SYNTHESIS AND CHARACTERIZATION OF GEL POLYMER ELECTROLYTE AND ZINC OXIDE FOR PHOTOELECTROCHEMICAL CELL

by

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for the degree of
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Abbreviations

CB	Conduction band
DSSC	Dye sensitized solar cell
e^-	electron
E_C	Top of the valence band
E_V	Bottom of the conduction band
EDX	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
GPE	Gel polymer electrolyte
HRTEM	High resolution transmission electron microscopy
J-V	Current density-voltage
LEDs	Light emitting diods
PV	Photovoltaic
PEC	Photoelectrochemical cell
PL	Photoluminescence test
PVC	Polyvinyl chloride
PEO	Polyethylene oxide
Pt	Platinum
SCE	Saturated Calomel Electrodes
UV	Ultra violet
VB	Valence band
XRD	X-ray diffraction

LIST OF SYMBOLS

Symbols	
A	Active area
Å	Ångströms
c	Speed of light
°C	Degree celcius
eV	Electron volt
E_a	Activation energy
E_g	Energy band gap
FF	Fill factor
hv	Photon energy
h	Planck constant
I	Current
k	Boltzmann constant
J	Current density
J_{SC}	Short circuit current density
J_{max}	Maximum current density
mA	Miliampere
nm	Nanometer
Pa s	Viscosity unit
$\mathrm{P_{in}}$	Incident light power
T	Absolute temperature
V_{OC}	Open circuit voltage
V_{max}	Maximum voltage
V	Volt
σ	Conductivity
σ_0	pre exponential factor
η	Overall conversion efficiency percentage
η	Viscosity
Ω	ohm
λ	Value of wave number

Au	Gold
C	Carbon
D	Dye
ITO	Indium tin oxide
I_2	Iodine
I^-/I_3^-	Iodide/triiodide redox reaction
$LiClO_4$	Lithium chloride
N-719	bis(tetrabutylammonium)-*cis*-(dithiocyanato)-*N*,*N*'-bis(4-carboxylato4'carboxylic acid-2,2'-bipyridine) ruthenium(II) dye
NaOH	Sodium hydroxide
NH_4I	Ammonium iodide
ZnO	Zinc oxide
ZnAc	Zinc acetate dehydrate

SINTESIS DAN PENCIRIAN ELEKTROLIT POLIMER GEL DAN ZINK OKSIDA UNTUK SEL FOTOELEKTROKIMIA

ABSTRAK

Projek ini dibahagikan kepada tiga bahagian: penyediaan dan pencirian elektrolit polimer gel berasaskan agar komersil; penghasilan dan pencirian serbuk nano partikel zink oksida (ZnO); dan fabrikasi sel fotoelektrokimia. Elektrolit polimer gel disediakan dengan melarutkan serbuk agar ke dalam gliserol. Pelbagai kepekatan ammonium iodida (NH_4I) dan iodin (I_2) ditambah ke dalam pes agar hingga mencapai nilai konduktiviti optimum. Nilai konduktiviti optimum ($(2.64 \pm 0.19) \times 10^{-3}$ S cm^{-1}) diperoleh dari sampel pes agar + 1.0 M NH_4I + 0.2 μM I_2 (A1.0N0.2I). Sampel A1.0N0.2I mempunyai nilai kelikatan terendah ((1.17 ± 0.29) Pa s). Semua sampel elektrolit polimer gel menunjukkan sifat Arrhenius dengan nilai tenaga pengaktifan terendah 0.25 eV (A1.0N0.2I). Sampel A1.0N0.2I mempunyai ciri fizikal terbaik. Serbuk nano partikel ZnO dihasilkan melalui sentrifugasi sol-gel pada pelbagai nilai pH. Sampel ZnO pH 9 mempunyai saiz kristal maksima (25.36 nm). Purata saiz partikel 49.98 dan 48.10 nm diperoleh dari mikroskop pengimbas pembebasan medan elektron dan mikroskop pengimbas transmisi elektron. Saiz antara kekisi ruang dan kekisi berdekatan ialah 5.900 Å. Purata saiz partikel mempengaruhi analisis spektroskopi inframerah transformasi fourier. Sampel ZnO pH 9 mempunyai ciri optikal terbaik dengan jurang tenaga (3.31 eV). Fabrikasi sel ITO-ZnO (pewarna N-719)/elektrolit polimer gel A1.0N0.2I /ITO menghasilkan nilai voltan litar terbuka = 1.38 V, ketumpatan arus litar pintas = 7.5 mA cm^{-2}, faktor pengisian = 0.18 dan peratusan keseluruhan kecekapan penukaran = 1.9 % di bawah pencahayaan 100 mW cm^{-2}.

SYNTHESIS AND CHARACTERIZATION OF GEL POLYMER ELECTROLYTE AND ZINC OXIDE FOR PHOTOELECTROCHEMICAL CELL

ABSTRACT

This project is divided into three sections: preparation and characterization of gel polymer electrolyte (GPE) based on commercial agar; synthesis and characterization of nanoparticles powders zinc oxide (ZnO); and fabrication of photoelectrochemical cell (PEC). The GPE was prepared by dissolving agar powder in glycerol. Various concentrations of ammonium iodide and iodine were added to the agar paste until an optimum conductivity was reached. The optimum conductivity of (2.64 ± 0.19) x 10^{-3} S cm^{-1} was obtained from a sample of agar paste with 1.0 M NH_4I and 0.2 μM I_2 (A1.0N0.2I). The A1.0N0.2I had the lowest viscosity values of (1.17 ± 0.29) Pa s. All GPEs showed Arrhenius behavior with the lowest activation energy value of 0.25 eV for A1.0N0.2I. A1.0N0.2I also showed good physical appearance. Meanwhile, the ZnO nanoparticles powders were synthesized by sol-gel centrifugation process at various pH. ZnO synthesized at pH 9 had the maximum crystallite size (25.36 nm). The average particles diameter sizes were 49.98 nm and 48.1 nm, respectively, measured from field emission scanning electron microscope and transmission electron microscope analysis. The lattice spacing is 5.900 Å between adjacent lattice planes. The average particle size affects the Fourier transform infrared peaks shift. The ZnO pH 9 had good optical properties with band gap energy of 3.31 eV. The fabrication of ITO-ZnO (N719 dye)/ A1.0N0.2I GPE/ ITO PEC had the open circuit voltage = 1.38 V, (V_{OC}) short circuit current density = 7.5 mA cm^{-2}, fill factor = 0.18 of and overall conversion efficiency percentage = 1.9 % under illumination of 100 mW cm^{-2}.

CHAPTER 1

INTRODUCTION

1.1 Background

The fundamental concept of photoelectrochemical cell (PEC) was developed by Fujishima and Honda in 1972 by introducing the semiconductor-liquid electrolyte junction. The PEC was directly related to a system in battery, fuel cell, or other types of electrochemical, and was composed of two electrodes and an electrolyte. However, batteries or fuel cells stored the energy in the reactants and released it through the electrical discharge during the formation of chemical reaction products. Meanwhile, the PEC utilized the input optical energy from the sun to drive electrochemical reactions.

The dye adsorbed into the semiconductor electrodes was introduced by replacing the conventional PEC electrode. This kind of cell was developed based on a nanoporous network of n-type oxide particles, such as the dye-sensitized solar cells (DSSCs) or Grätzel cells discovered by O'Regan and Grätzel (1991) using titanium dioxide (TiO_2) electrode. Zinc oxide (ZnO) is likely to be an alternating material for TiO_2. In addition, nanostructured ZnO working electrode showed a good PEC performance (Keis et al., 2002; Ranga Rao and Dutta, 2008).

In the beginning of the PEC research studies, organic liquid phase redox electrolytes and room temperature based on ionic liquid electrolyte were used. However, both electrolytes had lots of drawback, such as leakage of electrolyte. Recently, gel polymer electrolyte (GPE) was extensively studied to replace the volatile organic solvents in the PEC (Freitas et al., 2009). This is attributed to their high ionic conductivity, electrochemical stability, and non-volatility (Wu et al., 2006a).

1.2 Problem statement

To date, the nanocrystalline metal oxide TiO_2 electrodes are used more predominantly as a working electrode compared to other oxide semiconductors, such as tin oxide (SnO_2), zirconium oxide (ZrO), and indium oxide (In_2O_3) (Hara et al., 2000). However, the study conducted by Wang et al. (2001) found that TiO_2 electrode had a low PEC overall conversion efficiency compared to ZnO-covered TiO_2 electrode.

Generally, the properties of these oxide semiconductor materials (TiO_2, ZnO and etc.), such as the crystal structure, point of zero charge, energy level of the conduction band and the electron conductivity, influence the performance of the PEC working electrode. Among these oxide semiconductor materials, ZnO appears more flexible compared to TiO_2 electrode. Although both of these materials have same band gap of energy value (~3.2 eV), but there have different crystal structure. The wurtzite structure of ZnO make it become more flexible compared to anatase structure of TiO_2 (Boschloo et al., 2006).

In order to avoid electrolyte leakage and evaporation problems, the solid polymer electrolyte (SPE) based on PEO-chitosan blend polymer doped with ammonium iodide (NH_4I) and iodine (I_2) was employed for the ZnTe/polymer electrolyte/ITO solar cell (Mohamad et al., 2007). The value of open circuit voltage (V_{OC}) and short circuit current (I_{SC}) obtained from this work were in between 300 and 400 mV, and between 2 and 5 mA, respectively (Mohamad et al., 2007). Nonetheless, the properties of solar cell based on liquid electrolyte much higher which were V_{OC} = 0.56 V and short circuit current density (J_{SC}) = 1.3 mA cm^{-2} (Keis et al., 2002) in contrast with photovoltaic cell based on SPE.

According Rahman et al. (2004), a ITO/TiO_2/liquid electrolyte/ITO solar cell without dye-sensitizer produced had low V_{OC} of 17 mV and J_{SC} of 1.3 μA cm^{-2} compared to the solar cell using liquid electrolyte with dye-sensitizer (V_{OC} = 0.78 V and J_{SC} = 2.10 mA cm^{-2}) (Hara et al., 2000). However both of these kinds of solar cell liquid electrolyte had disadvantages such as heavy weight, shape flexibility, and instability.

To the best of my knowledge, there is no systematic study on the PEC based on ZnO working electrode combined with natural biopolymer GPE because most studies are focused on TiO_2 electrode sensitized with various kinds of dye mixed with liquid electrolyte and counter electrode. Thus, a study on synthesizing ZnO working electrode in conjunction with natural polymer material doped with iodide salt and iodine in gel form is deemed necessary to improve the PEC performance.

1.3 Objectives

The main objectives of this study are:

i) To prepare and find out the optimum conductivity of the GPE based on agar paste + NH_4I + I_2 in the range of ~ 10^{-3} S cm^{-1} for PEC electrolyte.

ii) To determine the hexagonal wurtzite structure, porous and nanoparticles morphology properties of ZnO in a range of ~ 50 nm synthesis by sol-gel centrifugation at pH 6 to 11.

iii) To fabricate and determine the current density-voltage (*J-V*) of ITO-ZnO (N719 dye)/GPE/ITO in range of 5.0 mA cm^{-2}.

1.4 Approach of study

This work mainly focuses on the evaluation of the ability of the GPE sandwich with ZnO working electrode for the PEC. In order to overcome the problems mentioned in Section 1.2, commercial agar paste is introduced as natural biopolymer electrolyte in the PEC. The characterization of ITO-ZnO (N719 dye)/GPE/ITO cell *J-V* performance has been determined to measure the PEC efficiency.

To achieve the overall objectives in Section 1.3, this project is divided into three sections. Firstly, the GPE from commercial agar powder was prepared as electrolyte for the PEC. The GPE characteristics include conductivity study at room and elevated temperature, determination of viscosity, chemical interaction, and physical of agar paste.

Secondly, for synthesis ZnO powder, the materials used were zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) precursor, methanol as solvent, and sodium hydroxide (NaOH) to vary pH. The successfully synthesized ZnO powder was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), and photoluminescence test (PL).

Finally, for the fabrication of ITO-ZnO (N719 dye)/GPE/ITO cell, the optimum conductivity of GPE at room temperature was selected as electrolyte and combined with the best characteristic of the ZnO powder coated on ITO glass sensitized with N-719 dye. The current density-voltage (*J-V)* performance of the PEC will be investigated under luminescence and dark condition. The V_{OC}, J_{SC}, maximum voltage (V_{max}) and maximum current density (J_{max}) will be calculated based on X-Y axis intercepts and the square area under *J-V* curves.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter provides a review of previous studies related to this research. It is divided into four sections as follows:

a) The discoveries of photoelectrochemical cell (PEC) will be emphasized in the introduction of solar energy and solar cell and the development of the PEC including construction and operation.

b) The suceeding discussions delve on the development of gel polymer electrolyte (GPE) together with a type of polymer electrolyte, solvents, and salts, aside from the application of agar and carrageenan polymer electrolyte.

c) The zinc oxide (ZnO) will be discussed as well as the synthesis techniques, structure, and performance of ZnO as the PEC working electrode.

d) The PEC current density and voltage (*J*-*V*) curve will be reviewed at the end of this chapter.

2.2 The Discoveries of Photoelectrochemical Cell

2.2.1 The Solar Energy and Solar Cell

Solar radiation resembles the radiation by an idea of a black body at 5762 K. According to Grätzel (2001), the sun is a gigantic energy supplier to the earth with 3.0×10^{24} J a year or about 10000 times more than the global population currently consumes. This gigantic energy source can cover 0.1% of the earth's surface with solar cells. The solar cell with overall conversion efficiency percentage (η) of 10% would satisfy the present needs (Li et al., 2006).

A solar cell or photovoltaic (PV) cell converts the incident of solar radiation energy from the sun into electrical energy. Incident photons are absorbed to the photogenerated charge carriers that pass through an external load to do an electrical work. Solar cell device applications cover a wider range of consumer electronics, such as solar cell calculator and small scale distributed power systems to centralized megawatt scale power plants.

The solar cell developments are categorized into three generations. For the first generation, cells consist of large-area, high quality, and single junction devices from silicon (Si). However, this technology involves high energy and employment inputs which prevent any significant progress in reducing production costs.

The second generation is focused on the solar cell alternative manufacturing techniques, such as electrodeposition and vapor deposition on silicon substrate or glass cover (thin-film technologies). These techniques have several advantages, such as relevant production cost and low temperature processing.

The new invention and improvement from the second generation was made in the third generation technology. The intention is to enhance the poor electrical performance of second generation while maintaining very low production costs. This generation consists of several types of solar cell, such as hybrid solar cell nanocrystal solar cell, and dye sensitized solar cell (DSSC), also known as the photoelectrochemical cell (PEC) (Smestad, 1998).

In general, the generation of photovoltage in solar cell involves several steps. Firstly, the absorption of light quanta with an energy equal to the band gap of the semiconducting materials or greater than the threshold energy. After the absorption of light occurs, the electrons will transfer from the valence band to the conduction band by leaving a net positive charge (or hole) in the valence band. Thus, each electron absorbs quanta of light which generates one electron-hole pair (Chandra, 1985).

Then, the photogenerated electron-hole pairs are separated with some built-in electric field within the cell. Hence, this separation process produces photocurrent (Chandra, 1985). The common types of PV cells are the p-n junction solar cells and the PEC. The differences between these two types of PV cells are described in Table 2.1.

2.2.2 The Photoelectrochemical Cell

Various kinds of PEC were discovered by researchers all over the world since Fujishima and Honda (1972) introduced the semiconductor-liquid electrolyte junction. Practical advances are gained every year by replacing the type of nanostructured working electrode, electrolyte, and counter electrode to increase the PEC performance. Table 2.2 shows the discoveries of nanostructured PEC since 1972.

Table 2.1: The difference between p-n junction and photoelectrochemical cell (Chandra, 1985).

Type of solar cells	p-n junction solar cells	Photoelectrochemical cell
Junction type	(a) p-n	(a) p-electrolyte, n-electrolyte
	(b) Solid-solid	(b) Solid-liquid
Potential barrier at the junction	(a) Have the barrier at the junction.	(a) Have the barrier at the junction.
	(b) The barrier is formed due to the interdiffussion of majority charge carriers between p- and n-region.	(b) The barrier is formed because of the transfer of majority carriers from semiconductor to electrolyte.
	(c) The potential drop or band bending in two regions of semiconductor is almost equal.	(c) Major potential drop is in semiconductor space charge layer, only a small fraction of the drop is in the electrolyte regions.
	(d) Facilitates flow of minority carriers and inhibits majority carrier flow.	(d) Same as in p-n junction.
Photoeffect	(a) Excess carriers are generated.	(a) Excess carriers are generated.
	(b) Mutual diffusion of excess photogenerated minority carriers in the two regions gives photovoltage.	(b) The excess photogenerated minority carriers transfer charge with ions of the electrolyte to give photovoltage or lead to electrolysis.

Table 2.2: The discoveries of nanostructured photoelectrochemical cells.

Year	Materials for solar cell	References
1972	Semiconductor-liquid electrolyte junction	Fujishima and Honda (1972)
1975	Photo effects at semiconductor electrodes for PEC cell	Gerischer (1975)
1982	Solid polymer electrolyte PV cell	Skotheim and Lundstörm (1982)
1982	Photoelectrochemistry at the n-silicon/polymer electrolyte interface	Inganas et al. (1986)
1981	Water in photoelectrochemical cells	Heller (1981)
1990	Additional of cyanide to cadmium chalcogenide electrodes of PEC	Litch and Peramunage (1990)
1991	Nanocrystalline DSSC	O'Regan and Grätzel (1991)
1996	PEC studies of an ion conducting polymer (PEO)/semiconductor (Si) junction	Battacharya et al. (1996)
1997	Solar cells based on nanostructured ZnO Electrodes	Rensmo et al. (1997)
1998	PEC studies of the junction between poly[3-(4-octylphenyl) thiophene)] and redox polymer electrolyte	Yohannes and Inganäs (1998)
1999	Solid-state PEC cell based on a polymer electrolyte	Philias and Marsan (1999)
2003	Coumarin dyes for efficient DSSC	Hara et al. (2003)
2004	PEC cells with polyacrylonitrile-based and polyethylene oxide-based polymer electrolytes	Ileperuma et al. (2004)
2004	Solar cells of ITO/TiO_2/PVC-$LiClO_4$/graphite	Rahman et al. (2004)
2007	ZnTe/PEO-chitosan blend electrolyte junction	Mohamad et al. (2007)
2008	Titania surface modification and PV characteristics with tungsten oxide	Cheng et al. (2008)
2010	TiO_2 / solid electrolyte junction solar cells with I^-/ I_3^- redox couple	Buraidah et al. (2010)

2.2.3 Photoelectrochemical Cell: Construction and Operation

PEC is generally consists of a transparent conducting oxide (TCO)-coated glass as substrate for semiconductor working photoelectrode, a dye, a redox electrolyte, and a counter electrode. The nanocrystalline PEC is similar to natural photosynthesis in two compliments. Firstly, the functions of the organic dye as light absorber and the production of a flow of electrons were like chlorophyll layer inside leaf. Secondly, it also uses multiple layers as leaf to enhance both light absorption and electron collection efficiency (Smestad, 1998).

Usually, a solution containing nanometer size particles of titanium dioxide (TiO_2) was distributed uniformly on a glass plate coated with a thin conductive and transparent layer of tin dioxide (SnO_2) to create nanocrystalline solar cell. Then, the TiO_2 film was dried and heated to form a porous, high surface area TiO_2 structure (Li et al., 2006).

This TiO_2 film on the glass plate was then dipped into a solution of a dye, such as a red ruthenium (Ru) containing organic dye or green chlorophyll derivative. In the meantime, a drop of liquid electrolyte containing iodide was placed on the film to penetrate into the pores of the membrane in order to complete the device. A counter electrode of conductive glass coated with a thin catalytic layer of platinum (Pt) or carbon (C) for instance was placed on top, and the sandwich was illuminated through the TiO_2 side (Smestad, 1998).

In the nanocrystalline PEC, each layer of dye did not absorb much light. However, the interconnected particles of the porous membrane with dye absorbed 90% of the visible light. Since the dye layer was so thin, almost all of the excited electrons produced from light absorption could be injected into the TiO_2 to produce electricity. The electrons lost by the dye via light absorption were quickly replaced by the mediator (Smestad, 1998).

Typically, iodide ion in the electrolyte solution acted as mediator in the PEC. The oxidized mediator forms iodide/triiodide (I^-/I_3^-), which in turn obtained an electron at the counter electrode after the electron flowed through the electrical load. This reaction occurred repeatedly while the PEC was exposed to the light. Figure 2.1 illustrates the reaction of produced energy in the nanocrystalline PEC.

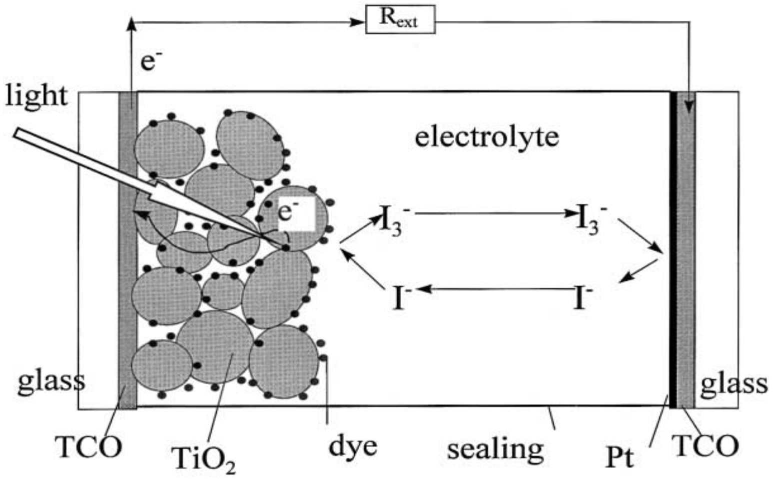

Figure 2.1: Schematic structure and reaction in PEC (Hauch and Georg, 2001).

2.2.4 Photoelectrochemical Cell: Working Electrode

Several semiconductor materials, including single-crystal and polycrystal forms of n-and p-Si, CdS-CdTe, n-and p-GaAs , n-and p-InP, and n-CdS were used as photoelectrodes. These materials can produce good performance when used with a suitable redox electrolyte (Hara and Arakawa, 2003).

The oxide semiconductor materials also have good stability under irradiation in solution (Hara and Arakawa 2003). However, the stable oxide semiconductors type could not absorb visible light because the semiconductors had wide band gaps. To solve this problem, the sensitization of wide band gap oxide semiconductor materials was made. The sensitization of TiO_2, zinc oxide (ZnO), and tin oxide

(SnO_2) with photosensitizers, such as organic dyes can enhance the potential of light absorption, excite, and inject, electrons into the conduction band of the semiconductor electrodes.

The combination of two kinds of oxide semiconductor photoelectrodes can also increase the PEC efficiency. Tennakone et al. (1999) used a porous film with a mixture of SnO_2 and ZnO sensitized with a Ru bipyridyl complex which showed a good PEC performance. Table 2.3 tabulated the photovoltaic performance of the PECs using various kinds of semiconductor working electrodes (Hara et al., 2000).

Table 2.3: Photovoltaic performance of various oxide semiconductors PEC (Hara et al., 2000).

Oxide semiconductor	J_{SC} (mA cm^{-2})	V_{OC} (V)
In_2O_3	2.38	0.39
TiO_2	2.10	0.78
ZrO_2	0.004	0.14
SnO_2	1.95	0.58
ZnO	7.44	0.52

2.2.5 Photoelectrochemical Cell: Electrolyte

At the beginning of the PEC research study, the electrolytes based on liquid were used. However, liquid electrolyte has numerous drawbacks, such as leakage, volatilization of liquid, possible desorption and photodegradation of the attached dyes, and corrosion of counter electrode. This would hinder practical application and limit the long term performance of the PEC (Wang, 2009).

The existence of solid polymer electrolyte (SPE) was used to replace the liquid electrolyte. It was found that the SPE can solve problems, such as stability, evaporation, leakage, and corrosion of harmful liquid. This makes SPE suitable for electrochemical devices. Nevertheless, the conductivity of SPE is lower compared to the liquid electrolyte and the gel polymer electrolyte (GPE). The lower conductivity value will affect the electrochemical devices performance later.

The GPE or quasi-solidification electrolyte using a gelator was used to substitute liquid electrolytes and SPE in a PEC. Gelation can be accomplished by adding gelator into the electrolyte (Hara and Arakawa, 2003). Kubo et al. (2001) developed the quasi-solid state PEC by using gelator. This PEC performance was comparable with PEC using liquid electrolyte studied by Keis et al. (2002).

Recently, biopolymer materials, such as chitosan (Buraidah et al., 2010), agarose, and carrageenan (Kaneko et al., 2004) were used as PEC electrolyte. A good PEC performance was attained by Kaneko et al. (2004) and was compared to another type of electrolyte. The list of electrolyte types in different physical forms and their performance are listed in Table 2.4. All the electrolytes are compared based on the type of electrolyte only. However, each of electrolytes had different type of working electrode and counter electrode for PEC construction.

Table 2.4: List of electrolytes for photoelectrochemical cell.

Materials of electrolyte	Physical form	J_{SC} (mA cm^{-2})	V_{OC} (V)	Reference
LiI/I_2 in methoxypropionitrile added 4-tertbutylpyridine	Liquid	1.3	0.56	Keis et al. (2002)
1-hexyl-3-methylimidazolium iodide (HMImI)	Gel	11.8	0.64	Kubo et al. (2003)
1-alkyl-3-methylimidazolium iodide	Liquid	16.6	0.72	Kubo et al. (2003)
Solid κ-carrageenan using acetonitrile (AN)/3-methyl-2 oxazolidinone (MOZ) with tetrapropylammonium iodide (Pr_4NI) + I_3^-	Solid	14.67	0.73	Kaneko et al. (2004)
Poly(butyl acrylate)/NaI/I_2	Solid	0.65	0.54	Kim et al. (2005)
Poly(acrylicacid)-poly(ethyleneglycol) (PAA-PEG) hybrid	Gel	11.41	0.72	Lan et al. (2007)

2.2.6 Photoelectrochemical Cell: Dye

Dye is a material used for the PEC regeneration based on a thin layer sandwich type electrode. Usually, a dye is sensitized on nanocrystalline semiconducor working electrode, such as TiO_2 and ZnO. Various compounds were investigated for semiconductor sensitizer, such as porphyrins (Mao et al., 1998), phthalocyanines (Fang et al., 1997), coumarin 343 (Rehm et al., 1996), mercurochrome (Hara et al., 2000), and natural product (Cherepy et al., 1997).

Transition metal complexes were the best among the photosensitizer investigation (Nazeeruddin et al., 1993). Among the three types of dye based on Ru, N-719 has been widely used with ZnO electrode for the PEC application due to its features. The good performance of ZnO/N-719 PEC was discovered by Saito and Fujihara (2008) wherein the value of J_{SC} and V_{OC} were 18.11 mA cm^{-2} and 0.62 V, respectively. The description of dye based on Ru complex is shown in Table 2.5. The different types of dye have their own advantages.

Table 2.5: Ru complex dye description (Desilvestro and Hebting, 2011).

Type of dye	Common name	Description
Cis-bis(isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylato ruthenium (II)	N-3	a) Pioneering dye for use in DSSCs. b) Sensitizes wide band gap semiconductors such as TiO_2 up to wavelengths of 700 nm.
Cis-bis (isothiocyanato) bis (2, 2’bipyridy1-4,4’dicarboxylato) ruthenium (II) bis-tetrabutylammonium	N-719	a) Modified dye to increase voltage. b) Highly studied, high performance dye.
Cis-bis(isothiocyanato)(2,2’-bipyridyl-4,4’-dicarboxylato)(4,4’-di-nonyl-2’-bipyridyl)ruthenium (II)	Z-907	a) Hydrophobic dye. b) Very efficiently sensitizes wide band gap TiO_2 up to 750 nm.

2.2.7 Phoelectrochemical Cell: Counter Electrode

Another important part in developing the PEC is counter electrode. Counter electrode is regularly constructed with a conducting glass, also known as indium tin oxide glass (ITO-glass) substrate coated with platinum (Pt) film (Ma et al., 2004). The role of the counter electrode is to collect electrons from the external circuit and to reduce I_3^- to I^- in electrolyte. To keep a low overvoltage at photocurrent densities up to 20 mA cm^{-2} and to reduce energy losses, the counter electrode should have low resistance and high electrocatalytic activity for I^-/I_3^- redox reaction (Fang et al., 2004; Li et al., 2009).

Diverse kinds of counter electrode were applied in previous studies in order to produce high overall conversion efficiency of the PEC instead of Pt, such as metal substrates, carbon (C) coated on glass substrate, polymer, polymer-C composite, and polymer-Pt composite (Kitamura et al., 2001; Ma et al., 2004). Electrocatalytic metals, such as Pt (Nazeeruddin et al., 2005) and gold (Au) (Singh et al., 2006), also known as efficient photo conversion materials, promote semiconductor PEC cells.

However, the ITO-glass without any coating also can be utilized as counter electrode (Mohamad et al., 2007; Buraidah et al., 2010). This is because the glass was already coated with a conducting material (ITO). The PEC which applied this kind of electrode showed a good PEC performance. The various types of counter electrode and the PEC performance are shown in Table 2.6. The comparisons were made based on the different type and performance of counter electrode only. Each of counter electrodes had various type of working electrodes and electrolytes for PEC construction.

Table 2.6: Previous researches of photoelectrochemical cells counter electrode.

Counter electrode substrate	Catalyst on counter electrode	J_{SC} (mA cm^{-2})	V_{OC} (V)	Reference
FTO-glass	Carbon black	0.10	0.72	Kitamura et al. (2001)
ITO-glass	PEDOT-TsO	11.2	0.67	Saito et al. (2004)
Au	PEDOT	2.6	0.68	Fukuri et al. (2004)
Stainless steel	Pt	12.4	0.70	Ma et al. (2004)
Au/FTO-glass	PEDOT	2.5	0.37	Senadeera et al. (2005)
Ni	Pt	11.18	0.69	Fang et al (2005)
ITO-glass	Au	2.67	0.49	Lin et al. (2007)
ITO-glass	-	0.002-0.005	0.30-0.40	Mohamad et al. (2007)
ITO-glass	-	0.019	0.26	Buraidah et al. (2010)
ITO-glass	PVP-capped Pt	12.11	0.69	Lan et al. (2010)

2.3 The Development of Polymer Electrolyte

2.3.1 Polymer Electrolyte

The development of crystalline solid materials with high ambient temperature conductivity started in late 1960s and early 1970s. The first polymer shown to conduct electricity was polyacetylene (Shirakawa et al., 1977). Since conducting polyacetylene was discovered, a number of other conducting polymers with unique properties were enormously developed. The polymer ionics eventually became the broader field of solid state ionics. These materials had excellent transport characteristics and stability for all solid state electrochemical cell.

2.3.2 Type of Polymer Electrolyte, Solvents and Salts

According to Gray (1996), there are five categories of polymer electrolyte as follows:

a) Liquid solvent free system. In this system, the salt was dissolved in a high molecular weight polar polymer matrix.

b) Gel electrolyte formed by dissolving a salt in a polar liquid and adding an inactive polymeric material to give the material mechanical stability.

c) Plasticized electrolyte. Basically, it is a gel electrolyte. However, it is usually associated with the addition of small amounts of high dielectric constant solvent to a conducting polymer electrolyte to enhance its conductivity.

d) Ionic rubber. It is a liquid electrolyte comprising of a low temperature molten salt mixture. A small amount of high molecular weight polymer was added to reduce rubbery condition. The ionic rubber electrolytes have some similarity with gel electrolyte structural level.

e) Membrane ionomer is also known as a proton conducting polymer electrolyte. The electrolyte is used as in proton exchange membrane (PEM) fuel cell or SPE fuel cell (SPEFC).

There are several kinds of solvent that can be used to dissolve the polymers. The degree of solvation depends on the ability of polymer cations co-ordination necessary for electrolyte formation. A variety of solvents were used in previous research on polymer electrolyte, such as tetrahydrofuran (THF) (Park et al., 2008), acetone (Saito et al., 2003), dimethylformamide (DMF), ethyl carbonate (EC), and polycarbonate (PC) (Renard et al., 2003).

Glycerol is another type of organic solvent used aside from plasticizer for polymer electrolyte research (Vieira et al., 2007). Glycerol is a chemical compound also commonly known as glycerine. It is a colorless, odorless, viscous liquid. Glycerol is a non-toxic, biodegradable, and recyclable liquid that is highly inert, stable, and compatible with many other non-toxic and non-irritating chemicals (Wolfson and Dlugy 2009).

Glycerol has three hydrophilic hydroxyl groups responsible for its solubility in water and hygroscopic nature. Figure 2.2 shows the glycerol chemical structure.

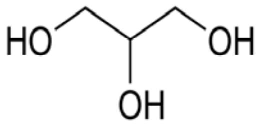

Figure 2.2: Glycerol structure.

Dashnau et al. (2006) examined the average number of hydrogen bonds per water (glycerol) as well as contributions from bulk water, solvation shell, and glycerol-water through both theoretical and experimental approaches. The effectiveness of glycerol in gellan films is most likely due to its small size. This would allow glycerol to be more readily inserted between the polymer chains. Consequently, glycerol exerted more influence on the film's mechanical properties (Yang and Paulson, 2000).

Glycerol has numerous advantages as solvent as it is more effective than sorbitol in plasticizing whey protein films due to its small size (Krochta and Mulder-Johnston 1994). The existence of polar groups (–OH) along glycerol chains is believed to have the ability to develop polymer-plasticizer hydrogen bonds to replace the polymer-polymer interactions in the biopolymer films (Gennadios et al., 1993). The molecular size, configuration, and total number of glycerol functional hydroxyl groups as well as its compatibility with the polymer could affect interactions between plasticizer and polymer.

Salt is another important part in polymer electrolyte studies aside from solvents. Gray (1996) claimed that salts are divided into two types: the cations and anions. The mixtures of iodides salts, such as lithium iodide (LiI), sodium iodide (NaI), potassium iodide (KI), tetraalkylammonium iodide (R_4NI), and imidazolium-derivative iodides with iodine (I_2) dissolved in nonprotonic solvents, such as acetonitrile, propionitrile, methoxyacetonitrile, and propylene carbonate, have been utilized for the PEC electrolyte.

In general, the enhancement of the PEC performance also depends on counter cations of iodides salts in electrolyte, such as Li^+, Na^+, K^+, and R_4N^+ (Cianca et al., 1997). These counter cations owe the different ionic conductivity from the electrolyte or adsorption on the oxide semiconductor surface. Thus, the counter cations lead to a shift in the conduction band level of the oxide semiconductor electrode (Hara et al., 2001). The PEC electrolyte also needs I^-/I_3^- redox ions to reduce the oxidized dye and functions as the charge carrier mediator in the regenerative PEC. Hence, both inorganic and organic iodide salts have significant influence on the performance of the PEC (Wang, 2009).

Ammonium iodide (NH_4I) is presented as one of the alkali iodide. NH_4I has potential to be used as salt in polymer electrolyte together with I_2 particularly for the PEC electrolyte. The complex of polyethylene oxide (PEO) with NH_4I salt film demonstrated a good ionic conductivity within a range of ~10^{-5} S cm $^{-1}$ (Maurya et al., 1992). Recently, PEO-chitosan complexed with $NH_4I + I_2$ has been employed as electrolyte for the PEC. Based on this study, the ionic conductivity of the polymer electrolyte attained was 4.32 10^{-6} S cm $^{-1}$ (Mohamad et al., 2007).

Herein, the NH_4^+ cation of NH_4I are linked together by N–O---H type hydrogen bonds when coordinated with the oxygen of the polymer. This attributed to the existence tetrahedral structure of NH_4^+ (Salihoğlu et al., 2002). Two of the four hydrogen of NH_4^+ ions are bound equally. The third hydrogen is bound more rigidly and the fourth more weakly. The weakly bound H of NH_4^+ can easily be dissociated under the influence of an electric field. These H^+ ions can hop via each coordinating site of the polymer (Hashmi et al., 1990).

For I^- anion of NH_4I and liquid I_2 reaction, the hopping mechanism can be expected to occur. It is well known that the triiodide species (I_3^-) is quite stable. Hence, the equilibrium constant for the reaction of I_3^- as follows (Gileadi and Kirowa-Eisner, 2006):

$$I^- + I_2 \leftrightarrow I_3^- \qquad (2.1)$$

Charge can be propagated by the movement of I^- from a I_3^- ion to an adjacent I_2 molecule:

$$[I–I–I]^- + [I–I] \rightarrow [I–I] + [I–I–I]^- \qquad (2.2)$$

In this process, a single I_2 atom moved a short distance, giving rise to a virtual movement of an I_3^- ion over a distance that is three or four times longer. As the charge propagates down the chain, it is a different I^- ion that moves and takes off to some level the hopping of protons from a charged to a neutral cluster of water molecules. For the mode of conductivity measurement, the species involved should be aligned linearly (Gileadi and Kirowa-Eisner, 2006). Therefore, the movement of H^+ cation from NH_4I and together along I_3^- anion from NH_4I and I_2 can contribute to the increasing ionic conductivity of the polymer electrolyte.

2.3.3 Gel Polymer Electrolytes

Gel polymer electrolytes (GPE) belong to the (salt-solvent-polymer) system, particularly in terms of achieving higher and more practical ionic conductivities. The GPE is often termed as polymer electrolytes because it is formed by dissolving a salt in a polar liquid and adding a polymer network to give the material mechanical stability. Generally, the solidity of GPE results from chain entanglements (Gray, 1996).

The GPE has been attracting attention because of several advantages, such as low vapor pressure, good long term stability, excellent contacting and filling properties between the nanostructured electrode and counter electrode (Spiekermann et al., 2001). The GPE also has higher ionic conductivity within a range of ~ 10^{-3} S cm^{-1} at ambient temperature compared to the SPE. Besides, GPE was found to be stable over wide potential range application (Groce, 1994; Liu and Osaka, 1997). Hence, the GPE is suitable for various solid state ionic devices (Osaka et al., 1994).

Nogueira and co-workers (2004) claimed that the GPE was usually obtained by incorporating a large amount of liquid plasticizer and/or solvent containing the desired ionic salts into a polymer matrix, giving rise to a stable gel with a polymer host structure. When gelation occurs, a dilute or more viscous polymer solution was converted into gel.

In order to improve the mechanical properties of the GPE, components that can be cross-linked and/or thermoset may also be incorporated into the GPE formulation. Thus, the GPE can be obtained as a result of either a chemical or a physical crosslinking process. Both processes lead to the formation of irreversible GPE. By contrast, the gel network formed via physical cross-linking is called entanglement network.

2.3.4 Gel Polymer Electrolytes: Agar and Carrageenan

Recently, most researchers used the polysaccharides due to their rich nature, very low cost, and biodegradable properties (Mattos et al., 2007). These biodegradable polymers, such as chitosan (Majid and Arof, 2007), cellulose (Samir et al., 2004), sago (Masri and Mohamad, 2009) and agarose (Kaneko et al., 2004) have been modified using different methods of converting them into the desired physical appearance, such as liquid electrolyte, GPE, or SPE.

Polysaccharides, particularly agarose and carrageenan, have been used as electrolyte for the PEC (Kaneko and Hoshi 2003). Agarose and carrageenan electrolyte have also been blended with polypyrrole (PPy) and polyaniline (PANi) (Humphrey et al. 1990). The conductivity values of agarose and κ-carrageenan electrolyte for the PEC were 4.36 and 2.82 x 10^{-3} S cm^{-1}, respectively. These conductivity values are compared to the conductivity value of liquid electrolyte (4.40 x 10^{-3} S cm^{-1}) for the same application (Kaneko et al., 2004). Other kinds of polysaccharides, like the chitosan, have also been used as electrolyte for the PEC. Table 2.7 lists the polysaccharides based electrolyte in different physical forms and its performance for the PEC application.

Table 2.7: Physical form and performances of polysaccharides electrolyte.

Materials of electrolyte	Physical form	J_{SC} (A cm^{-2})	V_{OC} (V)	Reference
κ-carrageenan	Solid	14.67 m	0.73	Kaneko et al. (2004)
Agar	Gel	7.93 m	0.83	Suzuki et al. (2006)
κ-carrageenan	Solid	8.67 m	0.75	Nemoto et al. (2007)
Chitosan	Solid	19.23µ	0.26	Buraidah et al. (2010)

Agar also known as agar-agar is typically a strong gelling component widely-used in the food industry as a thickening agent (E406), a vegetarian gelatin substitute, or a clarifying agent in brewing (Cherblanc et al., 2008). In general, the commercial agar powder contains agar (crispier texture), carrageenan (thickening, suspending, and gelling food products), konnyaku (creating viscous solutions), and permitted food conditioner.

Agar is linear polysaccharides made up of alternating β (1,3)-and α (1,4)-linked galactose residues. The repeating units are disaccharides. The (1,4)-linked residues are commonly but not regularly present as the 3,6-anhydride (Norman, 2006). It is a mixture of polysaccharides found in the cell matrix of red algae (Rhodophyta), especially from members of the Gelidiaceae and Gracilariaceae families (Armisen and Galactas, 1987).

Agar can also be considered as a heterogeneous mixture of two classes of polysaccharides: the agaropectin and agarose. Although both classes of polysaccharides share the same galactose-based backbone, agaropectin is heavily modified with acidic side-groups, such as sulfate and pyruvate (Labropoulos et al., 2002).

Agar differs from carrageenans, the other important class of red seaweed polysaccharides due to the (1,4)-linked residues which is the L-enantiomer, whereas in carrageenans, it is the D-enantiomer. However, the (1,3)-linked residues are D-galactose in both agars and carrageenans (Norman, 2006). Figure 2.3 shows the agar structure.

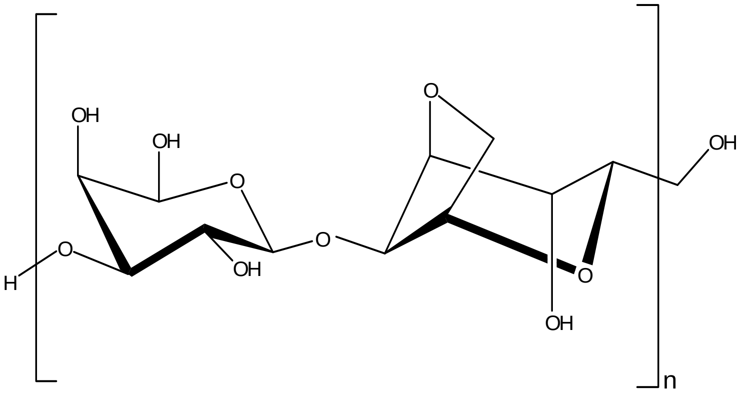

Figure 2.3: Agar structure (Ueno et al., 2004).

Meanwhile, carrageenan is an anionic polysaccharide extracted from Gigartina, Chondrus, Iridaea, and Eucheuma species. Carrageenan existed in three main forms like κ ι and λ. Among them, κ-carrageenan is characterized by its repeating disaccharide units of 3-linked β-D-galactose 4-sulfate and 4-linked 3,6 anhydro-α-D-galactose (Norziah et al., 2006).

The sulphate groups are covalently coupled via ester linkages to the carbon atoms C-2, C-4 or C-6 of individual galactose residues. The amount of $–O–SO_3^-$ in sulphated polysaccharides can be extensive and varies within the range of 0-41% (w/w), resulting in highly negatively charged polymers (De Ruiter and Rudolph, 1997). The carrageenan structure is revealed in Figure 2.4.