OPTIMIZATION OF HYDROGEN PRODUCTION BY WATER ELECTROLYSIS

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UNIVERSITI TEKNOLOGI MALAYSIA

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A thesis submitted in fulfillment of the
requirements for the award of the degree of
Master of Science (Physics)

Faculty of Science
Universiti Teknologi Malaysia

SEPTEMBER 2014

I lovingly dedicate this thesis to my precious, the sweetest and dearly loved lady in my life, my mom, Che ku Mahani Binti Che Ku Daud and her strong spirit caring man, always my hero, Azni Bin Muda, special mate of mine MHAB who always support me, beloved siblings, family and friends,

Love,

Siti Radhiana Binti Azni

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ABSTRACT

Recently, hydrogen has been considered as a future energy carrier. Hydrogen is believed to be the most important long-term option for addressing the energy, environmental and economic concerns since it is a renewable and clean energy resource. The simplest and cheapest way to produce hydrogen is by electrolysis. However, the process is inefficient. Therefore the objective of this study is to enhance the hydrogen production by optimizing the electrolysis parameters as well as the laser parameters. In this study, fixed volume of distilled water was employed as medium and sodium chloride used as catalyst. Graphite rods were used as electrodes which were supplied by varying voltage. Molybdenum sheets with various surface areas were utilized as a sacrifice agent to protect the cathode. Meanwhile, ethanol solution was used to compensate oxidation by donating an amount of electron in the electrolyte was deployed as supplement. Hence the electrolyte parameters were optimized by varying the voltage, the sacrifice agents and electron donor. In addition, the hydrogen production was also enhanced by illuminating light into the electrolysis chamber. The light source was also optimized by varying the wavelength and the power of the light. In this study, the light source used comprised of diode-pumped solid state laser at various wavelength including, 485 nm, 532 nm, 635 nm, while nitrogen laser and conventional UV light source were at 337 nm and 403 nm respectively. The results obtained showed that the hydrogen increased with the voltage as well as the sacrifice agent area. The larger the voltage, the more the water splitting and the larger the area of sacrifice agent, the more protection on the cathode. Thus, more hydrogen production was encouraged. In contrast, the addition of the supplementary element ethanol was limited to 7 mL and above 7 mL, it resisted the hydrogen production. In the case of illumination light, green laser at 532 nm had shown a pronounced result. This was due to the light that is transparent to the water, thus contributing to more electric field into the electrolysis system. Furthermore, the higher the power of the green laser into the electrolysis chamber the more hydrogen production was realized. Thus, the effectiveness as well as the efficiency of the hydrogen production do relies on the optimizing parameters.

ABSTRAK

Mutakhir ini, hidrogen telah dipertimbangkan sebagai pembawa tenaga pada masa hadapan. Hidrogen dipercayai menjadi pilihan jangka panjang yang paling penting bagi menangani tenaga, keprihatinan terhadap alam sekitar dan juga ekonomi kerana ia adalah sumber tenaga yang boleh diperbaharui dan bersih. Cara termudah dan termurah untuk menghasilkan hidrogen adalah melalui elektrolisis. Walau bagaimanapun, kaedah ini masih tidak cekap. Oleh itu, objektif kajian ini adalah untuk meningkatkan penghasilan hidrogen dengan mengoptimumkan parameter elektrolisis serta parameter laser. Dalam kajian ini, isipadu air suling yang digunakan sebagai medium elektrolisis ditetapkan dan natrium klorida digunakan sebagai mangkin. Rod grafit digunakan sebagai elektrod yang dibekalkan dengan pelbagai voltan. Kepingan molibdenum dengan pelbagai luas permukaan digunakan sebagai agen korban untuk melindungi katod. Sementara itu, larutan etanol digunakan untuk mengimbangi pengoksidaan dengan mendermakan elektron dalam elektrolit. Oleh sebab itu, parameter elektrolit dioptimumkan dengan perubahan voltan, agen korban dan penderma elektron. Di samping itu, penghasilan hidrogen juga dapat ditingkatkan dengan memancarkan cahaya ke dalam kebuk elektrolisis. Sumber cahaya juga dioptimumkan melalui perubahan panjang gelombang dan kuasa cahaya. Dalam kajian ini, sumber cahaya yang digunakan terdiri daripada diod yang dipam oleh laser dalam keadaan pepejal dengan pelbagai panjang gelombang, termasuk, 485 nm, 532 nm, 635 nm, sementara panjang gelombang bagi laser nitrogen ialah pada 337 nm dan sumber cahaya UV konvensional pada 403 nm. Keputusan yang diperoleh menunjukkan bahawa hidrogen bertambah dengan pertambahan voltan serta luas permukaan agen korban. Semakin tinggi voltan, semakin banyak pemecahan air yang berlaku dan semakin besar kawasan agen korban, semakin banyak perlindungan terhadap katod. Oleh itu, menggalakkan lebih banyak penghasilan hidrogen. Sebaliknya, penambahan etanol sebagai unsur penambah hanya terbatas kepada 7 mL sahaja dan lebih daripada 7 mL, ia merintangi penghasilan hidrogen. Dalam hal pancaran cahaya, laser hijau pada 532 nm menunjukkan keputusan terbaik. Ini disebabkan, cahaya ini adalah lutsinar kepada air, dengan itu dapat menyumbangkan lebih banyak medan elektrik ke dalam sistem elektrolisis. Tambahan pula, semakin tinggi kuasa laser hijau dalam kebuk elektrolisis, semakin banyak penghasilan hidrogen yang dikenalpasti. Oleh itu, keberkesanan serta kecekapan penghasilan hidrogen amat bergantung kepada parameter yang dioptimumkan.

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LIST OF SYMBOLS

A	-	Ampere
A	-	amplitude
Å	-	armstrong
amu	-	Atomic mass unit
aq	-	aquose
BMI.BF4	-	1-butyl-3-methyl-imidazolium-tetrafluoroborate
c	-	speed of light, 2.9888x 10^8 m/s
C_xH_x	-	Base
CH3OH5	-	Ethanol
CO_x	-	Carbon Oxide
CO_2	-	Carbon Dioxide
cm^2	-	centimeter square
CP	-	Cathodic Protection
DC	-	Direct Current
0°C	-	Degree
e^-	-	Negative charge
E	-	Electric Field
g	-	gas
G	-	Gibbs Energy
g	-	gram
GHz	-	Gigaheltz
H_2O	-	Water

H	-	Helmhotz
h	-	Planck constant
H^+	-	Hydrogen ion
H_2	-	Hydrogen gas
HER	-	Hydrogen Evaluation Reaction
HP	-	Hydrogen production
HTE	-	High Temperature Electrolysis
HTSE	-	High Temperature Steam Electrolysis
I	-	Current
I	-	Intensity
j	-	Current density
J	-	Joule
K	-	Kelvin
MHz	-	Megaheltz
mA cm^{-2}	-	Milli ampere per centimetre
ml	-	Millilitre
Mo	-	molybdenum
NaCl	-	Sodium Chloride
NaOH	-	Sodium hydroxide
NO_x	-	Nitrogen Oxide
nm	-	nanometre
N^2	-	Nitrogen
NH_3	-	ammonia
O_2	-	Oxygen gas
OH^-	-	Hydroxide ion
Pa	-	Pascal
%	-	Percent
P	-	Power
PV	-	photo-voltaic
S	-	Enthalpy
SO_x	-	Sulphur Oxide
STP	-	Standard Temperature Pressure
U	-	Internal Energy

UV	-	Ultraviolet
V	-	Volt
λ	-	lambda(wavelength)

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Today global energy requirements are mostly dependent on fossil fuels (about 80% of the present world energy demand) (Sims et al., 2007). This will eventually lead to the foreseeable depletion of limited fossil energy resources. Presently, the utilization of fossil fuels are causing global climate change mainly due to the emission of pollutants like CO_x, NO_x, SO_x, C_xH_x, soot, ash, droplets of tars and other organic compounds, which are released into the atmosphere as a result of their combustion (Benemann, 1996; Chen *et al.*, 2005; Fang, 2002). In order to remedy the depletion of fossil fuels and their environmental misdeeds hydrogen has been suggested as the energy carrier of the future. It is not a primary energy source, but rather serves as a medium through which primary energy sources (such as nuclear and/or solar energy) can be stored, transmitted and utilized to fulfill our energy needs.

Hydrogen is energy carrier, not an energy source. It must be produced from hydrogen containing compounds. Hydrogen is extremely abundant in our universe. Every molecule of water (H_2O) results from the combination of two hydrogen atoms and one oxygen atom.

Hydrogen is also found in the form of hydrocarbon (natural gas, oil and etc.) which are the bonding of carbon and hydrogen atoms (US Department, 2005). Hydrogen is making up about three-quarter of all matter. The atmosphere contains about 0.07 % hydrogen, while the earth's surface contains about 0.14 % hydrogen. Hydrogen is the lightest element. As we know, water covers 70 % of the Earth's surface. All living things in our planet, whether animal or plant, contain hydrogen, so the biomass is another potential source of hydrogen. Although it is abundant element on the planet, hydrogen practically not exists naturally in its pure state. So we have to convert it into energy supply if we could produce it in sufficient quantity.

According to the literature, for more than a century, hydrogen has been scientifically studied (Richards, 1901, Richards, 1896). Today hydrogen can be used to replace fuels. Hydrogen can be produced using many ways such as diverse, domestic resources including fossil fuels, such as coal (preferentially with carbon sequestration), natural gas, biomass or using nuclear energy and renewable energy sources, such as wind, solar, geothermal, and hydroelectric power to split water. Researchers are developing a wide range of technologies to produce hydrogen economically from a variety of resources in environmentally friendly ways. Therefore, one of a method to produce hydrogen with near-zero net greenhouse effect is by electrolysis.

At the preset of time, most of industrial production of hydrogen is achieved using the reforming of fossil or biofuels (CSIS, 2005). This approach is limited by cost or availability problems and, more dramatically, by environmental constraints associated with the production of CO_2, which is responsible for the greenhouse effect involved in global warming. An attractive alternative is the production of hydrogen by water electrolysis in clean and renewable process (Levine, 2003).

The following reactions take place inside the alkaline electrolysis cell:

Electrolyte: $4H_2O \longrightarrow 4H^+ + 4OH^-$

Cathode: $4H^+ + 4e^- \longrightarrow 2H_2$

Anode: $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

Sum: $2H_2O \longrightarrow O_2 + 2H_2$

The variety methods to enhance the hydrogen production from water were discovered. Hydrogen produced from electrolysis is clean fuel source. When testing the hydrogen from water electrolysis, some variables are tested which are (1) Different temperature of electrolyte (2) Voltage. Both temperature and voltage increases with the time. (3) The effect of concentration of electrolyte (ethanol). Recently, many researchers suggested that Ethanol is becoming popular alternative in replacing several conventional sources of energy and actually more susceptible to electrolysis than water, which is why they are being considered for use in fuel cells. Electrical efficiency can influence the hydrogen production and the important is the electrolyte quality. The higher the ethanol concentration in the feed was, the higher the currents were obtained under the application of a fixed potential (Caravaca, 2012). However, above an ethanol volume of 7 ml, the system started to be limited by ohmic losses since the conductivity of the membrane may decrease at high ethanol concentrations.

The effect of using molybdenum was also been observed. In previous research, it has been observed that the pure molybdenum is high electrocatalytic activity and stability. Molybdenum gives very high current density, *j*, 77.5 $mAcm^{-2}$ (Roberto et al., 2008). The larger sizes of molybdenum, the hydrogen production is higher too. Then, electrolysis process is repeated by using green laser.

Laser-induced chemical reactions are of particular interest because the laser provides the energy of activation. An increase in the production of hydrogen resulted in a corresponding increase in the power of laser irradiation of green laser 532 nm. Somehow, it is important that a catalyst should be used for hydrogen production (HP) and a catalyst that suitable for this electrolysis is sodium chloride (NaCl). Because the water is covalent and current cannot flow very well, so to make it ionic, have to use ionic substance, and it is NaCl.

1.2 Problem Statement

Hydrogen gas has a clean and safe characteristic that make it so suitable to replace fuels in future. A relatively new of exploration, the hydrogen gas can be produced by electrolysis process and it more been preferred to use this method as it green environmental. However, from normal electrolysis, the hydrogen produced is a few. Therefore, this work is to be carried out to observe the ways that can enhance the hydrogen production by electrolysis and also by photo-electrolysis which is by light. As far as we know, solar system can be used to generate HP through photocatalytic activity. But the solar energy is unpredictable it depend on season and weather although it is free. On the other hand, the usage of laser is quite costly but by using the diode pumped solid state laser can save the cost. Laser is more controllable light. This man made light is more promising for hydrogen production. In this present work, hydrogen production is planning to generate in more environmental and friendly ways with the aid of laser irradiation.

1.3 Research Objective

The main objective of this project is to enhance the hydrogen production from electrolysis technique. This is accomplished by the following tasks:

i. To produce the hydrogen economically from water
ii. To observe of variation rate of hydrogen production by using different temperature and voltage.
iii. To observe the variation rate of hydrogen production with different quantity of ethanol and molybdenum.
iv. To compare the amount of variation of hydrogen production with laser irradiation and without laser irradiation.
v. To investigate the rate of hydrogen production by using laser with different power rating.

1.4 Research Scope

This research only focused on hydrogen production by electrolysis and photo-electrolysis of distilled water which used sodium chloride, NaCl as catalyst. Besides that, during electrolysis process, the temperature and voltage were varied. The different amount of ethanol and sizes of molybdenum were added into the electrolysis cell to observe the hydrogen gas produced. Diode pumped solid state laser with second harmonic generation was used as a source for photolysis. Electric power supply was used to induce charges in electrolysis process. Graphite electrodes were provided to detect the breakdown current flows as well as collection of gases production.

1.5 Thesis Outline

The first chapter is the introduction to the research. It basically describes some past researches regarding the hydrogen production technique. It also includes the problem statement of the research together with the objective and scope of the study.

Chapter 2 is the theoretical chapter. It includes some fundamental theory as a background of this study. This chapter discusses about the water molecule and electrolysis process in details as well as the theoretical background in producing hydrogen gas and its process in details. Besides that, some variables that can enhance hydrogen production in electrolysis cell have been studied. Electrolysis with green laser 532 nm is also described in details in this chapter.

Chapter 3 contains the methodological information about this thesis. It discusses the step of electrolysis process on how variables that can enhance the hydrogen production. Besides that, this chapter also discusses the step of laser irradiation into the electrolysis process in order to get the higher amount of hydrogen gas.

Chapter 4 discusses about the characterization of the variables that can enhance the hydrogen production in normal electrolysis. The parameters of electrolysis have been discussed in this chapter. The parameters involved in this research are temperature, voltage, catalyst which is ethanol and molybdenum. Chapter 4 also discusses about the photo-electrolysis which involve light source in electrolysis. In lab work, the laser will be used as a light source. However, there is certain light that can really work in enhancing the hydrogen production. Then, the type of the laser and its stability region were determined.

Chapter 5 summarized the work done in this project. It contains the list of problem arise during the running of the project. Finally some recommendations and suggestion are proposed for future study.

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APPENDIX A

Presentations

1. Siti Radhiana Binti Azni, Noriah Bidin, Optimization of Hydrogen Production Based on Different Laser Wavelength. Laser Electro-Optic Seminar 2013 (LEOSH) Conference, July 2013, Pulai Spring Resort Johor.

2. Siti Radhiana Binti Azni has participated Laser Workshop 2013, Advance Photonic Science Institute (APSI), July 2013, Dewan Sri Iskandar, UTM.

3. Noriah Binti Bidin, Yaacob Bin Mat Daud, Siti Radhiana Binti Azni, Daing Hanum Farhana Binti Ab Munap, and Ali Kamel Mohsin. Enhancement Hydrogen Production By Laser Ablation. 15^{th} Industrial Art and Technology Exhibiton (INATEX) 2013 Dewan Sultan Iskandar, UTM, Johor Bahru.