POLY (VINYLIDENE FLUORIDE-CO-HEXAFLUORO PROPYLENE) / POLYETHYLENE OXIDE-BASED NANOPARTICLES REINFORCED GEL POLYMER ELECTROLYTES FOR DYE-SENSITIZED SOLAR CELL

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Field of Study: **EXPERIMENTAL PHYSICS**

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ABSTRACT

Solar energy is the most abundant and clean source of energy on the earth. Recently scientists have been able to develop a technology to harvest solar energy and today we are able to convert the sunlight directly to the electricity. Dye-sensitized solar cells (DSSCs) are one of the promising solar harvesting technologies with numerous advantages over the other technologies such as silicon based solar cells. Usually high performance DSSCs are obtained using liquid electrolyte which face several drawbacks for long term usage, such as leakage, electrolyte evaporation and interface corrosion. Gel polymer electrolyte can be an alternative to overcome these issues but the ionic conductivity of this gel polymer electrolytes must be improved to achieve high energy conversion efficiency. In this work we studied three gel polymer electrolyte (GPE) systems and the performance of DSSCs using GPEs have been analyzed. These GPEs are formulated by blending Poly(vinylidene fluoride-co-hexafluoro propylene) copolymer (PVdF-HFP) and polyethylene oxide (PEO) polymers. First, incorporation of sodium iodide (NaI) salt in different concentrations in the GPE system is investigated and later the addition of fumed silica (SiO_2) and zinc oxide (ZnO) nanofiller into the GPE system are studied. GPEs are examined using electrochemical impedance spectroscopy (EIS) to determine ionic conductivity values. The highest ionic conductivities of 6.38, 8.84 and 8.36 mS cm^{-1} are achieved after the incorporation of 100 wt.% of sodium iodide (NaI), 13 wt.% of fumed silica (SiO_2) and 3 wt.% of ZnO in each system, respectively. Temperature-dependent ionic conductivity study confirms that GPE systems follow Arrhenius thermal activated model. GPEs are characterized for structural studies using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. DSSCs are fabricated using GPEs and need to be recorded under 1 Sun simulator which produced

the significant highest energy conversion efficiency of 5.67, 9.44 and 9.08 % with incorporation of 100 wt.% of sodium iodide (NaI) with respect to the total weight of PEO:PVdF-HFP polymers, 13 wt.% of fumed silica (SiO_2) and 3 wt.% of ZnO in each system, respectively.

ABSTRAK

Tenaga solar merupakan sumber tenaga yang paling banyak dan bersih di muka bumi. Baru-baru ini, ahli-ahli sains telah membangunkan teknologi untuk mengumpul tenaga solar dan pada hari ini kami berupaya menukar tenaga matahari kepada tenaga elektrik. Sel solar yang sensitif kepada pewarna (DSSCs) merupakan salah satu teknologi mengumpul tenaga solar yang mempunyai banyak kelebihan dan berpotensi tinggi berbanding dengan teknologi lain seperti sel solar berasaskan silikon. Biasanya, DSSCs yang berprestasi tinggi diperoleh dengan menggunakan elektrolit cecair. Namun demikian, elektrolit cecair menghadapi masalah kebocoran, penyejatan elektrolit cecair dan hakisan pada antara muka. Gel polimer elektrolit boleh menjadi alternatif untuk mengatasi isu-isu ini tetapi kekonduksian ionik gel tersebut perlu diperbaiki untuk mencapai penukaran yang tinggi. Kami telah mengkaji tiga sistem gel polimer elektrolit (GPE) dan prestasi DSSCs yang difabrikasi dengan menggunakan ketiga-tiga GPEs telah dianalisis. Gel polimer elektrolit tersebut diperolehi dengan mengadunkan poli(viniliden florida-co-heksafloropropilena) (PVdF-HFP) kopolimer dan polimer polietilena oksida (PEO). Sistem GPE yang pertama dikaji dengan menggunakan pelbagai kepekatan garam natrium iodida (NaI). Kemudian sistem GPE yang terdahulu diteruskan kajiannya dengan penambahan silika wasap (SiO_2) dan zink oksida (ZnO) selaku pengisi bersaiz nano. GPE untuk setiap sistem telah dianalisis menggunakan spektroskopi impedan elektrokimia (EIS). Kekonduksian ionik tertinggi yang dicapai oleh setiap sistem melalui penambahan 100 % berat NaI, 13 % berat SiO_2 dan 3 % berat ZnO adalah 6.38, 8.84 dan 8.36 mS cm^{-1} masing-masing. Kajian kekonduksian ionik yang bergantung kepada suhu mengesahkan bahawa sistem GPE tersebut mematuhi model Arrhenius yang diaktifkan haba. Kajian struktur untuk GPE tersebut dilakukan dengan menggunakan pembelauan sinar-X (XRD) dan spektroskopi pengubah infra merah Fourier (FTIR). DSSCs yang difabrikasi

menggunakan GPEs telah dianalisis dengan menggunakan 1 Sun simulasi. Penambahan 100 % berat NaI, 13 % berat SiO_2 dan 3 % berat ZnO berdasarkan kepada jumlah berat polimer PEO:PVdF-HFP menunjukkan kecekapan penukaran tenaga yang ketara iaitu 5.67 , 9.44 and 9.08 %, masing-masing.

ACKNOWLEDGEMENTS

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LIST OF SYMBOLS AND ABBREVIATIONS

A		Area (cm^2)
DSSC	:	Dye-Sensitized Solar Cell
EIS	:	Electrochemical Impedance Spectroscopy
E_a	:	Activation Energy (meV)
FF	:	Fill Factor (%)
FTIR	:	Fourier Transform Infrared
FTO	:	Fluorine-Doped Tin Oxide
GPE	:	Gel Polymer Electrolyte
HOMO	:	Highest Occupied Molecular Orbital
σ	:	Ionic Conductivity (S cm^{-1})
I_2	:	Iodine
ITO	:	Indium Tin Oxide
J_{sc}	:	Short Circuit Current Density (mA cm^{-2})
k	:	Boltzmann constant (8.61×10^{-5} eV K^{-1})
L		Thickness (cm)
LUMO	:	Lowest Unoccupied Molecular Orbital
NaI	:	Sodium Iodide
OLED		Organic Light Emitting Diode
PEO	:	Polyethylene Oxide
PVdF-HFP	:	Poly (vinylidene fluoride-co-hexafluoro propylene)
Pt	:	Platinum
η	:	Photovoltaic Energy Conversion Efficiency (%)
$σ_o$	:	Pre-exponential factor
R_b	:	Bulk Resistance (Ω)

SiO$_2$	:	Fumed Silica
SPE	:	Solid Polymer Electrolyte
TiO$_2$	:	Titanium Dioxide
V$_{oc}$	:	Open Circuit Voltage (mV)
XRD	:	X-ray Diffraction
ZnO	:	Zinc Oxide

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CHAPTER 1: INTRODUCTION

1.1   Introduction of Research

Development of technology has affected every single household appliance to use electricity and it shows the intense human needs for energy. The total production of energy from various energy sources in 2014 was 22433 TWh. So far the non-renewable conventional energy resources such as fossil fuels such as oil, coal and gas obviated human demands for energy but they are not human preference due to their contributions to environmental pollution and global warming. 31% of deaths caused by air pollution are due to the power generation (Schillerby, 2015) and the year 2015 was the hottest year in the historical record (Gillis, 2016). Burning fossil fuels begets acidic rain and extraction of crude oil damages the marine ecosystem which kills many animals each year. So humans are looking for a clean, cheap and safe method to produce and store for their unlimited energy consumption. Solar cells are one of the latest green technologies for converting and storing the vast sun light to electricity. One hour of the sun light at the atmosphere has the power equal to the electrical power to turn on 120 trillion of 60 W light bulbs. Many researchers are working to improve the performance of solar cells by using environmental friendly and cheap materials because they believe on the capacity of solar cells for providing clean worldwide energy needs.

By using dye-sensitized solar cells (DSSCs), we can store the clean and lifelong energy of Sun with high efficiency and even without direct sunlight. This technology invented on 1991 by Michael Gratzel and Brian O'Regan and it is able to catch a wide spectral range of sunlight from near Infrared to ultraviolet. DSSCs can be easily fabricated from low cost materials and they could reach up to 12% sunlight energy conversion efficiency. DSSCs can be obtained by fabricating three parts of photo-anode, electrolyte and counter

electrode which are conducting glass commonly coated with TiO_2 and sensitized by dyes, electrolyte containing iodide/triiodide redox couples and a conducting glass which generally coated with Platinum (Pt) respectively. DSSCs are not an elaborate technology that are easy to fabricate and utilize as well as being cost effective and able to operate under indirect sunlight and cloudy weather hence these characteristics make them a reliable alternative for the silicon based solar cells.

Many research groups are working on each parts of DSSC nowadays in order to develop a more efficient and high performance system. Utilization of liquid electrolyte based DSSCs faces many problems, for instance potential instability, sealing defects caused by leakage and reacting to the temperature variations and also evaporation. Researchers could develop safe and more stable DSSCs using gel polymer electrolytes (GPEs). Although application of GPEs in DSSCs decrease the energy conversion efficiencies of DSSCs compare with the Gratzel liquid type of electrolyte but GPEs are safe, stable and have high ionic conductivity. Fabrication of DSSCs by using GPEs helps to overcome their long term usage drawbacks specially photo-corrosion and desorption of dyes and corrosion of platinum coating of counter electrode. GPEs can be obtained using polymers, gelling agents, iodine, alkali metal iodides, ionic liquids and plasticizers. Mobility of iodide/triiodide ions in the polymer matrix improves in presence of organic and inorganic nanoparticles as a filler into the GPE system. Moreover the efficiency of DSSCs that were fabricated using these GPEs will be enhanced as a result of enhanced ionic conductivity of GPE system.

In this study, we attempted to enhance the ionic conductivity of the GPEs for application in DSSC. Accordingly, iodide salt and two inorganic fillers were used in different GPE systems. DSSCs were fabricated by using GPEs that obtained in different systems and the performance of DSSCs were investigated. GPE systems are developed

by blending PEO and PVdF-HFP polymers as the host polymers. Ionic conductivity of GPE system is optimized in presence of sodium iodide (NaI) salt into the PEO/PVdF-HFP:NaI:I_2 system and furthermore, effect of fumed silica (SiO_2) and zinc oxide (ZnO) nanoparticles on the ionic conductivity of optimized PEO/PVdF-HFP:NaI:I_2 system are investigated in two different systems respectively.

1.2 Objectives of the Research

1. To prepare and optimize GPEs based on PVdF/HFP:PEO polymers and NaI salt for application of DSSCs as well as enhancing the ionic conductivity of GPEs in corporation of fumed silica (SiO_2) and ZnO nanoparticles as fillers into the optimized GPE system.

2. To characterize the GPEs using electrochemical impedance spectroscopy (EIS), X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) studies.

3. To investigate the performance of fabricated DSSCs using GPEs.

1.3 Scope of Thesis

This thesis intends to report the development process of GPE systems for fabrication of high performance and efficient DSSCs by focusing on enhancement in the ionic conductivity values of the GPEs. Chapter 1 explicitly explains need of the usage of sunlight as a source of energy and the advantages of using DSSCs as our preference and how we can develop this system. Chapter 2 is the literature review about the characteristics of DSSCs and its working principles, different types of polymer electrolytes, GPEs and their advantages and the properties of materials that are used in preparation of GPEs in this research.

Preparation of GPEs and their characterization methods is represented in Chapter 3. Chapter 3 also contains the informations about fabrication of DSSCs, preparation of their components and their photovoltaic studies. PVdF-HFP/PEO blended polymers were

chosen to enhance the mobility of ions in the intended GPE system. Chapter 4 contains the characterizations and discussions for three systems prepared in this work. NaI salt has been incorporated into the GPE system to provide more ions, especially I^- anions in the system and to increase the ionic conduction and facilitating I^-/I_3^- reduction process of the GPE. The amount of NaI salt was optimized in the PVdF-HFP:PEO:NaI:I_2 system and the electrochemical and structural properties GPEs were investigated. Effect of two different types of fumed silica (SiO$_2$) and ZnO nanoparticles on the electrochemical and structural properties of GPEs were studied and the photovoltaic performance of fabricated DSSCs using these GPEs was investigated. In chapter 5, the comparison between the electrochemical (EIS) and structural properties (XRD and FTIR) of GPEs in three systems was explained and the energy conversion efficiencies for fabricated DSSCs using GPEs in each system were also compared. The last chapter is allocated to the conclusions of this research and some ideas for the future studies.

CHAPTER 2: LITERATURE REVIEWS

2.1 Introduction

In this chapter, the literature reviews will be discussed for solar cells, DSSCs and their advantages and components. Different types of polymer electrolytes specially GPEs and their benefits, background of all the materials that were used for preparation of GPEs in this research, have also been reviewed. Various factors affecting the performance of DSSCs and ionic conductivity of GPEs have been reported.

2.2 Solar cells

Humans have been reached to a point that using a clean and unlimited source of energy is essential for their huge energy consumptions and preventing environmental pollutions. The limited and unrenewable source of energy especially oil resources are going to finish soon due to the heavy consumptions. Many scientists have worked hard for years to find a new unlimited source of energy which does not damage the earth environment and can be replaced to the conventional fossil fuels. Solar energy is the best candidate for our source of energy as it is unlimited, safe, powerful and it is available everywhere. According to Figure 2.1 energy consumption using solar cells has been grown worldwide and the price of electricity generated from solar panels has been reduced. In 1975, the price of electricity generated by photovoltaic cells was \$100/W which has been highly reduced to \$0.60/W in 2015 with 65,000 MW globally installed solar panels. So far many types of solar technologies exist with different mechanisms, costs and power efficiencies. Different categories of solar cells are briefly explained as bellow:

- Single-junction GaAs: single crystal, concentrator and thin-film crystal solar cells are in this category. These types of solar cells have efficiencies between

27.5 to 29.1 %. This is the most fundamental type of solar cell which use one p-n junction to produce electricity (Green et al., 2015).

- Multi-junction cells: two-junction (concentrator), two-junction (non-concentrator), three-junction (concentrator), three-junction (non-concentrator), four-junction or more (concentrator), four-junction or more (non-concentrator) solar cells are in this category. Their efficiencies vary between 31.6 to 46%. These types of solar cells have made by using several semiconductor materials with different P-N junctions and they have high energy conversion efficiencies due to the absorption of a wide range of sunlight wavelengths (Siddiki et al., 2010).

- Crystalline Si cells: single-crystal (concentrator), single-crystal (non-concentrator), multicrystalline, silicon heterostructures (HIT), thin-film crystal solar cells are in this category. Their energy conversion efficiencies varies between 21.2 to 27.6%. They are made of semicrystalline silicon which produce electricity when they absorb light and the electrons of silica atoms/molecules go to the excited state and go back to the orbital (Ndiaye et al., 2013).

- Thin-film technologies: CIGS (concentrator), CIGS, CdTe, amorphous Si:H (stabilized) solar cells are in this category. Their energy conversion efficiencies are between 13.6 to 23.3%. In this system sunlight make electrons to move between two n and p-type semiconductors (Suryawanshi et al., 2013).

- Emerging photovoltaic: DSSCs, perovskite cells, organic cells, organic tandem cells, inorganic cells and quantum dot solar cells are in this category. Their photovoltaic efficiencies are between 10.6 to 22.1%. these technologies are developed to increase the energy conversion efficiency of solar cells by using cost-effective materials (Park, 2015).

Figure 2.1: Variation of solar panel price per watt and global solar panel installation by time (Source: Earth Policy Institute).

2.3   Dye-Sensitized Solar Cells (DSSCs)

DSSC was invented on 1988 by Brian O'Regan and Michael Gratzel with inspiration from a discovery in 1960 which stated that electricity can be generated from the illuminated chlorophyll dyes extracted from spinach and in an oxide electrode. In this technology photoelectrons generate by dye molecules and a layer of semiconductor is used to conduct these electrons however in conventional silicon-based solar cells the semiconductor is as a source of both photoelectrons and electron conduction part. Photo-anode, electrolyte and counter electrode are different components of forming a DSSC. A transparent glass with a conducting layer face (FTO or ITO) which coated with TiO_2 and has been soaked in dye is a photo-anode for solar cell and this glass can be coated with platinum to form the counter electrode for this system. Dye molecules react to the sunlight and they induce to the excited state and photoelectrons produce and pass through the conducting TiO_2 layer which produce electricity. These electrons conduct to an external circuit from the conducting face of glass and they inject to the system by counter electrode

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and then the oxidation and reduction process by I$^-$/I$_3^-$ ions helps to give back those missed electrons of dye molecules and this process repeats for generating electricity. All three components effect on the performance and energy conversion efficiency DSSC (Hagfeldt et al., 2010).

2.3.1 Advantages of using DSSCs

DSSCs have been made of many materials and changing or processing each material can help us to optimize the performance of this solar cell. The performance of this solar cell is highly influenced by dye molecules which absorb sunlight and also the redox couples and their movements in the electrolyte. Many researches can be done on finding and applying variety of materials in this technology.

The materials used in DSSCs are usually cheap and green which reduce the cost of manufacturing and keeps our environment safe. DSSCs can be made of hazardous-free and bio materials which can be abundant in nature and cost effective. DSSCs can be very light and flexible since commercialy they can be made by coating materials on the flexible, cheap and light plastic substrate and this method makes them robust for long term usage. Moreover DSSCs do not need any protection for controlling their internal temperature in compare to the conventional silicon based solar cells and even under direct sunlight heat can easily pass through the transparent components of DSSC and the temperature of device will be controlled. All these properties help us in easy and inexpensive manufacturing process.

DSSCs have high efficiency in converting sunlight to electricity among the other types of solar cells and in compare to their price and this attributes makes them a superior choice for home or low-density application. Among all types of solar cells, DSSCs are the only ones which can produce electricity under indirect sunlight and cloudy weather because they have this ability to absorb a wide range of wavelengths of light spectrum, diffused

sunlight from objects and also fluorescent lights hence they are suitable even for the places with cloudy weather and no direct sunlight.

2.3.2 Working principles of DSSCs

Figure 2.2: Dye-sensitized solar cell configuration.

DSSCs consist of five components which are demonstrated in Figure 2.2.

1. A glass which is coated by a conductive substrate such as fluorine-doped tin oxide (FTO) or indium tin oxide (ITO) is the photo-anode.

2. Mesoporous semiconductor which is usually TiO_2 will be coated on the photo-anode to conduct electrons generated by dye.

3. Dye nanoparticles which are absorbed on the mesoporous semiconductor for sensitizing purpose and light absorption and generally Ruthenium based dyes are chosen.

4. Electrolyte which contains redox mediator to regenerating oxidized dye and it is generally I^-/I_3^-.

5. A counter electrode which is usually platinum for recycling the redox couples generation in the redox mediator.

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Figure 2.3: Operating principle of dye-sensitized solar cell (Miki, 2013).

The working principle for DSSC to produce electricity is demonstrated in Figure 2.3. One of the important rule in this technology is that the LUMO (Lowest Unoccupied Molecular Orbit) and HOMO (Highest Occupied Molecular Orbit) orbitals for dye molecules should be above orbital limit of semiconductor and below the potential of the redox mediator respectively (Flores et al., 2015). This property is essential for dye to inject the electrons efficiently in the system for electricity generation. Basically the sensitizer (S) go to the excited state (S^*) by absorbing a photon and this will make the excited dye (S^*) to infuse electron to the TiO_2 semiconductor conduction band and S^* changing to oxidized dye (S^+). The electrons diffuse in the mesoporous TiO_2 network and pass through the external circuit and then they will be collected by the counter electrode. Afterward electrons will reduce the redox mediator in the electrolyte/counter electrode surface and this process repeats again and again for electricity generation (Gong et al., 2012; Nazeeruddin et al., 2011). All the chemical equations for the processes explained above are as below:

$$S + h\nu \rightarrow S^* \tag{1}$$

$$S^* \rightarrow S^+ + e^- \tag{2}$$

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

$$2S^+ + 3I^- \rightarrow 2S + I_3^- \tag{4}$$

In electrolyte/TiO$_2$ surface there are two possibilities for the injected electrons a) they can combine with oxidized dye molecules (S^+) or b) they can combine with oxidized redox couples and these are the reasons which cause decline of energy conversion efficiency:

$$S^+ + e^- \rightarrow S \tag{5}$$

$$I_3^- + 2e^- \rightarrow 3I^- \tag{6}$$

2.3.3 The components of DSSCs

2.3.3.1 Transparent conducting films (TCFs)

As we can understand from transparent conducting films (TCF) name, they are films which are transparent namely glass which are coated with a conductive layer such as indium tin oxide (ITO) or fluorine doped tin oxide (FTO). Charges can be transferred and controlled on the surface of transparent conducting films by applying voltages and this property give them an advantage to be applied in LCD and organic light emitting diode (OLED) displays, thin-film solar technologies and electrochromic glasses to control light and heat. Many different types of TCFs are developed by scientists with various substrates and coatings which give them different characteristics such as being flexible and having high conductivity at high transmittance (Bergin et al., 2012; Ko et al., 2016). Both FTO and ITO glasses use for DSSC preparation but FTO is known to be stable under high temperature although it has less transmittance compared to ITO glass (Sima et al., 2010).

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2.3.3.2 Photo-anode

There should be a transparent, tin and mesoporous semiconductor layer such as TiO$_2$ to be deposited on the transparent conducting films which can absorb dye molecules and can conduct electrons toward the external circuit in DSSCs. A good semiconductor for photo-anode is the one which can prevent recombination of injected electrons by dye molecules with both oxidized dye molecules (S$^+$) and redox couples to give more energy conversion efficiency. The surface area of the semiconductor will affect the electron recombination at the photo-anode and this parameter can be controlled by the size of the thickness of the semiconductor layer coated on the transparent conducting glass and also the semiconductor particle size. For photo-anode preparation doctor blade coating method is generally used to control the thickness of the semiconductor layer coated on the transparent conducting film and after coating the semiconductor layer sinter at 450 ^{o}C to create electronic contacts between the molecules (O'Regan & Gratzel, 1991). The size of pores at the surface of the semiconductor will affect dye molecules absorption and the surface area for photo-anode. Photo-anodes prepared by using core-shell materials are reported to improve the performance of DSSCs by providing energy barrier against electron recombination on the photo-anode/dye/electrolyte interface and in this method a semiconductor material such as TiO$_2$ (band gap, 3.2 eV) will be used as a core material and another nanoparticle such as ZnO (band gap, 3.37 eV) can be applied as a shell for providing energy barrier (Zhang et al., 2016). For fabrication of flexible DSSC, the semiconductor layer needs to be coated on the flexible plastic substrate at low temperature hence a new technique of lift-off and transfer process is reported for preparation of semiconductor layer and by sintering at low temperature (Durr et al., 2005).

2.3.3.3 Sensitizing dye

A good sensitizer can absorb all the spectrum of lights from near infrared region to the lower wavelengths. It is very important that dye molecules graft firmly to the

semiconductor layer to facilitate the electron injection to the semiconductor conduction band by dye molecules when they get excited and base on this statement it is essential for dye molecules to contain some functional groups such as phosphonate or carboxylate in order for them to attach to the semiconductor layer (Hagfeldt & Grätzel, 2000). Basically there are two types of natural and ruthenium-base dyes and each type of dyes has its own advantages. Ruthenium based dyes such as N3, N719 and black dyes can absorb high range of light spectrum and they anchor to the surface of semiconductor layer well and it results high efficiency of DSSC. On the other hand, the organic dyes are cheap, environmentally friendly and easy to obtain in addition they can be easiy modified to have better connection with the semiconductor layer and have higher molar extinction coefficient (Arjunan & Senthil, 2013; Nazeeruddin et al., 1993; Nazeeruddin et al., 2001). Many natural and metal free dyes have been reported for high efficiency DSSCs namely cyanine, indoline and triphenylamine which show good properties for high performance DSSCs (Feldt et al., 2010; Horiuchi et al., 2004). The structure of some inorganic and natural dyes are represented in Table 2.1.

Table 2.1: Some ruthenium based and natural dyes with their corresponding structure.

dye		structure
Ruthenium-based dyes	N3	

Table 2.2 (continued): Some ruthenium based and natural dyes with their corresponding structure.

	N719	
	Black dye	
Organic dyes	Cyanine	
Organic dyes	Indoline	
	Triphenylamine	

2.3.3.4 Counter electrodes

Based on the working principle of DSSC explained earlier, the counter electrode plays an important role in reducing the triiodides in the electrolyte and producing iodide molecules. Generally platinum has been used as an efficient counter electrode for DSSC which is a costly material. Several types of counter electrodes have been developed using different materials for fabrication of DSSCs such as carbon-based, conducting polymer-based, transition metal nitrides and carbides-based, metal oxide-based, metal sulfide-based and the counter electrodes prepared by using composite materials. The best properties for a good counter electrode is to be cheap, environmental friendly and having high catalytic activity and conductivity for reduction of triiodide. There are different methods for preparation of platinum counter electrode in order to increase the active surface area for catalytic activity enhancement and also to make the preparation process easier and inexpensive (Dao & Choi, 2016). It is reported that composite materials with combination of two materials with high electrical conductivity and catalytic activity such as mesoporous carbon (MC) and VC as VC-MC composite electrode produce higher energy conversion efficiency compared to the common platinum (Wu et al., 2012). Carbon-based counter electrodes are quite promising as platinum-free counter electrodes for DSSCs by showing high energy conversion efficiencies, being cheap, highly conductive and corrosion resistant when they exposed to iodine. Many types of carbons such as carbon nanotubes, carbon black, graphite, graphene and grapheme oxide have been used for counter electrodes and among all of them graphene and mesoporour carbon counter electrodes shows very good performance especially for reducing triiodide and showing high energy conversion efficiencies for DSSCs which are comparable with platinum counter electrode (Chen et al., 2009; Hong et al., 2008; Imoto et al., 2003; Lee et al., 2012; Xu et al., 2013). Conductive polymers such as polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPY) can be a good candidate for

preparation of inexpensive, stable and highly catalytic active counter electrodes for DSSCs (Bu et al., 2013; Li et al., 2008).

2.3.3.5 Electrolytes

Electrolytes are one of the most important parts of DSSCs that contain redox couples for capturing electrons from counter electrode and giving those electrons back to the oxidized dyes for electricity generation. The traditional electrolyte for DSSC is the liquid electrolyte of organic acetonitrile containing I^-/I_3^- redox couple used by Gratzel. Kinetic properties of I^-/I_3^- makes fast injection of electrons to the TiO_2 conduction band as well as fast interaction between iodide and oxidized dye which does not allow high rate of electron recombination in the TiO_2/dye/electrolyte surface. Other types of redox couples have been tested in the electrolyte such as Co (II)/Co (III), Br^-/Br_3^-, $SeCN^-/(SeCN)_3^-$ and $SCN^-/(SCN)_2$. Traditional liquid electrolytes show many unfavorable behavior which deters production of stable, safe and efficient DSSCs for long term utilization. Corrosion of dye molecules and counter electrode, leakage, low stability and diminution of volatile ions concentration caused by evaporation are the undesirable results for fabrication of DSSCs by using liquid electrolytes. Many types of materials can be used for making liquid electrolyte and each of them can effect different parameters of DSSC so choosing the right materials and optimizing their concentration in the electrolyte system are essential for making a suitable electrolyte for high performance DSSC. Ionic liquids and different types of iodide salts with different cation sizes are the additives for providing more ions in the liquid electrolyte, enhancing thermal and chemical stability and effectively influence the DSSC parameters.

Besides liquid electrolytes there are two more types of solid-state and quasi solid electrolyte systems, have been developed to overcome the imperfections of using liquid electrolytes for fabrication of DSSCs. Although quasi solid and solid state electrolytes

have lower ionic conductivity compared to the liquid electrolytes but they have higher stability and are easy to handle for fabrication of DSSCs and each type of systems has its own advantages.

- Solid state electrolyte: researchers have been developing solid polymer electrolytes by using a suitable p-type semiconductor concordant with conduction band of TiO_2 and HOMO level of dye as electrolyte beside the n-type sensitizer dye which reminds the conventional silicon based solar cells with p-n junction. Dimension of crystals for the p-type semiconductor is very important for filling the TiO_2 pores and enhancing the energy conversion efficiency of DSSCs. These types of electrolytes are stable and safe for fabrication of DSSCs although they promote low energy conversion efficiencies (<5%) (Snaith & Mende, 2007).

- Quasi-solid electrolytes (gel electrolyte): quasi-solid or gel electrolytes are obtained by gelatinizing the liquid electrolytes by using gelling agents or using conductive polymers to have the high mobility of ions like liquid electrolyte as well as the cohesiveness of solid electrolyte. GPEs are a quasi-solid electrolyte where polymers are creating the gel networks and they can be dry standing film or wet semi solid polymer electrolyte obtained by using plasticizers to plasticize the polymer (Kubo et al., 2002). Composite polymer electrolytes are another type of quasi-solid polymer electrolyte where polymer electrolytes contain fillers namely metal oxides (SiO_2, TiO_2, ZnO, ZrO_2, etc.) to improve the mobility of ions and stability of the electrolyte (Wang, et al., 2003).

Quasi-solid polymer electrolytes have many advantages in compare to the other types of electrolytes which help to enhance the performance of DSSCs and manufacturing DSSCs in larger scale. They have high ionic conductivity in the room temperature,

they show high stability, very good contact with TiO_2 semiconductor layer, preventing leakage and evaporation of dye, preventing corrosion and dissolution of dye when they expose to electrolyte, being flexible and cost effective all are advantages of using quasi-solid/gel electrolyte for fabrication of DSSCs (Wu et al., 2007).

2.4   Gel polymer electrolytes (GPEs)

This type of electrolytes are obtained by plasticizing the polymers using different types of plasticizers and additives such as ionic liquids. Salts and fillers are used to increase the ionic conductivity of GPE system and make them suitable for application in DSSCs. Many different types of polymers have been used for preparation of GPEs such as poly(ethylene oxide) (PEO), poly(methylmethacrylate) (PMMA), poly(vinylidene fluoride) (PVdF), polyacrylonitrile (PAN), poly (vinyl chloride) (PVC), etc. (Ahn et al., 2010; Ren et al., 2002; Wang et al., 2004; Wu et al., 2006a; Yang et al., 2008). Many types of polymer electrolytes are obtained using the biopolymers consist of starch, cellulose derivatives, Chitosan and pectin (Andrade et al., 2009; Khiar & Arof, 2010; Sudhakar & Selvakumar, 2012; Xiao et al., 2014). Presence of copolymers obtained from different methods including electron beam radiation polymerization, UV, thermal radiation or photo-polymerization and using low molecular weight monomers in the GPE system show very high ionic conductivity and mechanical performance (Machado et al., 2005; Musil et al., 2015). DSSCs fabricated using polymer electrolytes generally have higher open circuit voltage (V_{oc}) since obstruction of recombination sites by polymer chains put off electron recombination with I_3^- ions in the TiO_2/dye/electrolyte interface. Basically the movements and diffusion of redox couple in the electrolyte is effecting the efficiency of DSSCs while the ionic conductivity value for polymer electrolytes show both anionic and cationic conductions in the system, so we can understand that in GPEs, solvents and plasticizers play an important role in mobility on anions rather than polymers (de Freitas et al., 2009). Since the approach in preparation of electrolyte for DSSCs is

facile mobility of anions which helps to enhance the performance of DSSCs, using alkaline salts with larger cations enhances mobility of ions in the GPE (Wang, et al., 2003). Properties of plasticizers and their concentration directly affect ionic conductivity of GPEs and need to be optimized in the system (Kang et al., 2003). Viscosity of GPEs need to be controlled in presence of additives since penetration of electrolyte in the pores of TiO_2 reduces by increasing viscosity of the GPE and reduction in the movements of polymer chains segments that causes decrease in the V_{oc} value of DSSC. Presence of nanoparticles in the GPEs increases the energy conversion efficiency of DSSC by controlling the recombination rate of electrons in the TiO_2/dye/electrolyte interface in addition to enhancing the stability and ionic mobility of GPEs (Stathatos et al., 2003).

2.5 PVdF-HFP and PEO

Figure 2.4 shows the structure of Poly (ethylene oxide) (PEO). PEO has been widely used in polymer electrolytes and for electrochemical applications since it has high mechanical and chemical stability and it is efficient for diffusion of ions in the polymer electrolyte system by being polar moiety and acting as a solvent for metal salts. Application of PEO-based polymer electrolytes in DSSCs enhances the mobility of I^- in the system due to the interaction between the ether oxygen and the dissociated cations in the polymer electrolyte system (Xia et al., 2006). Although PEO has semicrystalline nature and shows low ionic conductivity ($\sim 10^{-6}$ S cm^{-1}), many methods has been reported to reduce crystallinity of PEO and increase the conductivity to make this polymer idoneous for preparation of polymer electrolytes for DSSC application such as blending with other polymers, using nanoparticles and plasticizers. The energy conversion efficiency for N3-dye sensitized solar cell using PEO, PEO:EC, PEO:PC as electrolyte is 0.6%, 2.9% and 3.6%, respectively (Ileperuma, 2013). Addition of 2-Mercapto benzimidazole (MB) small rubber molecules in the PEO:I_2 system increased the ionic conductivity of the system as the amorphous phase of polymer electrolyte increased and

application of this polymer electrolyte in DSSC improved both J_{sc} and V_{oc} and the energy conversion efficiency (Muthuraaman et al., 2013). GPE based on PEO blended with 2-(2-methoxyethoxy)ethyl glycidyl ether) (P(EO/EM)) and with different concentration of γ-butyrolactone (GBL) shows high thermal stability and ionic conductivity enhance ment dye to the interaction between GBL, polymers and Li ions (Benedetti et al., 2014). Crystallinity of Poly(ethylene oxide)/poly(vinylidenefluoride-hexafluoropropylene) blend polymer based GPE system reduced in presence of tetraethylammonium tetra-fluoroborate (Et₄NBF₄) salt, the ionic conductivity and diffusion of redox couples increased in the system and the energy conversion efficiency of 6.2% have been reported for DSSC fabricated by using such GPE (Cui et al., 2013). Presence of fillers with large surface area in the PEO- based polymer electrolyte system prevents recrystallization of PEO in the system and decreases the crystalline phase of polymer electrolyte (Stergiopoulos et al., 2002).

Figure 2.4: Structure of Poly (ethylene oxide).

Figure 2.5 shows the structure of PVdF-HFP. It is noteworthy that Poly(vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP) has high ionic conductivity in compare with other polymers (between 10^{-8} to 10^{-10} S cm^{-1}) and high dielectric constant ($\varepsilon = 8.4$) that helps in dissociation of salt into ions in the polymer electrolyte system and results in ionic conductivity improvement (Prabakaran et al., 2015a). PVdF-HFP based GPE with incorporation of silica nanoparticles and 1-methyl-3-propylimidazolium iodide ionic liquid show high energy conversion efficiency of 6.7%

and this system preserve 90% of this efficiency after 30 days and under 80 ºC (Wang et al., 2004). PVdF-HFP polymer were used for preparation of GPE which uses tris(2,2'-bipyridine)cobalt(II)/(III) as redox couple and application of this GPE in DSSC has been reported the energy conversion efficiency of 8.7% (Xiang et al., 2013).

Figure 2.5: Structure of Poly(vinylidenefluoride-co-hexafluoropropylene) (PVdF-HFP).

Presence of blend polymers such as PEO/PVdF-HFP in many researches (Prabakaran et al., 2015c; Thankamony et al., 2015) is significant because of the unique features of these polymers. PEO and PVdF-HFP blend polymer is a very good choice as a host polymer to enhance mobility of ions in GPE and this is due to the high electro-negativity of fluorine and also high interaction between the C-O-C and CF_2 groups of PEO and PVdF-HFP respectively (Prabakaran et al., 2015a; Prabakaran et al., 2015b). Even though PEO based polymer electrolyte shows very good performance due to the fast transportation of ions (Prabakaran et al., 2015b) blending with PVdF-HFP can increase the ionic conductivity of the system by decreasing the crystallinity of the electrolyte. Polyethylene oxide (PEO) and Poly (vinylidene fluoride-co-hexafluoro propylene) (PVdF-HFP) blend polymers were used widely in preparation of polymer electrolytes for DSSC applications (Prabakaran et al., 2015c; Rong et al., 2015). Unique characteristics of PVdF-HFP and PEO polymers in GPE preparation, make them very suitable polymers for DSSC application. Strong interaction between CF_2 and C-O-C groups of PVdF-HFP and PEO respectively, helps in significant crystallinity reduction of GPE and high compatibility of these polymers for blending. PVdF-HFP provides a long term stability

of DSSC for practical usage due to its electrochemical stability beside TiO_2 and Platinum (Pt). High electronegative fluorine in PVdF-HFP and high number of channels between electrodes of DSSC provided by PEO polymer helps in highly conductive GPE preparation as a result of fast ion transportations (Prabakaran et al., 2015a) .

2.6   Iodide salts

Basically electrolytes for DSSCs contain iodide salt as a source of I^- and they effectively influence DSSC parameters. The size of cations in iodide salts effect the energy conversion efficiency of DSSCs as well as concentration of iodide in the electrolyte system.

Two different types of iodide salts have been used in preparation of electrolytes of DSSCs which are organic and inorganic iodide salts. The organic salts such as N-methyl pyridine iodide and 1-hexadecyl-3-methyl imidazolium iodide ($C_{16}MImI$) have better dissociation in organic solvents (Li et al., 2014; Wu et al., 2006b). Inorganic iodide salts such as potassium iodide (KI) and sodium iodide (NaI), lithium iodide (LiI) have been obtained by reaction between alkaline metal hydroxide or alkaline earth metal hydroxide and acidic iodide. It is reported that N-methyl pyridine iodide salt with large cations easily dissociated in γ-butyrolactone (γ-BL) organic solvent and release I^- anions in the electrolyte (Lan et al., 2007). PVdF polymer based GPE with tetrapropylammonium iodide (Pr_4NI) salt for DSSC showed better performance compared to the ZnI_2 and KI salts. It was reported that the V_{oc} of the DSSC fabricated by using GPE mentioned above increased since the big size Pr_4N cations palliate the movements of I_3^- ions in the electrolyte and reduce electron recombination rate at the TiO_2/dye/electrolyte interface (Madhushani et al., 2016). Polyphosphazene-based electrolyte with 1-methyl-3-propylimidazolium (PMII) content shows relatively higher anionic conductivity in compare to the equivalent electrolyte with NH_4I, NaI and LiI contents respectively and it

also shows a better performance as applied in DSSC (Lee et al., 2010). Interaction between ether-oxygen of PEO in PEO based polymer electrolyte and alkaline salt with larger cation facilitates dissociation of the iodide salts in the system and increase the open circuit voltage and energy conversion efficiency of DSSC (Shen et al., 2008).

Figure 2.6 shows the structure of sodium iodide (NaI). NaI has crystalline structure and can be obtained due to the interaction between NaOH and acidic iodides. Sodium iodide salt (NaI) has been used in many electrolytes as a source of I^- for application in DSSCs. NaI is cheap and soluble in many organic solvents such as acetone, acetonitrile and water and it has the melting and boiling point of 661 ℃ and 1304 ℃ respectively. High performance DSSCs have been obtained by using GPEs with NaI content as salt (Bella et al., 2013).

Figure 2.6: Sodium iodide (NaI) structure (Lide, June 17, 1999).

2.7 Fillers

Fillers are generally nanosized particles of ceramics and carbon materials. TiO_2, SiO_2, ZrO_2, Al_2O_3 and ZnO are some of the examples for ceramic fillers. Graphene and carbon nanotubes (CNTs) are some examples for carbon-based fillers. Presence of nanoparticles in the electrolytes increases the ionic conductivity by preventing crystallization and

increasing the amorphous phase in the system and these nanoparticles also promote electrolytes with high physical and electrochemical stability (Dissanayake et al., 2014). Addition of fillers to the electrolytes for application in DSSCs enhances the mobility of redox couples (I^-/I_3^-) and diffusion of ions in the system and enhances the performance and long-term stability of this device. Incorporation of graphene nanoparticles as filler into the PMMA-GPE enhances the ion diffusivity and the energy conversion efficiency of the relevant DSSC to 8.5% (Kang & Moon, 2015). GPE with TiO_2 content reported to have enhancement in ionic conductivity, stability and reduction in electron transfer resistance in the counter electrode/electrolyte interface of relevant DSSC where TiO_2 nanoparticles absorb on the platinum surface and draw out electrons into the GPE system (Venkatesan et al., 2016). Incorporation of TiO_2 nanoparticles into the poly(acrylonitrile-co-vinyl acetate) (PAN-co-VA) based GPE increased the gelation of the system and enhanced the energy conversion efficiency of pertaining DSSC from 8% to 8.3% (Venkatesan et al., 2015). In PAN based GPE containing activated carbon, space-charge layers as interfacial regions with electric field created in the system due to the interaction between activated carbon nanoparticles and the absorbed ionic liquid and these regions are responsible for enhancement in mobility of ions. Ionic conductivity of GPEs can be increased by reducing ion paring due to the Lewis acid surface groups of some fillers such SiO_2 nanofillers (Mohan et al., 2013). SiO_2 nanofibers provide feasible ion pathways by creating free volume and decreasing the viscosity of GPE in order to enhance the ionic conductivity of the system and applying this GPE in DSSC increasing recombination time of electrons and charge collection efficiency (Zhao et al., 2014).

2.8   Summary

Literature review has been discussed in this chapter. General informations about solar cells, DSSCs, their working principle and their advantages are discussed. The literature about components of DSSCs and effects of materials on the working principle and energy conversion efficiencies are provided. The literature background for materials used in this research are also discussed.

CHAPTER 3: METHODOLOGY

3.1   Introduction

In this chapter, materials and chemicals used for the preparation of GPEs and photo-anodes are discussed. The methodology for preparation of GPEs and photo-anodes, electrochemical and structural characterizations of GPEs, fabrication and characterization of DSSCs have also been explained.

3.2   Materials and chemicals

Table 3.1 and 3.2 demonstrate the list of materials used in the preparation of GPEs and photo-anode respectively.

Table 3.1: Materials used in preparation of GPEs.

Role	Material	Source
Solvent/plasticizer	Ethylene carbonate (EC)	Sigma-Aldrich
Solvent/plasticizer	Propylene carbonate (PC)	Sigma-Aldrich
Iodide salt	Sodium iodide (NaI)	Sigma-Aldrich
Polymer	Poly (ethylene oxide) (PEO)	Sigma-Aldrich
Polymer	Poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP)	Sigma-Aldrich
Redox couple	Iodine (I_2)	Friedemann Schmidt Chemical
Nanofiller	Silica, fumed (7 nm)	Sigma-Aldrich
Nanofiller	Zinc oxide nanopowder (<100 nm)	Aldrich

Table 3.2: Materials used in preparation of photo-anode.

Role	Material	Source
Blocking layer	TiO$_2$ P90 (14 nm)	AEROXIDE
Mesoporous layer	TiO$_2$ P25 (21 nm)	AEROXIDE
Inorganic dye	(N719) Ruthenium dye (Di-tetrabutylammonium cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II))	Sigma-Aldrich

3.3 Research design

In this research, three GPE systems were prepared with the aim of applying these GPEs for fabrication of DSSCs with high performance. First GPE system were optimized based on PVdF-HFP:PEO polymers and sodium iodide (NaI) salt and effect of NaI on the GPE system is investigated using EIS, temperature-dependent ionic conductivity, XRD and FTIR studies. For second and third GPE systems fumed silica (SiO$_2$) and zinc oxide (ZnO) were added, respectively, to the optimized GPE in first system as filler to improve the mechanical properties and also to enhance the ionic conductivity of prepared GPE. The ionic conductivity and temperature-dependent ionic conductivity studies were investigated by EIS. XRD and FTIR spectroscopy were used to investigate the molecular structures and interactions between the materials in the system. DSSCs were fabricated using GPEs and characterized under Sun simulator. Figure 3.1 demonstrates the steps for preparation of GPE systems investigated in this research.

Table 3.3, 3.4 and 3.5 shows designation of GPEs in first, second and third system respectively. Variation of NaI amount in the first system is compared to the total amounts of PVdF-HFP and PEO polymers. Variation in the amounts of fumed silica (SiO$_2$) and

ZnO in each GPE for system 2 and 3 have been shown in both weight percentage (wt.%) and milligram (mg).

Figure 3.1: Steps of preparation of three GPE system that investigated in this research.

Table 3.3: Designation of first gel polymer electrolyte system with NaI content. The amount of NaI is in compare to the total amount of PVdF-HFP and PEO polymers.

GPE designation	NaI (wt.%)	NaI (g)
PP-NaI-20	20	1.4
PP-NaI-40	40	2.8
PP-NaI-60	60	4.2
PP-NaI-80	80	5.6
PP-NaI-100	100	7

Table 3.4: Designation of second gel polymer electrolyte system in corporation of fumed silica (SiO_2) nanofiller.

Designation	[PVdF-HFP:PEO]:SiO_2 Composition (wt.%)	Fumed silica (SiO_2) (mg)
PP-NaI-Si-0	[40.0:60.0]:0	0
PP-NaI-Si-1	[39.6:59.4]:1	7
PP-NaI-Si-2	[38.8:58.2]:3	21
PP-NaI-Si-3	[38.0:57.0]:5	35
PP-NaI-Si-4	[37.2:55.8]:7	49
PP-NaI-Si-5	[36.4:54.6]:9	63
PP-NaI-Si-6	[35.6:53.4]:11	77
PP-NaI-Si-7	[34.8:52.2]:13	91
PP-NaI-Si-8	[34.0:51.0]:15	105

Table 3.5: Designation of third gel polymer electrolyte system in corporation of zinc oxide (ZnO) nanofiller.

Designation	[PVdF-HFP:PEO]:ZnO Composition (wt.%)	Zinc oxide (ZnO) (mg)
PP-NaI-ZnO-0	[40.0:60.0]:0	0
PP-NaI-ZnO-1	[39.6:59.4]:1	7
PP-NaI-ZnO-2	[39.2:58.8]:2	14
PP-NaI-ZnO-3	[38.8:58.2]:3	21
PP-NaI-ZnO-4	[38.4:57.6]:4	28

3.4   Preparation of gel polymer electrolytes

3.4.1   Preparation of gel polymer electrolytes (PVdF-HFP:PEO:EC:PC:NaI:I$_2$) - First system

PEO/PVdF-HFP:NaI:I$_2$ GPE were prepared using the heating and stirring process. At first, PEO and PVdF-HFP polymers were dissolved in the clear mixture of EC and PC plasticizers with the weight ratio of 1:1. The optimized weight percentage (wt.%) of 40:60 were obtained for the PEO and PVdF-HFP polymers, respectively. For the preparation of GPEs, 20, 40, 60, 80 and 100 wt.% of NaI salt (with respect to the total weight of PEO and PVdF-HFP polymers) were added to the EC:PC mixture first by stirring for 2 hour, at 60 ºC. Then PEO and PVdF-HFP polymers (40:60 wt.%) were dissolved into the EC:PC:NaI mixture by stirring under 100 ºC for overnight. Lastly, Iodine (I$_2$) (1/10 molar ratio of NaI), was added and dissolved into the homogeneous solution of PEO/PVdF-HFP:NaI.

Figure 3.2: Gel polymer electrolytes obtained in first system (PVdF-HFP:PEO:EC: PC:NaI:I$_2$).

3.4.2 Preparation of gel polymer electrolytes (PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$: I$_2$) - Second system

For preparation of the GPEs, the materials needed to be mixed in order and by continuous stirring and heating for better dissolution and gelatinization purpose. Ethylene carbonate (EC) and propylene carbonate (PC) with the same weight ratio (1:1) were mixed in a glass bottle by stirring under 60 °C for about 1 hr. Fixed and optimized amount of NaI salt was added to the mixture while the solution were continuously stirred at the same temperature for 4 hours. For each sample the fumed silica with different concentration was added to the solution followed by heating and stirring for overnight. For better dispersion of PVdF-HFP in the mixture, at first it was dissolved in 10 ml of acetone by continuous stirring and the known amount of PEO was added gradually. Then, EC:PC and salt mixture was added for complete dissolution. The temperature was adjusted to 80 °C for evaporation of all the acetone in the solution. When the evaporation of acetone ensured, iodine (10 M of NaI salt) was added to the mixture to provide the

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iodide/triiodide (I^-/I_3^-) redox couple and further stirred to get homogenous and gelatinized solution. The mixtures as GPEs were allowed to cool down to room temperature and directly characterized by using impedance spectroscopy at ambient temperature.

Figure 3.3: Gel polymer electrolytes obtained in the second system (PVdF-HFP:PEO: EC:PC:NaI:SiO$_2$:I$_2$).

3.4.3   Preparation of gel polymer electrolytes in (PVdF-HFP:PEO:EC:PC:NaI: ZnO:I$_2$)- Third system

Nanocomposite polymer electrolytes were prepared by mixing chemicals under continuously stirring and heating processes. Clear mixture of ethylene carbonate (EC) and propylene carbonate (PC) with the same weight ratio (1:1) were obtained by stirring under 60 °C and for 1 hour. For all the GPEs, optimized amount of sodium iodide (NaI) salt added to the mixture and dissolved by stirring for 4 hours at the same temperature (60 °C). ZnO nanoparticles were dried in oven for 4 hours and under 60 °C before use. Certain amounts of ZnO nanoparticle were dispersed into each sample by heating and stirring for about 8 hours. PVdF-HFP were separately dissolved in 10 ml of acetone by

stirring at room temperature and the resultant solution added to the mixture gradually. Intended amount of PEO added to the mixture and the temperature adjusted to 80 ℃ and this mixture further stirred at this temperature for 4 hours until evaporation of acetone in the mixture was obtained. At the end 0.118 g iodine (1/10 M of salt) was added to the mixture as a source or I^-/I_3^- redox couple and stirred until the homogeneous mixture was obtained. EIS studies investigated directly after all NCPEs obtained and cooled down to the room temperature.

Figure 3.4: Gel polymer electrolytes obtained in the third system (PVdF-HFP:PEO:EC: PC:NaI:ZnO:I_2).

3.5 Characterizations of gel polymer electrolytes

EIS for all GPEs in system 1, 2 and 3 were analyzed by using Hioki, 3532-50 LCR HiTESTER device. The ionic conductivity studies at ambient temperature and the temperature-dependent ionic conductivity studies were carried out under the frequency range of 50 Hz to 5 MHz. The XRD patterns were collected using PANalytical Empyrean diffractometer with Cu-Kα radiation wavelength of λ = 1.540600 Å in 2θ range of 5° to 80° at ambient temperature (45 kV and 40 mA). FTIR spectra were obtained for all the

GPEs in each system using FTIR-ATR PerkinElmer spectrum-400 spectrometer and the interaction between the materials was studied. The J-V curves of the fabricated DSSCs obtained under the sun simulator using the Keithly 2400 potentiometer. The light with incident light power (P_{in}) of 1000 (W m^{-2}) were used.

3.5.1   Electrochemical Impedance Spectroscopy (EIS)

A stainless steel cell with fixed thickness of 0.2828 cm and surface area of 2.27 cm^2 was filled with GPE completely and sandwiched between two stainless steel blocking electrodes as shown in the Figure 3.5.

Figure 3.5: Photograph of the stainless steel cell with two blocking electrodes used for electrochemical impedance spectroscopy (EIS) analysis of gel polymer electrolytes.

The following equation was used to calculate the ionic conductivity (σ) of the GPEs using EIS data

$$\sigma = \frac{L}{R_b A} \qquad\qquad 3.1$$

where σ is the ionic conductivity (S cm^{-1}) of the GPEs, L (cm) is the thickness of the stainless steel cell, R_b (Ω) is the bulk resistance and A (cm^2) is the area of the stainless steel cell.

The Cole-Cole plots were obtained for each GPE to determine the bulk resistance value (R_b) and the ionic conductivity values were calculated by using equation mentioned above. Figure 3.6 shows the typical Cole-Cole plot and the parameters can be obtained from this plot such as bulk resistance (R_b). The inset circuit represents the equivalent circuit of the cell.

Figure 3.6: Demonstration of Cole-Cole plot and the parameters.

3.5.2 Temperature-dependent ionic conductivity

Measuring ionic conductivity of GPEs in different temperatures known as temperature-dependent ionic conductivity helps to investigate thermal behaviour of the GPEs based on two generic thermal activated models of Arrhenius and Vogel-Tammann-Fulcher (VTF) thermal models as well as calculation of activation energies for each GPE in different system of this research (Angell & Smith, 1982).

The Arrhenius model which express the thermal behaviour of GPEs based on their ionic conductivity values at various temperatures shown below:

$$\sigma = \sigma_0 \exp\left[\frac{-E_a}{kT}\right] \qquad 3.2$$

where σ_0, E_a and k allude to the pre-exponential factor, activation energy (eV) and Boltzmann constant (eV/K), respectively. Activation energy values for each GPE calculated by using log σ versus 1000/T plot and equation 3.2.

Thermal behaviour of GPEs for VTF model should fit the following equation:

$$\sigma T^{1/2} = A \exp\left[\frac{-E_a}{k_B(T-T_0)}\right] \qquad 3.3$$

where T, A and T_0 are the temperature, pre-exponential factor and reference temperature (K) related to glass transition temperature (T_g), respectively.

Based on the regression values ($R^2 \sim 1$) obtained from log σ versus 1000/T plot, all the prepared GPEs in system 1,2 and 3 followed the Arrhenius thermal behaviour and the activation energies calculated by using equation 3.2. The ionic conductivity of all GPEs in each system were obtained at temperatures between 30 to 100 ^{o}C and by 10 ^{o}C difference by using Hioki, 3532-50 LCR HiTESTER device.

3.5.3   Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy is an important analysis to identify the molecular structure in the GPE system and assessment of interactions between materials in the GPE for quality identifications. Investigating interactions happens between molecules in the GPEs helps to explain identity of materials and the quality of GPE performance for applications in DSSCs. In this characterization GPEs expose to the infrared radiation and transmittance or absorbance of infrared light gives the fingerprint called FTIR spectrum for screening samples and further investigation of their structural properties by understanding the chemical bonds. Figure 3.7 shows the FTIR instrumentation and how a FTIR spectrum produces by this spectrometer.

Figure 3.7: Fourier transform infrared spectroscopy (FTIR) instrumentation (Vedantam, 2014).

The basic optical principle of FTIR spectrometer is base on the Michelson spectrometer demonstrated in Figure 3.8. A FTIR spectrometer has a light source that produces $g(\delta)$ over range of δ and a fixed mirror A, a movable mirror B and an beam splitter C with centre at O as shown in Figure 3.8. A computer attaches to the spectrometer to do computations for transforming the instant results to the spectrum. A parallel input beam splits into two beams at O and they travel to the mirrors A and B and recombine at O. in the distance between O and two mirrors are same (OA=OB=L) then the beam travel the distance equal to 2L before cocombination at O. mirror B moves a distance L and the optical path differnce $\delta = 2L$. If $L = \lambda/4$ (λ = wavelenght of the monochromatic input light) then $\delta = \lambda/2$ so the beams interfere destructively at O and the resultant beam has intensity equal to zero. When $L = \lambda/2$ and $\delta = \lambda$, the splitted beam interfere constructively at O and the resultant beam has the maximum intensity (Bates, 1976).

Figure 3.8: The components of Michelson spectrometer.

Interaction between ions, polymers, salts and solvents helps to track the movements of ions and understanding the pathways created in the GPEs for facilitating the mobility of ions. The FTIR spectra have been obtained in the wavenumber range from 4000 to 500 cm^{-1} for the pure materials used in the preparation of the GPEs and all the GPEs in system 1, 2 and 3.

3.5.4   X-ray Diffraction Spectroscopy

X-ray diffraction analysis has been used to study the structure of atom and molecules by using X-ray. X-ray radiations are high energy electromagnetic radiations with short wavelengths that can easily penetrate into the solid objects. Sample holder, X-ray tube and X-ray detector are the components of an X-ray diffractometer. X-ray tube is where the X-ray produces by applying a voltage for acceleration of electrons generated by heating a filament. Filters were used to produce monochromatic radiation from X-rays and the resultant radiation collimated and concentrated toward the sample. If radiations interfere with the sample constructively based on the Bragg's law ($n\lambda=2d \sin \theta$) they produce diffracted rays. X-ray detector detected the diffracted rays for counting. Figure 3.9 show the structure of an X-ray diffractometer.

Figure 3.9: X-ray diffractometer (He et al., 2000).

The X-ray diffraction analysis over 2θ angle can detect all diffracted radiations from the lattice in all direction. Figure 3.9 shows diffraction of X-ray through the sample and base on the Bragg's law.

Figure 3.10: Diffraction of X-ray by interfering with sample (Liao, 2007).

The X-ray radiations can penetrate into the sample to dislodge electrons from the inner shells to ionize the atoms and produce different type of intensities (K_α and K_β) in the X-ray spectra of the sample.

The XRD pattern for all GPEs in system 1, 2 and 3 and the pure materials used in preparation of GPEs obtained in 2θ range of $5°$ to $80°$ at ambient temperature to investigate the amorphous nature of GPEs.

3.6   Dye-sensitized solar cell (DSSC) fabrication

DSSCs were fabricated after preparation of photo-anode, counter electrode and GPEs. Preparation of photo-anode is in three steps of coating first TiO_2 layer (P90), coating second TiO_2 layer (P25) and preparation of dye solution for soaking the coated FTO glasses.

3.6.1   Preparation of photo-sensitized electrode

For the preparation of photo-electrode (anode electrode), two TiO_2 layers were coated with two different methods such as spin coating and doctor bladed method on the FTO glasses. For Second layer, TiO_2 with bigger particle size (25 nm) was used to produce porous surface and to trap more molecules of sensitizing dye. The prepared photo-electrodes were immersed in the N719 dye solution for 24 hours and dried. The complete procedure is explained in the following sessions. Figure 3.11 shows materials used for preparation of photo-anodes.

Figure 3.11: Materials for photo-anode preparation.

3.6.1.1 Conducting glass (FTO) cleaning

In this work fluorine doped tin oxide (FTO) substrates were used for preparation of photo-anodes. Before coating TiO_2 layer we need to clean the FTO glasses properly with the following procedure. The FTO glasses was placed into a beaker and washed with few drops of soap and rinsed under running water. After the FTO glasses totally rinsed with water, distilled water was poured into the beaker until all of the FTO glasses were covered then 2 drops of H_2SO_4 were added to the beaker and the FTO glasses sonicated in this solution for 10 minutes. The solution inside beaker totally disposed to the disposal bottle and 2-propanol poured into the beaker to cover all the FTO glasses again. The FTO glasses in the beaker filled with 2-propanol placed on the hot plate and heated until some small bubbles appeared inside. The FTO glasses taken out from the beaker by tweezers and wiped with tissue gently.

3.6.1.2 First layer of photo-sensitized electrode

The first layer of TiO_2 was coated on the FTO glass by spin coating method. 0.5 g of TiO_2 (P90) was ground for 30 minutes in the agate mortar and later 2 ml HNO_3 in pH=1 added to the TiO_2 powder and mixed very well using mortar until a homogeneous solution obtained. Half of the FTO glass covered with magic tape and placed on the spin coater. One drop of the solution dropped on the surface of the FTO glass and spin coated for 2 seconds at 1000 rpm and immediately for 60 seconds at 2350 rpm. After spin coating the substrate was sintered at 450° C for 30 minutes and kept in the furnace until they cooled down to the ambient temperature stilly. Figure 3.11 shows the steps for coating the first layer of TiO_2.

Figure 3.12: Procedures of coating the first layer of TiO$_2$ (P90).

3.6.1.3 Second layer of photo-sensitized electrode

The second layer of TiO$_2$ were coated on the FTO glass by doctor blading method. 0.5 g of TiO$_2$ (P25) was ground for 30 minutes in the agate mortar and later 2 ml HNO$_3$ in pH=1, 1 drop of Triton X-100 and 0.1 g Carbowax added to the TiO$_2$ powder respectively and mixed very well using mortar until a homogeneous solution obtained. Doctor blade

method were used for coating the second layer of TiO$_2$. In this method two FTO glasses with the same thickness placed on the both side of the substrate and fixed with magic tape to control the thickness of the TiO$_2$ layer. After coating the second layer, substrate was sintered at 450 ºC for 30 minutes and kept in the furnace until they cooled down to the ambient temperature stilly.

Figure 3.13: Coating the second layer of TiO$_2$ by doctor blade method.

3.6.1.4 Dye solution

After FTO glasses were coated with two TiO$_2$ layers, they were soaked into the dye solution to absorb dye molecules on the porous surface of TiO$_2$ layer. For preparation of dye solution, 5 mg of dye (N719) added to 10 ml ethanol and mixed for 10 minutes by stirring at room temperature. Later they were soaked in this solution for 24 hours to complete preparation of photo-anodes. Figure 3.14 shows the container of N719 dye solution covered with aluminum to avoid any radiation of light.

Figure 3.14: Dye solution.

3.6.2 Preparation of counter electrode

For preparation of counter electrode the commercial platinum solution was coated on the FTO glass for three time. For the first and second layers, the platinum solution was dropped on the surface of FTO glass and spin coated at 1000 rpm for 4 seconds and immediately after at 2350 rpm for 45 second and later the counter electrode were sintered at 450 ºC for 30 minutes. Procedure for the third layer is the same but the only difference is that the substrate sintered at 450º C for 30 minutes.

3.6.3 Fabrication of DSSCs

For fabrication of DSSCs all GPEs were sandwiched between photo-anode and counter electrode. The components of DSSCs were fixed tightly with a clip and a silicon tape was used to cover the back surface of photo-anode and made an active area on the surface of photo-anode to control illumination of light into the DSSC. Based on Figure 3.15 the configuration of DSSC is FTO glass/TiO$_2$ (P90)/ TiO$_2$ (P25)/dye (N719)/ GPE /platinum/FTO glass.

Figure 3.15: The components used in fabrication of dye-sensitized solar cell.

An incident light power (P_{in}) of 1000 (W m^{-2}) was used to analyze the fabricated DSSCs and their J-V curves were obtained under the sun simulator. Figure 3.16 shows a sample of the fabricated DSSC in this research and Figure 3.17 shows the experimental setup for characterization of DSSCs under solar simulator.

Figure 3.16: Fabricated dye-sensitized solar cell.

Figure 3.17: Experimental setup for characterization of fabricated dye-sensitized solar cell under solar simulator.

3.6.4 Photovoltaic studies of DSSCs

DSSCs were fabricated by sandwiching all GPEs from system 1, 2 and 3, between the working and counter electrodes to investigate the changes on the parameters and efficiency values of the DSSCs in each system. The J-V curves of the fabricated DSSCs were obtained under the sun simulator using the Keithly 2400 potentiometer. The light with incident light power (P_{in}) of 1000 (W m^{-2}) was used to generate electricity based on the principle explained in chapter two. Variation of voltage with current values that generated in DSSCs were collected. The current density (J) values were calculated and the plot of J (mA cm^{-2}) versus voltage (V) obtained for all fabricated DSSCs with various GPEs. Figure 3.18 shows a model of a J-V characteristic curve with position of J_{sc} and V_{oc} parameters that can be obtained from this curve.

Figure 3.18: The J-V characteristic curve with parameters.

The efficiency values of DSSCs were calculated using the following equation:

$$\eta = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{in}}$$

3.4

where P_{in} is the incident light power, and J_{sc} (mA cm^{-2}), V_{oc} (V) and FF are the short-circuit current density, open circuit voltage and fill factor, respectively. The fill factor for all the DSSCs was calculated using the equation below:

$$FF = \frac{P_{max}}{J_{sc}V_{oc}}$$

3.5

where P_{max} (mW cm^{-2}) is the maximum power of solar cell. The fabricated solar cell were analyzed under the solar simulator with incident light power of 1000 (W cm^{-2}).

3.7   Summary

   In this chapter, the materials and chemicals that were used in this research and their roles and also the research design were discussed. The experimental methods for preparation of GPEs and electrodes and also the characterization methods for both GPEs and fabricated DSSCs were discussed.

4.1   Introduction

The results obtained for all the GPEs in three systems based on the electrochemical impedance spectroscopy (EIS), temperature-dependence ionic conductivity, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) studies were reported in this chapter. The photovoltaic performance of DSSCs were also reported based on the GPEs in each system.

4.2   PVdF-HFP:PEO:EC:PC:NaI:I$_2$ gel polymer electrolytes

PEO/PVdF-HFP blend based GPEs are containing ethylene carbonate (EC) and propylene carbonate (PC) as solvent with different concentrations of sodium iodide (NaI) salt. The concentration of NaI salt was calculated with respect to the total amount of polymers (PEO:PVdF-HFP) which means 20 wt.% concentration of NaI is equal to 20 weight percent of the fixed amount of PEO and PVdF-HFP. NaI based GPEs in this system are PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80, PP-NaI-100 with 20, 40, 60, 80 and 100 wt.% NaI content. Effect of NaI on the GPE system was investigated using EIS, temperature-dependent ionic conductivity, XRD and FTIR studies. DSSCs were fabricated using GPEs and tested under Sun simulator.

4.2.1   Ionic conductivity studies at ambient temperature

The Cole-Cole plots for PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 GPEs were obtained and the ionic conductivity values were calculated. Figure 4.1 shows the Cole-Cole plots for PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 GPEs in PEO/PVdF-HFP:NaI:I$_2$ system.

Figure 4.1: Cole-Cole plots for (a) PP-NaI-20, (b) PP-NaI-40, (c) PP-NaI-60, (d) PP-NaI-80 and (e) PP-NaI-100 gel polymer electrolytes.

Table 4.1 shows the designation for the GPEs and the relevant ionic conductivity values. Figure 4.2 shows the variation of the ionic conductivities of the GPEs in presence of different concentration of sodium iodide (NaI) from 0 to 100 wt.%.

Table 4.1: Designation with the corresponding ionic conductivity and bulk resistance values of the gel polymer electrolytes.

GPE designation	NaI content with respect to PEO:PVdF-HFP (wt.%)	Bulk resistance R_b (Ω)	σ (mS cm^{-1})
PP-NaI-20	20	54.4	2.29
PP-NaI-40	40	32.9	3.78
PP-NaI-60	60	24.8	5.02
PP-NaI-80	80	21.4	5.82
PP-NaI-100	100	19.5	6.38

PP-NaI-100 has the lowest bulk resistance value of 19.5 Ω among all the GPEs in system one. Improvements in the ionic conductivity values can be observed in the presence of the NaI salt where the highest ionic conductivity value of 6.38 mS cm^{-1} obtained after incorporation of 100 wt.% of NaI salt for PP-NaI-100 GPE. The ionic conductivity of GPEs was enhanced due to the incorporation of NaI salt. Dissociation of NaI salt in the GPEs provided more ions in the system and enhanced the ionic conductivity value of GPE. Contribution of NaI in the system increases the charge carriers where I$^-$ ions from dissociation of NaI in the system could be considered as the source of the I$^-$/I$_3^-$ redox couple next to the Iodine (I$_2$).

Figure 4.2: Variation of ionic conductivity in presence of different concentrations of NaI salt in the gel polymer electrolyte system.

4.2.2   Temperature-dependent ionic conductivity studies

The ionic conductivity for PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 GPEs was measured at different temperatures from 303 K to 373 K and the results were demonstrated in Figure 4.3. The ionic conductivity values increased by increasing the temperature. This could be due to enhancement in mobility of ions in less viscous medium and increased in the polymer chain flexibilities by increasing temperature (Ramesh & Arof, 2001).

Figure 4.3: Temperature-dependent ionic conductivity results for PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 gel polymer electrolytes.

Increasing the ionic conductivity with temperature shows the fast mobility of ions in the system and it may be due to the increasing in the amorphous phase of the host polymers where the PEO and PVDF-HFP have low glass transition temperatures specially compared with the EC and PC plasticizers (Ataollahi et al., 2012; Dissanayake et al., 2016).

The thermal ionic conductivity behaviour of all the GPEs shows almost straight line with the regression values ~ 1 according to the Arrhenius thermal activated model. Table 4.2 shows the activation energy values that were calculated by using the equation 3.3, for all the GPEs with different concentration of NaI content. The activation energy value decreases by increasing the concentration of NaI salt in the system and it starts to decrease from 117 meV for the GPE with 20 wt.% NaI content to 98 meV which is the lowest activation energy value and corresponds for the highest conducting GPE with 100 wt.% NaI content. Activation energy has direct relationship with mobility of ions in the GPE system. The lower is the activation energy value, the ions have less barrier for movement to overcome in the GPE system. NaI salt provides more ions in the GPE system and based on the ion hopping mechanism more ions can easily transfer to conduction sites in the system using less energy which entail less activation energy values (Sørensen & Jacobsen, 1982).

Table 4.2: Designation with the corresponding ionic conductivity and activation energy values of the gel polymer electrolytes.

GPE designation	NaI content (wt.%)	E_a (meV)
PP-NaI-20	20	117
PP-NaI-40	40	114
PP-NaI-60	60	108
PP-NaI-80	80	105
PP-NaI-100	100	98

4.2.3   FTIR studies

The interaction between PEO, PVdF-HFP and NaI salt in the GPE systems was investigated using the FTIR analysis. Figure 4.4 shows FTIR spectra for Pure PEO, PVdF-HFP and pure NaI salt.

Figure 4.4: FTIR spectra of pure PEO, PVdF-HFP and NaI.

Table 4.3 represents the band assignments of the pure PEO, PVdF-HFP and NaI salt. The interaction between NaI salt and the host polymers can be understood by investigating any changes in these characteristic peaks in the combined FTIR spectra for all the GPEs with different amounts of NaI content from 20 to 100 wt.%. The FTIR spectra for GPEs with different NaI contents are represented in Figure 4.5.

Table 4.3: The FTIR absorption bands for the pure polymers and NaI salt that were used in preparation of the gel polymer electrolytes.

Material	Wavenumber (cm^{-1})	Band assignments	References
Pure PEO	2879	CH band	(Choi et al., 2015; Farheen & Mathad, 2015; Na et al., 2016)
	1466	CH_2 scissoring	
	1359, 1059	C-O-C stretching	
	1341	Waging vibration	
	1279, 1241	C-O band	
	1144, 1092	C-O-C band	
	841	CH vibration	
Pure PVdF-HFP	3026, 2985	Symmetric and antisymmetric stretching vibration of CH_2	(Saikia & Kumar, 2005; Shalu et al., 2015)
	1400	C-F stretching vibration	
	975	C-F stretching	
	872	Combined CF_2 and CC symmetric stretching vibrations	
	840	Mixed mode of CH_2 rocking	
	796	CF_3 stretching vibration	
	761	CH_2 rocking vibration	
NaI	1605, 3414	The sodium iodide characteristic peaks	(Abiddin & Ahmad, 2015)

Figure 4.5: FTIR spectra for PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 gel polymer electrolytes.

The characteristic peak of NaI at 3414 cm^{-1} is shifted to 3559, 3567, 3559, 3560 and 3579 cm^{-1} in PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100, respectively, after NaI is complexed with PEO and PVdF-HFP polymer blends. These changes in the NaI characteristic band may be due to the interaction between Na$^+$ cation and the fluorine in the PVdF-HFP polymer when NaI dissolved in the GPE system and dissociated into I$^-$ anion and Na$^+$ cation. Moreover, the peak at 2879 cm^{-1} in PEO and two peaks at 3026 and 2985 cm^{-1} in PVdF-HFP, after blending and complexation with NaI salt are shifted to lower wavenumbers in PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 based on the values mentioned in Figure 4.5. The peak at 1554 cm^{-1} in the PP-NaI-20 spectrum is due to the interaction between the CH$_2$ scissoring band of PEO and C-F stretching vibration band of PVdF-HFP polymers which increase to 1556 cm^{-1} by increasing the concentration of NaI salt up to 100 wt.%. The wavenumber at 848 cm^{-1} is shifted to 849 cm^{-1} which is due to the interaction of NaI salt with the mixed mode of CH$_2$ rocking of PVdF-HFP and CH vibration of PEO polymers. The peak at 772 cm^{-1} in PP-NaI-20 spectrum is shifted to 773 cm^{-1} in PP-NaI-100 spectrum due to the interaction between the CF$_3$ stretching vibration of PVDF-HFP and NaI and the wavenumber at 893 cm^{-1} in PP-NaI-20 spectrum decreased in intensity in PP-NaI-100 spectrum due to the interaction between combined CF$_2$ and C-C symmetric stretching vibrations of PVdF-HFP and addition of NaI. All the changes in the wavenumbers on increasing the amount of NaI salt in the GPE system up to 100 wt.% prove the interaction and complexation between the NaI salt and the other materials in the system.

4.2.4 X-ray Diffraction (XRD) studies

Figure 4.6 represents the XRD patterns for pure polymers (PEO and PVdF-HFP), PEO/PVdF-HFP polymer blend and NaI salt. The XRD patterns for PEO shows two sharp peaks at $2\theta = 19°$ and $23°$. The XRD patterns for PVdF-HFP shows semicrystalline nature of this copolymer (Ataollahi et al., 2012) with the crystalline sharp peaks at $2\theta = 20°$, $29°$

60

and 38°. The XRD patterns for PEO/PVdF-HFP blend system show the amorphous morphology which proves the complete blending of these polymers in the system and as a result increasing amorphous phase by preventing the re-crystallization in the system. The sharp peaks of NaI represented in Figure 4.6 shows the highly crystalline nature of this salt (Rani et al., 2013).

Figure 4.7 shows the XRD pattern for PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 GPEs. The crystalline peaks of the NaI salt does not appear in the XRD results of the PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 GPEs due to the full dissolution of NaI into the GPE system. Based on Figure 4.7, the semicrystalline peak in PEO/PVdF-HFP blend polymer system decreases in intensity in presence of 20 wt.% NaI salt and it continues decreasing with the addition of NaI salt up to 100 wt.% due to the complexation between NaI and the other materials in the system (Rani et al., 2013).

Figure 4.6: XRD patterns for NaI salt, PEO, PVdF-HFP and PEO/PVdF-HFP polymers.

Figure 4.7: XRD patterns for PEO/PVdF-HFP and PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 gel polymer electrolytes.

4.2.5   Photocurrent density vs voltage characteristics (J-V)

The J-V characteristic curves for all GPEs are represented in Figure 4.8 and the effect of NaI salt on the efficiency of DSSCs fabricated using PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 GPEs were investigated.

Figure 4.8: J-V characteristic curves for the DCCSs fabricated using PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 gel polymer electrolytes.

Enhancement in the efficiency of the DSSCs with increasing the NaI content in the GPE system can be observed in Figure 4.8. All the photovoltaic parameter values of the fabricated DSSCs are represented in Table 4.4. The highest efficiency value of 5.67 % was obtained for DSSC which was fabricated using PP-NaI-100 with 100 wt.% NaI salt

content and highest ionic conductivity value. The performance of DSSCs developed due to the contribution of NaI salt in I^-/I_3^- redox couple generation in GPE system and also by facilitation in the movement of ions in the system.

Table 4.4: The values of the Photovoltaic parameters for the fabricated DSSCs using PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 gel polymer electrolytes.

Electrolyte	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	Efficiency, η (%)
PP-NaI-20	13.39	654	56.9	4.98
PP-NaI-40	12.03	665	62.7	5.02
PP-NaI-60	12.22	675	62.9	5.19
PP-NaI-80	14.45	600	63.2	5.48
PP-NaI-100	13.93	639	63.7	5.67

4.3   PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ gel polymer electrolytes

Novel GPEs were prepared using poly(vinylidene fluoride-co-hexafluoro propylene) copolymer (PVdF-HFP) and polyethylene oxide (PEO) in presence of fumed silica nanofiller with the designated system of PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$. GPEs were examined using electrochemical impedance spectroscopy (EIS) and Temperature-dependent ionic conductivity study to measure the ionic conductivity and understanding the thermal ionic conductivity behavior of GPEs. GPEs were characterized for structural studies using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. GPEs were used to fabricate DSSCs and tested under 1 Sun irradiation.

4.3.1   Ionic conductivity studies in ambient temperature

The Cole-Cole plots for PP-NaI-Si-1, PP-NaI-Si-2, PP-NaI-Si-3, PP-NaI-Si-4, PP-NaI-Si-5, PP-NaI-Si-6, PP-NaI-Si-7 and PP-NaI-Si-8 GPEs were obtained as shown in Figure 4.9. The ionic conductivity values were calculated.

Figure 4.9: Cole-Cole plots for (a) PP-NaI-Si-1, (b) PP-NaI-Si-2, (c) PP-NaI-Si-3, (d) PP-NaI-Si-4, (e) PP-NaI-Si-5, (f) PP-NaI-Si-6, (g) PP-NaI-Si-7 and (h) PP-NaI-Si-8 gel polymer electrolytes.

PP-NaI-Si-7 GPE with [PVdF-HFP:PEO]:SiO$_2$ composition of [34.8:52.2]:13 wt.% has the lowest bulk resistance value of 14.1 Ω and accordingly the highest ionic conductivity value of 8.84 mS cm^{-1}. The ionic conductivity and bulk resistance values are tabulated in Table 4.5. The ionic conductivity of the GPE system was increased in presence of fumed silica (SiO$_2$) filler compared with the GPE without fumed silica (SiO$_2$) (6.38 mS cm^{-1}). Figure 4.10 shows the variation of ionic conductivity with fumed silica (SiO$_2$) content with error bars.

Table 4.5: Designation, ionic conductivity and bulk resistance values for gel electrolyte system in presence of fumed silica (SiO$_2$) nanofiller.

Designation	[PVdF-HFP:PEO]:SiO$_2$ Composition (wt.%)	Fumed silica (SiO$_2$) (mg)	R_b (Ω)	σ (mS cm^{-1})
PP-NaI-Si-0	[40.0:60.0]:0	0	19.5	6.38
PP-NaI-Si-1	[39.6:59.4]:1	7	17.8	6.99
PP-NaI-Si-2	[38.8:58.2]:3	21	17.2	7.24
PP-NaI-Si-3	[38.0:57.0]:5	35	17.1	7.28
PP-NaI-Si-4	[37.2:55.8]:7	49	16.9	7.37
PP-NaI-Si-5	[36.4:54.6]:9	63	16.8	7.42
PP-NaI-Si-6	[35.6:53.4]:11	77	16.4	7.59
PP-NaI-Si-7	[34.8:52.2]:13	91	14.1	8.84
PP-NaI-Si-8	[34.0:51.0]:15	105	16.7	7.46

Presence of fumed silica nanoparticles in the GPEs, in addition to the improvements in mechanical properties of the system improves the ionic conductivity of the GPEs by decreasing the crystallinity of the host polymer and also by the Lewis acid-base interactions between the silanol surface groups of fumed silica and the ions in the GPE which enhances the mobility of I^- and I_3^- ions by immobilizing the Na^+ cations (Sethupathy et al., 2013; Zhao et al., 2014). Based on EIS results, the presence of fumed silica filler increases the ionic conductivity by decreasing the crystallinity of the system and providing the micro-channels for ion transportation and at the same time creation of conductive interfacial layer with polymers, resulting improves the ionic conductivity of the system (Kumar et al., 2015). Polymers and fumed silica particles can absorb together by different types of bindings such as hydrophobic interaction, hydrogen binding or electrostatic binding. Here, mobility of ions were increased by hydrogen bonding between chains of polymers and the hydroxyl groups on the surface of fumed silica (Zeyghami et al., 2014). The hydrogen bindings between the hydroxyl groups of the fumed silica itself, can increase dispersion of fumed silica particles in the GPE system and formation of three dimensional and uniform gel structure for improvements in the mobility of ions (Sharmin et al., 2012). Incorporation of fumed silica into the PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ GPE system increases the ionic conductivity by development of amorphous regions in the GPE system. Interactions between the fumed silica and polymers increase the polymer chains flexibility which helps to increase the ionic conductivity and formation of uniform GPE structure (Abdollahi et al., 2015; Lee et al., 2012). Moreover the interfacial charged layers on the surface of fumed silica nanoparticles overlap on each other and provide the pathways for mobility of ions. These charged layers also increase dissociation of salt into ions when the positive ions attract to the oxygen on the surface of fumed silica that can increase the ionic conductivity value of the GPE effectively (Shuchi et al., 2016).

Figure 4.10: Variation of ionic conductivity values for gel polymer electrolytes with different fumed silica (SiO$_2$) content.

4.3.2 Temperature-dependent ionic conductivity studies

The ionic conductivity for PP-NaI-Si-1, PP-NaI-Si-2, PP-NaI-Si-3, PP-NaI-Si-4, PP-NaI-Si-5, PP-NaI-Si-6, PP-NaI-Si-7 and PP-NaI-Si-8 GPEs was measured in different temperatures from 303 K to 373 K and Figure 4.11 exhibits the temperature-dependent ionic conductivity behavior of the GPEs in presence of the fumed silica filler in PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ system.

Figure 4.11: Temperature-dependent ionic conductivity results for gel polymer electrolytes with different amounts of fumed silica (SiO_2).

The ionic conductivity values increase by increasing the temperature based on what explained in session 4.1.2. Based on the regression values ($R^2 \sim 1$), all the prepared GPEs followed the Arrhenius behavior and the activation energies were calculated by using the Arrhenius equation.

Table 4.6: Designation, ionic conductivity and activation energy for gel polymer electrolyte system in presence of fumed silica (SiO_2) nanofiller.

Designation	[PVdF-HFP:PEO]:SiO$_2$ Composition (wt.%)	E_a (meV)
PP-NaI-Si-0	[40.0:60.0]:0	98
PP-NaI-Si-1	[39.6:59.4]:1	96
PP-NaI-Si-2	[38.8:58.2]:3	95
PP-NaI-Si-3	[38.0:57.0]:5	94
PP-NaI-Si-4	[37.2:55.8]:7	92
PP-NaI-Si-5	[36.4:54.6]:9	90
PP-NaI-Si-6	[35.6:53.4]:11	91
PP-NaI-Si-7	[34.8:52.2]:13	85
PP-NaI-Si-8	[34.0:51.0]:15	88

Table 4.6 shows the variation of activation energy values, E_a with athe ionic conductivity of the GPEs with different amounts of fumed silica content in PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ system. Results show the addition of fumed silica filler up to 13 wt.% into PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ system has enhanced the mobility of ions and, as a result, it has improved the ionic conductivity and at the same time, the activation energy value has been decreased by increasing the mobility of ions in the GPEs which means the ions in the GPE need less energy to move (Yilmaz et al., 2011).

4.3.3   FTIR studies

Analyzing the changes in the IR absorption peaks in presence of fumed silica filler helps to understand the complexation between the fumed silica and the other components of the GPE system and the effect of fumed silica on the chemical bonds of the materials in the system. Figure 4.12 shows the FTIR spectra in the wavenumber range from 4000

to 650 cm^{-1} for the pure materials used in the preparation of the GPEs. Table 4.7 shows

the essential absorption peaks and the relative band assignments for the pure materials

used in preparation of GPEs.

Figure 4.12: FTIR spectra for the pure materials (PVdF-HFP, PEO, NaI and fumed silica (SiO$_2$)).

Table 4.7: The essential absorption peaks and relative band assignments for the pure materials (PEO, PVdF-HFP, NaI and fumed silica (SiO_2)).

Materials	Wavenumbers (cm^{-1})	Band assignments	References
Pure PEO	2879	CH band	(Choi et al., 2015; Farheen & Mathad, 2015; Na et al., 2016)
	1466	CH_2 scissoring	
	1359, 1059	C-O-C stretching	
	1341	Waging vibration	
	1279, 1241	C-O band	
	1144, 1092	C-O-C band	
	841	CH vibration	
Pure PVdF-HFP	3026, 2985	Symmetric and antisymmetric stretching vibration of CH_2	(Saikia & Kumar, 2005; Shalu et al., 2015)
	1400	C-F stretching vibration	
	975	C-F stretching	
	872	Combined CF_2 and CC symmetricstretching vibrations	
	840	Mixed mode of CH_2 rocking	
	796	CF_3 stretching vibration	
	761	CH_2 rocking vibration	
NaI	1605,3414	The sodium iodide characteristic peaks	(Abiddin & Ahmad, 2015)
Fumed silica (SiO_2)	3331	O-H stretching	(Agnihotry et al., 2004; Fu et al., 2003; Sharma & Sekhon, 2007)
	1636	O-H deformation of the surface hydroxyl group of fumed silica	
	1088, 806	Si-O vibration	

Figure 4.13 represents the Fourier transform infrared (FTIR) absorption peaks in the wavenumber range between 4000 and 500 cm^{-1} for the PP-NaI-Si-1, PP-NaI-Si-2, PP-NaI-Si-3, PP-NaI-Si-4, PP-NaI-Si-5, PP-NaI-Si-6, PP-NaI-Si-7 and PP-NaI-Si-8 GPEs in system PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ with different concentrations of fumed silica filler.

The wavenumbers for the IR absorption peaks of the PP-NaI-Si-0 (without fumed silica (SiO$_2$)) are represented in Table 4.7 and the relative band assignments for the peaks show the changes in the wavenumbers due to the interaction between the materials in the GPEs without filler compared with the characteristic peaks represented in Table 4.7 for the pure materials. In presence of fumed silica into the GPE system the peak at 3579 cm^{-1} changes to the lower wavenumbers due to the interaction between fumed silica and NaI salt according to Figure 4.13. The peak at 1799 cm^{-1} appears in the GPE containing 13 wt.% fumed silica (PP-NaI-Si-7) FTIR spectra and due to the complexation between the fumed silica and NaI the peak at 1770 cm^{-1} moves to higher wavenumber at 1775 cm^{-1} with lower intensity. All the peaks in the entire PP-NaI-Si-7 FTIR spectra show decreasing in intensity, and at 1166, 1634, 716 and 715 cm^{-1} wavenumbers, all the peaks show the higher wavenumbers and lower intensity peaks compared with the other GPEs which were incorporated with 1, 3, 5, 7, 9, 11 and 15 wt.% of fumed silica. All of these changes have confirmed the complexation between PVdF-HFP copolymer, PEO polymer, NaI salt and fumed silica.

Figure 4.13: FTIR spectra for PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ system.

4.3.4   X-ray Diffraction (XRD) studies

The XRD patterns for fumed silica (SiO$_2$), PEO, PVdF-HFP, PVdF-HFP:PEO and NaI are represented in Figure 4.14. The XRD patterns for PVdF-HFP show the semicrystalline morphology of the PVdF-HFP copolymer with sharp peaks at $2\theta = 18^o$ (100), 19° (020), 26° (110), 29° (021) and 38° (211) are corresponding for crystalline peaks of PVdF (Kumar & Dek, 2010). Two sharp peaks at $2\theta = 19^o$ and 23° are represented in the XRD results for PEO. The XRD patterns for PVdF-HFP:PEO blend in Figure 4.14 shows low intensity with slightly broadening due to the interaction between PEO and PVdF-HFP when these two polymers were blended homogenously and the crystallization in the system was reduced. Moreover, NaI salt shows high crystalline morphology and fumed silica represents amorphous characteristic based on the XRD results in Figure 4.14.

Furthermore, the XRD patterns of PP-NaI-Si-4, PP-NaI-Si-5, PP-NaI-Si-6, PP-NaI-Si-7 and PP-NaI-Si-8 GPEs with different amounts of fumed silica filler are represented in Figure 4.15. All the GPE show the amorphous characteristic due to the interaction between the fumed silica and the other materials in the system and specially interaction with the polymers caused by making disordered polymer chains in presence of fumed silica filler and also well dispersion of fumed silica filler in the system (Prabakaran et al., 2015b).

Figure 4.14: XRD patterns for pure materials (PVdF-HFP, PEO, NaI and fumed silica (SiO$_2$)) used in preparation of gel polymer electrolytes in PVdF-HFP:PEO: EC:PC: NaI: SiO$_2$:I$_2$ system.

Figure 4.15: XRD patterns for PP-NaI-Si-4, PP-NaI-Si-5, PP-NaI-Si-6, PP-NaI-Si-7 and PP- NaI-Si-8 gel polymer electrolytes.

4.3.5 Photocurrent density vs voltage characteristics (J-V)

DSSCs were fabricated by sandwiching the GPEs with and without fumed silica between the working and counter electrodes to investigate the effects of the fumed silica on the efficiency of the DSSC. The photovoltaic characteristics of DSSCs using PP-NaI-Si-1, PP-NaI-Si-2, PP-NaI-Si-3, PP-NaI-Si-4, PP-NaI-Si-5, PP-NaI-Si-6, PP-NaI-Si-7 and PP-NaI-Si-8 GPEs were investigated. The fabricated solar cells were analyzed under the solar simulator with incident light power of 1000 (W cm^{-2}). Table 4.8 shows the DSSC parameters.

Table 4.8: DSSC parameters using the gel polymer electrolytes in PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ system and with different fumed silica (SiO$_2$) content.

Electrolytes	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	Efficiency, η (%)
PP-NaI-Si-0	13.93	639	63.7	5.67
PP-NaI-Si-1	17.23	604	62.0	6.45
PP-NaI-Si-3	18.93	639	64.2	7.76
PP-NaI-Si-4	22.26	600	59.4	7.92
PP-NaI-Si-5	22.29	574	62.6	8.01
PP-NaI-Si-6	23.22	584	63.0	8.54
PP-NaI-Si-7	27.31	564	61.3	9.44
PP-NaI-Si-8	18.94	584	59.1	6.53

The J-V results indicate that the presence of fumed silica nanofiller in the GPE systems, namely PP-NaI-Si-1, PP-NaI-Si-3, PP-NaI-Si-4, PP-NaI-Si-5, PP-NaI-Si-6, PP-NaI-Si-7, PP-NaI-Si-8, increases the short circuit current density J_{sc} of the fabricated DSSCs. Incorporation of 13 wt.% fumed silica filler (PP-NaI-Si-8) led to the highest conversion efficiency of 9.44%. Figure 4.16 exhibits the J-V characteristics of DSSCs using PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ GPE system.

Figure 4.16: J-V results for the DSSCs using gel polymer electrolytes without fumed silica (PP-NaI-Si-0) and with different amounts of fumed silica (SiO_2).

The J-V results reveal that J_{sc} is increased with the addition of fumed silica to the GPE system that enhances transportation of ions. The J_{sc} and efficiency values follow the conductivity trend however V_{oc} and FF values does not change much and are in the range 564 to 649 mV and 0.591 to 0.642, respectively. Presence of fumed silica in the GPE system increases the ionic conductivity and efficiency of GPEs, which can be due to increasing the mobility of ions in the GPEs (Kim et al., 2004).

4.4 PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ gel polymer electrolytes

GPEs were prepared by blending poly (vinylidene fluoride-co-hexafluoro propylene) copolymer (PVdF-HFP) and polyethylene oxide (PEO) polymers and incorporation of ZnO inorganic nanofiller (PVdF-HFP:PEO:EC:PC:NaI:I$_2$:ZnO). Electrochemical impedance spectroscopy (EIS) and temperature-dependent ionic conductivity behavior of GPEs analyzed. Structural studies of GPEs was carried out by using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy analysis. GPEs are used to fabricate DSSCs. Enhancements in the solar light to electricity conversion efficiency (η) of DSSCs were observed in the presence of ZnO inorganic nanofiller.

4.4.1 Ionic conductivity studies in ambient temperature

The bulk resistance values for GPEs in PEO/PVdF-HFP:NaI:I$_2$:ZnO system were investigated by plotting the Cole-Cole plots for PP-NaI-ZnO-0, PP-NaI-ZnO-1, PP-NaI-ZnO-2, PP-NaI-ZnO-3 and PP-NaI-ZnO-4 GPEs and the ionic conductivity values were calculated. Figure 4.17 shows the Cole-Cole plots for PP-NaI-ZnO-0, PP-NaI-ZnO-1, PP-NaI-ZnO-2, PP-NaI-ZnO-3 and PP-NaI-ZnO-4 GPEs and based on these plots, the trend for variation of bulk resistance values (R$_b$) in presence of ZnO inorganic nanofiller in PEO/PVdF-HFP:NaI:ZnO:I$_2$ system can be observed.

Figure 4.17: Cole-Cole plots for (a) PP-NaI-ZnO-0, (b) PP-NaI-ZnO-1, (c) PP-NaI-ZnO-2, (d) PP-NaI- ZnO-3 and (e) PP-NaI-ZnO-4, gel polymer electrolytes.

The ionic conductivity value is inversely proportional to the bulk resistance value. Table 4.9 shows the designation for the GPEs and the relevant ionic conductivity values. Figure 4.18 shows the variation of ionic conductivity values of GPEs with ZnO nanoparticles content.

Table 4.9: Designation, ionic conductivity and bulk resistance values for gel polymer electrolytes in PVdF-HFP:PEO:EC:PC:NaI:ZnO:I_2 with different amounts of ZnO nanoparticle.

Designation	[PVdF-HFP:PEO]:ZnO Composition (wt.%)	Bulk resistance, R_b (Ω)	σ (mS cm^{-1})
PP-NaI-ZnO-0	[40.0:60.0]:0	19.5	6.38
PP-NaI-ZnO-1	[39.6:59.4]:1	18.0	6.92
PP-NaI-ZnO-2	[39.2:58.8]:2	17.1	7.30
PP-NaI-ZnO-3	[38.8:58.2]:3	14.9	8.36
PP-NaI-ZnO-4	[38.4:57.6]:4	18.5	6.73

Incorporation of ZnO nanoparticles into the GPE system significantly enhanced the ionic conductivity up to 8.36 mS cm^{-1} for PP-NaI-ZnO-3 compared to the polymer electrolyte without ZnO nanoparticle (6.38 mS cm^{-1}). It is inferred that ZnO nanoparticles provide three dimensional channels for more ion transportations via Grotthuss mechanism, by increasing the amorphous phase of the GPE system (Ludueña et al., 2011). The ionic conductivity values for each GPE are listed in Table 4.9. In addition to the improvements in ionic conductivity and the mechanical flow of the GPEs, contribution of ZnO nanoparticles enhanced the electron recombination in the electrolyte by inducing electrons from conduction band of TiO_2 layer on photo-anode to the oxidation/reduction potential of iodide/triiodide (Chang et al., 2016).

Figure 4.18: Ionic conductivity values for each gel polymer electrolyte in PEO/PVdF-HFP:NaI:I$_2$:ZnO system with different ZnO content.

4.4.2 Temperature-dependent ionic conductivity studies

The ionic conductivity of PP-NaI-ZnO-0, PP-NaI-ZnO-1, PP-NaI-ZnO-2, PP-NaI-ZnO-3 and PP-NaI-ZnO-4 GPEs at different temperatures from 30 to 100° C were obtained and the temperature-dependent ionic conductivity of GPEs were investigated. The ionic conductivity of GPEs increased by increasing temperature. Figure 4.19 represents the temperature-dependence ionic conductivity behavior of all GPEs in PEO/PVdF-HFP:NaI:ZnO:I$_2$ system and with incorporation of different amounts of ZnO nanoparticles.

Figure 4.19: Temperature-dependence ionic conductivity for gel polymer electrolytes in PVdF-HFP:PEO:EC:PC:NaI:ZnO:I_2 system with different ZnO content.

According to the unity of regression values ($R^2 \sim 1$), it is concluded that GPEs in PEO/PVdF-HFP:NaI:ZnO:I_2 system follows Arrhenius thermal behaviour hence the activation energies of GPEs were calculated by using the Arrhenius equation. Activation energy values for GPEs with different ZnO nanoparticle content are listed in Table 4.10.

PP-NaI-ZnO-3 GPE with highest ionic conductivity value has the lowest activation energy value of 95 meV compared to other GPEs in the PVdF-HFP:PEO:EC:PC:NaI:ZnO;I_2 system.

Table 4.10: Designation, ionic conductivity and activation energy values for gel polymer electrolytes in PVdF-HFP:PEO:EC:PC:NaI:I$_2$:ZnO with different amounts of ZnO nanoparticle.

Designation	[PVdF-HFP:PEO]:ZnO Composition (wt.%)	E$_a$ (meV)
PP-NaI-ZnO-0	[40.0:60.0]:0	98
PP-NaI-ZnO-1	[39.6:59.4]:1	97
PP-NaI-ZnO-2	[39.2:58.8]:2	96
PP-NaI-ZnO-3	[38.8:58.2]:3	95
PP-NaI-ZnO-4	[38.4:57.6]:4	97

4.4.3 FTIR studies

Figure 4.20 shows the FTIR spectra for PVdF-HFP and PEO polymers, NaI salt and ZnO nanoparticles in the range from 4000 to 450 cm^{-1} and their pertinent band assignments were listed in Table 4.11.

GPEs were analyzed by infrared spectroscopy to investigate the effect of ZnO nanoparticles on the structural properties of GPEs and chemical bonds of materials in the system. Figure 4.21 shows the FTIR peaks for all GPEs with different amounts of ZnO nanoparticles in the PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ system in the range from 4000 to 450 cm^{-1}. The absorption peaks of GPE without ZnO nanoparticles (PP-NaI-ZnO-0) are investigated in compare with the characteristic peaks of pure materials represented in Table 4.11.

Figure 4.20: FTIR spectra for polymers (PVdF-HFP and PEO), salt (NaI) and ZnO nanoparticles that were used in preparation of gel polymer electrolytes.

Table 4.11: FTIR spectra for PVdF-HFP and PEO polymers, NaI salt and ZnO nanoparticles.

Materials	Wavenumbers (cm^{-1})	Band assignments	References
PVdF-HFP	761	CH$_2$ rocking vibration	(Saikia & Kumar, 2005; Shalu et al., 2015)
	796	CF$_3$ stretching vibration	
	840	Mix mode of CH$_2$ rocking	
	872	Combined CF$_2$ and C-C symmetric stretching	
	975,1400	vibrations	
	3026,2985	C-F stretching vibration	
		Symmetric and antisymmetric stretching vibration of CH$_2$	
PEO	841	C-H vibration	(Choi et al., 2015; Farheen & Mathad, 2015; Na et al., 2016)
	1144,1092	C-O-C band	
	1279,1241	C-O band	
	1341	Waging vibration	
	1359,1059	C-O-C stretching	
	1466	CH$_2$ scissoring	
	2879	C-H band	
NaI	1605 and 3414	Characteristic absorption peaks of sodium iodide	(Zainal Abiddin & Ahmad, 2015)
ZnO	488	Zinc oxide characteristic peaks	(Ambrožič et al., 2010; Martinez et al.)
	1392,1536	Symmetric and antisymmetric stretching of C=O for zinc acetate	
	1545,3389	bending and stretching modes of O-H	

Figure 4.21: FTIR spectra for all gel polymer electrolytes prepared in PVdF-HFP:PEO: EC:PC:NaI:I$_2$:ZnO system.

According to the FTIR spectra for PP-NaI-ZnO-3, the broad absorption band at 3579 cm^{-1} shifts to 3565 cm^{-1} with lower intensity due to complexation between ZnO nanoparticles and NaI. The C-H band at 2929 cm^{-1} moves to higher wavenumber at 2931 cm^{-1} due to the interaction between ZnO nanoparticles and PEO along with symmetric and asymmetric stretching vibration of CH$_2$ in PVdF-HFP. The new peak at 1710 cm^{-1} appears in FTIR spectra of PP-NaI-ZnO-3, by incorporation of 3 wt.% ZnO nanoparticles and it corresponds with complexation between ZnO nanoparticles, NaI and host

polymers. For all GPEs the peaks at 2362 and 1967 cm⁻¹ moves to lower wavenumbers due to the incorporation of ZnO nanoparticles in to the PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ system. The band at 1635 cm⁻¹ responsible for C=O stretching, shifts to 1636 cm⁻¹ for PP-NaI-ZnO-3 and the peak intensity decreases due to the interaction between C=O stretching of zinc acetate and C=O stretching of ethylene carbonate and propylene carbonate (Indran et al., 2016). The peak intensity for the bands at 1389 and 1354 cm⁻¹ decrease due to the interaction between symmetric and asymmetric C=O stretching of zinc acetate and C-O band of PEO respectively. The band at 1221 cm⁻¹ attributes to C-O-C stretching of PEO, decrease in peak intensity in presence of ZnO nanoparticles in the PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ system. The bands at 773 and 715 cm⁻¹ shifts to higher intensity due to the interaction between ZnO nanoparticles and CF$_3$ stretching and CH$_2$ rocking vibration of PVdF-HFP respectively.

4.4.4   X-ray Diffraction (XRD) studies

The X-ray diffractogram for pure PVdF-HFP, PEO, NaI and ZnO and also PVdF-HFP:PEO film has been shown in Figure 4.22. The peaks and their pertaining planes indicated in the XRD patterns of PVdF-HFP at 2θ= 18° (100), 19° (020), 26° (110), 29° (021) and 38° (211) are corresponding to α and γ-phase of crystalline PVdF in this co-polymer respectively and the XRD pattern is indicative of the semicrystalline nature of PVdF-HFP co-polymer (Hoque et al., 2016; Ulaganathan et al., 2012). Two intense diffraction peaks at 2θ= 19° and 23° observed in the XRD pattern of pure PEO (Poonam, 2012). The XRD pattern for PVdF-HFP:PEO shows one low intensity and broaden peak which corresponds for semicrystalline morphology due to the interaction between PVdF-HFP and PEO that have been enhanced the amorphous regions in the PVdF-HFP:PEO system. The diffraction peak at 20.2° for PVdF-HFP:PEO XRD pattern shows the overlap of the peak for (200) plane for β-phase of PVdF in PVdF-HFP co-polymer and the peak at 19.2° for PEO when non-polar and crystalline α-phase turn to the electro-active β-phase

due to the interaction between PVdF-HFP and PEO polymers by blending (Hoque et al., 2016). The XRD pattern for NaI with several diffraction peaks ascertains high crystalline nature of this salt. ZnO X-ray diffractogram of ZnO shows crystalline morphology and high intensity diffraction peaks with pertaining planes at 2θ= 31.9° (100), 34.6° (002), 36.4° (101), 47.7° (102), 56.7° (110), 63° (103), 66.5° (200), 68.1° (112), 69.2° (201) (Mallakpour & Zeraatpisheh, 2012). Figure 4.23 shows the X-ray diffractogram for PP-NaI-ZnO-0, PP-NaI-ZnO-1, PP-NaI-ZnO-2, PP-NaI-ZnO-3 and PP-NaI-ZnO-4.

The XRD pattern for all the GPEs ascertains the semicrystalline morphology. The broad diffraction peak in the X-ray diffractogram of PP-NaI-ZnO-1, PP-NaI-ZnO-2 and PP-NaI-ZnO-3 nanocomposite polymer electrolytes slightly decrease in intensity due to the disordered polymer chains produced by ZnO nanoparticles in the system that enhanced amorphous phase of the system.

Figure 4.22: XRD patterns for polymers (PVdF-HFP and PEO), salt (NaI) and ZnO nanoparticles that were used in preparation of gel polymer electrolytes.

Figure 4.23: XRD patterns for nanocomposite polymer electrolytes in PVdF-HFP:PEO: EC:PC:NaI:I$_2$:ZnO system with different ZnO content.

4.4.5 Photocurrent density vs voltage characteristics (J-V)

GPEs with different amounts of ZnO nanoparticles were sandwiched between photo-anode and counter electrode for fabrication of DSSCs. Solar light to electricity conversion efficiency of DSSCs were calculated on incorporation of different amounts of ZnO nanoparticles into the PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ system. Simulated incident light power of 1000 (W cm^{-2}) were used to analyze the fabricated DSSCs. DSSC parameters for DSSCs fabricated using PP-NaI-ZnO-0, PP-NaI-ZnO-1, PP-NaI-ZnO-2, PP-NaI-ZnO-3 and PP-NaI-ZnO-4 GPEs are listed in Table 4.12.

Table 4.12: DSSC parameters for all gel polymer electrolytes (PVdF-HFP:PEO:EC: PC:NaI:ZnO:I_2).

Gel polymer electrolytes	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	Efficiency, η (%)
PP-NaI-ZnO-0	13.93	639	63.7	5.67
PP-NaI-ZnO-1	21.20	560	61.0	7.00
PP-NaI-ZnO-2	22.53	560	60.1	7.68
PP-NaI-ZnO-3	24.54	620	60.2	9.08
PP-NaI-ZnO-4	23.06	600	59.0	8.13

Based on the results shown in Table 4.12, incorporation of ZnO nanoparticles into the PVdF-HFP:PEO:EC:PC:NaI:ZnO:I_2 system has increased the short-circuit current density (J_{sc}) values. The J_{sc} values are enhanced due to the improvement of ion transportation through transmittal channels created in presence of ZnO nanoparticles in the GPEs. V_{oc} value slightly decrease for GPE with incorporation of 1 wt.% ZnO (PP-NaI-ZnO-1) due to the increase in electron recombination rate in presence of ZnO nanoparticles in the GPE system as mentioned earlier. V_{oc} values increased for PP-NaI-ZnO-2 and PP-NaI-ZnO-3 and by increasing the ionic conductivity and it decreased for PP-NaI-ZnO-4. The filling factor values decrease by increasing ZnO nanoparticles content in the GPE system. The highest sunlight to electricity conversion efficiency value of 9.08 % were obtained for DSSC fabricated by using PP-NaI-ZnO-3 and by incorporation of 3 wt.% ZnO nanoparticles. Unlike V_{oc} and FF, J_{sc} and efficiency values follow the same trend as ionic conductivity. Figure 4.24 represents the combined J-V characteristic curves for DSSCs fabricated by using GPEs with incorporation of different amounts of ZnO nanoparticles. Incorporation of ZnO nanoparticles in the GPE system

increased the J_{sc} and energy conversion efficiency values, as a result of enhancement in the mobility of ions in the system (Vijayakumar et al., 2015).

Figure 4.24: Photocurrent density (J) versus cell potential (V) for DSSCs fabricate by using polymer electrolyte without ZnO nanoparticles and gel polymer electrolytes with different amounts of ZnO nanoparticles.

4.5 Summary

The results for three GPE systems of PVdF-HFP:PEO:EC:PC:NaI:I$_2$, PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ and PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ were elaborated in this chapter based on the electrochemical impedance spectroscopy (EIS), temperature-dependence ionic conductivity, X-ray diffraction (XRD) and FTIR studies. Results for the photovoltaic performance of DSSCs were also elaborated based on the GPEs in each system. PP-NaI-100, PP-NaI-Si-7 and PP-NaI-ZnO-3 GPEs showed the highest ionic

conductivity values of 6.38, 8.84 and 8.36 mS cm^{-1} in system one, two and three respectively. DSSCs based on NaI-100, PP-NaI-Si-7 and PP-NaI-ZnO-3 GPEs also represented the highest energy conversion efficiency values of 5.67, 9.44 and 9.08 %.

CHAPTER 5: SUMMARY OF THE RESEARCH

In the first system (PVdF-HFP:PEO:EC:PC:NaI:I_2), the PEO/PVdF-HFP blend based GPEs with different amounts of NaI salt from 20 to 100 wt.% with respect to PEO:PVdF-HFP were prepared and these were employed in fabrication of DSSCs. Increasing the ionic conductivity of the GPEs by increasing the NaI content up to 100 wt.% with respect to PEO:PVdF-HFP, were observed and the highest ionic conductivity of 6.38 mS cm^{-1} was achieved with PP-NaI-100 after incorporation of 100 wt.% of NaI salt. The temperature-dependent ionic conductivity of all the GPEs was proved the Arrhenius behavior and the activation energy value decreased up to 98 meV for PP-NaI-100. The XRD pattern for all the GPEs showed the semi-crystalline nature of the GPEs with the addition of salt. Increasing the amount of NaI salt in the system proved the complexation between PEO/PVdF-HFP polymer blend and NaI salt in the system. The absorption peaks in the FTIR spectra shows the shifting in the wavenumbers by increasing the NaI amount up to 100 wt.% NaI salt which proved the interaction between NaI salt and PEO/PVdF-HFP polymer blend in the system. The performance of all the fabricated DSSCs using PP-NaI-20, PP-NaI-40, PP-NaI-60, PP-NaI-80 and PP-NaI-100 GPEs were analyzed under the Sun simulator with 100 mW cm^{-2}. From the J-V results, the efficiencies were calculated. The DSSC fabricated with PP-NaI-100 GPE showed the highest efficiency value of 5.67 %.

In the second system (PVdF-HFP:PEO:EC:PC:NaI:SiO_2:I_2), the novel PVdF-HFP:PEO based GPEs were prepared and the fumed silica was incorporated into GPE system. The effects of fumed silica nanofiller into the system were studied by characterization of samples using EIS, XRD and FTIR spectroscopy. Fumed silica increased the ionic conductivity of the GPE as a result of enhanced ionic transportation

and increased the amorphous phase of the system based on the XRD results. Furthermore, interaction between Na^+ cations and the silanol surphase groups of fumed silica increase the mobility of I^- and I_3^- ions and increased the ionic conductivity of GPE. The highest ionic conductivity of 8.84 mS cm^{-1} was achieved after incorporation of 13 wt.% of fumed silica (PP-NaI-Si-7). The PP-NaI-Si-7 shows the lowest activation energy value (85 meV). Temperature-dependent ionic conductivity studies showed that all GPEs followed the Arrhenius thermal activated model. FTIR and XRD studies confirmed the interaction and complexation between the PEO, PVDF-HFP:PEO polymers, NaI and fumed silica. The highest energy conversion efficiency of 9.44% was achieved for the highest conducting GPE with 13 wt.% of fumed silica content (PP-NaI-Si-7). This high energy conversion value is achieved as a result of high ionic conductivity and presence of good contact with the photo-electrode (Kim et al., 2004). Based on the J-V and efficiency (η) trend, increasing in mobility of ions in presence of fumed silica filler that improved the photovoltaic performance of fabricated DSSC.

In the third system (PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$), GPEs incorporated with different amounts of ZnO nanoparticles were prepared and intended DSSCs were fabricated using these GPEs. GPEs were characterized by using electrochemical impedance spectroscopy (EIS), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) and effect of ZnO nanoparticles into the GPE system were investigated. The ionic conductivity of GPEs increased by increasing mobility of ions by Grothuss mechanism and ion transportations through transmittal channels created by ZnO nanoparticles in the GPE system. The highest ionic conductivity value (8.36 mS cm^{-1}) obtained for PP-NaI-ZnO-3 GPE. X-ray diffractogram has shown the enhancement in the amorphous phase of GPEs in presence of 1, 2 and 3 wt. % ZnO nanoparticles in the PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ system. All nanocomposite polymer electrolytes proven to follow Arrhenius thermal model based on the temperature-dependent ionic conductivity

results. The constructive interaction between ZnO nanoparticles, NaI, PVdF-HFP and PEO are confirmed by XRD and FTIR studies. Energy conversion efficiency and photovoltaic performance of DSSCs enhanced as the mobility of ions increased in the GPEs in presence of ZnO nanoparticles. The highest sunlight to energy conversion efficiency of 9.08 % was achieved for the highest conducting GPE and by incorporation of 3 wt. % ZnO nanoparticles content.

In both of the second and third GPE systems, incorporation of fumed silica and zinc oxide nanoparticles as filler, increased the ionic conductivity values. In the first system the highest ionic conductivity value of 8.84 mS cm^{-1} was achieved by incorporation of 13 wt.% of fumed silica in the PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ GPE system which is higher than the highest ionic conductivity value of 8.36 mS cm^{-1} that was achieved by incorporation of 3 wt. % ZnO in the (PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$) GPE system. Higher energy conversion efficiency value (9.44%) was achieved in the second GPE system in compare to the highest energy conversion efficiency value (9.08 %) that was achieved in the third system. Higher ionic conductivity of PP-NaI-Si-7 GPE, produced higher current density value and also higher energy conversion efficiency compared to the related results for PP-NaI-ZnO-3 GPE in the third system. Well dispersion of nanoparticles in the electrolyte system, size of nanoparticles and interfacial layers are some of the main factors which can increase the ionic conductivity of GPE (Shuchi et al., 2016). Fumed silica particles has tiny size of 7 nm in compare to the zinc oxide (~100 nm). The hydroxyl groups on the surface of the fumed silica produced the amorphous and uniform GPE system with high ionic conductivity value due to the interaction of these particles with polymer chains and their contribution in dissociation of salt in the GPE. These reasons may be responsible for higher ionic conductivity and energy conversion efficiency values obtained in the second system compared to the related results in the third system and by incorporation of zinc oxide nanoparticles.

CHAPTER 6: CONCLUSIONS AND FUTURE WORKS

6.1   Conclusions

In this research three GPE systems were developed for application in fabrication of DSSCs with high performance. First GPE system were optimized based on PVdF-HFP:PEO polymers and sodium iodide (NaI) salt and the highest ionic conductivity value of 6.38 mS cm^{-1} were achieved for the PP-NaI-100 GPE after the addition of 100 wt.% of NaI salt with respect to weight of PEO/PVdF-HFP polymers. PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ and PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ GPE systems were studied as second and third systems in this research, respectively. For second and third GPE systems fumed silica (SiO$_2$) and zinc oxide (ZnO) were added respectively to the optimized GPE in first system as filler to enhance the ionic conductivity of prepared GPE. The highest ionic conductivity values of 8.84 mS cm^{-1} and 8.36 mS cm^{-1} were obtained for PP-NaI-Si-7 and PP-NaI-ZnO-3 GPEs in PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ and PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ GPE systems respectively. DSSCs were fabricated using GPEs prepared in system one, two and three and characterized under Sun simulator. The highest energy conversion efficiency values for DSSCs fabricated using GPEs in PVdF-HFP:PEO:EC:PC:NaI:I$_2$, PVdF-HFP:PEO:EC:PC:NaI:SiO$_2$:I$_2$ and PVdF-HFP:PEO:EC:PC:NaI:ZnO:I$_2$ systems using PP-NaI-100, PP-NaI-Si-7 and PP-NaI-ZnO-3 GPEs were 5.67, 9.44 and 9.08 % respectively.

6.2   Future works

Optimization of each components of DSSCs (photo/anode/electrolyte/counter electrode) can enhance the performance of this technology. If the focus of the research is on the fabrication of DSSCs based on GPEs then increasing the ionic conductivity of

GPEs can help to enhance the performance of DSSCs by improving the short circuit current density (J_{sc}). There are many methods in order to increase the mobility of ions in the GPEs such as:

- Applying different types of amorphous polymers as host polymer for GPE preparation.

- Blending different typed of polymers to increase the amorphous phase of GPEs for enhancing the mobility of ions as well as increasing the stability of the GPE system which makes them suitable for application in DSSCs.

- Applying different types of iodide salts with different cation sizes as well as using two types of iodide salts (binary salt system) to increase the mobility of iodide/triiodide ions in the GPE system.

- Applying ionic liquids as a source of ions to enhance the ionic conductivity of GPEs.

- Applying different types of nanoparticles such as carbon nanotubes (CNTs) and graphene oxides (GO) as filler into the GPE system to increase the stability and ionic conductivity of GPEs.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

List of Publications

Negar Zebardastan, Khanmirzaei,M.H., Ramesh, S., & Ramesh, K. (2016). Novel poly(vinylidene fluoride-co-hexafluoro propylene)/polyethylene oxide based gel polymer electrolyte containing fumed silica (SiO2) nanofiller for high performance dye-sensitized solar cell. Electrochimica Acta, 220 (2016), 573-580. (Published)

Zebardastan, N., Khanmirzaei, M. H., Ramesh, S., & Ramesh, K. (2017). Presence of NaI in PEO/PVdF-HFP blend based gel polymer electrolytes for fabrication of dye-sensitized solar cells. Materials Science in Semiconductor Processing, 66, 144-148. (Published)

Zebardastan, N., Khanmirzaei, M. H., Ramesh, S., & Ramesh, K. (2017). Performance enhancement of poly (vinylidene fluoride-co-hexafluoro propylene) /polyethylene oxide based nanocomposite polymer electrolyte with ZnO nanofiller for dye-sensitized solar cell. Organic Electronics. (Published)

List of Conferences

Negar Zebardastan, Khanmirzaei, M.H., Ramesh, S. & Ramesh, K. (2016). Presence of NaI in PEO/PVdF-HFP blend based gel polymer electrolyte for fabrication of dye-sensitized solar cells. Oral presented at International conference on emerging research in science and humanities (ERSH 2016), May 16-17 (2016), Kuala Lumpur, Malaysia.