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HIGH PERFORMANCE PLASMA ELECTROLYSIS REACTOR FOR HYDROGEN GENERATION USING A NaOH-METHANOL SOLUTION

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ABSTRACT

In the plasma electrolysis process, hydrogen generation around the cathode is affected by the amount of evaporation energy. Utilizing a veil, minimizing the cooling in the liquid phase, and maximizing the cooling in the gas phase become important parameters to improve the process efficiency of hydrogen production. This research aims to obtain an optimum high-efficiency electrolysis plasma reactor based on decreased energy consumption and increased hydrogen gas production. The research method varied the NaOH concentration, voltage, veil length, cathode depth, and the volume of the methanol additive. In characterizing the current and voltage, as the concentration increases, the voltage needed to form the plasma will decrease. As the concentration and voltage increase, the rate of production, hydrogen content percentage, and the hydrogen ratio also increase, while the energy consumption decreases. The optimum condition, based on variations of veil length, is 5 cm when the depth of the cathode is 1 cm below the surface of the solution. Improving the efficiency of the hydrogen production process can be done by adding methanol. The best result was achieved using 15% volumes of methanol additive in 0.01 M NaOH, and higher hydrogen-ratio plasma-electrolysis results were found in comparison with Faraday electrolysis: the hydrogen ratio was 151.88 mol/mol, the lowest energy consumption was 0.89 kJ/mmol, and the highest hydrogen production rate was 31.45 mmol/min. The results show that this method can produce hydrogen 152 times more than Faraday electrolysis.

Keywords: Electrolysis plasma reactor; Energy consumption; Hydrogen generation

1. INTRODUCTION

CO_2 emissions in the atmosphere have increased because of the utilization of fossil fuels as the main non-renewable energy source. The increase in atmosphere temperature and the extreme climate change in the past 100 years have encouraged the search for clean and environmentally friendly renewable energy sources. These days, leading nations, in particular the United States, have been developing infrastructure for utilizing hydrogen as the energy source for fuel cells on vehicles (U.S. Department of Energy, 2007).

The formation of hydrogen and oxygen from water via the electrolysis process has been commercialized since 1890. A commercial electrolyzer can today reach up to 73% system efficiency with an energy consumption of 753.4 kWh/kg H_2 at 1 atm and 25°C (Turner et al., 2008). The hydrogen production cost from water electrolysis is more expensive than the conventional process that uses hydrocarbon as the source material.

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The plasma electrolysis is the electrolysis process with a high enough voltage to form the electric spark and produce the plasma on the electrolyte solution. The plasma will produce a large amount of reactive species that can increase the bond breaking in the water so that it increases the formation of hydrogen and oxygen several times more than the Faraday electrolysis process (Mizuno et al., 2005). This method was developed just five years ago, so there are still many issues with the reaction process that have not been solved. The main problem in the development of plasma electrolysis technology is the selection of the electrode, the solution, the additional material, the additive in the solution, and the reactor's coolant system.

In this research, a non-thermal plasma electrolysis process is designed, and it includes the plasma generator which can produce DC voltage up to 700 V and the plasma electrolysis reactor, which provides the cooling system. The addition of methanol as an additive in the electrolyte solution in this research is predicted to increase the hydrogen productivity.

2. EXPERIMENTAL SETUP

This research has been developed based on prior studies that investigated the potential of plasma technology in the conversion of a methanol solution to hydrogen using non-thermal plasma electrolysis via a glow discharge plasma model reactor, which has proven to be more effective for producing hydrogen. The flow diagram can be seen in Figure 1.

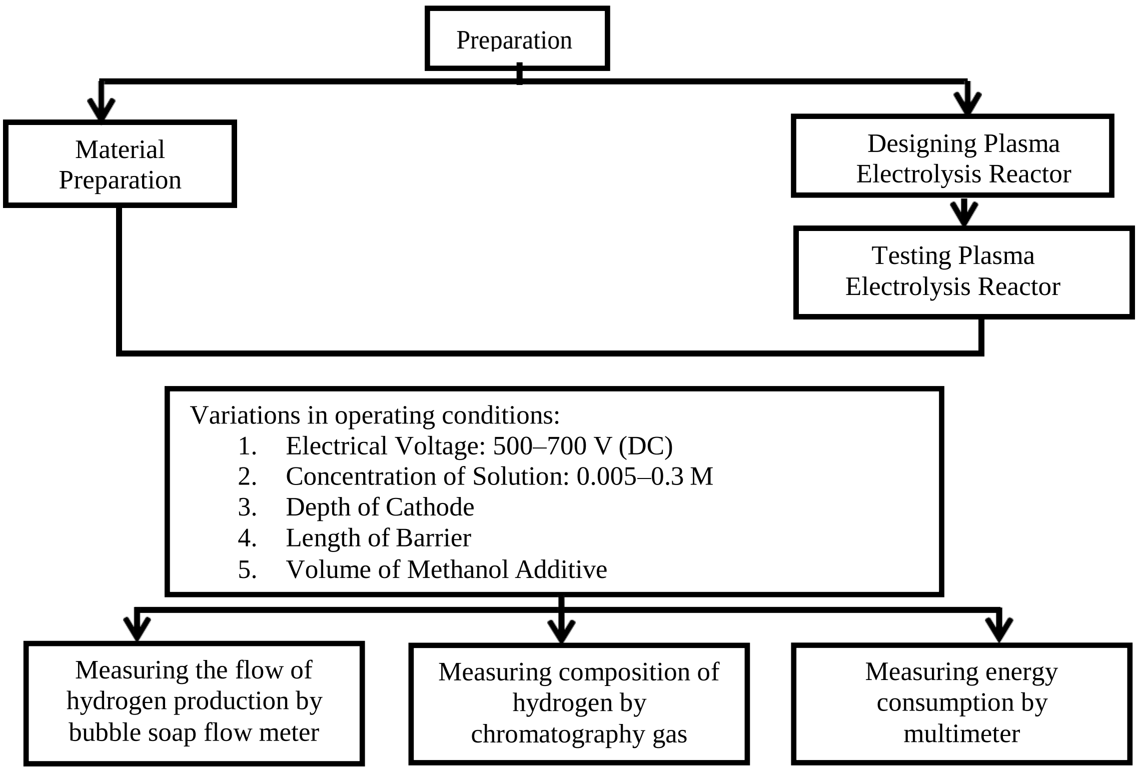

Figure 1 Experimental flow diagram

2.1. Data Processing of Equipment Test Results in Hydrogen Production System

The independent variables in this research are the voltage and the concentration of the NaOH solution. The dependent variables are the electrical current, the amount of mole hydrogen in comparison with the conventional electrolysis produced by the Faraday Law, and the electrical energy consumption in the process for hydrogen production.

1. The electric power is the power needed to convert electrical energy into heat and kinetic energy. The calculation of the electric power during the plasma electrolysis process is as follows:

$$P\left(W\ atau\frac{J}{s}\right) = V(volt) \times I(ampere) \tag{1}$$

2. The calculation of the consumed energy during electrolysis process is done using the following equation (Yan et al., 2008):

$$Wr\left(\frac{kJ}{mmol}\right) = \frac{V.Q}{V_{gas}} \tag{2}$$

3. The calculation of the hydrogen gas flow is as follows:

$$\eta_{hidrogen} = \frac{V_{gas}.Komposisi\ H_2.X}{22{,}4} \tag{3}$$

V_{gas} = production flow
X = 1 (comparison of the coefficient of the hydrogen to the total gas product)

4. $G(H_2)$ is the comparison of the mole number of the hydrogen product in the experimental results of the plasma electrolysis process with the theoretical mole number of the hydrogen product based on the Faraday electrolysis Equation 4.

$$G(H_2) = \frac{V_{gas}\frac{mL}{s}/22{,}4}{Q/2F} \tag{4}$$

F = 96500 c/mol

3. RESULTS AND DISCUSSION

The plasma electrolysis phenomena can be explained by the characterization of the current and voltage with varying concentrations of NaOH. While the current and voltage relationship is proportional, the process is still going on electrolysis zone which means that high energy consumption is needed to produce greater percentage of hydrogen. At a point called breakdown voltage, when the voltage is further increased, the current begins to drop and fluctuate, which is followed by the appearance of plasma. This indicates that it begins to enter the plasma electrolysis zone, where the current decreases when the voltage increases, so the plasma electrolysis process will be more efficient in terms of energy consumption when compared to the electrolysis process. The results of the current characterization in this experiment can be seen in the current-voltage curve, as shown in Figure 2.

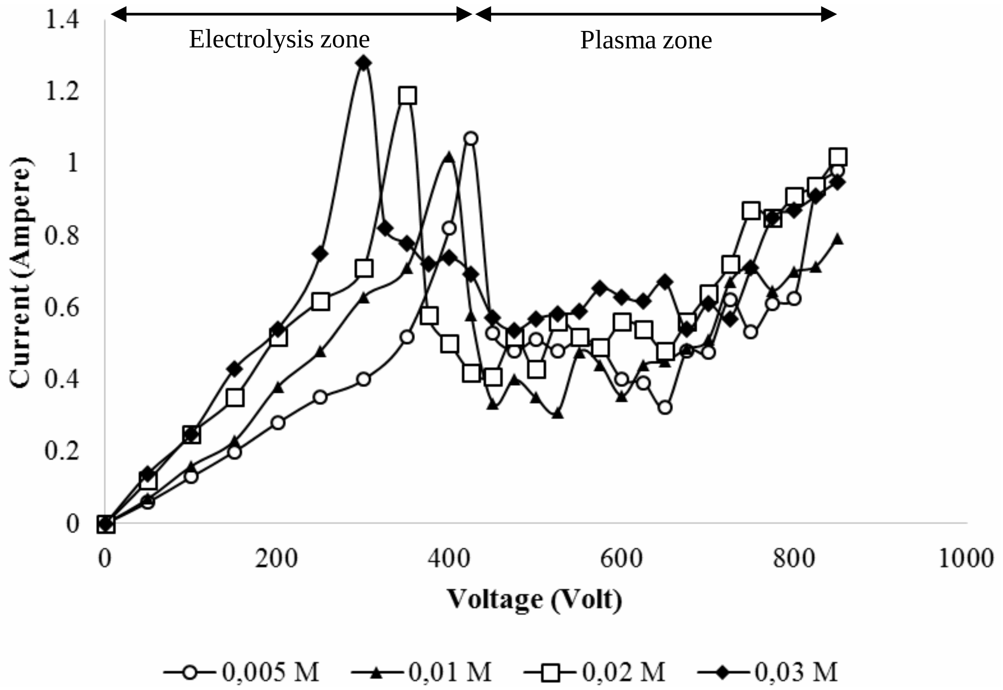

Figure 2 Characterization of current and voltage by varying concentrations of NaOH

Figure 2 is divided into two zones: the electrolysis zone and the plasma zone. The electrolysis zone is characterized by increased electrical current with increased voltage. In this electrolysis zone, the plasma has not appeared, but there is a little bubble around the cathode, which is also known as the Ohmic region. The plasma zone begins when the current reaches a maximum value, which is then followed by a decrease in the current until it reaches a critical point. The decrease in the current after reaching the maximum value occurs because of the obstruction of positive ions toward the cathode due to the formation of gas bubbles that cover the cathode (Saksono et al., 2012). In this condition, the radicals in the solution will be excited, which leads to the appearance of glowing plasma. In addition, the plasma zone occurs as a result of energy-scattering collisions between electric charges and saturated gas. This increases the temperature around the cathode, thereby triggering increased electrical resistance that leads to the decline in the current.

3.1. Effect of Voltage and Solution Concentration on Hydrogen Gas Production and Energy Consumption

Voltage is an important parameter in plasma electrolysis. The plasma electrolytic process requires a high enough voltage to form plasma in the solution. The plasma will not form when the voltage is below the critical voltage, and the ongoing process is the process of Faraday electrolysis with redox (reduction-oxidation). Increasing the voltage will increase the thickness of the layer of gas, which can increase the volume of plasma in the plasma electrolysis process (Yan et al., 2009). The effect of this voltage was examined using a veil length of 5 cm and a cathode depth of 1 cm (below the surface of the solution) with various concentrations. Figure 3 proves that at the same concentration, the higher the voltage, the greater the increase in hydrogen gas production. This condition occurs because as the voltage increases, the electron density will also increase, which leads to a higher excitation process, so the hydrogen gas production will increase. According to Mizuno (Mizuno et al., 2005), the voltage change will affect the ratio of H_2 and O_2, so when the voltage is increased, it will also increase the ratio of H_2 and O_2 as the time increases.

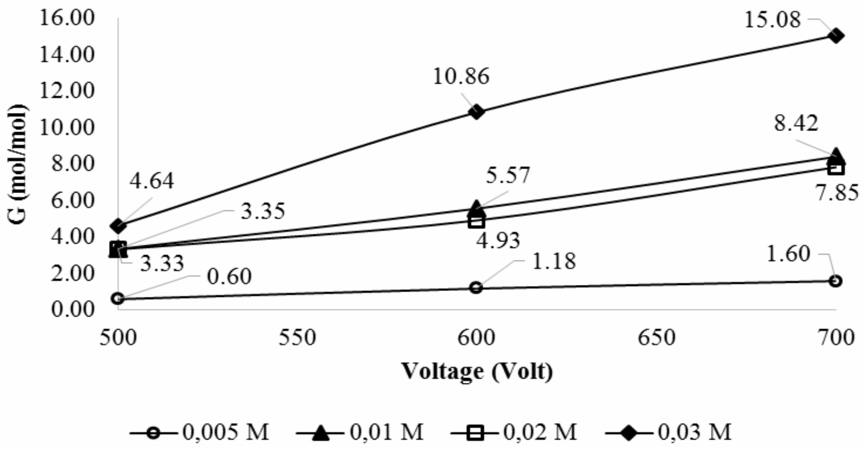

Figure 3 Effect of voltage variation on the value of G (H_2) at each concentration of NaOH using a veil length of 5 cm and a cathode depth of 1 cm

In the plasma zone, the higher the voltage, the higher the electron excitation energy that produces radicals (Saksono et al., 2016). The conversion of electrical energy into heat energy causes the solution around the cathode evaporate and form a gas veil. The formation of gas veil will trigger the excitation electrons. This excitation can lead ion radicalization that causes appearing of plasma. Plasma stability is affected by the Joule heating effect: the higher the voltage, the more energy is produced, which means that the hydrogen gas production also increases.

Table 1 Wr data on voltage variations and NaOH concentrations using a veil length of 5 cm and a cathode depth of 1 cm

NaOH Concentration (M)	Wr (kJ/mmol)		
	500 V	600 V	700 V
0.005	161.34	98.04	84.56
0.010	28.77	20.78	16.05
0.020	28.94	23.50	17.21
0.030	20.80	10.66	8.96

In the plasma electrolysis, the increase of voltage also affects the efficiency of energy consumption. In Table 1, the declining value of Wr with the increasing voltage indicates a decrease in the ratio of electrical energy used for every liter of hydrogen gas produced. While the resulting current increases with the voltage, the rate of hydrogen production also increases, which causes the ratio of electrical energy used for every liter of hydrogen gas will decrease because the value of Wr to the production rate of hydrogen is inversely proportional.

3.2. Effect of Veil Length to Hydrogen Gas Production and Energy Consumption

The utilization of a veil made from acrylic glass can reduce the space that needs to be heated so that the formation of plasma will be stable. Using a veil around the cathode improves the process forming the gas veil, so the formation of plasma will also be stable. The formation of stable plasma will have an impact on the hydrogen gas production rate. The rate of production will have an effect on the ratio of G (H_2). The greater the hydrogen gas production rate, the lower the current, so the G (H_2) value will be even greater. This can be seen in Table 2.

Based on Table 2, at a concentration of 0.03 M NaOH, with a voltage of 700 V and a cathode depth of 1 cm, the optimum result is obtained when using a veil with a length of 5 cm; with a production rate of hydrogen gas for 15 minutes (i.e., 2.75 mmol/min), the average current is 0.58 A, the energy consumption is 8.82 kJ/mol, and the mole ratio of hydrogen production is 15.33 mol/mol. It means the mole ratio of hydrogen production from plasma electrolysis process is 15.33 more times compared to Faraday electrolysis process. Optimum results can be categorized because of the high hydrogen gas production rate, G (H_2), and low energy consumption.

Table 2 Variation of veil length using 0.03 M NaOH

Veil length (cm)	Current (Ampere)	Production rate of hydrogen gas (mmol/minute)	Composition (%)	$G(H_2)$ (mol/mol)	Power (J/s)	Energy = Wr (kJ/mmol)
Without	0.60	1.72	20.95	9.21	420.7	14.66
5	0.58	2.75	27.71	15.33	403.9	8.82
8	0.57	2.48	27.43	14.06	397.6	9.61
12	0.55	2.02	24.02	11.85	384.3	11.40

In Table 2, it can be seen that the longer the veil length (the electron path will also grow longer), the higher the impact of resistance. The greater the resistance, the lower the current that is generated, so the power that is used will also be lower. However, energy consumption will be more efficient when using the shortest length of veil. The loss of energy to the environment can be minimized by using a veil, which means that the energy required will decrease. Thus, utilization of the veil can help localize the heat generated by the plasma formation in the cathode and reduce energy consumption. It can be concluded that the best conditions for producing hydrogen gas with lower energy can be achieved using the shortest veil, which is 5 cm.

3.3. Effect of Cathode Depth to Hydrogen Gas Production and Energy Consumption

The deeper the cathode, the greater the generation of current. This condition occurs because the contact surface area between the cathode and the solution affects the movement of the electrons to the cathode. At a cathode depth of 0.5 cm below the surface solution, the contact area between the cathode and the solution decreases, so the movement of electrons toward the cathode is decreased than the deeper cathode. However, in terms of energy consumption, the shallower cathode depth has lower energy consumption than the deeper cathode. This is due to the deeper the cathode, the more energy is needed to continue forming the gas veil. The energy is needed to maintain the hydrostatic pressure from the electrolyte solution, whereby the deeper the cathode, the greater the hydrostatic pressure.

Figure 4 shows the energy consumption (Wr) at the lowest cathode depth of 1 cm below the surface of the solution. This condition occurs because the power required is low enough and it has the highest hydrogen production rate. In terms of the mole ratio for the hydrogen gas produced in the electrolysis plasma experiment with the Faraday equation, the highest value of G (H_2), when the cathode depth was 1 cm below the surface of the solution, was 15.32 mol/mol. At a cathode depth of 2 cm, the current generated increased, but this was not followed by an increase in the production of hydrogen gas in terms of both the production rate and the value of G (H_2). This shows that at a cathode depth of 2 cm, electrolysis is the dominant zone and this leads to the formation of unstable plasma. It can be concluded that the optimum condition is a cathode depth of 1 cm, as this has the highest hydrogen production rate and G (H_2) and the lowest energy consumption (Wr). The effect of cathode depth on the hydrogen production and energy consumption can be seen in the chart below.

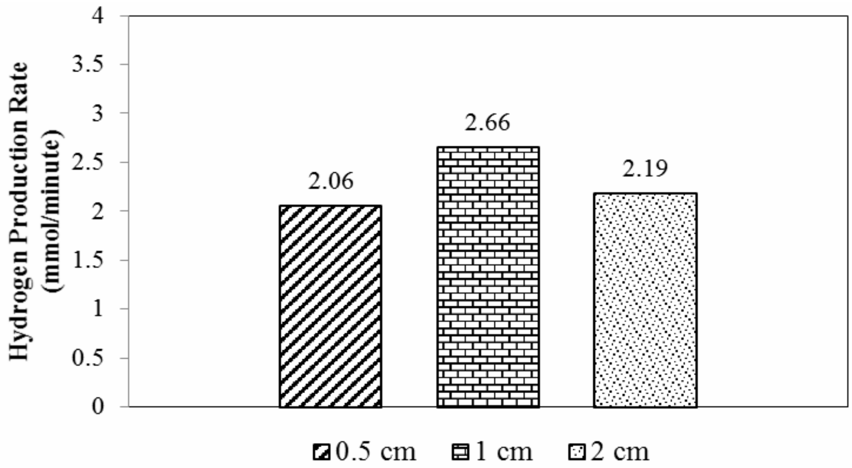

Figure 4 The effect of variations in the cathode depth on the hydrogen production rate with 0.03 M NaOH, 700 V, and a 5 cm veil length

3.4. Effect of the % Volume of Methanol Additive on Hydrogen Gas Production and Energy Consumption

The addition of the methanol additive aims to improve hydrogen production because methanol can contribute active species, such as •OH and H•, which can lead to bonds breaking in water decomposition (Yan et al., 2008). Yan et al (2008), using a methanol solution of 99.5% mole (equivalent to a volume of 97.8%) and NaOH as the electrolyte, produced a ratio of H_2 moles up to 2300 times greater than the H_2 produced by Faraday's law. Methanol concentration in the solution can increase the concentration of water in the surrounding gas veil. High energy electrons will break the bond between hydrogen and oxygen in the water to produce hydrogen gas. In terms of the value of G (H_2), at the same voltage, the greater the % volume of additive methanol, the greater the value of G (H_2). The addition of 15% volume methanol in 0.01 M NaOH with a voltage of 700 V can reach 151.88 mol/mol of G (H_2). It means the mole ratio of hydrogen production from plasma electrolysis is 151.88 more times compared to Faraday electrolysis. The results for the variation of the % volume of methanol and voltage can be seen in Table 3 and Table 4. Based on the variation of the % volume of methanol, the best results were obtained with an additive of 15% volume methanol in 0.01 M NaOH solution with a voltage of 700 V, as the value of G (H_2) reached 151.88 mol/mol and the Wr was 0.89 kJ/mol.

Figure 5 Visualization of glowing plasma with variations in the % volume methanol: (a) 5% volume; (b) 10% volume; and (c) 15% volume with 0.01 M NaOH solution, 700 V, a veil length of 5 cm and a cathode depth of 1 cm

Based on Figure 5, the diameter of the plasma increases with an increase in the % volume of methanol. The larger the diameter of the plasma, the greater the decomposition of the compound into active radicals and ion species that trigger hydrogen gas formation. With the increases in the volume of methanol, more active species of •OH and H• are formed, which trigger the formation of hydrogen gas; this can be seen as the mechanism of hydrogen gas formation from methanol.

Table 3 Effect of variations in the % volume of methanol and the voltage on the hydrogen gas production rate with 0.01 M NaOH, a veil length of 5 cm, and a cathode depth of 1 cm

%Volume	H_2 Gas Production Rate (mmol/minute)		
Methanol	500V	600V	700V
0	0.50	1.05	1.68
5	10.78	11.72	12.95
10	16.28	21.02	24.60
15	19.62	24.54	31.45

Table 4 Effect of variations of the % volume methanol and the voltage on the G (H_2) with 0.01 M NaOH, a veil length of 5 cm, and a cathode depth of 1 cm

%Volume	G (H_2) (mol/mol)		
Methanol	500V	600V	700V
0	3.35	5.57	8.42
5	62.39	64.77	63.30
10	93.54	111.78	119.71
15	107.39	129.20	151.88

4. CONCLUSION

This research has successfully made a plasma electrolysis reactor that is able to produce hydrogen with high efficiency. The utilization of a veil localizes the heat produced by the cathode in plasma generation, which increases the hydrogen production. The best energy consumption was 0.89 kJ/mmol of hydrogen, which is up to 152 times more than the Faraday electrolysis process in the same reactor configuration.

5. ACKNOWLEDGEMENT

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6. REFERENCES

Mizuno, T., Akimoto, T., Ohmori, T., 2005. Confirmation of Anomalous Hydrogen Generation by Plasma Electrolysis. *In*: 4th Meeting of Japan CF Research Society. Iwate, Japan: Iwate University

Saksono, N., Ariawan, B., Bismo, S., 2012. Hydrogen Productions System using Non-thermal Plasma Electrolysis in Glycerol-KOH Solution. *International Journal of Technology*, Volume 1, pp. 8–15

Saksono, N., Nugraha, I., Ibrahim, Febiyanti, I., 2016. Hydroxyl Radical Production on Contact Glow Discharge Electrolysis for Degradation of Linear Alkylbenzene Sulfonate. *Environmental Progress & Sustainable Energy*, Volume 35(4), pp. 962–968

Turner, J., Sverdrup, G., Mann, M.K., Maness, P.-C., Kroposki, B., Ghirardi, M., Evans, R.J., Lake, D., 2008. Renewable Hydrogen Production. *International Journal of Hydrogen Energy*, Volume 32, pp. 379–407

U.S. Department of Energy, 2007. *Fuel Cells and Hydrogen Infrastructure Technologies Program*. Multi-Year Research, Development and Demonstration Plan, U.S. Department of Energy

Yan, Z.C., Li, C., Wang, H.L., 2008. Hydrogen Generation by Glow Discharge Plasma Electrolysis of Ethanol Solutions. *J. Phys. D: Appl. Phys.*, Volume 41, pp. 1–7

Yan, Z.C., Li, C., Wang, H.L., 2009. Hydrogen Generation by Glow Discharge Plasma Electrolysis of Methanol Solutions. *International Journal of Hydrogen Energy*, Volume 34, pp. 48–55