The development of photo-anode film for photo-electrochemical (PEC)reactor producing hydrogen (H2)

By

Muhammad Hafiz Abdul Rahim

(1331210966)

A thesis submittteed in fulfillment of the requirements for the degree of Master of Science in Environmental Engineering

School of Environmental Engineering

UNIVERSITI MALAYSIA PERLIS

2016

ACKNOWLEDGEMENTS

First of all, my grateful thanks to Allah S.W.T and honour to the Prophet Muhammad S.A.W.

I would like to express my appreciation and gratitude to my main supervisor, Dr. Umi Fazara binti Md. Ali and also to Dr. Mohd Nazree bin Derman for their high quality guidance, support, counseling, publication, correction and critical review that has contributed to the completion of this research project and preparation of this thesis.

Sincere thanks to all staff in the School of Environmental Engineering and Material Engineering for their advices, critics and valuable ideas. I wish to express my sincere appreciation to all Laboratory and Workshop staffs for their kind assistance as well.

Respectfully, I would like to send my deepest gratefulness to my family, without their encouragement and support; I might not be able to finish this thesis.

MUHAMMAD HAFIZ

DISEMBER 2015

©This item is protected by original copyright

TABLE OF CONTENTS

©This item is protected by original copyright

©This item is protected by original copyright

© This item is protected by original copyright

LIST OF TABLES

©This item is protected by original copyright

LIST OF FIGURES

©This item is protected by original copyright

©This item is protected by original copyright

LIST OF EQUATIONS

©This item is protected by original copyright

LIST OF ABBREVIATIONS

PEC	Photo-electrochemical
TCO	Transparent Conducting Oxide
FTO	Fluorine Tin Oxide
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
XRD	X-ray Diffraction
TW	Tera Watt
eV	Electron Volt
PV	Photovoltaic
REDOX	Reduction and Oxidation
SCLJ	Semi-conductor-liquid junction

©This item is protected by original copyright

LIST OF SYMBOLS

H_2	Hydrogen
O_2	Oxygen
α-Fe_2O_3	Hematite
TiO_2	Titanium Dioxide
WO_3	Tungsten Trioxide
CO_2	Carbon Dioxide
TEOS	Tetraethyl orthosilicate

Pembangunan Filem Foto-Anod untuk Reaktor Foto-Elektrokimia (PEC) Menghasilkan Gas Hidrogen (H_2)

ABSTRAK

Dunia kini menggunakan tenaga pada kadar 13 TW. Walau bagaimanapun, permintaan untuk tenaga akan berganda pada tahun 2050 dan lebih daripada tiga kali ganda menjelang akhir abad ini. Petroleum sebagai sumber tenaga adalah tidak mapan kerana ia terikat kepada pemanasan global, hakikatnya kebanyakan diperoleh daripada negara-negara dengan geopolitik yang tidak stabil, dan ia adalah sumber yang terhad. Satu sumber tenaga alternatif adalah tenaga solar. Tenaga solar boleh ditangkap melalui elektrolisis air dan disimpan di dalam bentuk tenaga hidrogen padat. Satu aspek penting dalam sel elektrolisis berkuasa solar adalah elektrod. Hematit adalah sesuai photo-anod kerana jurang jalur kecil daripada 2.1-2.2 eV yang membolehkan kecekapan penukaran sehingga 16%. Tambahan pula ia juga adalah stabil secara kimia dalam persekitaran berair, yang boleh didapati secara meluas, dan kos rendah yang menjadikan ia menarik untuk kegunaan industri. Untuk mengoptimumkan penggunaan hematit, itu didepositkan ke Flourine Tin Oxide (FTO) substrat pada suhu 300 ° C, 400 ° C dan 500 ° C sebagai filem nipis dengan teknik semburan pirolisis. Tambahan unsur dengan iaitu timah (Sn) dan silika (Si) digunakan untuk meningkatkan ketumpatan pembawa cas; ke substrat. Pencirian daripada substrat untuk penambahan kedua-dua jenis unsur ditentukan dengan merujuk kepada morfologi yang diperolehi daripada SEM profil, foto-elektrokimia dengan menggunakan voltammetri linear manakala struktur telah ditentukan dengan menggunakan XRD. Selepas itu keupayaan untuk filem nipis hematit untuk menjana hidrogen (H_2) ditentukan. Hematit yang didopkan dengan timah pada 300 ° C menyumbang kepada jumlah tertinggi kutipan hidrogen (H_2) yang merupakan 0.4 mL. hematit yang terbentuk kelompok yang besar apabila suhu substrat untuk hematit telah meningkat daripada 300 ° C hingga 400 ° C. Bilangan tepi hematit seolah-olah kekal agak yang sama untuk kedua-dua suhu tetapi sedikit bulat dalam bentuk untuk proses doping pada 400 ^{o}C. Pada suhu substrat 500 ° C, rangkaian hematit boleh diperhatikan, tetapi zarah hematit telah bergumpal hingga titik bahawa mereka hilang tepi tajam mereka. Dari segi analisis foto-elektrokimia di semasa gelap dan terang, hematit didopkan dengan timah pada 300 ° C mempunyai prestasi yang lebih baik berbanding dengan hematit yang tidak didop pada suhu yang sama, dengan kawasan yang dikira daripada 7.277×10^{-4} AVcm^{-2} dan 1.084×10^{-5} AVcm^{-2} masing-masing. Hematit (Fe_2O_3) puncak diperhatikan dalam corak XRD di 2θ sudut 32.98 dan 67.81, manakala puncak tambahan bersamaan dengan pembentukan oksida campuran Fe dan Sn diperhatikan pada sudut 2θ 21.76, 29.53 dan 46.24.

© This item is protected by original copyright

The Development of Photo-Anode film for Photo-Electrochemical (PEC) Reactor Producing Hydrogen (H_2)

ABSTRACT

The world now uses energy at a rate of 13 TW. However, demand for energy will double by 2050 and more than triple by the end of the century. Petroleum as an energy source is unsustainable because it tied to global warming, the fact that it is mostly sourced from countries with unstable geopolitics, and the fact it is a finite resource. One alternative energy source is solar energy. Solar energy can be captured through electrolysis of water and stored in the form of energy dense hydrogen. One important aspect of the solar powered electrolysis cell is the electrode. Hematite is a suitable photo-anode due to its small band gap of 2.1-2.2 eV which enables conversion efficiencies of up to 16%. Furthermore it is also chemically stable in aqueous environments, widely available, and low cost which makes it attractive for industrial application. To optimize the use of hematite, it is deposited onto Flourine Tin Oxide (FTO) substrate at temperature 300°C, 400°C and 500 °C as a thin film by spray pyrolysis technique. The doping with impurities particularly tin (Sn) and silica (Si) is used to increase charge carrier density; onto a conducting substrate. The characterizations of the substrate for the addition of these two kinds of impurities were determined by referring to the morphology obtained from SEM, photo-electrochemical profile by using linear voltammetry whilst the structure was determined by using XRD. Subsequently the ability for hematite thin film to generate hydrogen (H_2) was determined. Hematite doped with tin at 300°C contributes to the highest volume of hydrogen (H_2) collection which was 0.4 mL. The hematite formed a large cluster when the substrate temperature of hematite was increased from 300°C to 400°C. The number of hematite edges seems to remain relatively the same for both temperature but slightly rounder in shape for the doping process at 400^{o}C. At substrate temperature of 500°C, a network of hematite can be observed, but the hematite particles have agglomerated till the point that they lost their sharp edges. In terms of photo-electrochemical analysis at dark and light current, hematite doped with tin at 300°C has a better performance compared to undoped hematite at the same temperature, with a calculated area of 7.277×10^{-4} AVcm^{-2} and 1.084×10^{-5} AVcm^{-2} respectively. Hematite (Fe_2O_3) peaks were observed in the XRD patterns at 2θ angle 32.98 and 67.81, while additional peak corresponding to the formation of mixed oxides of Fe and Sn were observed at 2θ angle 21.76, 29.53 and 46.24.

©This item is protected by original copyright

CHAPTER 1

INTRODUCTION

This chapter includes the background of photo-electrochemical (PEC) cell; mainly on the solar as energy sources, hydrogen as the energy carrier and the principle of electrolysis; the chosen metal oxide as the photo-anode for the PEC; and the scope and objectives of this project.

©This item is protected by original copyright

1.1 Solar energy

Generally, there is only one true energy source which is the sun. Others are only different forms of energy carriers or batteries. The sun deposits 120,000 Terawatt (TW) of radiation on the surface of the Earth. Lewis (2005) reported that by covering 0.16% of Earth's land with 10% solar conversion systems would provide 20 TW of power, which is more than enough to meet the current energy demand. Yet still in 2001, solar electricity provided less than 0.1% of the world's electricity. One of the main challenges on utilizing solar energy is to convert solar energy to chemical energy in a form that allows its use in mobile applications. On the other hand, solar energy must be able to compete economically with fossil fuels, provided that the price of world's oil has slump recently to below $30 (RM 125.00) per barrel (Davidson, 2010).

Research on solar as a potential energy resource had been for ages, Becquerel (1839) observed that a voltage and a current were produced when silver chloride electrode is immersed in an electrolytic solution and connected to a counter metal electrode illuminated with white light. However, the modern photovoltaic (PV) solar cell was invented in 1954, when Chapin et al. (1954) demonstrated 5-6 % efficient solar cells based on p-n junctions in single crystal silicon.

Fujishima (2000) discovered that titanium dioxide (TiO_2), when spiked with nitrogen ions or doped with metal oxide like tungsten trioxide (WO_3), is a photo-catalyst. It was a ground-breaking discovery and he published his paper in 1972. The photo-catalytic property on the surface of the doped TiO_2 that is able to split water was named the Honda-Fujishima effect. As mentioned by Ingler et al. (2004), the band gap value of hematite is 2.2 eV, which allows it to harness a much wider part of the sunlight energy than TiO_2. Hence, hematite was chosen as subject of photo-anode to be studied in this research.

©This item is protected by original copyright

1.2 Hydrogen as an energy carrier

Interest in hydrogen (H_2) began when Jones (1970) first discussed the economic and technical aspects of replacing hydrocarbon fuels for air and vehicular transport with liquid hydrogen. Hydrogen is an interesting energy carrier, particularly in transport application because it has a high energy density by weight. In a zero emission vehicle symposium held in 2006, the Bureau of Motor Vehicle (BMV) pointed out that an Otto cycle internal-combustion engine powered by hydrogen have a maximum efficiency of about 38% compared to 30% for a gasoline powered one (Davidson, 2010).

The second advantage of H_2 as a fuel is that it does not emit any pollutant such as particulate matter or carbon dioxide (CO_2) at the point of end use, if environmentally sound ways such as those derived from solar power are used to produce hydrogen. National Academy of Engineering (2004) carried out a study and found that the use of H_2 would not release as much CO_2 as gasoline in hybrid electric vehicles and that significant reduction in CO_2 emissions is attainable if carbon capture sequestration is carried out at the site of hydrogen production, even more if hydrocarbons are not used in the first place. In addition, H_2 can be used to produce ammonia through the Haber process. In the Haber process, Clark (2013) explained that 1 mole of nitrogen gas is reacted with 3 moles of hydrogen at high temperature and pressure. Ammonia is a fertilizer and can support the agriculture industry in feeding the growing population.

©This item is protected by original copyright

As stated by Haslego (2010), H_2 is also used to purify hydrocarbon streams from sulphur and nitrogen in hydrocracking. Hydrocracking break down complex fossil fuels into its lighter more useful fractions to produce mainly jet fuel and diesel, and can also produce high octane rating gasoline fractions and liquid petroleum gas. One way to produce H_2 is via electrolysis of water.

1.3 Electrolysis of water to convert solar into chemical energy

Electrolysis can be used to convert the sun's energy into useful chemical form by splitting water into hydrogen and oxygen. In this study, photo-anode fabricated from hematite will catalyse the water splitting process to evolve oxygen and hydrogen in the presence of light. This is called a photo-electrochemical (PEC) cell system where a semiconducting photo-anode is illuminated in a liquid cell and drives electrochemical reactions at both electrodes. As highlighted in Section 1.1, hematite (α-Fe_2O_3) was chosen as the photo-anode in this study.

1.4 Iron oxide as photo-anode in photo-electrochemical (PEC) cell

The selection of iron oxide or commonly known as hematite (α-Fe_2O_3) as the photo-anode in a PEC is due to its ability to absorb solar radiation. It gets its reddish brown hue from the fact that it strongly absorbs radiation from the yellow region to the ultraviolet region, and transmits radiation from the orange to the infrared region. Valdes (2011) discovered the potential of hematite as a suitable photo-anode material due to its small band gap of 2.1 eV, which in principle enables conversion efficiencies of up to 16%. Furthermore, it is chemically stable in aqueous environments, widely available, and relatively low cost, making it an attractive candidate for water photo-oxidation.

Based on previous research (Prakasam et al., 2006), hematite was seen as a popular semiconducting material for the evolution of hydrogen using the energy that

©This item is protected by original copyright

comes from solar. Other known materials such as magnetite and FeO cannot be utilized due to the metal-like behaviour and has a small band gap of less than 1 eV.

According to Ingler et al. (2004), the band gap value of hematite is 2.2 eV which permits absorption of a wider section of the sunlight energy compared to TiO_2 (a popular semiconducting material). Hematite is known as a material that absorbs in the visible light circa 388% of the photons of the solar spectrum (Ingler et al., 2004). In addition to that, hematite has excellent stability properties; it is abundantly available and sells at reasonable price.

There are a few researches (Glasscock et al., 2007) in the disadvantages of hematite such as having low charge carrier mobility which caused high resistivity, slow electron or hole recombination rate, as well as slow surface kinetics. To overcome this, Glasscock et al. (2007) suggested that the incorporation of what in the semiconductor lattice of a doping material, in order to reach significant efficiencies may be required. Secondly, the conduction band energy level is measured lower than the redox potential of H^+/H_2. Hence a bias potential has to be added to account for the losses contributed from the ohm drop in the electrolyte and over potentials at the anode and cathode. Thirdly, as per discussed hematite is chemically stable over a wide range of pH, nevertheless the electrochemical stability might be questioned. The electrochemical characterizations that will be studied in this research will address the stability issues.

Figure 1.1 illustrates the PEC cell structure separated with a Nafion membrane. The case presented by Aurora (2010) was the photo-generated holes and electrons are believed to oxidize and reduce hematite (Schoonman and Krol 2011). Hence he

©This item is protected by original copyright

suggested that if a deposition process can be applied on the surface with catalysts such as RuO_2 or IrO_2 on the anode or Pt on the cathode, this situation can be overcomed. These catalysts would make oxygen and hydrogen evolution faster, as a result preventing the consumption of the charge carriers for the oxidation or the reduction (REDOX) of hematite.

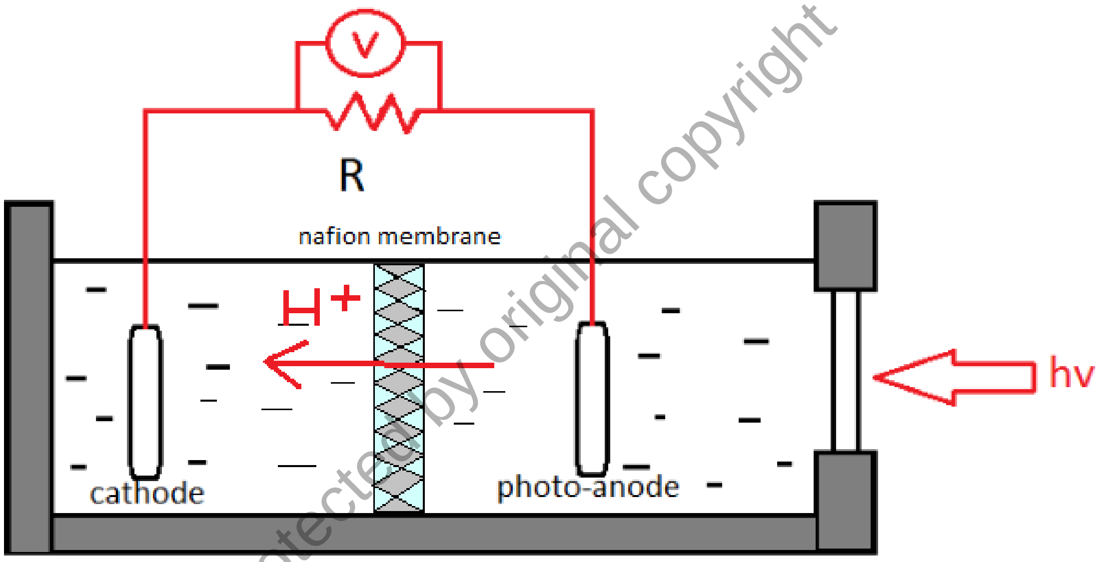

Figure 1.1: The PEC cell structure with Nafion membrane (Schoonman & Krol, 2011).

©This item is protected by original copyright

The powder suspension system has been used in many processes of water splitting but several problems are limiting the application of photo-catalysts in the aqueous solutions. The thin films of TiO_2 are much more suitable to be used in the aqueous solution since it is immobile in the thin film state.

Hematite has certain drawbacks toward oxygen evolution. First, the hole which is better known from the absence of electrons diffusion length is relatively short as compared to the light penetration depth. Next, the poor oxygen evolution kinetics at the hematite semi-conductor– liquid junction (SCLJ), necessitates the application of a large over potential. Finally, the position of the conduction band in hematite is too low to allow spontaneous water reduction by the photo-generated electrons (Valdes et al., 2011).

The use of hematite to split water can be optimized by several ways, such as addition of impurities (doping) to increase charge carrier density, using it in tandem with other photo-catalytic material, or novel nano-deposition methods to increase available sites for reaction. In this study, the electrolysis of water by using hematite as photo-anode with the presence of solar energy will be studied as well as the potential of this photo-electrochemical to absorb energy and then producing hydrogen gas.

©This item is protected by original copyright

1.5 Problem statement

Solar hydrogen seems to have a bright future as a clean energy in the coming decades. However, many difficulties need to be overcome to make it economically viable as a fuel or an energy carrier. There are many processes to generate hydrogen which is one of them by using photo-electrochemical, a method that give very low impact to environment.

An ideal material as semiconductor in photo-electrochemical should be cheap, be able to harness visible light, avoid as much as possible the recombination of charge carriers and be photo-electrochemically stable. Various techniques have been tested to improve the efficiency of photo-electrochemical, one of them is doping. Cheap semiconductors, with already known and good enough photo-electrochemical properties which is Fe_2O_3 will then be used. The Fe_2O_3 will be compared with Fe_2O_3 doping with tin (Sn) and tetraethyl orthosilicate (TEOS) to see the effect of morphology, photo-electrochemical profile and hydrogen production. The photo-anode will be tested by comparing to the experiment with having light and without light.

1.6 Scope of research

Hematite has a potential as a suitable photo-anode material due to its small band gap of 2.1-2.2 eV for photo-electrochemical cell. Therefore, this project is examining the development of hematite by using a simple, relatively low cost method. The hematite will be doped by tin and silica to study the effect of doping towards the hematite performance. The prepared samples are subjected to physicochemical characterization as well as observing the potential of photo-anode to produce hydrogen gas through photo-electrochemical process. The following are the list of project objectives that has to be fulfilled.

©This item is protected by original copyright

1.7 Objective of research

i) To investigate the efficiency of hematite as photo-anode and the effect of doping to the hematite.

ii) To characterize the developed hematite morphology by using a scanning electron microscope and its electrochemical profile using linear voltammetry.

iii) To study the performance of hematite as a photo-anode by its ability to evolve hydrogen.

©This item is protected by original copyright

CHAPTER 2

LITERATURE REVIEW

Although the fossil fuels are still available while the price slumps during recent years, fossil fuels are always subjected to depletion. Hence, the needs of developing alternatives energy are still important concerns. This chapter includes review of extensive studies and research that have been done on photo-electrochemical Cell (PEC) and hematite as the photo-anode for the PEC. The loopholes on the subject matter will be discussed at the end of this chapter.

©This item is protected by original copyright

2.1 Depletion of fossil fuels and future energy

World's energy consumption was reported at a rate of 13 TW according to (Lewis, 2005). Demand for energy will double by 2050 and increase to more than triple by the end of the century. Unfortunately, even improvements in existing energy networks will still be inadequate to supply this demand sustainably. Until today, the main source of energy production is fossil fuels. Davidson (2010) explained that the process to form fossil fuels takes anywhere from 250 to 500 million years. Deep underground, heat and pressure transform the decomposed material into pockets of gas and unrefined oil in the absence of air. The oil and gas then move through the ground and then collect in reservoirs. US Energy Information Administration (2012) explained that since we consume fossil fuels at a higher rate than it can be replenished, so for all practical purposes, fossil fuel is considered a finite and non-renewable resource.

According to Blackstone et al. (2004), the human population is growing, and so is the economy. There are more of us in numbers living in energy consumptive lifestyles; this is the reason for the accelerated increase in energy demand. Yergin (2011) reported that since fossil fuel is a finite resource, supplies will sooner or later reach 'peak oil'. Peak oil is a point when the maximum rate of fossil fuel extraction has been reached. After this point, fossil fuel extraction rate will decline terminally. An increase in energy demand while there is a decrease in energy supply will cause an energy shortage.

Energy consumption can be linked to growth and development of a country; however the prices of fossil fuel are affected by external factors beyond our control. Wars, recessions, and devastating weather are the main causes that drive up oil prices. In 2005, Hurricane Katrina halted oil production along the Southern Gulf Coast of the United States. Supply was cut but the demand did not decrease causing the price of oil to spike to over $70 a barrel which was equivalent to RM 227.29. Most of our fossil fuel are produced by a powerful few, namely from the Middle East, and supply is subjected to its unstable geopolitics. In July of 2008, wars in both Iraq and Afghanistan affected the delivery mechanism of oil to the rest of the world. Suppliers were unable to convince buyers that they would be able to properly deliver oil. As a result, oil prices reached over RM 441.59. Nonetheless, the current trend is vice versa, but fossil fuels are always subjected to depletion unlike renewable energy such as solar (Davidson, 2010).

©This item is protected by original copyright

Fossil fuels contain carbon as it is derived from organic matter. This carbon is released to the air in form of carbon dioxide and carbon monoxide when it is burned to generate electricity. These carbon gasses prevent outgoing radiation from leaving the atmosphere and therefore increases the local temperature. Since this is happening everywhere on earth, the effect becomes global, and we have global warming. Singh (2013) explained that global warming cause artic ice to melt, sea levels to increase, animals' behavioural patterns to change and economical damage hitting perhaps most severely, agriculture.

With these unpleasant aspects to using fossil to fuel our civilization, more of us are trying to wean ourselves from it. Alternative energy sources, one of which is solar, will be of our concern in this project. As PEC will be used in this research, selection of photo-anode is the main priority.

©This item is protected by original copyright

2.2 Semiconducting photo-anode

A semiconducting photo-anode is an electrode that is made from a conductive material in which electrical current can pass through. A photo-anode is an anode that must be able to harvest solar photons, from the solar energy and thus, the photolytic splitting of water can be carried out (Zhu et al., 2011). For a semiconducting photo-anode that will be used in the PEC cell for the purpose of water splitting process, the semiconductor chosen must have band gap energy more than the band gap of water.