Analysis of Hydrogen Generation for Hydrogen Fuel Cell Electrical System

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Abstract

This paper presents the analysis of hydrogen produced from a sodium hydroxide-aluminium electrolysis process, in which hydrogen is used as fuel for a hydrogen fuel cell electrical system. Different molar concentrations of sodium hydroxide and cross sectional areas of aluminum electrodes are used to experiment the rate of hydrogen produced. Analysis of the rate of hydrogen produced is then performed with the intention to derive a theoretical expression to fit the experimental results. In conclusion, the derived theoretical expression is able to fit well with the experimentally measured rate of hydrogen produced.

Keyword: hydrogen, electrolysis, aluminium, sodium hydroxide, and molar concentration.

I. Objective

The objective of this research paper is to derive a theoretical expression for the rate of hydrogen produced from a sodium hydrogen-aluminium electrolysis system that can fit the experimentally measured rate of hydrogen produced.

II. Introduction

A hydrogen fuel cell electrical system that used hydrogen as fuel was constructed to produce electricity for lighting gallium nitride-phosphor white light emitting diode (LED). The electrolysis system must be able to produce sufficient hydrogen as the fuel to feed the system. Consequently, the rate of hydrogen produced at room temperature and standard pressure conditions becomes a main concern. Therefore, taken into consideration of cost and complexity of the design, various types of electrolysis methods were being experimented. Finally, an electrolysis system that uses aluminium as electrodes and sodium hydroxide (NaOH) as electrolyte is selected. [1]

In the experiments, the rates of hydrogen produced were recorded with various molar concentrations of sodium hydroxide with a fixed cross sectional area of aluminium electrodes and different cross sectional areas of aluminium electrodes with a fixed molar concentration of sodium hydroxide.

Analysis of the rate of hydrogen produced is performed to derive a theoretical expression that can fit the experimental results.

III. Design and Experimental Setup of Electrolysis System

The design of sodium hydroxide-aluminium system begins with the design of aluminium electrode. The electrode is designed in plate form with the dimensions shown in Fig. 1.

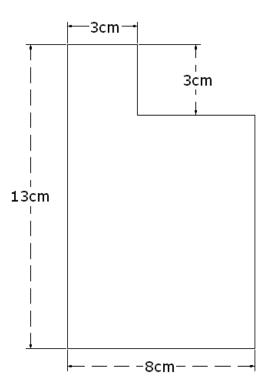


Figure 1: Aluminum electrode plate and its dimensions

Three cathode and three anode plates were constructed and connected in parallel and physically they were placed in alternating sequence as shown in Fig. 2 aiming to produce sufficient amount of hydrogen to feed the hydrogen fuel cell electrical system.

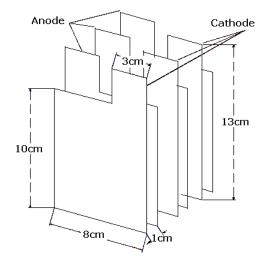


Figure 2: Arrangement of cathode and anode electrodes

The width between anode and cathode plates was designed to be 1.0cm throughout the experimental measurements. These electrodes were immersed in sodium hydroxide solution. A 12V battery was connected between electrodes to provide electric current flow to initiate the electrolysis process.

Two experiments were conducted to determine how the molar concentration of sodium hydroxide and cross sectional area of electrodes affects the rate of hydrogen produced.

First experiment was conducted to determine the relationship between molar concentration of sodium hydroxide and rate of hydrogen produced. The width between electrode plates was fixed at 1.0cm and cross sectional area of electrodes was fixed at 80.0cm². The molar concentrations used were 0.0001 molcm⁻³, 0.0002 molcm⁻³, 0.0004 molcm⁻³, 0.0008 molcm⁻³, and 0.0011 molcm⁻³ respectively. The rate of hydrogen produced was measured in volume cm³ per second with sodium hydroxide of molar concentration as stated.

The second experiment was conducted to observe how the cross sectional area of the electrode affect the rate of hydrogen produced. By setting the space between electrode plates fixed at 1.0cm and concentration of sodium hydroxide fixed at 0.0004mol/cm³, four cross sectional areas, which are 40.0cm², 64.0cm², 72.0cm², and 80cm² are used to determine their effects on the rate of hydrogen produced.

IV. Results

The rate of hydrogen produced with varying molar concentrations of sodium hydroxide and fixed cross sectional area of the electrodes, and fixed molar concentration of sodium hydroxide with various cross sectional area electrodes are graphically shown in Fig. 3 and Fig. 4 respectively.

Rate of Hydrogen Produced Vs Molar Concentration of NaOH

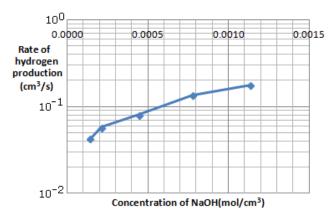


Figure 3: Rate of hydrogen produced with different NaOH molar concentrations

As shown in Fig. 3, an increase in molar concentration of sodium hydroxide causes an increase in the rate of hydrogen produced. At molar concentrations of 0.0001 molcm⁻³ and 0.0002 molcm⁻³, there is no appreciable increase in the rate of hydrogen produced. However, for higher molar concentrations, the rate of hydrogen produced shows exponentially increases.

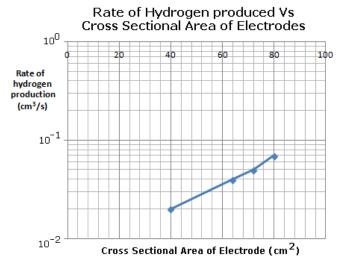


Figure 4: Rate of hydrogen production with different cross-sectional areas of electrodes

From the results shown in Fig. 4, the rate of hydrogen produced increases exponentially with increase of cross sectional area of the electrodes.

V. Discussion

In Fig. 3, the rate of hydrogen produced increases with increase of molar concentration of sodium hydroxide. With the increase of molar concentration, the quantity of OH ions will be increased. Hence, the average distance between ions decreases and the concentration of OH ions at the surface of the electrodes increase that will react easily with the surrounding ions of opposite charge. ^[2] Thus, it shortens the time of ion reaction with ions of the opposite charge. The consequence is increase probability of attachment lead to increase of rate of hydrogen produced.

From Fig. 4, the rate of hydrogen produced increases with increase of the cross sectional area of the electrode. With increase surface area, the amount of available aluminium atoms increases. Thus, it increases the chance of reaction. Consequently, the rate of hydrogen produced increases.

Hydrogen is produced at cathode of electrolysis system is shown in equation (1).

Cathode (reduction) [3]:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
 (1)

From this chemical reaction, it can explain how surface area affects the amount of hydrogen produced. Larger surface area of electrode provides higher chance of chemical reaction. There is more ions can be attached. Eventually more reactions are occurred. Thus, the amount of hydrogen produced increases.

Electrolysis is one of the critical processes of the whole electrical system whereby it produces the hydrogen. The rate of the hydrogen produced is primarily due to the chemical reaction between water and the electrode when electrical current is passed through it. The chemical process is shown in equation (2) [4] [5].

$$2Al + 6H2O \rightarrow 2Al(OH)3 + 2H2$$
 (2)

However, when sodium hydroxide is added into water, it acts as catalyst and electrolyte that increases the efficiency of the electrolysis. The chemical reaction is shown in equation (3) [4] [5].

$$2Al + 6H2O + NaOH \rightarrow 2NaAl(OH)4 + 3H2$$
(3)

From the equation (3), it is a redox reaction between cathode and anode of the electrolysis system. The negative ion in the solution, which is OH ion, loses electron to form a neutral species with aluminium forming aluminium hydroxide (Al(OH)₃). Two H ions in the electrolyte gains two electrons at the cathode to form hydrogen (H₂). Sodium hydroxide is added to increase the quantity of ions. Hence it decreases the average distance and travelling time for ions produced at the electrodes to encounter ion of the opposite charge [2] Consequently, the rate of hydrogen produced can be increased by adjusting the concentration of the sodium hydroxide and the surface area of the aluminium electrode.

The volume (V) of electrolyte between two electrodes is expressed in equation (4).

$$V = AxS (4)$$

where A is the cross sectional area of the electrode and S is the separation between the electrode respectively. The number of mole sodium hydroxide in this volume (V) is shown in equation (5).

Number of Mole of NaOH =
$$ASM$$
 (5)

where M is the molar concentration. The number of OH in volume (V) is governed by equation (6).

Number of
$$OH^-$$
 ion = $\frac{1}{2} \cdot ASMA_o$ (6)

where A_0 is the Avogadro number, which has value $6.02214x10^{23}$ atom/mole and 1/2 denotes half mole of NaOH is OH⁻ ion.

If one assumes 100% of OH ions are converted into hydrogen molecule (H₂), the number of hydrogen molecule can be produced in volume (V) is equal to

Number of
$$H_2 = \frac{1}{4} \cdot ASMA_o$$
 (7)

Half is used to denote that it needs two water molecules to produce one hydrogen molecule as shown in equation (1).

If the drift velocity of the OH^- ion is V_{drift} , then the mobility (μ) of OH^- ion is expressed by equation (8). [6]

$$\mu = \frac{V_{\text{drift}}}{E} \tag{8}$$

where E is the electric field across the electrodes, which is defined as V/S. V is the voltage across the electrodes and S is separation between electrodes.

The maximum time (t_{max}) taken for OH ion to travel from cathode to anode is equal to

$$t_{\text{max}} = \frac{S^2}{uV} \tag{9}$$

Since not all OH^- ions are at the extreme end of the electrode and for a more precise calculation of travelling time of ion, an average time (t_{avg})

is taken. It can be calculated with expression (10).

$$t_{avg} = \frac{1}{S} \int_{0}^{S} \frac{S^{2}}{\mu V} ds$$
 (10)

The maximum rate of hydrogen molecule produced per second (R_{H2}) can be calculated by taken equation (7) divided by equation (9), which yields equation (11).

$$R_{H2} = \frac{\frac{1}{4} \cdot AMA_{o}\mu V}{S}$$
 (11)

At normal atmospheric pressure and room temperature, based on ideal gas law, one molar of gas occupied 22.4 litres volume ^[7]. Therefore, the density of hydrogen is 2.6874x10¹⁹ molecules per cm³. The rate of hydrogen produced in cm³ per second is equal to expression (12).

$$R_{H2}/s = \frac{\frac{1}{4} \cdot AMA_o \mu V}{2.6874 \times 10^{19} S}$$
 (12)

Based on equation (3), the ratio of aluminium and water in the reaction is 1:3. A factor of 1/3 needs to be added to equation (12). The electrolysis system has three cathodes and three anodes connected in parallel. Thus, a factor of 3 has to be added to equation (12). As the consequence, the maximum rate of hydrogen produced remains as shown in equation (12).

With the considering factors which affect the theoretical maximum rate of hydrogen produced, equation (12) has to be modified to equation (13).

$$R_{H2}/s = \frac{\frac{1}{4} \cdot AMA_o \mu_n V \alpha PP_{site}}{2.6874 \times 10^{19} Sn}$$
 (13)

where A_0 is the Avogadro number, which is 6.02214 x 10^{23} per mole ^[8]. α is the mobility degradation factor, which is taken to be equal to 0.3 since the molar concentration of sodium hydroxide is higher than 10^{18}cm^{-3} . P and P_{site} are the probability of attachment of OH^- ion and the factional number of available OH^- ion to be attached on the surface of aluminium electrode. n is the number of mole of hydrogen.

Since the scattering is high, the probability P of attachment to form hydrogen is taken to be ranged from 10% to 50% for the mentioned molar concentrations. Fractional number P_{site} of available OH⁻ ion for attachment on the surface of aluminium electrode is calculated from equation (14).

$$P_{\text{site}} = \frac{\text{Surface density of Al electrode}}{\text{Surface density of OH}^{-} \text{ in NaOH}} (14)$$

The intrinsic mobility (μ) of OH⁻ ion is taken to be 209cm²/V-s. Since hydrogen is emitted in a confined volume, the number of mole of hydrogen produced is taken to be ranged from 1.00 to 1.05 for the mentioned molar concentration.

Based on equation (13), the theoretical rate of hydrogen produced is plotted together with the experimental rate of hydrogen produced for both experiments. The results are shown in Fig. 5 and Fig. 6 respectively.

Rate of Hydrogen Produced Vs Molar Concentration of NaOH

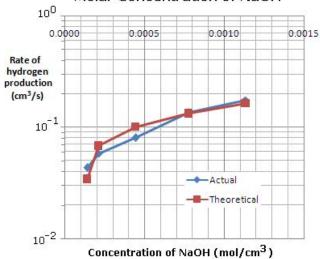


Figure 5: Theoretical and experimental results in different molar concentration of NaOH for a fixed 80cm² aluminium electrode

Rate of Hydrogen Produced Vs Cross Sectional Area of Electrode

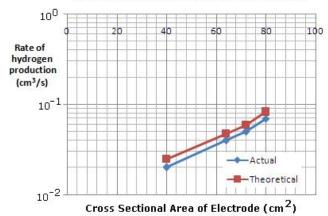


Figure 6: The theoretical and experimental results for different cross sectional area of electrodes with fixed molar concentration 0.0004mol/cm³

From the results shown in Fig. 5 and Fig. 6, it shows that the theoretical rate of hydrogen produced fits well with the experimental rate of hydrogen produced for both experiments.

Let's consider the factors be taken when calculating the theoretical rate of hydrogen produced. According to Ideal Gas Law, PV = nRT, the gas molecules do not interact with each other. All collisions between molecules or with the wall of the container are completely elastic, which means that the kinetic energy of the molecule remains unchanged and size of the gas molecule is small compared to the distance between them. [9] However, in this experiment, the condition is not ideal gas condition. This is because higher molar concentration and larger electrodes would produce more hydrogen molecule leads to higher pressure in a confined volume. Thus, the number mole (n) of hydrogen molecule produced has to be adjusted according to the pressure in the confined container. n is taken to be ranged from 1.00 to 1.05 for the mentioned molar concentration.

In ideal case, no matter what is the molar concentration of sodium hydroxide, the OH ion will be 100% convert to the hydrogen. However, in the real case, it is not achievable. It is a fact that when the concentration is getting higher, the chance of the OH ion to be converted into the hydrogen will be higher. However, at extreme high molar concentration condition, the conversion rate will not be further increased. It is because surface area of electrode is fixed and the probability of attachment has attained its maximum value.

In this electrolysis system, aluminium is used as electrode. For different cross sectional area of the electrode, the number of atom available on the surface is different that can be calculated with known lattice constant of aluminium. The number of atoms on the surface of electrode is also the available site for the attachment of OH ion to undergo the chemical reaction and be converted to hydrogen. In this

case, increase of molar concentration until a certain optimum level will not increase the conversion to hydrogen. This is due to the number of available site for the reaction of OH⁻ ion is fixed. No matter how much of OH⁻ ion is present. It cannot undergo further conversion.

The mobility of OH ion is affected by molar concentration of sodium hydroxide. The higher the molar concentration, the higher will be the scattering. Thus, the degradation factor (α) of 0.3 is added to reflect the effect of scattering since the concentration is higher than 10^{18}cm^{-3} .

VI. Conclusion

In conclusion, with the consideration of measurement error is small, the theoretical derivation of an expression as stated in equation (13) is able to fit the experimental results of the sodium hydroxide-aluminium electrolysis system well that is used to produce hydrogen as the fuel for hydrogen fuel cell electrical system.

VII. Reference

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