HYDROGEN GENERATION BY KOH-ETHANOL PLASMA ELECTROLYSIS USING DOUBLE COMPARTMENT REACTOR

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Abstract

This study has successfully investigated the generation of hydrogen using double compartment reactor with plasma electrolysis process. Double compartment reactor is designed to achieve high discharged voltage, high concentration, and also reduce the energy consumption. The experimental results showed the use of double compartment reactor increased the productivity ratio 90 times higher compared to Faraday electrolysis process. The highest hydrogen production obtained is 26.50 mmol/min while the energy consumption can reach up 1.71 kJ/mmol H\textsubscript{2} at 0.01 M KOH solution. It was shown that KOH concentration, addition of ethanol, cathode depth, and temperature have important effects on hydrogen production, energy consumption, and process efficiency.

\textit{Keywords:} Double compartment reactor, Ethanol, Hydrogen, KOH, Plasma electrolysis

Introduction

Hydrogen is widely manufactured from steam reforming and electrolysis process. The weaknesses of steam reforming are the high carbon emissions and not renewable feedstock (natural gas). Meanwhile, the main obstacles of electrolysis are the lack of production and high energy consumption [1].

Alternative way to produce hydrogen is plasma electrolysis. This method has a similar process like common electrolysis but it uses higher voltage that is able to create electrical sparks and form plasma. Plasma will produce large amounts of reactive species that can break H\textsubscript{2}O binding. Mizuno used KOH solution at a temperature of 80°C and 230 V that can lower energy consumption eight times compared with Faraday electrolysis [2]. High discharged voltage causes the process efficiency more optimal [3].

Saksono, using 0.1 M KOH solution at 85°C and 300 V, obtained hydrogen production rate 13.4 times higher compared with Faraday electrolysis for the same amount of power electricity [4]. Higher discharged voltage increases excitation energy. It produces large amount of radicals so that the production of hydrogen increases.

Hydrogen atom and hydroxyl radical production are increased by addition of methanol. These active species are produced from the hemolytic dissociation of water molecules by plasma. The addition of 15 \% (v/v) methanol in 0.01 M NaOH solution at 700 V increases hydrogen production nineteen times higher than without additives [5].

Therefore, high discharged voltage and additives are main criterias in designing a reactor to produce large amount hydrogens. In a single reactor, the distance between the anode and cathode is very close. At this condition, high discharged voltage will increase electrical current and power electricity that causes operation system less safety. Double compartment...
reactor enlarges the distance between anode and cathode so that the electrical current which flow in the system will be much lower due to the increase of flow resistance. Utilization of double compartment reactor on the production of chlor gas showed reactor capability to increase production rate, minimize energy consumption, and reduce explosion possibility, especially at higher voltage and concentration [6].

The objective of using double compartment on this research is to achieve process condition at higher concentration with low electrical current flow. The addition of additives is needed to obtain higher hydrogen production rate. This study will examine independent variables such as discharged voltage, KOH concentration, ethanol concentration, cathode depth, and temperature effects on hydrogen production, energy consumption, ratio of energy consumption per mmol of product (Wr), and the ratio plasma electrolysis moles product per Faraday electrolysis moles product (G(H2)).

Experimental

The design of the reactor is shown in Figure 1. The reactor has two compartments: one compartment is equipped with a tungsten cathode and the other is equipped with a stainless steel anode. The reactor is a semi batch system made from an acrylic housing filter connected to a globe valve. The electric source is connected to a 3 kVA slide regulator that is then connected to a transformer. A diode bridge is used to rectify the electric current. The current is measured from a multimeter Yuhua A830L. The hydrogen gas produced is then passed into gas chromatography 8A Shimadzu. Bubble soap flowmeter is used to measure hydrogen production rate. This study analyses the formation of plasma by varying KOH concentrations from 0.05 M to 0.1 M within 600–800 V. Furthermore, an examination of energy consumption is conducted by measuring the amount of electrical current and time of process.

Figure 1 Experimental Set-up

Power electricity (P) is defined as the amount of electrical energy used in t second (eq. 1)

\[ P = V \times I \]  

(1)
V : Discharged voltage (V)
I : Electrical current average (A)

Hydrogen production mol rate (mmol/s) \( V_{H_2} \) is calculated by measuring product flow rate using bubble-soap flowmeter and then calculate it using equation 2:

\[
V_{H_2} = \frac{V_{gH_2}}{22.4}
\]  

(2)

\( V_{gH_2} \) : Hydrogen gas product flow rate (mL/s)

\( W_r \) (kJ/mmol) is defined as ratio of energy consumption per mmol product (eq. 3) dan \( G(H_2) \) is defined as ratio of plasma electrolysis moles product per Faraday electrolysis moles product (eq. 4).

\[
W_r = \frac{V \times Q}{V_{H_2}}
\]  

(3)

\[
G(H_2) = \frac{V_{H_2}/22.4}{Q/2F}
\]  

(4)

V : Discharged voltage (V)
Q : Electricity load (C)
F : Faraday Contant ( 96500 C/mole)

Results and Discussion

Effects of KOH Concentration

Figure 2 shows that the increasing of KOH concentration increases the hydrogen gas production rate. The highest production is 26.50 mmol/min at 0.1 M KOH solution with addition of ethanol 10% volume. Higher concentration more than 0.1 M will potentially cause an explosion.

Figure 2 Hydrogen Production Rate in KOH + Ethanol 10%v at 800 V and 90°C

The increasing of KOH concentration in solution increases the number of OH\(^-\) and K\(^+\) ion. Plasma transforms OH\(^-\) into OH\(^{\bullet}\). OH radicals (OH\(^{\bullet}\)) are decomposed into hydrogen and oxygen as shown in the following reactions [3]:

\[
2OH^{\bullet} \rightarrow H_2 + O_2
\]
Large amount of ion in solution makes conductivity higher. Higher conductivity facilitates the mobilization of electrons so that electric current flowing in the system becomes higher. Therefore, energy consumption increases along with the increase of concentration.

At 0.1 M plasma spark brightestly and stable. The highest production rate is obtained at highest concentration. Wr decreases because the increase of production rate is higher than the increase of energy consumption. Figure 3 shows that at higher concentration, Wr which means energy consumption required per mole product becomes minimum. At this conditions G(H₂) obtained is 90.

**Figure 3** Wr in KOH + Ethanol 10%v at 800 V and 90°C

**Effects of Ethanol Addition**

The addition of ethanol increases the production rate significantly as shown in Figure 4. At 600 V, production rate reaches up 23 times higher compares without using ethanol. The ethanol additive function is to donate active species H● and OH● which in turn leads to the termination of the binding energy in the decomposition of water.

**Figure 4** Hydrogen Production Rate in KOH 0.05 M at 90°C

Plasma dissociates ethanol in solution as shown in the following reactions [7]:

\[
\begin{aligned}
4H^+_{(aq)} + 4e^- &\rightarrow 4H\bullet & \quad (5) \\
4OH^-_{(aq)} &\rightarrow 4OH\bullet + 4e & \quad (6) \\
4H^+_{(aq)} + 4OH^-_{(aq)} &\rightarrow 4H\bullet + 4OH\bullet & \quad (7) \\
2H\bullet + 2H\bullet &\rightarrow 2H_2(g) & \quad (8) \\
4OH &\rightarrow 2H_2(aq) + 2O_2(aq) & \quad (9)
\end{aligned}
\]
Three reactions directly generate H₂ and two other reactions generate H●. The H● then recombines with each other to produce H₂. Dissociation reactions indicate that the presence of ethanol increases the production of H₂.

At higher voltage, energy that is used to excite electrons increases. This phenomenon is visualized by the presence of large and stable plasma in the reactor. Large and stable plasma accelerates the formation of radical species thus accelerating the reaction of hydrogen formation. At 800 V with addition of ethanol 15% v, G(H₂) obtained is 82.8 as shown in Figure 5.

![Figure 5 G(H₂) in KOH 0.05 M at 90 °C](image)

![Figure 6 Electrical Current Characteristic Curve in KOH 0.05 M + Ethanol 20 % V at 800 V, Cathode Depth 1 cm](image)

Addition of ethanol until 20%v causes G (H₂) decreased. This phenomenon can be described quantitatively by fluctuating current read on multimeter. The addition of ethanol 20%v makes the electrical current flowing in the system larger and more fluctuating which is
visualized by high peaks as shown in Figure 6. At these high peaks, plasma inside reactor slightly dimmed accompanied the increase of current which affects to increase energy consumption.

**Cathode Depth Effects**

The brightest plasma spark happens when the cathode position is on the solution surface. Short electrode is utilized to achieve high current density to facilitate joule heating effect [8]. Joule heating effect around the cathode produces a gas sheath that surrounds the cathode. The presence of gas sheath triggers electron excitation to form plasma.

| Cathode Depth (cm) | H₂ production rate (mmol/minute) |
|-------------------|----------------------------------|
| 0                 | 3.52                             |
| 1                 | 17.3                             |
| 2                 | 5.18                             |

**Figure 7 Cathode Depth**

Cathode depth is the length of cathode submerged in solution as shown in Fig. 7. Fig. 8 shows that the highest hydrogen production rate is 17.3 mmol / min at 1 cm cathode depth. At solution surface, hydrogen production rate is lower than 1 and 2 cm although the brightest plasma spark was formed at solution surface. At solution surface, high energy electrons produced by plasma is not effective attacking OH⁻ and H⁺. OH⁻ and H⁺ ions are not only found on the surface but scattered in the solution. Therefore, at 1 cm position depth, plasma is more effective to form radicals that increase hydrogen production.

**Figure 8 Hydrogen Production Rate in KOH 0.05 M + Ethanol 10% v at 800 V, 90 °C**

At deeper cathode position, cathode will face higher hydrostatic pressure. At 2 cm below solution surface, the production of H₂ declines. At this position, the formation of bubbles on the submerged part of the cathode is more dominant than the formation of vapor around cathode surface solution so that the gas sheath formed was unstable. The presence of bubbles on the submerged part indicates that Faraday electrolysis was dominantly occurred than plasma electrolysis. This phenomenon increased energy consumption as shown in Fig. 9.
Fig. 9 shows that the highest hydrogen production rate is produced at 90°C. High temperature leads to the formation of bubbles (vapor bubbles on the surface of the solution). The bubbles will be ionized and form plasma when attacked by electron excitated [2].

Temperature Effects

Figure 10 Hydrogen production rate in KOH 0.05 M + Ethanol 10% v at 800 V, 90 °C

Figure 11 Wr and G(H₂) in KOH 0.05 M + Ethanol 10% v at 800 V, 90 °C
At temperature of 90°C H₂O molecules are more easily broken down into its constituent atoms compared to the liquid phase with a lower temperature. In bubbler form, the space between water molecules becomes more tenuous so that collisions of high-energy electrons in the water molecules become easier. Figure 11 shows that the process becomes more optimal due to the increase of temperature.

**Double Compartment Effects**

The reactor consists of two double compartment where anode and cathode are separated in different room in order to extend the distance between electrode. Longer distance increases electrical current resistance and extend electron pathway so that electrical current flowing in system can be minimalized.

Utilization of double compartment reactor also aims to purify the products. In single compartment reactor, the hydrogen and oxygen are produced in one reactor. In double compartment reactor, hydrogen concentrates in cathode compartment while oxygen in anode compartment as shown in Figure 12.

![Figure 12 Plasma electrolysis reactor (a) single compartment (b) double compartment](image)

**Table 1 Comparison result between single and double compartment reactor in KOH 0.1 M, 1 cm cathode depth.**

| Process Variable | Single Compartment Reactor | Double Compartment Reactor |
|------------------|---------------------------|-----------------------------|
| Max. discharged Voltage (V) | 300 | 800 |
| I_average (A) | 3.32 | 0.95 |
| G (mol/mol) | 21.8 | 90.05 |
| Wr (kJ/mmol) | 2.62 | 1.71 |

Double compartment reactor is equipped with cooling system. It aims to maintain the stability of operating temperature. Table 1 shows a comparison result between single and double compartment. Through double compartment reactor, high voltage (800 V) can be obtained with low electrical current flow and minimum Wr.
Conclusions

The application of plasma electrolysis in double compartment reactor can be implemented in the generation of hydrogen gas. The highest hydrogen production obtained is 26.50 mmol/min while the energy consumption can reach up 1.71 kJ/mmol H₂ at 0.01 M KOH solution. The experimental results showed that the use of double compartment reactor increased the productivity ratio 90 times higher compared to Faraday electrolysis process.

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