still drawbacks that need to put effort in order for the replacement of liquid electrolytes to a certain extent and the gelator that might react with other chemicals of the electrolytes which may cause the drop in the gel polymer electrolyte performances (Burschka et al., 2013).

Thus, we propose the usage of poly(propylene) carbonate into the gel polymer electrolytes. We also have incorporated inorganic salts such as sodium iodide (NaI) into

the gel polymer electrolytes. We have introduced two different types of imadazolium ionic liquid into the electrolytes as well such as 1-methyl-3-propylimidazolium iodide (MPII) and 1-butyl-3-methylimidazolium iodide (BmimI). The ionic conductivity, structural study and DSSCs performance of GPEs are studied.

1.2 Objectives of Research

The objectives of the research are as below:

- To prepare PPC based gel polymer electrolytes (GPEs) which are applicable to fabricate DSSCs.
- To characterize the resulting PPC based GPEs using several techniques such as X-ray Diffraction spectroscopy (XRD) and Fourier Transform Infrared spectroscopy (FTIR) for structural studies.
- 3) To investigate the ionic conductivity and DSSC performance of the GPEs with the addition of inorganic iodide salts (NaI).
- 4) To improve the electrical and DSSC performances of the GPE with two different types of ionic liquids (BmimI and MPII).

1.3 Scope of thesis

The current thesis is expressed in 6 chapters. Chapter 1 is an introduction of the present work. Literature review is included in Chapter 2 containing history of solar cell, the basic principles of dye-sensitized solar cells, benefits of dye-sensitized solar cells and the component of DSSCs. The factor that influence the ionic conductivity of gel polymer electrolytes as well as the strategy to improve are presented in Chapter 2. Chapter 3 is about experimental methods in four section introducing materials in this work, preparation methods, dye-sensitized solar cells fabrication procedures and characterization. The results and discussion of the present work including three systems are described in Chapter 4. The ionic conductivity study and structural characterization including XRD and FTIR, and dye-sensitized solar cells (DSSCs) characterization for all the three systems discussed in Chapter 4. In Chapter 5, discussion on differences and comparisons between three systems based on the results obtained. Finally, conclusion and suggestion for the future work are represented in Chapter 6.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction of the chapter

In this chapter, the available literature on solar cell, dye sensitized solar cells, type of polymer electrolytes are discussed. The factors that could influence the performances of the gel polymer electrolytes and a way that can be used to improve the performance of these gel polymer electrolytes, have also been explained.

2.2 Solar cells

Noble Laureate Richard E. Smalley stated that in the next 50 years, we will face the humanity's top 10 problems on the energy and environment issues (Chen et al., 2010). The three growing issues of energy problem were included as i) the increase of energy demand, ii) the depletion of fossil fuel keeps increasing year by year and iii) fossil fuel combustion that caused greenhouse effect. Presently, the concern of the growth of technological endeavor of renewable and green energy has attracted the awareness worldwide. By 2020, the European Union (EU) has set a goal that 20% of EU's final energy consumption should be renewable energy. In addition, American Recovery and Reinvestment Act estimated about \$80 billion will be used to reduce greenhouse gas emission by 28% in clean energy development before 2020 (Chiron et al., 2014).

Today, around 13% of energy production is from renewable sources. Among all of the renewable energy sources, solar energy gets so much interests from researchers due to its advantages and potential for power generation. Photovoltaic cell (PV) or solar cell, is an electrical device that converts the light energy directly into electricity by the photovoltaic effect. From Figure 2.1, within the 5 years (between end of 2010 to the end of 2015), the annual growth rate of solar photovoltaic energy generation has shown an increment at 42% and it was fastest among all the renewable technologies (Lu et al., 2013).



Figure 2.1: Average annual growth rates of renewable capacity, between the ends of 2010 to the end of 2015 (Source: REN21).

When photons from the sun hit the solar panel, the semiconducting materials such as silicon will absorb the photons. Consequently, the electron from the atom in the cell would accept the energy release from the photons. As the electron gets enough energy, it will move from original place to the external electrical circuit and form a 'hole' which is needed to fill by another electron (Lim et al., 2011).

In order to produce the required voltage to light up external load such as an LED, electric field is needed. To create the electric field from solar cells, p-type (positive) and n-type (negative) of semiconductors are required to be sandwiched together. The n-type silicon contains more electrons while p-type has more holes. When these two types come together, they will create p-n junction and then the electric field will be formed. The extra electrons from the n-type flows to the p-type and vacating the holes. This phenomenon creates the electric field at the surface allowing the electrons to hop from semiconductor to the surface. These electrons would flow into the external electrical circuit and light up the external load. The holes that are emptied by the electrons would then wait for another new electron to vacant (Ng et al., 2015).

There are many different solar cells studied in the past decades and is summarized below:

- Multijunction Cell (y=31 to 44%): the most expensive solar cells as the cells contain different layers of technologies have been built inside.
- Single-Junction Cell (y=33.7%): usually they are made with Gallium-Arsenide which are the expensive raw materials. Thus, they merely are used in satellite applications.
- Crystalline Si Cells (y = 20 to 27%): the cells are made of slices of silicon. This cell gives better pricing and easy to install compared with the other solar cells which attract many practical application.
- Thin Film technologies (y=13 to 23%): this cell is made of active material such as silicon that sandwiched between two panels of glass. Compared to the other cells, this cell is much thinner and cheaper but it does not get much attention due to its low performance.
- Emerging PV (y=9 to 15%): Mostly the cells are still undergoing research as they have considerably low performance compared to the other cells. Nonetheless, it's getting an increasing improvement throughout the decades.

Even though silicon solar cells are widely explored among other solar cell technologies, the emerging type of PV cells are still being improvised. Thus, it is expected PV cell will be able to overtake these existence solar panels. The emerging types of PV such as dye-sensitized solar cell (DSSC) are one of the upcoming devices and it is the main focus in this research.

2.3 Dye-sensitized Solar Cells (DSSCs)

The first and second generation of solar cells have achieved excellent performance in power conversion efficiency but due to the high production cost and environmental issues

have limited their comprehensive application and the suggestion of environmental friendly as well as low cost solar cell as replacement are required (Seo et al., 2014). After approximately 2nd decade of research and development, the third generation of solar cells have been introduced. Dye-sensitized solar cell (DSSC) is one of the new generations of solar devices that has been invented.

In 1991, O'regan and Gratzel developed the DSSC that based on nanocrystalline TiO₂ working electrode (O'Regan & Grätzel, 1991). These DSSCs were found to have relatively high efficiency which exceeding 7% in 1991 and further increase 10% in 1993 (Rong et al., 2013). This simple and low cost technology have caught of a great interest from researchers to improve the efficiency as it is important for commercial use (Ramesh & Ng, 2011).

2.3.1 Benefits of using DSSCs

In comparison with the other technology based on silicon, the DSSC is one of the best candidates in terms of pricing due to its simple fabrication which composed of conductive glasses, a porous wide band gap semiconductor, a molecular dye and a redox couple. Most of the materials used in the DSSC were low cost materials and cheap. It is also enable to print on any flexible surface without required any apparatus. The DSSCs are the best suitable for low density application as the overall peak energy efficiency is around 11%. Even though, the performance of DSSC is still considered low compared to the other thin film solar cells, it gains attention and preferable to others because of the obtained price to performance ratio obtained (Rani et al., 2014).

Besides, DSSC is made of light weighted materials as compared to other thin-film solar cells. However, they do not require any extra protection from the rain, trees or any other harsh objects. They are easy to use and able to maintain as it is made mechanically robust. In addition, for long time being exposed to sunlight, it will not degrade and hence it have long lifetime of the cells and the replacement of the cells will be minimized.

The usage of dye in the DSSC enables to absorb diffused sunlight and fluorescent light which shows that these DSSCs could work under illumination below certain ranges as other traditional cells cannot succeed to do so. Therefore, the DSSCs could work in any condition such as cloudy or low light without giving an effect on the performance of the efficiency. Furthermore, the size of DSSC can be adjustable whether small or big and also flexible. So, it is suitable to apply on some small devices indoor (Hsu et al., 2013).

Moreover, the DSSC is able to work at the internal temperature as well. This because it's made with a thin layer of plastic where the heat could be able to radiate easily away. Comparable to the traditional cells, as the temperature rises which causes the electrons in the semiconductor is pushed to conduction band mechanically. Hence, silicon cells need more protection by covering it with glass box or other methods. Otherwise, it will get heated easily and then caused the efficiency be affected due to the internal temperature.



2.3.2 Basic principles of DSSCs

Figure 2.2: Schematic diagram of operation principle of a DSSC (Bandara et al., 2010).

Figure 2.2 represent typical schematic diagram and the operation principle of a DSSC. There are four fundamental components for a DSSC (Singh et al., 2008):

- Photo-anode A transparent conducting oxide layer (commonly fluorine-doped tin oxide (FTO) or Indium-doped tin oxide (ITO)) will be coated with a mesoporous oxide layer (typically TiO₂, ZnO, SnO₂ and etc).
- Dye A monolayer of charge transfer material that bonded to the surface of the mesoporous oxide layer to enhance light absorption.
- Electrolyte A redox mediator such as I^-/I_3^- .
- Counter electrode a catalyst (usually platinum) coated on a conductive oxide layer to facilitate electron collection.

When exposed to sunlight, the dye will start to get excited as it absorbs the photon or light from any source. The absorbed dye molecule will inject electrons into the TiO₂ working electrode and thus becomes oxidized. There is recombination between the injected electron in the conduction band of semiconductor and the hole on the oxidized dye. Then, the photo induced electrons diffuse through porous TiO₂ layer and are extracted at FTO surface. These generated electrons have been utilized at the external load through the circuit and finally being collected by electrolyte at the counter electrode where the reduction process has occur. The I^-/I_3^- pair will complete the cycle by reducing the oxidized dye. This process will be repeated billions of times per second inside the cell, thus an electrical current will be produced from the sunlight (Wu et al., 2015).

The summarized operating cycle in chemical reaction is as following (Tang et al., 2012):

At anode:

$$S + hv \rightarrow S^*$$
 Absorption (1)

$$S^* \rightarrow S^+ + (TiO_2)$$
 Electron injection (2)

$$2S^+ + 3I^- \rightarrow 2S + I_3^-$$
 Regeneration (3)

At cathode:

$$I_3^- + 2e^-(Pt) \to 3I^- \tag{4}$$

Cell:

$$e^{-}(Pt) + hv \to 3I^{-} \tag{5}$$

There is no chemical substance in nature has released during the working cycle as shown in the cell reaction (5).

2.3.3 The component of the DSSCs

2.3.3.1 Semiconductor film electrode

Firstly, the transparent conducting film is a very important element in the DSSCs. It can be made with organic and inorganic materials. In the DSSCs application, a very thin layer of transparent conducting oxide such as indium tin oxide (ITO), fluorine doped tin oxide (FTO) and the doped zinc oxide (ZnO) are the examples of inorganic material that have been used for this past years in the DSSC (Tiautit et al., 2014). This substrate is an important component as mesoporous oxide layer will be coated on it.

Working electrode or photoanode electrode normally consists of wide band gap semiconductor which coated on the transparent conducting substrate. Semiconductor material that widely used in DSSC is example TiO_2 which is having anatase band gap of 3.2 eV. There is also some other types of semiconductor materials such as ZnO, SnO₂ and NiO that can be used as the replacement for TiO_2 . However, there are some advantages of TiO_2 to get more attention by the researchers. It is considered as low-priced material, non-toxic, long lasting and it is an abundant material which is easy to obtain. In addition, TiO_2 is broadly used in paints, sunscreens as well as in food industries (Subba Reddy et al., 2003).

There are several deposition methods used for thin layer preparation for example screen printing and doctor blading. The thickness usually are around 1-15µm. Both of the methods are involving the deposition of viscous colloidal TiO₂ paste onto the conducting substrate. By using a stable glass rod, the doctor blading can be conducted. It is used to spread the viscous colloid on the conducting substrate surface. The thickness was controlled using a tape frame and then removed it after the evaporation of the solvent. After that, sintering would be performed at certain temperature usually 450° to 500 °C after the deposition of the semiconductor materials. The electrical interconnection between the nanoparticles could occur with the application of high temperature and then it will form a nanostructured porous electrode. After sintering, subsequently the electrode will go through dye sensitization process which the electrode will be immersed into a dye solution for specific time (typically 24 hours) (Su'ait et al., 2015). With the electrode containing the porous nature, it will produce larger surface region that allowed more dye molecules to be absorbed. Hence, more efficient light can be harvested compared to the other type of electrodes.

2.3.3.2 Photosensitizers

In the DSSCs application, the photosensitizers or sensitizing dyes are the most necessary materials. The sensitizing dye acts by absorption of sunlight or proton into the DSSCs. For the past decades, many investigations have been taken place and a lot of work has been put in order to introduce the new and novel dyes. Hence, it could be improvised efficiency of the DSSCs. There are two types of dye in the DSSCs application: (i) inorganic dye and (ii) organic dye (Bandara et al., 2015).

Nevertheless, most of the researchers are more favored to the ruthenium based complexes as it could achieve higher efficiency about 11 to 12%. Nowadays, there are some types of ruthenium dyes that getting a lot of attention from research community: (i) N3 dye, (ii) N719 dye (Bandara et al., 2015) and (iii) black dyes (Burschka et al., 2013). Table 2.1 shows the structure of N3, N719 and black dyes.

2.3.3.3 The counter electrodes

Other important component in DSSCs is called counter electrode. The counter electrode is used to collect the electrons from the external circuit and acts as a catalyst in the reduction of redox electrolytes. As the function of counter electrode is to transfer the electron flow from external circuit back to the redox couple in the electrolytes, it must have photocurrent over the width of each solar cell. Hence, the materials should be conducting and shown a low overvoltage for reduction of the redox couple. There are several good counter electrode materials such as platinum (Pt), gold (Au) and silver (Ag). For liquid electrolyte systems, Pt is widely used as it is good in the reduction of the redox couples. While, for solid state electrolytes Au and Ag are better choices as they have a excellent ability in hole transfer. But, these materials are costly.

An interesting alternative material which has cost efficient is carbon due to sufficient conductivity, heat resistance, corrosion resistance as well as good electrocatalytic activity for triiodide ions reduction (Chou et al., 2015). Besides, porous C are easy to form from the graphite powder. The process is consisting of plate like crystal which the deposition of liquid dispersion and drying will produce align of the counter electrode. However, even with carbon is great alternative that can be used. In this research work, the conventional type of Pt counter electrode is used as we more focused on the investigation on electrolytes.



Table 2.1: The complexes of N3, N719 and black dye.

2.3.3.4 Electrolytes

The importance parameters of DSSCs performance are short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) normally depend on the electrolytes. The electrolytes are well known as redox mediator. The most successful redox mediator that has been used is liquid electrolyte with redox couple such as iodide/triiodide (I^-/I_3^-) . The diffusion of iodide/triiodide is the mechanism of the mobility of charge carriers which is able to complete the circuit of the solar cell devices. The electrochemical potential at the platinum counter electrode normally would receive a command from the redox potential

of the redox couple. At the working electrode, the reduction of the oxidized dye reaction will occur by iodide reduced to triiodide. While at the counter electrode, reduction of triiodide to iodide has occurred.

The redox couple is usually from the electrolyte which containing iodide salts and iodine as well as some additives. The different sizes of iodide also could provide the various size of cations into the system. The example of iodide salts such as lithium iodide (LiI), sodium iodie (NaI) as well as potassium iodide (KI). The additives such as room temperature ionic liquid are also added into system for example 1-hexyl-3methlimidazolium iodide (HMII). These various additives will affect the energetics of the important DSSCs parameter interface. In order to get the effective dye regeneration process, a suitable redox potential is required. This is prescribed by the success of the iodide/triiodide couple. Currently, to avoid the leakage and the uncertainty drawback that causes by liquid system, researchers have introduced the non-volatile type of redox mediator. The RTILs are used as electrolytes instead of additives because of the advantages such as non-volatility, high thermal and chemical stability and higher ionic conductivity. Sadly, the limitation of mass transport has occurred when DSSCs are used this highly viscous ionic liquid, this will lead to drop in the photovoltaic performance. On the contrary, other types of electrolytes such as solid state electrolytes have attracted interest of researchers where they use a hole-hopping mechanism to transport the ions. But, the increasing charge recombination, pore filling problems and less free mobile ions are the disadvantages that limit the usefulness nowadays. Until today, researchers are still finding the best type of redox mediator and it is the major challenge for the future of DSSC research. Hereby, polymer electrolytes are getting popular among the researchers nowadays because of the advantages of being flexible of going liquid, solid or gel types of polymer electrolytes.

2.4 Polymer electrolytes

In early of 1970s, solid-state materials like ceramic, glass and polymer electrolytes have started their development (Miyamoto, 1973). Fenton and his co-workers were the first researchers who introduced the polymer electrolytes to the scientific community (Rajendran et al., 2007) and the importance of the technologies application has been discovered in early 1980s. The past few decades, due to its usefulness in electrical/electrochemical power generation, storage and conversion system application have attracted so much attention from the nation.

Polymer electrolyte is defined as a membrane that consists of dissolution salt in a polymer network with high molecular weight. It has ionic conduction properties, thus it is so useful in electrochemical devices such as solid-state batteries, rechargeable batteries especially lithium-ion batteries. At present, polymer electrolytes have other potential in electrochemical devices such as supercapacitors, fuel cells, dye-sensitized solar cells, rechargeable batteries, and electrochemical sensors.

Polymer electrolytes are well known due to their advantages over the conventional liquid electrolytes. If comparable to liquid ionic solution, polymer electrolytes have high potential in the transport ion properties. Besides, it also has other interesting properties such as transparent material, solvent-free, light weight, flexible, able to form thin film, excellent in ionic conductivity, easy to process, and has wide electrochemical windows. Furthermore, it also can enhance the safety as it prevent some problem such as leakage, short internal, corrosion that caused by high concentration solvent, emission of harmful gas and presence of non-combustible reaction product on the electrode surface.

The polymer electrolytes can be categorized in five types (Azzahari et al., 2016):

• **Type I: classical electrolytes.** Low molecular weight solvent is mixed with the salts. The example of this category is liquid electrolytes.

- **Type II: gel polymer electrolytes.** These polymer electrolytes comprise polymer matrix that is swollen with the first type of polymer electrolytes.
- **Type III: solid polymer electrolyte**. High molecular weight polymer is mixed with the salts to obtain thin solid films.
- **Type IV: dry single ion conductors.** The ions are covalently bound to the polymer backbone and ion solvation is participated by the polymer.
- **Type V: solvated single-ion conductors.** The mixture of single ion conductors and low molecular weight solvents such as water.

2.4.1 Gel polymer electrolytes

Gel polymer electrolytes (GPEs) are also known as gel like structure which are made by adding liquid solution as plasticizer in the solid phase system. Until now, the GPE has been widely used due to its better properties that is including excellent ionic conductivity, electrochemical stability, safety and mechanical and electrical stability. Besides, it is also light in weight, solvent free, high energy density, better volumetric stability, and easy to shape into desired sizes. Moreover, the use of GPEs can reduce the leakage, corrosion and internal shorting and hence leads to long life time of the devices. These particular properties of GPE made it as better choice of the electrolyte type to replace the liquid electrolytes.

With the good performing properties of GPEs, it actually found to be suitable with the dye sensitized solar cells application. As it is formed by trapping the liquid electrolytes in the polymer matrix which makes it applicable for the application of DSSCs. The properties such as very low evaporation rate and excellent resistance to high temperature make it better electrolytes compared to others. Besides, being like gel, this type of electrolyte can improve the contact between the GPEs and the electrodes. Thus, a DSSC based on GPE would have long term stability and give a solution to the liquid electrolyte drawbacks. A high ionic conductivity is needed in order to achieve an excellent

photovoltaic performance as the short current density (J_{sc}) could be lower if the ionic conductivity is not higher enough. Unfortunately, the ionic conductivity of GPEs is still consider lower compared to liquid form. After the gelatinization process has taken place, there would be a decrease of gas because of the lower ionic conductivity but the open circuit voltage (V_{oc}) in this situation will increase due to the suppression of dark current by the polymer chains covering the surface of the TiO₂ electrode. Thus, the high energy conversion efficiency could be achieved and it can be comparable or could be improved compared to the liquid electrolytes based DSSCs (Ng et al., 2015).

Despite of all the advantages of GPEs, they are still some drawbacks into the electrochemical application especially for DSSCs. Based on DSSCs, the performance is still lower compared to the liquid electrolytes. They still have a problem regarding photovoltaic performance and stability of the DSSCs even some of the polymers could gelate the liquid electrolytes properly. The polymer network that form gel will causes restriction of ion movement in the GPEs and the gelators also might have reacted with the other materials like salts and additives of the GPEs. Hence, some of effective approaches should be done to improve the performance of the GPEs as well as photovoltaic performance.

2.4.2 Factors influencing ionic conductivity of GPE and the photovoltaic performance of their DSSCs

2.4.2.1 Polymer concentration

The higher ionic conductivity could be achieved if the polymer concentration is decreased due to the polymer matrix that trapped liquid electrolytes become larger, therefore the liquid electrolytes existence will contribute more freely moving ions. On the other hand, polymer blending where it consists of various ionic conductivities and viscosities, with the decrease amount of polymer it will increasing the ionic conductivity under same salt concentration. For example, the conductivity of PEO/PPC polyblend decreased with the decreasing amount of PEO (Yu et al., 2010). The reasons are:

- i. A PEO-salt complex had higher conductivity compared to PPC-salt complexes under same salt concentration.
- ii. The decrease in viscosity with increasing amount of PEO in the system exempt the segmental mobility and hence increased the conductivity of the system.

2.4.2.2 The iodide salts

As we know, the doping of salts was widely used as it acts as an important role in the ionic conductivity of the GPEs. There are several examples of the salts such as MgTf₂, LiTF and LiBOB. For DSSC applications, the energy conversion is the injection of the electrons from the excited dye into the conduction band of semiconductor electrode on the absorption light. For regenerate the photo-electrochemical cells, the redox couple such as I^{-}/I_{3}^{-} is used to reduce the oxidized dye and functions as the charge carrier mediator. Thus, the iodide salts such as (KI, NaI, LiI, TPAI, etc.) were used to be given an improvement result in the energy conversion efficiency studies. Besides, as iodide salts being added into the electrolytes it could also affect the iodide ion conducting in the gel polymer electrolytes and can be related to the changes in the *J*_{sc} of DSSCs. Hence, the photovoltaic performance of DSSCs will be improved (Khanmirzaei et al., 2015a).

2.4.2.3 Temperature

As the temperature that applied into GPEs increase, the ionic conductivity will increase too. The relation between conductivity and temperature can be explained by Arrhenius thermal activated model using the following formula:

$$\sigma(T) = \sigma_0 \exp\left[\frac{-E_a}{kT}\right]$$
(2.1)
where *T* is temperature (K), σ_0 is pre-exponential factor, E_a is activation energy (eV) and *k* is Boltzmann constant (eV/K). This can be explained that ionic conductivity depends on the thermal hopping of ions as the ion mobility process involves intermolecular ion hopping (Sanad et al., 2015).

There is another model that can explain the temperature-dependent ionic conductivity of the GPEs which is the free volume model. It is explained that the polymer matrix is amorphous and contain larger amount of free volume space. As more heat applied, it causes more area and thus leads to more mobility of ions and then higher ionic conductivity of the GPEs.

2.5 Strategy to improve the properties of the GPE and their DSSCs

The first ionic liquid was synthesized by Paul Walden in 1914. It is defined as the molten salt with the temperature lower than 100 °C. Walden synthesized the ionic liquid by neutralization of ethylamine with concentrated nitric acid to yield ethylammonium nitrate [EtNH₃][NO₃]. In 1980s, Hussey and coworker were first researcher that synthesized the most used cations in the recent work. However, these new emerging imidazolium ionic liquids were very sensitive to moisture as it will react with other chemical materials such as chloroaluminate (AlCl₃). Then, the imidazolium ILs which are stable to air and water were first synthesized in the 1992 by using nitrate (NO₃), tetrafluoroborate (BF₄) and acetate (CH₃COO) anions. Thus, nowadays there is more stable ionic liquid that becoming useful and common in its field especially in polymer electrolytes.

Ionic liquids usually have low melting points. Due to their larger size of anions that they have contained where the ions are big, have high flexibility organic groups and highly delocalized charges. These attributes result in small lattice enthalpy changes for crystallization and much bigger in the entropy changes for them to melt. Thus, the liquid state is more favorable. Moreover, electrolytes that containing imidazolium based ionic liquid such as 1-propyl-3-methlylimidazolium iodide (MPII) and 1-butyl-3-methylimidazolium iodide (BmimI) ionic liquids implement a excellent efficiencies, ionic conductivity and great stability for dye-sensitized solar cells (Singh et al., 2008; Khanmirzaei et al., 2015b).

The 1-propyl-3-methylimidazolium iodide (MPII) ionic liquid ($C_7H_{13}IN_2$) has molar mass of 252.10 g/mol. The MPII ionic liquid structure is shown in Figure 2.3. On the other hand, 1-butyl-3-methylimidazolium iodide (BmimI) ionic liquid ($C_8H_{15}IN_2$) has molar mass of 266.12 g/mol. The structure of BmimI has one extra of CH₂ compared to MPII ionic liquid as represented in Figure 2.4.



Figure 2.3: Structure of MPII ionic liquid (Aldrich).



Figure 2.4: Structures of BmimI ionic liquid (Aldrich).

2.6 Poly(propylene) carbonate (PPC)

Poly(propylene) carbonate is one of the synthetic polymer that utilize CO_2 as direct starting material for polymer synthesis (Zhou et al., 2013). PPC also has similar structure to carbonate-based organic solvents presently used in conventional gel electrolytes as shown in Figure 2.5. It also may have good compatibility with the salts used in polymer electrolytes as well as offer good interfacial contact with the electrode in electrochemical devices especially DSSC. PPC-based electrolytes are highly transparent if compare with PEO and (PVdF-co-HFP) because of amorphous nature of PPC. Furthermore, the T_g of PPC is lower compare to PMMA as it close to room temperature. Hence, it can be turned into a rubbery state by incorporating of ionic liquid and thus can facilitate the movement of ions in the polymer (Choi et al., 2011). With above-mentioned advantages make PPC a promising candidates for host polymer used in this work.



Figure 2.5: Structure of Poly(propylene) carbonate. (Aldrich).

2.7 Summary of the chapter

This chapter discussed the current literature related to solar cells, DSSCs, polymer electrolytes, gel polymer electrolytes. The factors that influence the ionic conductivity of GPE and the photovoltaic performance of their DSSCs have been discussed in this chapter. It is also discussed about the strategies that can be used to overcome the disadvantages of the GPE.

CHAPTER 3: METHODOLOGY

3.1 Introduction of the chapter

The materials and chemicals used are discussed in this chapter. It proceeds with the discussion on the methodology for the gel polymer electrolytes preparation, dye sensitized solar cell fabrications as well as characterizations (electrochemical impedance spectroscopy studies, structural studies and solar cell characterizations).

3.2 Materials

The materials used are divided into two parts: gel polymer preparation and electrode preparation. For gel polymer electrolytes preparation, polymer, iodide salt and some imidazolium iodide as ionic liquid were used. Poly (propylene) carbonate (PPC) was used as host polymer. Sodium iodide (NaI) was used as iodide salts. Ethylene carbonate (EC) and propylene carbonate (PC) were used as solvent/plasticizer. 1-methyl-3-propylimidazolium iodide (MPII) and 1-butyl-3-methylimidazolium iodide (BmimI) were used as ionic liquids. All the materials were purchased from Sigma-Aldrich. Iodine (I₂) was purchased from Friedemann Schmidt Chemical. For electrode preparation, two different sizes of TiO₂: (i) P90 (14 nm) and (ii) P25 (21 nm) were purchased from AEROXIDE. The Triton X-100 was purchased from Sigma Aldrich. The carbowax was purchased from Supelco Analytical. N719 ruthenium dye (Di-tetrabutylammonium cisbis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)) was used as inorganic dye and was purchased from Sigma-Aldrich.

3.3 Preparation of Gel Polymer Electrolyte

In this research work, three different gel polymer electrolyte systems were prepared. Firstly, the system was started with only PPC polymer and sodium iodide salts based system. Then, continued with another two systems which are ionic liquid based systems. Further detailed information of the preparation was explained in the Figure 3.1.



Figure 3.1: Overview of prepared systems of the gel polymer electrolytes.

3.3.1 Iodide salt based system (1st system)

The first system was prepared using poly(propylene) carbonate (PPC) and sodium iodide salt (NaI). The designations and composition are illustrated in Table 3.1. The system of gel polymer electrolytes follow the equation PPC:EC:PC:*x*NaI, where *x* is 20, 40, 60, 80 and 100 wt.% with respect to the PPC weight. The amount of PPC, EC and PC were optimized and remained unchanged at 1.0 g, 1.25 g and 1.25 g, respectively. For dye-sensitized solar cells, the iodine amount was one tenth of the molar ratio NaI salts (1:10). The iodine is introduced as redox mediator which provide I/I_3^- redox. The applicable amount of EC, PC, NaI and I₂ were mixed in a closed bottle and then continuously stirred at 100 °C until all the chemicals completely dissolved. Afterwards, PPC was added slowly into the mixture and stirred at 100 °C for 2 hours to get gelatinized and homogenous mixture. Then the resulting electrolyte was cooled down at room temperature. This series of step were repeated with different compositions as indicated in Table 3.1.

Designation	NaI (wt.%) composition with respect to PPC weight
PNa-1	20
PNa-2	40
PNa-3	60
PNa-4	80
PNa-5	100

Table 3.1: Designation and composition of 1st system (PPC:EC:PC:xNaI system)

3.3.2 Imidazolium iodide based ionic liquid systems (2nd system and 3rd system)

These two systems were prepared with incorporation of PPC polymer, NaI salts, BmimI (2nd system) and MPII (3rd system) ionic liquid. The optimization of NaI salt from 1st system was used to prepare the last two systems (60 wt.% of NaI). These two systems follow the equation PPC:EC:PC:NaI:yIL where *y* is 20, 40, 60, 80 and 100 wt.% with respect to the PPC weight (IL=BmimI and MPII). The designation and composition were tabulated in the Table 3.2 and Table 3.3 for BmimI and MPII, respectively. Firstly, the appropriate amounts of EC, PC, NaI, I₂ and BmimI/MPII were blended in the closed bottle at 100°C. The mixture were continuously stirred until all the chemical dissolved and lastly PPC was added slowly while stirring at 100°C for 2 hours until the mixture completely dissolved and homogenous. The resulting electrolyte was then cooled down at room temperature. This method also was repeated for different ratio of electrolyte as presented in Table 3.2 and Table 3.3.

Designation	BmimI (wt.%) composition with respect to PPC weight
BMIM-1	20
BMIM-2	40
BMIM-3	60
BMIM-4	80
BMIM-5	100

Table 3.2: Designations and composition of 2nd system (PPC:EC:PC:NaI:yBmimI system)

Table 3.3: Designations and composition of 3rd system (PPC:EC:PC:NaI:yMPII system)

Designation	MPII (wt.%) composition with respect to PPC weight
MPII-1	20
MPII-2	40
MPII-3	60
MPII-4	80
MPII-5	100

3.4 Preparation of working electrode

Firstly, the fluorine doped tin oxide (FTO) was cleaned before prior to use. The mesoporous TiO_2 layer was used as base materials of the deposition of the sensitizers. The working electrode consists of two different layers of TiO_2 (P90 and P25). The working electrode was fabricated by coating two layers of TiO_2 on FTO glass; spin coating on the first layer followed by doctor blade for the second layer (Khanmirzaei et al., 2015a). For the first layer, the mixture consist of 0.5 g of TiO_2 (P90) and 2ml of nitric acid (HNO₃) (pH=1) were grounded for 30 min using the mortar agate and then spin

coated at i) 1000 rpm for 2 s and followed by ii) 2350 rpm for 60 s on the FTO glass. The resulting P90 coated on FTO glass then was sintered at 450 °C for 30 min and let it to cool down at room temperature. The second layer was then prepared using the mixture of TiO_2 (P25), 2 ml of nitric acid (HNO₃), a few drop of Triton X-100 and 0.1 g of carbowax. The mixture then was coated on the first layer using doctor-blade method and sintered at 450 °C for 30 min. The thickness was controlled by using magic tape. Lastly, the resulting electrode was immersed in ethanolic dye solution containing Ruthenium dye N719 (Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)) for 24 hr before used.

3.5 Preparation of counter electrode

The counter electrode was prepared by dripping an aqueous solution of chloroplatinic acid (H₂PtCl₆) and isopropyl alcohol (C₃H₇OH) with the ratio 1:1 on the FTO glass and then air dried. The electrode then was sintered at 100 °C for 5 min and followed by 500 °C for 30 min. The resulting Pt electrode was washed carefully using ethanol. This procedure was repeated 2 to 3 times until the desired Pt electrode was obtained.

3.6 DSSCs Fabrication

In this research work, two electrodes which are working electrode and Pt counter electrode, and the prepared GPEs were used to fabricate the DSSC. The prepared GPEs were sandwiched between working electrode and Pt counter electrode as illustrated in Figure 3.2 and the assembled DSSCs were kept in the fixed position as shown in Figure 3.3. The assembled DSSC was then tested under the illumination in the range of 100 mWcm⁻² simulated sunlight from ABET sun simulator, with an Autolab potentiostat for fabrication of DSSCs. The measurement of J-V characteristic was repeated for three times and the average value of the results were reported in this work.



Figure 3.2: Illustration diagram of assembled DSSC.



Figure 3.3: Assembled DSSC.

3.7 Characterization techniques

Several types of instruments were used to analyze gel polymer electrolyte for various types of studies. The studies were done as the following:

- Ionic conductivity and temperature-dependent ionic conductivity studies using Electrochemical Impedance Spectroscopy (EIS).
- Structural studies using X-ray Diffraction spectroscopy (XRD) and Fourier Transform Infrared spectroscopy (FTIR).
- 3) Photovoltaic studies.

3.7.1 Electrochemical Impedance Spectroscopy (EIS) studies

HIOKI 3532-50 LCR HiTESTER bridge interface with computer were used to conduct impedance spectroscopy in order to study the electrochemical properties of gel polymer electrolytes. Gel polymer electrolytes were sandwiched between two stainless steel electrodes as it function as blocking electrode for ions as shown in Figure 3.4. Frequency range from 50 Hz to 50 MHz was used for the measurements.



Figure 3.4: Image of stainless steel electrodes.

At every single frequency, a set of complex impedance, Z^* values were obtained and from the Z^* value new sets of real impedance, Z' and imaginary impedance, Z'' were obtained. It was calculated by the following equations:

$$Z' = |Z(\omega)|\sin\theta \tag{3.1}$$

$$Z'' = |Z(\omega)|\cos\theta \tag{3.2}$$

The complex impedance data, Z^* can be represented by its real, Z' and imaginary, Z'' parts by relation:

$$Z^* = Z' - iZ'' \tag{3.3}$$

where *i* is a "imaginary unit".

3.7.1.1 Ionic conductivity measurement

From all the impedance data obtained, the complex impedance plot can be formed. An imaginary impedance component (Z'') versus the real impedance component (Z') can be plotted as a complex impedance graph or known as Cole-Cole plot. Typical Cole-Cole plot was presented in Figure 3.5. A spike can be observed from the Cole-Cole plot for each samples. From the plot, the bulk resistance value (R_B) can be obtained by intersection of the arc on the Z_{real} x-axis which is the R_B value was important component to be used to calculate ionic conductivity. The ionic conductivity can be calculated by using the following formula:

$$\sigma = \frac{L}{R_B A}$$
(3.4)

where σ is the ionic conductivity (S cm⁻¹), *L* is the thickness of the gel film (cm), *R*_B is the bulk resistance (Ω) and *A* is the area of the electrode that touched with the sample (cm²).



Figure 3.5: Typical Cole-Cole impedance graph for sample PNa-0.

3.7.1.2 Temperature-dependent ionic conductivity measurement

By studying the temperature-dependent ionic conductivity, the researchers are able to find out the investigated electrolyte system follow which model. There are two important model that have been introduced in the polymer electrolytes: i) Arrhenius model and ii) Vogel-Tammann-Fulcher (VTF) model (Dissanayake et al., 2013). The relation between ionic conductivity and temperature can be explained by Arrhenius thermal activated model following formula in Equation 2.1.The value of activation energy can be obtained from Equation 2.1 and calculated from the graph of log σ against 1000/*T*.

While for the VTF model, from the VTF equation below it can be expressed the behavior of the sample:

$$\sigma T^{1/2} = A \exp\left[\frac{-E_a}{k_B(T-T_0)}\right]$$
(3.5)

where *T* is the temperature (K), *A* is pre-exponential factor, T_0 is reference temperature related to glass transition temperature (T_g) (K) (Xia et al., 2006).

The temperature-dependent behaviors of GPEs were conducted by using HIOKI 3532-50 LCR HITESTER with convection oven (YIHDER-DK-500D) at the temperature between 303 K to 373 K with the increment of 10. The activation energy for all GPEs were calculated using Equation 2.1 as all the samples followed Arrhenius thermal activated model.

3.7.2 X-ray Diffraction (XRD) studies

A rapid analytical technique called XRD is used to describe crystalline nature of the material and provide more information about the dimensions of the cell unit. The XRD was discovered by Max von Laue which he found that crystalline substance literally can act as tree-dimensional diffraction grating for the X-ray wavenumber and it is related to the spacing of the planes in a crystal lattice. X-ray diffraction is based on the constructive interference of the monochromatic X-ray and crystalline pattern. A cathode ray tube was used to generate these X-rays and then it is filtered to produce monochromatic radiation. Subsequently, the monochromatic radiation is collimated to accumulate before directed towards the samples. When there is interaction of the X-ray with the sample, constructive interference and a diffracted ray will be produced with the conditions that satisfy the Bragg's Law as shown below:

$$n\lambda = 2d \sin\theta$$
 (3.6)

where *n* is positive integer, λ is wavelength of incident wave (nm), *d* is the distance (nm) and θ is the scattering angle (degrees).

This law is related to the wavenumber of the electromagnetic radiation diffraction angle and the lattice spacing in the crystalline sample. The XRD then detected, processed and studied. All possible diffraction direction of the lattice could be achieved due to the random orientation of the powder material, thus all sample must be scanned at the range of 2θ angles. To determine the relative abundance of the crystalline compounds, heterogeneous mixture are characterized by using XRD.

In this research. XRD is used to study the structure of the gel polymer electrolytes. By XRD Siemens D 5000 diffractometer (40 kV, 40 mA) with Cu-K α radiation and wavelength of λ =1.540600 Å for 2 θ range of 5 to 80° at ambient temperature, the analysis was conducted.

3.7.3 Fourier transform infrared spectroscopy (FTIR) studies

By FTIR spectroscopy, the fundamental vibration of the polymer electrolytes were studied with the wavenumbers region between 4000 and 500 cm⁻¹ at a resolution of 1 cm⁻¹ using Thermo Scientific Nicolet iSIO Smart ITR machine. Resonance frequencies is that a particular molecules will absorb light energy at the specific wavenumber.

When the beam of infrared light passes through the sample, the spectrum of FTIR of a sample is collected. At each wavenumbers, the transmitted light could exposed its energy that has already absorbed. The FTIR spectrometer could assist in measuring all the wavenumber at once. The instrument will produce the transmittance and absorbance spectrum. The details about the molecular structures of a sample could be known by analyzing the absorption characteristics.

3.7.4 Photovoltaic studies

DSSC efficiency was determined by its photocurrent density versus voltage (J-V) characteristics under the standard illumination conditions with an intensity of 100 mWcm⁻ ² which also represented as 1 sun. The sunlight usually would be affected by different conditions of the atmosphere on the incident angle. Thus, the illumination conditions were provided by a calibrated lamp source from the solar simulator.

By adjusting the external load which is from zero load (short-circuit circumstances) to infinite load (open-circuit circumstances), the photocurrent density versus voltage characteristic were controlled. Figure 3.6 shows the typical J-V curve of photovoltaic performances.

When the photocurrent and the voltage is at its maximum, the maximum power is produced. The electrical power (P) is defined by current density (J) time voltage (V):

$$P=JV \tag{3.7}$$

The fill factor (FF) were formulated by the degree of the squared shape of the JV curve in the equation following:

$$FF = (J_{max} \times V_{max})/(J_{sc} \times V_{oc})$$
(3.8)

The ratio between the power generated and power of incident light are called as the DSSC efficiency as shown in equation below:

$$\eta = P_{out}/P_{in} = (J_{sc} \times V_{oc} \times FF)/P_{in}$$
(3.9)



Figure 3.6: Illustration of Photocurrent density-voltage characteristics of a DSSCs (Kniepert et al., 2015).

3.8 Summary of the chapter

The procedures including GPE preparations and designations for each system, DSSC

fabrications and related characterizations are discussed in this chapter.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Introduction of the chapter

PPC based gel polymer electrolyte (GPE) systems were analyzed and discussed in this study using various characterizations of method such as EIS, FTIR, XRD and photovoltaic studies.

4.2 PPC:EC:PC:NaI gel polymer electrolytes (system 1)

4.2.1 Electrochemical impedance spectroscopy (EIS) studies

Electrochemical impedance spectroscopy (EIS) can be used to characterize the electrical properties of the interface between the electronic and ionic conducting phases. Using EIS, we can also determine the dynamics of bound or ion movement in the bulk or interface regions of different type of solid or gel conducting materials (Vijayakumar et al., 2015). The EIS study of GPE samples for system 1 were divided into two part which is room temperature ionic conductivity and temperature-dependent ionic conductivity in the sections 4.2.1.1 and 4.2.1.2, respectively.

4.2.1.1 Room temperature ionic conductivity studies

Polymers can be categorized as ionic and electronic insulators. In a polymer electrolyte, the ionic conduction is normally coming from the diffusions of the ions through the free space inside the polymer network. That's the reason of adding an inorganic salt into the polymer in order to form a mixture that backing ionic conduction (Vijayakumar et al., 2015). In our work, the salt used was NaI which is smallest in size compared to potassium iodide (KI) or ammonium iodide (NH₄I) salts. The salts will play an important role inside the polymer electrolyte to boost the ionic conductivity will be explained in the discussion later.

Table 4.1 shows the values of bulk resistance for pure PPC (PNa-0), and all GPE sample with different composition of NaI salts (PPC:EC:PCNaI); PNa-1, PNa-2,PNa-

3,PNa-4 and PNa-5. The Cole-Cole plot for pure PPC (PNa-0) was demonstrated in the Figure 4.1. The figure shows a semicircle and straight line which indicates the big bulk resistance (R_b) and low ionic conductivity. This shows that it behaves like an insulator.



Figure 4.1: Cole-Cole plot for Pure PPC (PNa-0).

While, Figure 4.2 exhibits the Cole-Cole plot for all GPE samples in PPC:EC:PC:NaI system (a) PNa-1, (b) PNa-2, (c) PNa-3, (d) PNa-4 and lastly (e) PNa-5. As shown in Figure 4.2, the bulk resistance, R_b for sample PNa-3 is lowest compared to other samples. It indicates that the highest ionic conductivity is achieved when the R_b is the lowest. The PNa-0 is the sample of pure PPC with the addition of EC and PC only in order to form a gel polymer electrolyte. As seen in the Figure 4.1, the typical impedance behavior has shown. A semicircle region can be seen in the high frequency and then followed by a straight line or spike which indicates as the residual tail at low frequency.

It can be explained by the phenomenon of a resistor where it shows there are ion movements through the network of gel polymer electrolytes. A capacitor is represented that there is static polymer chain becomes polarized in the alternating field. Thus, the existence of semicircle that have been observed at high frequencies are because the presence of the ion mobility and large amount of polarization that are in parallel (Kim & Oh, 2000; Ng et al., 2015).



Figure 4.2: Cole-Cole plot for all GPE samples in the PPC:EC:PC:NaI system.

Designation	Nal salts composition (wt.%) with respect to PPC weight	Bulk resistance R_b (Ω)
PNa-0	0	420
PNa-1	20	74
PNa-2	40	66
PNa-3	60	62
PNa-4	80	90
PNa-5	100	100

 Table 4.1: Bulk resistances in PPC:EC:PC:NaI system.

Consequently, the semicircle that can be seen in the PNa-0 sample is faded in the Cole-Cole plot for most of sample in the system 1. At the low frequencies, the linear region refer to the effect of blocking electrodes and the conduction process in the bulk of the complex was related to the semicircle at high frequencies. Hence the disappearance of the semicircle can be explained that charge carrier was contained with the mostly ions and the total conductivity was mainly caused by ion conduction only. There is also showing an excellent interface contact between the electrodes and polymer electrolytes (Kim & Oh, 2000).

The ionic conductivity was calculated using Equation 3.4 where the bulk resistance (R_b) was obtained from the Cole-Cole plot for all the samples. The value of ionic conductivity for all the samples in the system 1 were tabulated in Table 4.2. The ionic conductivity value for each sample also was plotted in Figure 4.3. From the results we can observe that there is an increment in the ionic conductivity when NaI was added into the gel polymer electrolyte which is from 3.11×10^{-1} mS cm⁻¹ (PNa-0 sample) to 1.68 mS cm⁻¹ (PNa-1 sample). After that we can observe that the ionic conductivity increases up to 60 wt.% of NaI salt content. Then, there is a drop in the ionic conductivity after further addition of NaI salts. The highest ionic conductivity of 2.01 mS cm⁻¹ was achieved at 60 wt.% of NaI.

At the low concentrations of NaI salt, the ionic conductivity is low due to less amount of charge carriers in the gel polymer electrolytes. It can be said that at this point the ionic conductivity was dependent on the mobility of the ions and the ion conduction pathways. As the number of charge carriers that generated by NaI was increased, this leads to the increment of ionic conductivity.

Designation	Conductivity, σ (mS cm ⁻¹)
PNa-0	3.11×10^{-1}
PNa-1	1.68
PNa-2	1.89
PNa-3	2.01
PNa-4	1.38
PNa-5	1.25

Table 4.2: The variation of ionic conductivity for all GPEs in the PPC:EC:PC: NaI system.



Figure 4.3: Variation of ionic conductivity as a function of NaI salt content in GPEs.

NaI salts consists of Na⁺ and I⁻ ions. When there is more of these charge carriers present in the electrolytes, it can prevent the loss of the Na⁺ ions and hence it helps the ions to decouple. After further addition of NaI salts, the ionic conductivity start to drop. This is due to the GPEs already achieved the optimum threshold that electrolytes can take in (Jun et al., 2013). Moreover, there is formation of excess mobility of ions that can cause the agglomeration between the ions. The mobility of charge carriers can be disturbed by the forming of ion pairs from the overabundance of charge carriers (Kim et al., 2003).

4.2.1.2 Temperature-dependent ionic conductivity studies

The Arrhenius plot is shown in Figure 4.4 for the ionic conductivity versus temperature. The ion conduction mechanism has followed Arrhenius theory as we can observes the straight line from the graph in the range of 0.96 to 0.99.

By obeying Arrhenius theory, the ion movements in the GPE are hopping from other place to another place which is show that the mobility. As the temperature increases, the energy also increases which leads more the ions to move around the network chain. Hence this can cause the increment of ionic conductivity too (Lai et al., 2009). The minimum energy required to start the chemical reaction is called as activation energy. This energy is used for ions to hop from its own site to another neighboring site. From Figure 4.4, the activation energy can be calculated using the gradient of the graph. Where the activation energy is represented as E_a and the unit is in the electron volt (eV). Table 4.3 exhibits the value of E_a calculated for all GPE samples in the PNa:EC:PC:NaI system. It can be observed that sample PNa-3 has the lowest value of E_a which is 0.150 eV and it is lower compared to other samples in this system. It can be explained that the ions need less energy to hop from one location to another location. Thus, it will have greater mobility of ions and then augment the ionic conductivity.



Figure 4.4: Arrhenius plot for PNa-1, PNa-2, PNa-3 and PNa-4.

Table 4.3: The activation energy, E_a value for all GPE samples of PPC:EC:PC:NaI system.

4.2.2 XRD studies

The XRD patterns confirm the complexation between the PPC and NaI salt in the system 1. The XRD patterns of pure material and GPEs are highlighted in Figure 4.5(a) and Figure 4.5(b) respectively. Figure 4.5(a) shows XRD patterns of Pure PPC (PNa-0) and Pure NaI salt while Figure 4.5(b) shows the XRD patterns of samples PNa-2, PNa-3 and PNa-4. From Figure 4.5(a), XRD pattern of NaI salt were shown two sharp peaks at $2\theta = 21^{\circ}$ and 34° which indicate the crystalline characteristic of NaI salt. For pure PPC XRD patterns, show amorphous characteristic with two broad peak available at angles of $2\theta = 10^{\circ}$ and 22° .

The crystalline peak of NaI salt that observed earlier started to disappear into PPC: EC:PC:NaI based gel polymer electrolytes. This situation can be explained that the NaI was completely complexed with the PPC polymer. It also starts to show amorphous behavior after the addition of NaI salt as the appearance of the broad characteristic peak. Besides, the complexation can be confirmed based on the changes in the intensity of the gel polymer electrolytes. It can be seen that the intensity was dropped after the addition of NaI up to 60 wt.% (PNa-3) and then slightly increased after that. Thus, it is shown that the degree of crystallinity decreases then it increases the amorphous area in the gel polymer electrolytes hence the increment of ionic conductivity has occurred. Moreover, with the increase in the flexibility of polymer backbone the ion mobility could move faster inside the polymer matrix and hence leads to increase the ionic conductivity(Lu et al., 2013).



Figure 4.5: XRD patterns for (a) Pure PPC, pure NaI (b) PNa-2, PNa-3 and PNa-4.

4.2.3 FTIR studies

FTIR spectroscopy was used to study and prove the occurrence of complexation within the materials. After the addition of various materials into a system, it can be observed that there is changing in the FTIR spectra. Besides, the different concentration that have been added into the system also could cause the changes in the FTIR spectra (Noor et al., 2014). Figure 4.6 illustrates the FTIR spectra of pure PPC, pure NaI and three different concentrations of NaI in the system of PPC:EC:PC:NaI (PNa-2, PNa-3 and PNa-4). The band assignments of PPC were compiled and tabulated in Table 4.4. Figure 4.7 demonstrates the FTIR spectra with different region of wavenumbers; (a) region between 2000-2500 cm⁻¹ and (b) region between 1200-1000 cm⁻¹ for pure PPC, PNa-2, PNa-3 and PNa-4.

In Figure 4.7(a), the band at 1801 cm⁻¹ can be referred to the stretching vibration of the C=O bond in pure PPC. After the addition NaI salt, the band at 1801 cm⁻¹ is broadened due to the new band existence at lower band wavenumber and there is two bands blend together into a broad band (Zhou et al., 2013). This is proven that there is interaction between the Na⁺ and the carbonyl oxygen of PPC. On the other hand, the band at 1165 cm⁻¹ which is represented the C-O-C stretching vibration band (Figure 4.7(b)) can be seen. The band was shifted from 1165 cm⁻¹ to 1160 cm⁻¹ after the addition of NaI salt into the system. This is because the complexation has occurred between the pure PPC and the NaI salt.



Figure 4.6: FTIR spectra of Pure PPC, NaI salt, PNa-2, PNa-3 and PNa-4.

Wavenumbers (cm ⁻¹)	Band Assignments	References
3600-3000	O-H stretching (v)	(Bandara et al., 2010)
2990	C-H ₂ deformation (m) -(CH ₂)	(Bandara et al., 2010)
1710-1780	C=O(stretching)(s)	(Zhou et al., 2013)
1456	C-H bending (v) - (CH_2)	(Zhou et al., 2013)
1390	C-O-H bending, C-H twisting (CH ₂)	(Zhou et al., 2013)
1300-1100	C-O-C stretching (<i>s</i>)	(Wu et al., 2015)
1074	C-O-H bending (v)	(Wu et al., 2015)
973	C-H bending (v)	(Wu et al., 2015)
852	C-H deformation	(Dissanayake et al., 2013)
775	C-O-H bending (v)	(Zhou et al., 2013)

Table 4.4:	Band	assignments	of Pure	PPC.
I ubic iiii	Dunu	assignments	011010	110.

Note: (s) = strong, (m) = medium, (v) = variable



Figure 4.7: FTIR spectra in the region (a) 2000-1500 cm⁻¹ and (b) 1200-1000 cm⁻¹ for Pure PPC, PNa-2, PNa-3 and PNa-4.

4.2.4 Photocurrent versus voltage (J-V) characteristics

The photocurrent density versus voltage (J-V) curves for all GPE samples are illustrated in the Figure 4.8. In Table 4.5, the results of the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and energy conversion efficiency (η) were tabulated and summarize. It can be noted that the photovoltaic performance is influenced by the increasing amount of NaI content. In particular, η and J_{sc} values varied widely in the investigated domain, while the variation of FF is not much but still appreciated. The open-circuit voltage, V_{oc} instead seems not dependent on the change in the concentration as it does not change much. It is observed that J_{sc} increases NaI concentration increases and this would be explained by the increase of the iodide ion conduction.

It can be observed that the value of J_{sc} normally related to the movement of ions which is identical to the ionic conducting mechanism (Noor et al., 2014).Furthermore, as the mobility of ions increase will provide more diffusion ability of triiodide, I_3^- and then it caused the regeneration capability of the dye molecules to increase as well. Hence, it can also improve the photovoltaic performance (Khanmirzaei et al., 2015b). Thus, J_{sc} plays main role in the variation of the photovoltaic performances for these GPE samples. The highest energy conversion efficiency was achieved at PNa-3 which is 6.38% with J_{sc} of 22.88 mAcm⁻², V_{oc} of 0.458 V and fill factor of 60.9%.



Figure 4.8: Photocurrent density versus cell potential (J-V) curves for all GPE samples in the PPC:EC:PC:NaI system.

Electrolyte	J _{sc} (mA cm ⁻²)	$V_{oc}\left(\mathbf{V} ight)$	FF (%)	Efficiency, η (%)
PNa-1	8.93	0.550	61.0	2.99
PNa-2	20.42	0.483	59.7	5.89
PNa-3	22.88	0.458	60.9	6.38
PNa-4	15.91	0.463	61.7	4.55
PNa-5	10.70	0.483	60.3	3.12

Table 4.5: Dye-sensitized solar cell parameter for PPC:EC:PC:NaI system.

4.3 PPC:EC:PC:NaI:BmimI gel polymer electrolyte system (system 2)4.3.1 Electrochemical Impedance Spectroscopy (EIS) studies

The EIS study of GPE samples for system PPC: NaI: BmimI were divided into two part which is room temperature and temperature dependence in the sections 4.3.1.1 and 4.3.1.2 respectively.

4.3.1.1 Room temperature ionic conductivity studies

Cole-Cole plot for all GPE samples in the PPC:EC:PC:NaI:BmimI system were depicted in the Figure 4.9. The graph shows that the bulk resistance, R_b is increased when BmimI ionic liquid was added in the GPE system. The R_b value for all samples were tabulated in Table 4.6.



Figure 4.9: Cole-Cole plot of all GPE samples in the PPC:EC:PC:NaI:BmimI system.

Designation	BmimI ionic liquid composition (wt. %) with respect to PPC weight	Bulk resistance, R_b (Ω)
BMIM-0	0	62
BMIM-1	20	56
BMIM-2	40	46
BMIM-3	60	26
BMIM-4	80	34
BMIM-5	100	44

Table 4.6: The bulk resistance, R_b values for all GPE samples in the PPC:EC:PC:NaI:BmimI system.

The effect of BmimI ionic liquid addition on the ionic conductivity of the GPE samples was investigated and the summarized data were tabulated in Table 4.7 and represented in Figure 4.10. There is an increase up to 60 wt.% of BmimI content in ionic conductivity which is 4.79 mS cm⁻¹, then there is a drop after further addition of BmimI ionic liquid into the GPE system. The increment in ionic conductivity after addition of ionic liquid is due to the increase of mobility of charge carriers which are from BmimI ionic liquid (Bmim⁺ and I⁻) and NaI salt (Na⁺ and I⁻). Moreover, due to the high self-dissociating and ion transporting properties of the ionic liquid more charge carriers in the GPE will be provided. Hence, the ionic conductivity is increased. On the contrary, one of the main function of ionic liquid is plasticizing effect where it softens the polymer backbone. This will increase the amorphous region inside the electrolytes and gain more ion transports to decouple (Ng et al., 2015). However, after further addition of BmimI ionic liquid we can observe dropping in ionic conductivity. This is because of the agglomeration of the extra mobile ions and lead to the formation of ions (Kim et al., 2007).

Designation	BmimI ionic liquid content (wt.%) with respect to PPC weight	Conductivity, σ (mS cm ⁻¹)
BMIM-0	0	2.01
BMIM-1	20	2.22
BMIM-2	40	2.71
BMIM-3	60	4.79
BMIM-4	80	3.66
BMIM-5	100	2.83

Table 4.7: Variation of ionic conductivity of GPE samples in the PPC:EC:PC:NaI:BmimI system.



Figure 4.10: The ionic conductivity of all GPE samples in the system of PPC:EC:PC:NaI:BmimI.

4.3.1.2 Temperature-dependent EIS studies

By obeying Arrhenius theory, the ion transport mechanism of the PPC: NaI: BmimI GPE system was explained. The Arrhenius plot was expressed in Figure 4.11 by varying the temperature range from 303 K to 373 K. The regression value in the range of 0.96-0.98 was proved that all GPEs sample in this system follow Arrhenius theory after the addition of BmimI ionic liquid. Arrhenius theory defined that mobility of ion increases by hopping from its own site to the neighboring vacant site as the temperature is increased as well. In the amorphous phase, the ionic conductivity also dependent on the transporting of charge carrier. Thus, the ion conduction became higher as the temperature increases.

The activation energy, E_a of GPE samples can be obtained by calculating each of the gradient of the GPE samples. With the minimum energy required, the ions able to hop from first place to another places. Thus, GPEs with lowest E_a value is expected to have more of free movement ions and hence, it shows surpassing ionic conductivity. Table 4.8 was tabulated with the variation of activation energy, E_a of each GPEs sample in this system. It is expected that BMIM-3 have the lowest E_a as it has highest ionic conductivity.



Figure 4.11: Arrhenius plot for all GPE samples in the PPC:EC:PC:NaI:BmimI system.

Electrolytes	Activation energy, E_a (eV)
BMIM-1	0.202
BMIM-2	0.185
BMIM-3	0.144
BMIM-4	0.169
BMIM-5	0.224

Table 4.8: Variation of activation energy, E_a of all the GPE samples in the PPC:EC:PC:NaI:BmimI system.

4.3.2 XRD studies

Figure 4.12(a) and Figure 4.12(b) are illustrated the XRD patterns for the samples of system 2. For earlier system where NaI salt was added to the host polymer, PPC:EC:PC:NaI, the XRD patterns was shown a broad peak or amorphous phase. The XRD patterns also consists of two broad peak. So with the addition of BmimI ionic liquid, we expected the XRD patterns would have similar as previously pattern too. In order to

confirm the complexation that happen inside the GPEs, through the observation of the changes of the intensity of the peak after the addition of BmimI ionic liquid and the shifting of the main intensity peaks in XRD pattern (Bandara et al., 2015).

The characteristic peaks found in $2\theta = 10^{\circ}$ and 22° was found to be shifted to 2θ of 9.5° and 20° for BMIM-2, to 8.5° and 23° for BMIM-3, and to 9° and 24° for BMIM-4. This shifting is also another way to confirm the complexation between the PPC, NaI salts and BmimI ionic liquid (Lee et al., 2012). This complexation can be further confirmed based on the changes in the peak of the gel polymer electrolytes. From the Figure, it can be seen that the peak become broader after the addition of ionic liquid and the intensity for sample BMIM-3 was decrease and then slight increases at BMIM-4. This have proven that there is complexation between the PPC polymer, NaI salt and BmimI ionic liquid in these electrolytes. It proved that the degree of crystallinity decreases and hence increase the amorphous area in the polymer electrolytes which could eads to an increase in the ionic conductivity. The decrease in the crystallinity is probably due to the plasticizing effect of ionic liquid which it could able to weaken the interaction of polymer backbone inside these electrolytes.


Figure 4.12: (a) XRD patterns of Pure PPC, Pure NaI salts and Pure BmimI (b) XRD patterns of BMIM-2, BMIM-3 and BMIM-4.

4.3.3 FTIR studies

FTIR spectra of pure PPC, pure NaI, pure BmimI, BMIM-2, BMIM-3 and BMIM-4 were displayed in the Figure 4.13. Figure 4.14 showed FTIR spectra of pure PPC, BMIM-2, BMIM-3 and BMIM-4 with two different regions of wavenumbers; (a) 2000-1500 cm⁻¹ and (b) 1200-1000 cm⁻¹. After the addition of BmimI ionic liquid, the band at 1801 cm⁻¹

¹ of PPC was shifted to 1780 cm⁻¹ of three GPEs sample (BMIM-2, BMIM-3 and BMIM-4) which represented C=O or carbonyl band. Moreover, the band becomes more broadened after the addition of BmimI ionic liquid. The shifting and broadening of the carbonyl band has proven that there is strong interaction between BMIM⁺ and carbonyl oxygen of PPC. This will cause the complexation between Na⁺ and C=O band of PPC becomes less and hence produce larger free Na⁺ ions inside the polymer electrolytes.

The presence of more Na⁺ will improve the ionic conductivity of the polymer electrolytes. Besides, the band at 1074 cm⁻¹ which also represented C-O-C band of PPC was shifted to 1070 cm⁻¹ after the addition of BmimI ionic liquid into the system. It is also weakening the band. Thus it shows there is complexation of PPC polymer and BmimI ionic liquid.



Figure 4.13: FTIR spectra of Pure PPC, NaI salts, Pure BmimI, BMIM-2, BMIM-3 and BMIM-4.



Figure 4.14: FTIR spectra in the region (a) 2000-1500 cm⁻¹ and (b) 1200-1000 cm⁻¹ for Pure PPC, BMIM-2, BMIM-3 and BMIM-4.

4.3.4 Photocurrent versus voltage (J-V) characteristics

In the PPC:EC:PC:NaI:BmimI system, all of GPE samples were used to fabricate DSSC. The photovoltaic (J-V) curve is plotted in the Figure 4.15 and all of the parameters used in the DSSCs were tabulated in Table 4.9. From the Figure, it can be seen that as the BmimI ionic liquid content increases, the current density J_{sc} also shows an increment. This is due to the plasticizing effect from the ionic liquid. One of the role of ionic liquids are soften the backbone of polymer matrix and then promoting more amorphous region

which leads to more ions to flow more freely. Thus, it will increase the ionic conductivity of the electrolytes and current density J_{sc} as well. This is because J_{sc} are normally related to the mobility of charge carriers where the mechanism is similar to the ion conduction. The highest energy conversion efficiency of 6.14%, exhibited by BMIM-3 with shortcircuit current density J_{sc} of 17.56 mA cm⁻², open circuit voltage V_{oc} of 0.539 V and fill factor of 64.9%. However, the energy conversion efficiency of these system is lower compared to energy conversion efficiency of PPC:EC:PC:NaI system. It show that the highest energy conversion efficiency of PPC:EC:PC:NaI is 6.38% (J_{sc}: 22.88 mA cm⁻², V_{oc}: 0.458 V and fill factor: 60.9%) which is higher than PPC:EC:PC:NaI:BmimI system with highest efficiency of 6.14% (J_{sc} :17.56 mA cm⁻², V_{oc} : 0.539 V and fill factor : 64.9%). The decreased of short-circuit current density, J_{sc} could be explained by assuming that in that cell, different limitation processes are dominant. 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 TiO₂ electrode, diffusion of triiodide to the counter electrode to the counter electrode and its reduction at the counter electrode (Munirah et al., 2016).



Figure 4.15: Photovoltaic curve of all GPEs sample in the PPC: NaI: BmimI system.

		-		-
Electrolyte	J _{sc} (mA cm ⁻²)	Voc (V)	FF (%)	Efficiency, η (%)
BMIM-1	11.625	0.529	62.9	3.87
BMIM-2	13.069	0.514	68.7	4.61
BMIM-3	17.560	0.539	64.9	6.14
BMIM-4	14.557	0.554	67.5	5.44
BMIM-5	13.221	0.524	63.4	4.39

Table 4.9: Parameters of DSSCs for GPE samples in the PPC: NaI: BmimI system.

4.4 PPC:EC:PC:NaI:MPII gel polymer electrolyte system (system 3)4.4.1 Electrochemical Impedance Spectroscopy (EIS) studies

The EIS study of GPE samples for PPC:EC:PC:NaI:MPII system were divided into two parts which is room temperature ionic conductivity and temperature-dependent ionic conductivity in the sections 4.4.1.1 and 4.4.1.2 respectively.

4.4.1.1 Room temperature ionic conductivity studies

The impedance plots for all GPE samples of PPC: NaI: MPII system were displayed in the Figure 4.16 and the values of bulk resistance for all GPEs were tabulated in the Table 4.10. From the Figure, it can be observed that there is a single spike in all of GPE samples. This is because there was a very good contact between the electrode and the GPEs and the main current carriers are the free ions which contribute to the electrical conductivity of these electrolytes (Ng et al., 2015). Besides, the R_b value decreased as the MPII ionic liquid was added to this system and increased after further addition of MPII ionic liquid.



Figure 4.16: Cole-Cole plot of all GPE samples in the PPC:EC:PC:NaI:MPII system.

Designation	MPII ionic liquid composition (wt. %) with respect to PPC weight	Bulk resistance, $R_b(\Omega)$
MPII-0	0	62
MPII-1	20	56
MPII-2	40	46
MPII-3	60	38
MPII-4	80	25
MPII-5	100	32

Table 4.10: The value of bulk resistance, R_b for all GPE samples in the PPC:EC:PC:NaI:MPII system.

Figure 4.16 exhibits the variation of ionic conductivity with the different MPII content. The values of ionic conductivity with different composition of MPII are shown in Table 4.11. From the Figure 4.17, we can see that there is an increment of ionic conductivity up to 80 wt.% of MPII content was added into the electrolytes. This is due to presence of more mobility of ions in these electrolytes which are MPIm⁺ and Γ ions. These new ions will help to improve the dissociation of NaI where it helps to decrease the solvation of Na⁺ cations. Due to its high self-dissociating, great in ions hopping and high mobility of ion in the polymer structure, it helps the ions to decouple. Thus, there is an increase in ionic conductivity (Ng et al., 2015).

Furthermore, one of the role of ionic liquid is plasticizing effect. The ionic liquid could soften the backbone of the polymer and provide more conducting pathways where the ions can move more freely. As the amorphous nature increases, the ionic conductivity of the GPEs were increased as well (Ng et al., 2015). The highest ionic conductivity was achieved at 80 wt.% which is 4.98 mS cm⁻¹. Then, it shows that ionic conductivity drop after further addition of MPII ionic liquid. This is because the electrolytes have achieved their optimum threshold after 80 wt.% of MPII content. Besides, the agglomeration of the

excess charge carriers and the formation of ion pairs has occurred (Ng et al., 2015). The formation of ion pairs will reduce the movement of ions inside the polymer network.



Figure 4.17: Variations of ionic conductivity with different MPII content.

Designation	MPII ionic liquid composition (wt. %) with respect to PPC weight	Conductivity, σ (mS cm ⁻¹)
MPII-0	0	2.01
MPII-1	20	2.22
MPII-2	40	2.71
MPII-3	60	3.28
MPII-4	80	4.98
MPII-5	100	3.89

Table 4.11: The ionic conductivity of GPE samples in the PPC: NaI: MPII system.

4.4.1.2 Temperature-dependent ionic conductivity studies

Arrhenius plot is demonstrated in Figure 4.18 where the ionic conductivity versus temperature with range between 303 K to 373 K. From the Figure, it can be observed that all GPE samples have the regression value in the range of 0.95 to 0.98 which almost linear. Thus, the mechanism of ion conduction obeyed Arrhenius theory. This phenomenon can be explained by increasing of ion hopping from other places to another places inside the electrolytes as the temperature increases. The ionic conductivity increases when the temperature increases. This is due to the more amorphous space inside the electrolytes which ions can move more freely in the polymer matrix (Kim et al., 2003).

From the Arrhenius plot, the activation energy, E_a , can be calculated from the gradient of the graph. For ions to hop from its own site to another site as it is required a minimum energy which is called activation energy, E_a . For the electrolytes to achieve higher ionic conductivity, the activation energy is expected to be less where there is greater in the free moving ions and the ions also can easily hop inside the polymer network (Kim et al., 2003). The value of activation energy, E_a , was tabulated in the Table 4.13. We can observe that sample MPII-4 has the lowest activation energy, E_a , as it has the highest ionic conductivity compared to the other samples.

Electrolytes	Activation energy, E_a (eV)
MPII-1	0.2641
MPII-2	0.2003
MPII-3	0.2142
MPII-4	0.1966
MPII-5	0.1973

Table 4.12: Activation energy, E_a of all the GPE samples in the PPC:EC:PC:NaI:MPII system.



Figure 4.18: Arrhenius plot for all GPE samples in the PPC:EC:PC:NaI:MPII system.

4.4.2 XRD studies

The XRD patterns were represented in the Figure 4.19(a) and (b) for the PPC: NaI: MPII system. A broad peak was seen in the XRD pattern in this system as it is same as the XRD patterns of system 1. With the addition of MPII ionic liquid, the GPE samples show only two broad peaks at $2\theta = 10^{\circ}$ and 24° for MPII-3, MPII-4 and MPII-5. Same as the previous systems, the complexation between the PPC polymer, NaI salt and MPII ionic liquid only can be proven by observing the intensity of the peak once the MPII ionic liquid was added into these GPE samples.

It can be seen that the peak ($2\theta = 10^{\circ}$ and 24°) becomes much broader after the addition of MPII ionic liquid into these electrolytes. Besides, the intensity of the sample MPII-4 was decrease and slightly increase back in intensity at MPII-5. Hence, it implies that there is complexation between the PPC polymer, NaI salt and MPII ionic liquid in the polymer network. It also implies that the addition of MPII further decreases the crystallinity of the gel polymer electrolytes until the optimum threshold of the GPE. This is due to the plasticizing effect of the ionic liquid which the MPII ionic liquid actually helps to soften the polymer structure. With the crystallinity decreases, it shows that the ionic conductivity of the sample increases as well. The results of the XRD patterns show the similar trend with ionic conductivity which already explained in the previous part.



Figure 4.19: (a) XRD patterns of pure PPC, pure NaI and pure MPII and (b) XRD patterns of MPII-3, MPII-4 and MPII-5.

4.4.3 FTIR studies

Figure 4.20 exhibits the FTIR spectra of pure PPC, pure NaI, pure MPII, MPII-3, MPII-4 and MPII-5. The FTIR spectra with two different range of wavenumbers (a) 2000-

1500 cm⁻¹ and (b) 1200-1000 cm⁻¹ of Pure PPC, MPII-3, MPII-4 and MPII-5 are shown in Figure 4.21. After the addition of MPII, the bands of all sample were shifted to the lower wavenumbers. The shifting from 1801 cm⁻¹ to 1780 cm⁻¹ and the broadening of band were indicated to C=O stretching of PPC. This shows that C=O band was interacted with MPIm⁺ ions (Ng et al., 2015). There is also shifting from 1165 cm⁻¹ to lower wavenumbers after the addition of MPII content. The band was corresponded to C-O-C stretching band of PPC. Due to the changes in the intensity and peaks shifting, it proves that there is complexation between PPC polymer, NaI salt and MPII ionic liquid.



Figure 4.20: FTIR spectra of pure PPC, NaI salt, pure MPII, MPII-3, MPII-4 and MPII-5.



Figure 4.21: FTIR spectra in the region (a) 2000-1500 cm⁻¹ and (b) 1200-1000 cm⁻¹ for pure PPC, MPII-3, MPII-4 and MPII-5.

4.4.4 Photocurrent versus voltage (J-V) characteristics

Figure 4.22 demonstrated the photocurrent density versus voltage (J-V) curves for DSSCs with the GPE samples in the PPC: NaI: MPII system. The parameter of the DSSCs such as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and energy conversion efficiency (η) were tabulated in Table 4.13. From the results, we can observe that the trend of J_{sc} has similarity with the trend of energy conversion efficiency (η) in this system. After the addition of MPII ionic liquid into the first system, the variation of photovoltaic performance was caused by the short-circuit density, J_{sc} . This

can be explained that the increasing of J_{sc} are caused by the increasing of MPII content in these electrolytes. Besides, iodide ion from the MPII and the intercalation of the cations into the TiO₂ electrode also increases. As we know, small cation from NaI salt which is Na⁺ can be used to reduce the movement of the electrons through the TiO₂ as the cations intercalate into the traps in the layer of working electrode. Thus, the positive shifting of the conducting band will happen and then increases the charge injection rate and it will help to improve the J_{sc} .

Nevertheless, MPIm⁺ (the bulkier cations) cases, the positive conduction band shift becomes much smaller, but it could produce more iodides (**I**[•]) due to its high ionic dissociation rate. As shown in the ionic conductivity studies earlier, with the advantages of having two different cations, the charge injection rate well increased and then will improve the J_{sc} and the efficiency of the DSSCs as well (Bandara et al., 2010). Furthermore, one of the advantages of using ionic liquid is plasticizing effect where it can increase the amorphous region of the polymer electrolyte structure and produce more contact of GPEs with the working TiO₂ and Pt counter electrode (Cells et al., 2011). Hence, it enhances the J_{sc} and photovoltaic performances. The highest photovoltaic performance was achieved at MPII-4 sample with η of 7.72%, J_{sc} of 23.67 mA cm⁻², V_{oc} of 0.544 V and fill factor of 59%.



Figure 4.22: The photovoltaic curve of DSSCs for PPC:EC:PC:NaI:MPII system.

Electrolyte	J_{sc} (mA cm ⁻²)	Voc (V)	FF (%)	Efficiency, η (%)
MPII-1	18.893	0.559	58.0	6.17
MPII-2	20.500	0.544	56.0	6.22
MPII-3	20.471	0.554	56.0	6.40
MPII-4	23.672	0.544	59.0	7.72
MPII-5	17.902	0.544	63.0	6.10

 Table 4.13: The parameter of DSSCs of GPEs sample in the PPC:EC:PC:NaI:MPII

 system

4.5 Summary of the chapter

The PPC based GPEs were well prepared and fabricated into DSSC. Sample of MPII-4 and its DSSC were found to be giving the highest ionic conductivity and energy conversion efficiency with the value of 4.98 mS cm⁻¹ and 7.72% respectively. All of the PPC based GPE samples was found to be following the Arrhenius behavior. Meanwhile, the complexation of the materials used was confirmed using FTIR and XRD techniques.

CHAPTER 5: DISCUSSION

In this work, three different gel polymer electrolyte systems such as PPC:EC:PC:NaI, PPC:EC:PC:NaI:BmimI and PPC:EC:PC:NaI:MPII have been developed. The fundamental properties such as ionic conductivity and structural properties were studied using EIS, XRD and FTIR. The photovoltaic performances of all the system also was studied.

The EIS data for the first system (PPC:EC:PC:NaI) show an enhancement of ionic conductivity with the addition of sodium iodide, NaI salt. PNa-3 showed the highest ionic conductivity. Further addition of NaI salt showed a decreasing trend in ionic conductivity. The EIS data for ionic liquid based show ionic conductivity increment with the addition of BmimI and MPII ionic liquids compared with the PPC: NaI system without ionic liquid. There is no ionic conductivity differences until 40 wt.% of BmimI and MPII in both systems. But, after the addition of 80 wt.% of ionic liquid, it showed an increment of ionic conductivity with incorporation of MPII compared with BmimI. Moreover, for PPC:EC:PC:NaI:BmimI system, the ionic conductivity is achieved as the highest and reached the optimum threshold at 60 wt.% of ionic liquid whereas for MPII, at 80 wt.% of ionic liquid obtained the optimum performance. This can be due to more plasticizing effect of MPII which increases the number of charge carriers due to high self-dissociating and mobility of ions abilities of the ionic liquid (Ng et al., 2015; Vijayakumar et al., 2015). Among all three systems, PPC:EC:PC:NaI:MPII achieved highest ionic conductivity enhancement which in MPII-4 of 4.98 mS cm⁻¹ with 80 wt.% of MPII.

The results for temperature dependent ionic conductivity show that ionic conductivity of all GPEs in this study, increases with increasing of temperature. Besides, the results show that the activation energy decreases with an increment of ionic conductivity. All three systems show that they obey Arrhenius thermal activated model behavior based on the temperature-dependent results.

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FTIR spectra in three systems in this study show confirmation of complexation between PPC polymer, NaI salt and ionic liquids (BmimI and MPII). It can observe that frequencies shift to another frequencies in all three system. Moreover, the shifting to lower frequencies in all system can be observed like shifting of frequency to lower in NaI based system. This is due to more or less accumulation and aggregation of NaI salt and ionic liquids (Khanmirzaei & Ramesh, 2013; Rani et al., 2014). The XRD patterns in all systems generally show more broadening after increase of NaI salt or ionic liquids. Besides, the broadening in systems PPC: NaI: BmimI and PPC: NaI: MPII shows more broadening compared to the first system without ionic liquid. This is due to presence of ionic liquid in GPEs after addition of ionic liquid, which can increase the ion mobility and flexibility.

DSSC performance is significantly improved in MPII-4. Besides, the current density in MPII-4 is slightly higher than PNa-3. The open-circuit voltage and efficiency in MPII-4 also is higher than PNa-3. Hence, it shows that DSSC has higher performance fabricated with MPII-4 with incorporation 80 wt.% of MPII ionic liquid. This is due to higher plasticizing effect of MPII which causes it has higher flexibility of polymer backbone and then leads to increase in ions mobility.

When the ionic liquid contents reach to 60 wt.% and 80 wt.% which means BMIM-3 and MPII-4 respectively, the efficiency in BMIM-3 and MPII-4 has been evaluated as 6.14 and 7.72 % respectively. This is due to higher current density in MPII based GPEs which results in higher short-circuit current density and higher energy conversion efficiency. The efficiency of PPC:EC:PC:NaI:BmimI system is lower compare to the efficiency of PPC:EC:PC:NaI:MPII system. This because MPII ionic liquid has lowest viscosity compare to BmimI (Fredlake et al., 2004; Pringle et al., 2002). The lowest viscosity of ionic liquid able to reduce the mass transport limitation of triiodide in the electrolytes. Hence it increases the performance of DSSCs (Munirah et al., 2016).

In addition, compared to other works in literature, this work exhibits significant energy conversion efficiency enhancement of DSSC based gel polymer electrolyte after addition ionic liquid. Table 6.1 shows the comparison of efficiency of this work with the other work. It shows that the significant improvement of efficiency up to 7.72% in this work which is comparable with some other works with the highest achieved efficiencies of 5.41% (Bandara et al., 2015), 5.0% (Azzahari et al., 2016) and 4.75% (Chou et al., 2015) with incorporation of GPE in fabrication of DSSC.

Table 5.1: Comparison of this work with other works on efficiency enhancement.

Compositions	Conductivity, σ (S cm ⁻¹)	Efficiency, η (%)
PAN: EC: PC: BMII: Pr4NI: LiI	~ 10 ⁻³	5.41 (Bandara et al.,
(GPE)		2015)
PhCh: EC: DMF: TPAI (GPE)	~10 ⁻³	5.00 (Azzahari et al.,
		2016)
PVDF-HFP: LiI: DMPII: MPN	~10 ⁻³	4.75(Chou et al.,
(GPE)		2015)
MPII-4 (this work) (GPE)	~10 ⁻³	7.72

CHAPTER 6: CONCLUSIONS

6.1 Conclusions

A set of three gel polymer electrolyte systems were prepared for the DSSC application. It was optimized and divided into three categories: 1st system based on PPC polymer with the addition of NaI salt, 2nd and 3rd based on PPC, NaI salt and different types of BmimI and MPII ionic liquids into the gel polymer electrolyte. As discussed in each section, important information has been collected and reported in this thesis.

PPC was used as host polymer with NaI as an inorganic salt, and BmimI and MPII ionic liquids were used in this research. The highest ionic conductivity of 2.01 mS cm⁻¹ have been obtained with the addition of NaI system into the gel polymer electrolytes. The suitability of the ionic liquid with PPC based gel polymer electrolyte was tested on the first system (PPC:EC:PC:NaI system) and an excellent gel polymer electrolyte could be formed. The ionic conductivity of 2nd system (PPC:EC:PC:NaI:BmimI) was achieved at 4.79 mS cm⁻¹ upon the addition of 60 wt.% of BmimI ionic liquid content. On the other hand, the ionic conductivity was reached to a maximum value of 4.98 mS cm⁻¹ with doping of 80 wt.% MPII ionic liquid and it was the best PPC based gel polymer electrolyte prepared in this entire research.

For all the PPC based gel polymer electrolyte systems, the ionic conductivity were directly proportional with the temperature. It exhibits that all of them were obeyed the Arrhenius model which they have ion hopping mechanism following inside the polymer network of the GPE samples.

In addition, FTIR spectroscopy studies have been done and the complexation of the PPC, NaI, BmimI and MPII has been confirmed through the shifting of the peaks, intensity, shape and appearance of new peaks. The ions inside the electrolytes such as Na⁺, BMIM⁺ and MPIm⁺ were found to be interacting with both C=O group and C-O-C

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group of PPC polymer. X-ray diffraction (XRD) studies have been done in this research. It is found that the higher degree of amourphous behavior of the gel polymer electrolytes increased the ionic conductivity of the samples by disturbing the structure of polymer matrix, causing the reducing in the crystallinity and hence causing the enhancement of free mobile ions inside the polymer matrix after the addition of NaI salt, BmimI and MPII ionic liquid.

Furthermore, all samples from different systems have been used to fabricate the DSSCs and all of them were favorable. The 1st system has shown the highest energy conversion efficiency of 6.38% upon addition of 60 wt.% of NaI content. However, by adding BmimI ionic liquid into the the highest ionic conductivity of PPC:EC:PC:NaI system, the energy conversion efficiency has slightly drop to 6.14% at 60 wt.% of BmimI content but it's still can be considered comparable efficiency. Then, by adding MPII ionic liquid into the PPC:EC:PC:NaI system, the energy conversion efficiency increases to 7.72% upon 80 wt.% addition of MPII content. The best energy conversion efficiency was achieved among the other three systems in this research with open-circuit voltage (V_{oc}) at 544mV, short-circuit current density (J_{sc}) of 23.67 mA cm⁻² and fill factor at 59% in MPII-4 sample.

6.2 Future works

Further investigation could still be carried out to improve the performances of these PPC based gel polymer electrolytes and its DSSCs. Several works that can be done to improve the performance as follow:

I. The usage of binary salt systems to replace the single salt in the system. This may enhance the ionic conductivity of the GPEs and also the increment of short circuit current density of the DSSCs and hence increase the efficiency of the DSSCs.

- II. Addition of nano particles such as Ni₃PO₄ to the highest conducting sample. This may enhance the ionic conductivity by decreasing the degree of crystallinity and provide more pathways for ion conduction.
- III. Improvement in the techniques of electrode preparation could be introduced to achieve better photovoltaic performances of DSSC using the PPC based GPEs.

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LIST OF PUBLICATION AND PAPER PRESENTED

List of Publications

Farhana, N.K., Khanmirzaei, M.H.,Fatin Saiha Omar, Ramesh, S., & Ramesh, K. (2017). Ionic conductivity improvement in poly(propylene) carbonate-based gel polymer electrolytes using 1-butyl-3-methylimidazolium iodide (BmimI) ionic liquid for dye-sensitized solar cell application. *Ionics*. DOI 10.1007/s11581-017-1979-z.

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List of Conferences

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