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HYDROGEN PRODUCTION VIA CATALYST OF GREEN LASER, MOLYBDENUM AND ETHANOL

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Graphical abstract

Abstract

Electrolysis is an electrochemical process which is known as a green technology. Laser irradiation and the presence of catalyst in water electrolysis are identified as ways of improving the efficiency and increment of hydrogen production. The enhancement of hydrogen production through water electrolysis is obtained by adding molybdenum to increase the current in electrochemical cell and ethanol as an agent in photochemical reaction. In addition, diode pumped solid-state laser green laser at 532 nm is employed with the purpose to compensate the residual electrical field effect. The combination of the three catalysts is found more powerful to cause water splitting, thus produced 5 times greater H_2 production in comparison to the action of individual catalyst.

Keywords: Electrolysis, hydrogen, sacrificial anode, molybdenum, green laser, water splitting

Abstrak

Elektrolisis adalah satu proses elektrokimia yang dikenali sebagai teknologi hijau. Penyinaran laser dan kehadiran pemangkin dalam elektrolisis air dikenal pasti sebagai cara untuk meningkatkan kecekapan dan peningkatan hidrogen. Peningkatan penghasilan hidrogen melalui elektrolisis air diperoleh dengan menambah molibdenum untuk meningkatkan arus di dalam sel elektrokimia dan etanol sebagai agen dalam tindak balas fotokimia. Di samping itu, laser hijau pepejal dipam oleh diod pada 532 nm digunakan bagi tujuan untuk mengimbangi kesan baki medan elektrik. Kombinasi ketiga-tiga pemangkin didapati lebih kuat untuk menyebabkan pemisahan molekul air, sekali gus menghasilkan lima kali ganda pengeluaran H_2 berbanding dengan tindakan satu pemangkin sahaja.

Keywords: Elektrolisis, hidrogen, anod pekorban, molibdenum, laser hijau, pemisahan molekul air

1.0 INTRODUCTION

Electrolysis is well-known as a 'clean' process to produce hydrogen. Electrolysis was first observed by William Nicholson and Anthony Carlisle in 1801. Two platinum electrodes were immersed into a dilute salt solution and allowed electricity to flow by using voltaic pile battery. Consequently the water molecule decomposed into two separated gases (oxygen and hydrogen) at the electrodes.

Since then, the study of electrolysis is grown rapidly with upgrading techniques to produce low cost hydrogen and environmentally friendly. There were more than 80 hydrogen production routes that can be narrowed into four different categories that are; biological, chemical, electrochemical (water electrolysis, photoelectrochemical, halide electrolysis, etc.) and thermal electrolysis [1]. In water electrolysis, there are four methods proposed to produce hydrogen gas; alkaline electrolysis; proton exchange membrane (PEM) water electrolysis; steam electrolysis; and chlorine-alkali production of which hydrogen as a byproduct [2].

Basically, in electrolysis, there are some parameters that effect the hydrogen production such as the type, size and distance between the electrodes. A presence of molybdenum actually adding the size of an electrode thus the current density as well as the hydrogen production is expecting to be increased. According to Roberto *et al.,* [3] pure molybdenum has high electrocatalytic activity and stability to improve the efficiency, cost and stability of the hydrogen production process at room temperature. They had used different commercial electrodes and compared the performance of resistance to corrosion [3]. However, those works are limited only on the hydrogen production increased by electrical efficiency.

The purpose of this study is to increase the volumetric of hydrogen by adding catalyst of molybdenum, ethanol (as an agent in photochemical reaction [4]) and green laser to reduce the water polarization effect. Initially the investigation was carried out by using individual catalyst. Later on, by combining two catalysts and lastly to combine all of them together at once.

Figure 1 Electrolysis cell with catalysts

2.0 EXPERIMENTAL

Electrolysis chamber was filled with 500 ml of distilled water and 0.532 g of sodium chloride NaCl as an ionic substance consists of Na^+ and Cl^- ions.
A graphite electrode was selected because carbon is an ideal electrode for the electrolysis. The hydrogen yield was measured by using 15 ml test tubes. Initially, the test tube was filled with distilled water then it turns upside down into the chamber to vaccumize the air and cover the electrode. The reduction of water in the test tube at the cathode is the same volume of hydrogen gas collection. The same experiment was conducted with the presence of green laser irradiation to investigate the effect of laser irradiation upon electrolysis efficiency. A schematic diagram of the experimental set-up is shown in Figure 1.

A diode pumped solid state laser with wavelength of 532 nm and power of 184 mW was employed to compensate the reduction electrical field due to water polarization effect. A DC power supply was provided to electrify the electrodes. The voltage was kept constant at 10 V. The volume of H_2 was measured through the inverted test tube (at cathode) for every minute. A photograph of the whole experimental set-up in the real field is depicted in Figure 1.

Later the experiment was carried out by adding ethanol solution at various volumes of 3 mL, 5 mL, 7 mL, and 9 mL to reveal more electron donor in the water electrolysis. For each additional volume of ethanol, hydrogen production was collected for every 3 minutes till 15 minutes duration.

3.0 RESULTS AND DISCUSSION

The effect of green laser irradiation 532 nm on hydrogen production has been described in other texts [5].Green laser overcomes the residual electric field effect induced by water polarization. The external electric field assists the conductivity or mobility of the charges in the water electrolysis [5].High transparency of the green laser in water allows the electric field carried by the beam to fully utilized. The existence of such external electric field in water electrolysis assists in conducting more ions or charges to each terminal thus result in more hydrogen production.

3.1 The Effects of Molybdenum on Hydrogen Production

Figure 2 shows the progressive of hydrogen production by adding molybdenum at the presence of laser irradiation.

When molybdenum was added, the current in the electrolysis process is increased hence the hydrogen production also increases. This is because molybdenum has special property like high current density (77.5 mA cm^{-2}). As a result, it is capable to collect larger charge densities (301.0Ccm^{-2}) compared to the other metals such as aluminum or zinc. It could achieve efficiencies, η, as high as 99.2 % [6].This will cause abundant hydrogen production at the cathode since more electrons are transferred to the anode during the process.

The hydrogen production is noticed to be the lowest with the absence of molybdenum and ethanol as shown in Figure 2. This is due to its proton-donating properties. In contrast with the presence of molybdenum, actually additional area of electrode is occurred which leads increasing in current density thus allows more hydrogen production. The cathodic behavior of molybdenum electrode plays an important role in electrochemical protection of electrodes. Furthermore, the cathodic behavior is very important not only in application of the cathodic protection itself, but also in anodic protection.

Molybdenum (Mo) can activate the water easily. It is also claimed as a good material for hydrogen evolution reaction (HER) [7].Molybdenum is a good electrocatalyst compared to Platinum at temperature below 333 K. However it becomes weaker at higher temperature. Hence, Mo is suitable to be used as an electrocatalyst due to the properties of high current density which enable the increment of the current in electrolysis system and high stability. Besides, Mo is a low cost material which is affordable to sustain the hydrogen economy [3].

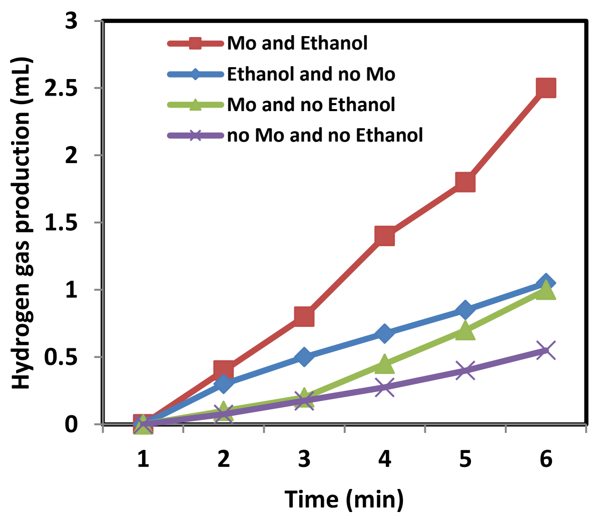

Figure 2 The effect with and without Molybdenum and Ethanol on the hydrogen production at 10 V

Figure 2 illustrates the production of Hydrogen by combination of Molybdenum, Ethanol and laser as catalysts. Optimum rate of Hydrogen production is realized when the three catalysts were used together during electrolysis. Nonetheless, the hydrogen production is almost similar when only Ethanol or Molybdenum was used as catalyst during the electrolysis. This shows that the similarity important role play by both of catalyst.

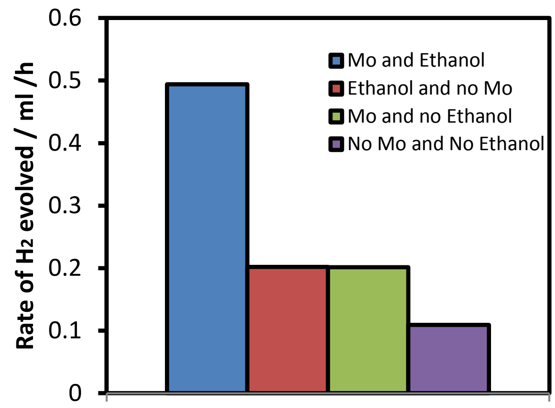

Figure 3 Time course of hydrogen gas evolved with the effect of the following catalysts

As indicated in Figure 3, the rate of Hydrogen production is recorded to be 0.1093 ml h^{-1}, the lowest rate of Hydrogen produced when Molybdenum and Ethanol are not presence in water electrolysis. This means the Hydrogen production is strongly depended on the presence of Molybdenum and Ethanol as catalysts. The highest rate of Hydrogen yield of 0.4943 $mLh^{-1}$is achieved with the presence of Molybdenum and Ethanol as the catalyst. This indicates that with the combination of the catalyst together the hydrogen production can be achieved five times higher as compared without them. On the other hand, the rate of Hydrogen evolved during laser electrolysis with single catalyst either Ethanol or Molybdenum is double the amount of hydrogen production without Molybdenum and Ethanol in the solution. The rate of hydrogen produced is 0.2021 ml $h^{-1}$and 0.2014 ml h^{-1} by adding Ethanol and Molybdenum as catalysts respectively. Almost similar rate is achieved with the individual present of the catalyst. This indicated the presence either of the catalyst is equally important in water electrolysis.

3.2 The Effect of Corrosion

The hydrogen production due to the effect of corrosion on Molybdenum also carried out in this study. The results are presented in Figure 4. The hydrogen production is compared with and without corrosion. Obviously the results showed that the hydrogen production without corrosion occurred on Molybdenum is higher than with corrosion. The rate of hydrogen production is higher showing that corrosion does affect the activity of electrolysis. The conductivity in the electrolysis is subjected to be less when corrosion on the molybdenum occurred therefore reduced the hydrogen production. The molybdenum is oxidized spontaneously when connected to anode. This is the way how the molybdenum protects the electrode from corrosion. It is also known as a sacrificial anodes. Molybdenum acts as part of a galvanic couple.

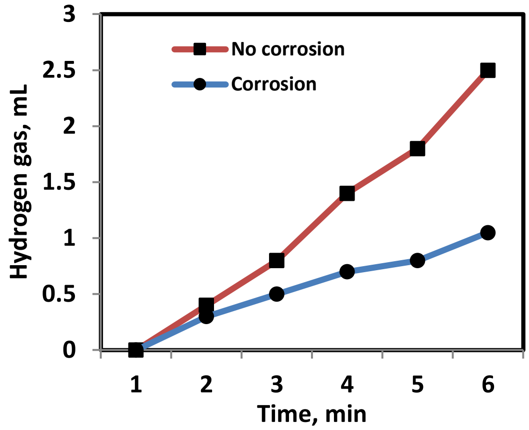

Figure 4 The effects of corrosion on Molybdenum

3.3 Effects of Ethanol on Hydrogen Production

Electrical efficiency is very important in electrolysis as it is related to passage of current. Eventually, ethanol as sacrificial electron donor and relatively increase the current density in the electrolyte.

According to Caravaca *et al.,* [6] the chemical reactions involving ethanol in the electrolysis is expressed as;

$$CH_3CH_2OH \longrightarrow CH_3CHO + 2H^+ + 2e^- \quad (1)$$
$$CH_3CH_2OH + 2H_2O \longrightarrow CH_3COOH + 6H^+ + 6e^- \quad (2)$$
$$CH_3CH_2OH + 3H_2O \longrightarrow 2CO_2 + 12H^+ + 12e^- \quad (3)$$
$$H_2O \longrightarrow OH + H^+ + e^- \quad (4)$$

In contrast, CH_3COOH is partially ionized in solution and approximately 5% of the displaceable hydrogen in the acid is present in solution as hydrogen ion, H(+).The activity of electrolysis rises directly with current.

Figure 5 depicted the effect of different volume of Ethanol on the hydrogen production. The higher the ethanol concentration, the higher the currents were obtained under the application of a fixed potential [4]. Without ethanol, rate of hydrogen gas is obtained as 0.666 $mLmin^{-1}$. Rate of hydrogen gas produced by using 3 mL of ethanol is 0.825 mL min^{-1}. At 7 mL of ethanol, the maximum rate of hydrogen production is achieved at approximately 3.00 $mLmin^{-1}$. Using 7 ml of ethanol, optimum hydrogen production is achieved. By adding 9 mL of ethanol into the electrolysis cell the rate of hydrogen gas decrease to 2.6 mL min^{-1} since the electrolyte has been concentrated and causes the reducing of conductivity as mentioned previously.

The rate of hydrogen production based on ethanol concentration is shown in Figure 6. It is found that initially the hydrogen production is increased linearly with the ethanol concentration. However, more than 7 mL of ethanol's (C_2H_5OH) the system started to be limited by Ohmic losses.

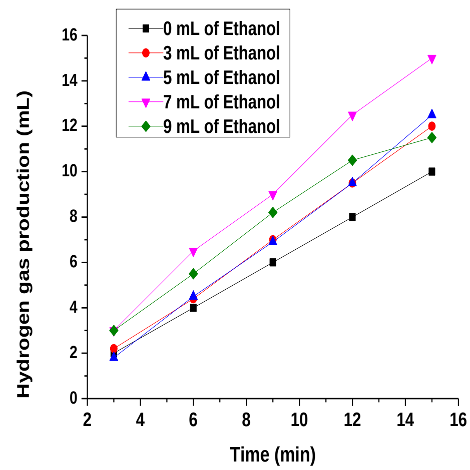

Figure 5 Effect of different volume of Ethanol on the hydrogen production

The conductivity of the ions is decreased with ethanol concentrations. Actually when 9 mL of ethanol is added into the electrolysis system, a lot of gas bubbles appeared at the entire surface including the chamber wall and surrounding of electrode. The bubbles covered almost all surfaces trigger ohmic resistance in the electrolysis. The present of heavy bubbles induce unstable current and reduce the conductivity of ions. Such condition causes a higher level of ohmic voltage drop [8].

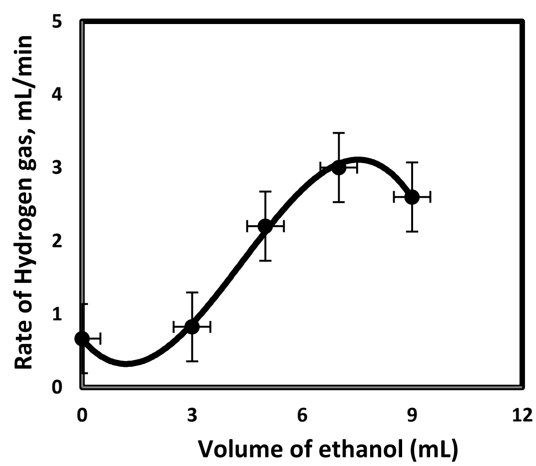

Figure 6 Rate of hydrogen production as a function of ethanol concentration

4.0 CONCLUSION

The catalyst of green laser, molybdenum and ethanol have significant role in improving the hydrogen production. The green laser compensates the polarization of water effect. The laser beam provides external electric field to overcome the residual electric field effect. The molybdenum is depending on its surface area; the larger surface area of molybdenum, the higher hydrogen production. However the corrosion on the molybdenum due to oxidation did affect the hydrogen production. On the hand ethanol is important as an electron donor. But it has limitation. The optimum ethanol allows in electrolysis is 7 mL which generated almost 3 mL/min the rate hydrogen production. Greater than optimum concentration causing in an ohmic voltage drop which due to heavy bubble formation. The combination of the optimized catalysts permitted the hydrogen production 5 times higher than the original one.

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