

## Effect of Operating Parameter on H<sub>2</sub>/CO<sub>2</sub> Gas Separation using Electrochemical Cell

Fung Yun Ru<sup>1</sup>, Nurul Noramelya Zulkefli<sup>2</sup>, Nur Yusra Mt Yusuf<sup>3</sup> and Mohd Shahbudin Masdar<sup>4,\*</sup>

<sup>1,2,3,4</sup> Department of Chemical and process engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.

\*Corresponding author

<sup>4</sup>Orcid: 0000-0001-5714-7415

### Abstract

Hydrogen (H<sub>2</sub>) gas produce from biological process also contains impurity gases. In order to enhance the H<sub>2</sub> production, the biohydrogen undergoes a purification techniques as electrochemical method which known as polymer electrolyte membrane (PEM). By applying direct current to the (PEM), protons are moved across membrane from anode to cathode. The selectively transportation of protons across the membrane enable the separation of H<sub>2</sub> from the impurity. In this investigation, the effects of electric current (0 – 2.5A), feed flow rate (90 mL/min – 300 mL/min) and temperature (25°C and 50°C) had studied and the optimum operating conditions are determined. The gas mixture H<sub>2</sub>/CO<sub>2</sub> with composition 50 vol.%: 50 vol.% at pressure 1 atm had fed into the anode side of the H<sub>2</sub> electrochemical purifier. Purity of H<sub>2</sub> gas is determined from the concentration of carbon dioxide (CO<sub>2</sub>) at cathode that measured by CO<sub>2</sub> analyser. The purity of gas and recovery is at the maximum value 93.62% and 60.45% when current, *I*, equal to 2.5A. Yet, performance of purification process is decreasing with the rise of amount of feed flow rate. The purity and the recovery of H<sub>2</sub> gas are higher, 93.36% and 75.83%, respectively at 90 mL/min. Moreover, at 50°C the purity of H<sub>2</sub> gas is higher compared to 25°C which increased from 93.32% to 96.27%. However, the highest H<sub>2</sub> flux at 0.429 mL/min·cm<sup>2</sup> occur at temperature of 25°C instead of 50°C. The relatively simple electrochemical method in purification process had preferred as required less energy and able to produce H<sub>2</sub> gas with high purity (> 90%). This is very important for the fuel cell application because fuel cell require continuous supply of high purity H<sub>2</sub> to function orderly.

**Keywords:** Gas purification, biohydrogen, electrochemical cell and PEM.

### INTRODUCTION

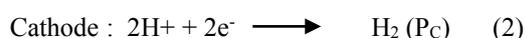
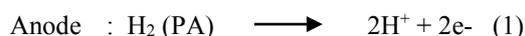
Biohydrogen produced from biomass fermentation contains two types of product which are major product (H<sub>2</sub> and CO<sub>2</sub>), and minor products (carbon monoxide (CO), hydrogen sulphide (H<sub>2</sub>S) and methane (CH<sub>4</sub>)) [1,2]. The minor product also known as impurities. The CO and H<sub>2</sub>S from the impurity gases cause poisoning of Pt catalyst, which degrades the efficiency of fuel cell [3].

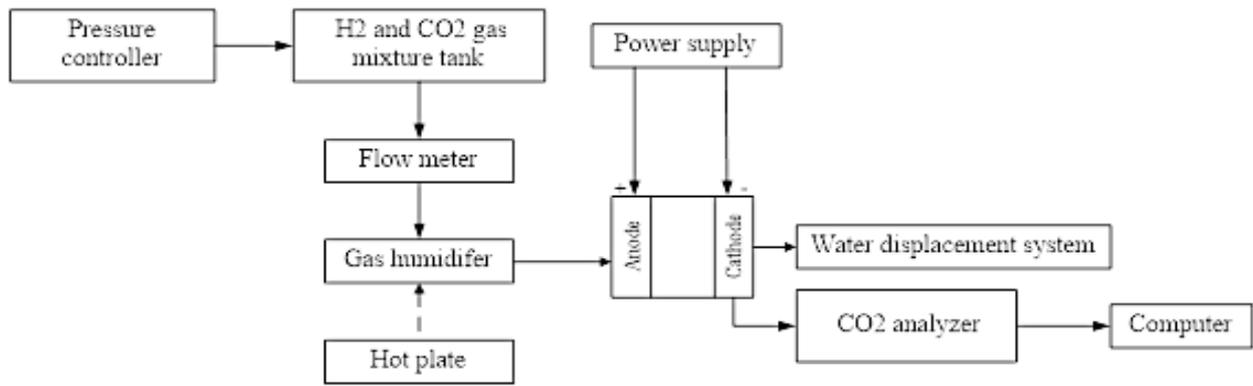
Moreover, the H<sub>2</sub> gas have high energy density source. This trait makes it a promising fuel source to be used within internal combustion engine. H<sub>2</sub> produces energy of 122kJ/kg which had potential to substitute hydrocarbon fuel. In order to generate electricity, the H<sub>2</sub> implemented into fuel cell [1]. However, the side product produce was water only which proved the H<sub>2</sub> gas are green energy source. Hence, purification technologies of H<sub>2</sub> gas had developed.

There are a few existing methods to purify H<sub>2</sub>, which are pressure swing absorption (PSA), absorption, cryogenic and electrochemical method [5, 7]. From the comparison above, PSA, absorption and cryogenic are challenging to implement. PSA and cryogenic are both energy intensive, which reduces their deployment flexibility. Besides, PSA, absorption and cryogenic technique have extreme operational temperature which requires as low as -80°C during the purification process [5].

In contrary, the mechanism of electrochemical method is simple and efficient. Electrochemical method consumes very low energy as low as 1V during its operation [6]. Despite having advantages during operation, it requires further optimization until commercially ready. Electrochemical hydrogen purifier, which also known as electrochemical hydrogen pump is the key component in electrochemical method [7]. Electrochemical hydrogen purifier is designed to perform electrolysis. Hence, electrical current is supplied to the purifier.

During the purification, gas mixture of H<sub>2</sub> and CO<sub>2</sub> is inserted at the anode end at low pressure (PA). Pt catalyst within the electrochemical hydrogen purifier will separate H<sub>2</sub> to proton (H<sup>+</sup>) and electrons. Then, proton (H<sup>+</sup>) is transported through PEM selectively from anode to cathode, while electron flows through the external circuit. In the end, electron will rejoin H<sup>+</sup> and H<sub>2</sub> gas is formed at the cathode [8].





**Figure 1.** Schematic diagram of experiment setup.

According to Fig. 1, the hydrogen recovery fraction of electrochemical can peak at 90%. However, it drops significantly below 60% when the feed flow rate of gas mixture increases [9]. In order to make this technique to be commercially ready, the recovery fraction of hydrogen must be consistently high to ensure continuous delivery of H<sub>2</sub> gas to fuel cells. The performance of electrochemical hydrogen purifier correlates to its operational parameters. Hence, limiting rate analysis can be done to optimize its operational parameters.

Most of the researches focus on a few parameters, which are the types of membrane used, thickness of membrane, humidity problem of membrane, as well as temperature, gas composition, electric current and voltage, while flow rate of gas mixture and pressure are less concerned.

Thus, this research optimizes a few operational parameters of H<sub>2</sub> purification in room temperature. Not only the optimum electrical current and voltage, but the optimum gas mixture flow rate and pressure will be identified as well in the end of this study. Finally, the relationship between electrical current, voltage, gas mixture flow rate and gas mixture pressure will be discussed further.

## EXPERIMENTAL

### A. Electrochemical Cell

The electrochemical cell consists of MEA, gasket, anode, cathode, bipolar plates and end plates. The size of the electrochemical cell used was 14 cm (H) x 10 cm (L) x 3.3 cm (W). The MEA chosen was Nafion®117 with an active area 32 cm<sup>2</sup> and 0.183 mm. This structure ensures the stability of Nafion in the process of oxidation and reduction for a long time [7]. Both anode and cathode loading 5 mg/cm<sup>3</sup> catalyst of platinum-ruthenium, Pt/Ru and Pt/C, respectively. The anode is fed with the gas mixture H<sub>2</sub>/CO<sub>2</sub> with composition 50 vol. % :50 vol. %. All experiment will be conducted for one hour.

### B. Electrochemical Cell Operation

The important of the experimental work were to investigate the effect of electrical power on the H<sub>2</sub> purification process and to study the influence of feed flow rate with operating

temperature on the performance of electrochemical cell. Figure 1 shows the schematic diagram of experiment setup. Whereas, Figure 2 indicate the real application set up. Gas mixture H<sub>2</sub>/CO<sub>2</sub> with composition 50 vol. % :50 vol. % is fed into the Büchner flask. Büchner flask is filled with distilled water and known as gas humidifier. Then the gas humidifier had fed to the anode of electrochemical cell. Then, the operating temperature parameter for gas mixture H<sub>2</sub>/CO<sub>2</sub> in the humidifier varied by heated the gas with hot plate. The power supply switch on and the reaction occurred to separate the H<sub>2</sub> gas from CO<sub>2</sub> gas. The CO<sub>2</sub> analyser connected to the cathode. The CO<sub>2</sub> analyzer used to measure the change of concentration of CO<sub>2</sub> gas with time in the duration of 30 minutes. Data for the concentration of CO<sub>2</sub> gas recorded automatically in graph form by using the computer. Then, the cathode connected to the water displacement system for 30 minutes to measure the volume of gas discharged from the cathode.

The gas mixture had fixed to feed at 90 mL/min for effect of different operating current. The operating conditions was at ambient temperature (25°C) and pressure (1atm). In this study, the galvanostatic mode had used to operate the H<sub>2</sub> electrochemical purifier for measured the cell voltage. Then, the current varies between 0.0A to 2.5A. The concentration of CO<sub>2</sub> gas contained in the cathode stream measured by using CO<sub>2</sub> analyser. Recovery of each applied current had determined by the volume of H<sub>2</sub> gas produced for 30 mins collected using water displacement method.

The effect of different flow rate had investigated by varied the value of feed flow rate in the range of 90 mL/min to 300 mL/min. The operating current then fixed at 2.5A. After all, the concentration of CO<sub>2</sub> gas contained in the cathode stream measured by using CO<sub>2</sub> analyser. Then, the recovery of each applied current determined by the volume of H<sub>2</sub> gas produced for 30 mins by collected using water displacement method.

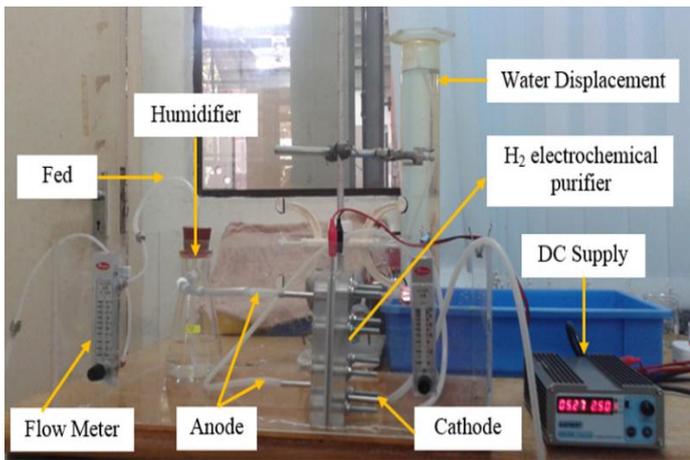


Figure 2. Actual photo for an experiment setup

The effect of different temperature had been studied in this research. The optimum operating voltage and flow rate that obtained from previous study are used in this experiment. The temperature varies between 25°C and 50°C. The concentration of CO<sub>2</sub> gas in a function of current had measured. Next, the recovery of each applied current had investigated by the volume of H<sub>2</sub> gas produced for 30 mins collected from water displacement method.

C. Measuring the Purity, Recovery and Flux of H<sub>2</sub>

The change of concentration of CO<sub>2</sub> gas with time had measured and plotted in a curve. The purity of H<sub>2</sub> gas had assumed as the concentration of H<sub>2</sub> gas discharged at the cathode. Therefore, the purity of H<sub>2</sub> in this study calculated based on the equation below:

$$\text{Purity of H}_2 \text{ gas} = 100\% - \text{Concentration of CO}_2 \text{ (\%)} \quad (4)$$

The recovery defined as the ratio of recovered H<sub>2</sub> gas, H<sub>R</sub> to the amount of H<sub>2</sub> gas fed, H<sub>F</sub>. However, the recovery of gas H<sub>2</sub> was depending on the volume of gas discharged and the purity of H<sub>2</sub> gas available at cathode side.

$$\text{Recovery of H}_2 \text{ gas} = \frac{H_R}{H_F}$$

$$\text{Where, } H_F = \frac{(\text{Purity of H}_2 \text{ gas}) \times \text{Feed flow rate}}{100} \quad (5)$$

$$H_R = \frac{(\text{Purity of H}_2 \text{ gas}) \times \text{Outlet flow rate}}{100} \quad (6)$$

$$\text{Outlet flow rate} = \frac{\text{Initial olume of water} - \text{Final volume of water}}{30 \text{ minit}} \quad (7)$$

The theoretical H<sub>2</sub> gas product was a function of current density only. By assuming H<sub>2</sub> gas as ideal gas, where the molar volume equal to 24.465 L/mole, the formula then derived further in order to obtain the value of H<sub>2</sub> gas flux.

$$\text{Flux of H}_2 \text{ gas (theoretical)} = \frac{i}{2F} \times \frac{24.465 \text{ L}}{1 \text{ mol}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{60 \text{ s}}{1 \text{ min}} \quad (8)$$

RESULTS AND DISCUSSION

A. Effect of Current Supply

The cell voltage is a driving force of the system. Whereas, the current density refers to the rate of H<sub>2</sub> gas production at the cathode. Therefore, in the galvanostatic operating mode, the current density had assigned. While, the cell voltage had measured.

Figure 3 indicates the graph of concentration of gas CO<sub>2</sub> versus time at different applied current. Current varied between 0.0A – 2.5A. The concentration of CO<sub>2</sub> gas was constant at the initial stage. After that, the concentration of CO<sub>2</sub> gas increased and reach a constant value. Nonetheless, the time to reach the constant value varied for each applied current. For an instance, for current, I = 0.5A, the time required for the CO<sub>2</sub> gas to reach the constant value was after 25 minutes; for current, I = 1.0A, then, the time required was 15 minutes; for current, I = 2.0A and I = 2.5A, the time required was only 12 minutes. From the figure, CO<sub>2</sub> notable as high concentration, 25.42% in the product stream when there is no current supplied (0.0A). Hence, the flux of CO<sub>2</sub> across the membrane and also reduce the performance of separation [8]. Generally, the concentration of CO<sub>2</sub> gas contained in the discharge from cathode decrease with the increasing of applied current.

Figure 4 shows the concentration of CO<sub>2</sub> gas and purity of gas H<sub>2</sub> versus applied current. The purity of gas H<sub>2</sub> increases with the applied current. The highest purity of gas H<sub>2</sub>, 93.62% occurs at current 2.5A. The purity of gas H<sub>2</sub> had been improved for 26% from 74.585% at 0.0A. The increasing trend was due to the H<sub>2</sub> oxidation reaction at anode. As the electric current increase, the oxidation rate also raised, hence, the protons flux that pass through the membrane enhanced by increasing the applied current. At the same time, gas CO<sub>2</sub> which is the impurity penetrate through the membrane without any changes.

Figure 5, illustrates the changes of recovery against applied current. The recovery of gas H<sub>2</sub> increases when the value of applied current increased. This can be explained as the applied current represent the rate of production. Consequently, when the applied current rise in the value, more protons drove through the membrane and boost the recovery of gas H<sub>2</sub> from the cathode.

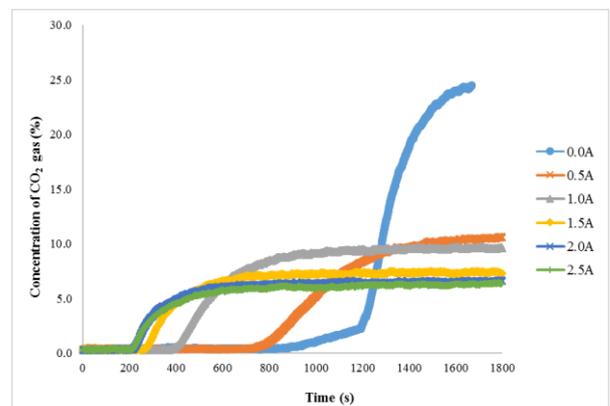


Figure 3. Concentration of gas CO<sub>2</sub> versus time at different applied current

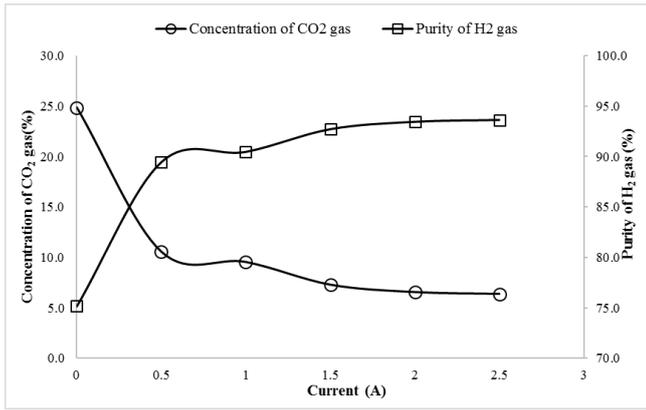


Figure 4. H<sub>2</sub> gas purity at different applied current to the cell

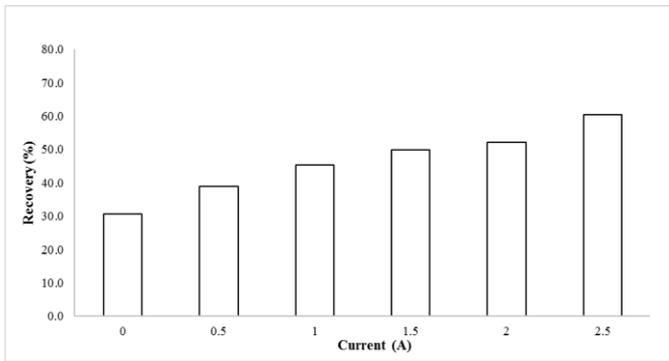


Figure 5. H<sub>2</sub> recovery percentage at different applied current to the cell

**B. Effect of Feed Flow Rate**

Then, the experiment had carried out under ambient condition at 25°C and 1 atm. The composition of gas mixture remained as the same ratio 1:1. The electric power had set at optimum value where current, I fixed at 2.5A. The feed flow rate varied in the range of 90 mL/min to 300 mL/min. Figure 6 shows the concentration of CO<sub>2</sub> gas versus time for different feed flow rate. The concentration of CO<sub>2</sub> contained in the product stream increase with feed flow rate. Hence, the higher concentration of CO<sub>2</sub> resulted for the lower of H<sub>2</sub> gas purity.

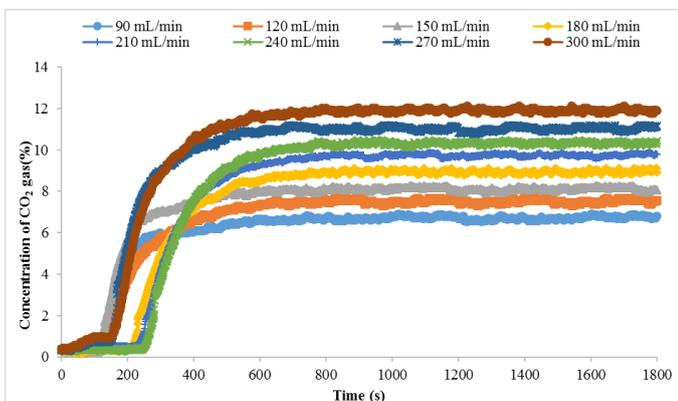


Figure 6. The concentration of CO<sub>2</sub> gas at different feed gas flow rate

The purity of H<sub>2</sub> gas can considered as in the equation (Eq. 1.0). Figure 7 shows the graph of concentration of gas CO<sub>2</sub> and purity of H<sub>2</sub> gas at different feed flow rate. The purity of H<sub>2</sub> gas that comes out from cathode decreases as the feed flow rate at the anode side increases. At the feed flow rate 90 mL/min, the H<sub>2</sub> gas purity is 93.32%. However, the H<sub>2</sub> gas purity drops drastically 88.096% when the feed flow rate increases to 300 mL/min. The purity reduced by 5.6% at the end of experiment.

This phenomenon had caused by the insufficient supply of electrical power. In a study by Casati et al. found the relationship of current density was directly proportional to the feed flow rate [9]. However, the current density will achieve stationary phase where the value of current density will remain constant. This happens when the higher feed flow rate supplied to the electrochemical system. Due to this, the lower feed flow rate, current density had dependent on the H<sub>2</sub> gas fed. While, at higher feed flow rate, the electric resistance was the limiting factor in the purification system.

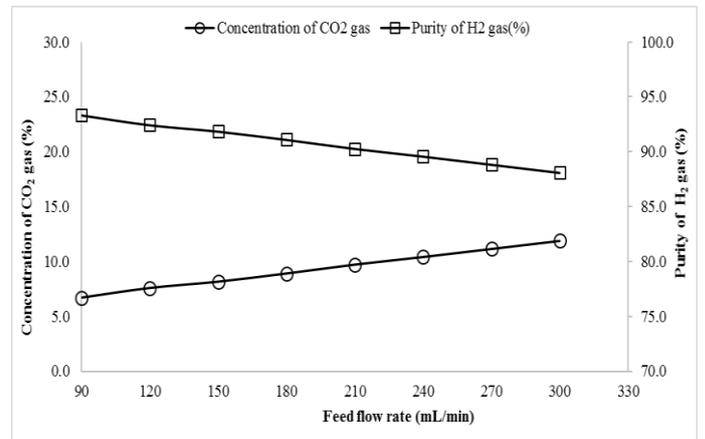


Figure 7. H<sub>2</sub> gas purity at different applied feed gas flow rate

**C. Effect of Temperature**

The comparison between the performances of electrochemical purification in the case of temperature had been investigated. The temperature had set at two different values, 25°C (298 K) and 50°C (323 K). Figure 8 represents the purity of gas H<sub>2</sub> versus applied current at different temperature. At the same temperature, the H<sub>2</sub> gas purity increased with the inclining of applied current. The increasing temperature had enhanced the H<sub>2</sub> gas purity. At temperature 50°C, the highest purity achieved was 96.27% while at temperature 25°C, the purity was only 93.62%.

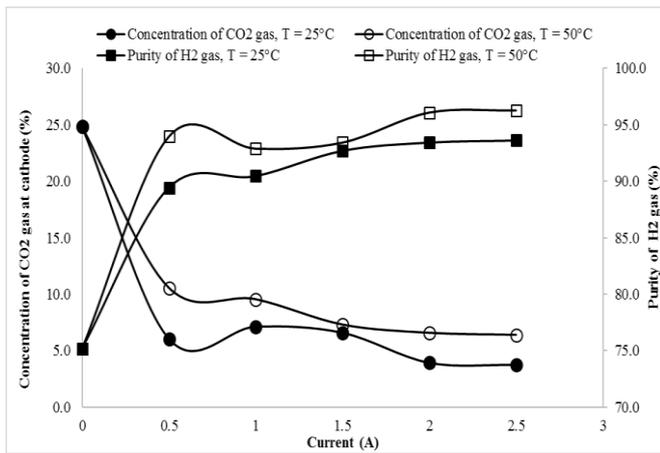


Figure 8. Concentration of CO<sub>2</sub> gas and purity of gas H<sub>2</sub> versus applied current at different temperature

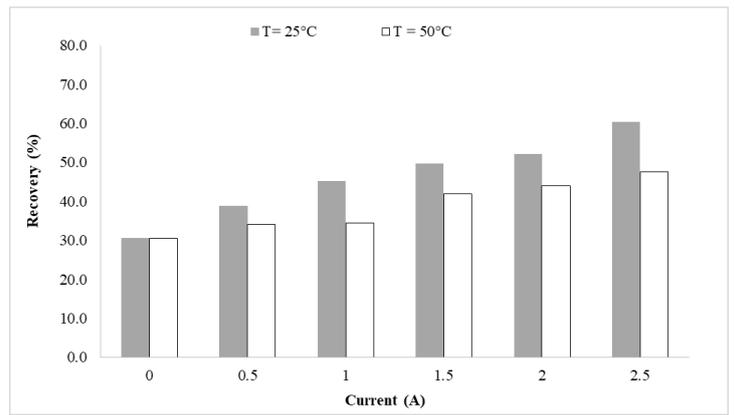


Figure 9. Recovery versus applied current at different temperature

The rise of temperature could be able to reduce the effect of ohmic and non-ohmic overpotential. Moreover, the membrane conductivity also can be improved. Membrane conductivity depends on the water diffusivity across the membrane. However, water diffusivity across the membrane relies on the humidity of reactant gas and electroosmosis drag. Electroosmosis drag refers to transportation of protons (contain water molecule) from anode to cathode. Hence, relative humidity (RH) of the reactant gas increases by the raise of temperature. Normally, the relative humidity of feed for purification purpose was nearly equal to 100%. Full hydration of membrane ensures the optimal performance and long-lasting service of the electrochemical purifier [6].

Figure 9 illustrates the performance of recovery versus applied current at different temperature. From the graph, the recovery at temperature 50°C was much lower than the recovery at temperature 25°C. Table 1 and Figure 10 had shown the theoretical and experimental flux of H<sub>2</sub> gas at different current. From the table, the theoretical flux of H<sub>2</sub> gas is proportional to the raise of electric current. It is the same as the experimental result at the temperature of 25°C and 50°C. Yet, it can be observed that under the same applied current,  $I = 0.5A$ , the H<sub>2</sub> gas flux at temperature 50°C is 0.051 mL/min·cm<sup>2</sup>. This value was much lower if compare to the value available at temperature 25°C, 0.121 mL/min·cm<sup>2</sup>. As the evidence, the study of Lee et al. 2004 claimed that the flux at temperature 50°C was more than the flux obtained at temperature 50°C. The reason of lower recovery at higher temperature was due to the efficiency drop of H<sub>2</sub> electrochemical purifier. Impurity gas CO<sub>2</sub> hinder the active site on the catalyst and impair the active area of catalyst. This phenomenon was known as degradation of catalyst [10]. While, the major was due to the high or excessive water content at temperature of 50°C and it cause flooding condition in electrochemical cell. Due to high water content had blocked the route for protons transportation and leading to unstable power supply.

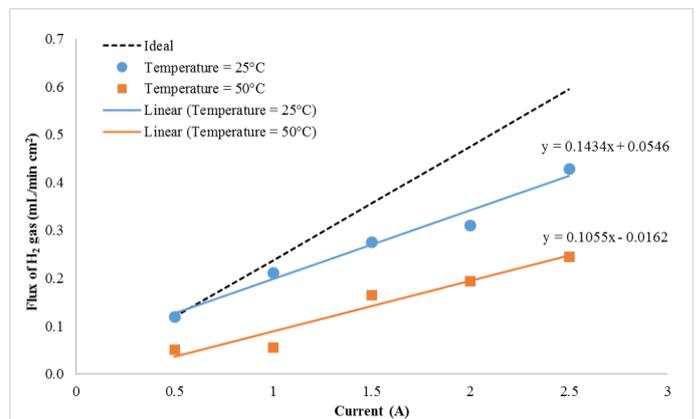


Figure 10. Flux of H<sub>2</sub> gas at different temperature

## CONCLUSION

The characteristic of voltage-current, purity and recovery of H<sub>2</sub> gas in separation process had been determined through a series of experiments. The optimum operating conditions occur at feed flow rate, 90 mL/min While, current,  $I = 2.5A$  produces the best efficiency from other set up, which contributes 93.62% purity and 60.45% recovery of H<sub>2</sub> gas at the cathode. The purity of H<sub>2</sub> gas also enhanced by the rise of temperature from 25°C to 50°C. For the feed flow rate parameter, performance of purification process decreased with the rise of amount of feed flow rate. Then, the minimum concentration of CO<sub>2</sub> was available at the cathode when the feed flow rate set at 90 mL/min. Hence, the purity and the recovery of H<sub>2</sub> gas was higher at 93.36% and 75.83%, respectively. Besides, the capability of electrochemical purification technique can be improved by increasing temperature. Purity of H<sub>2</sub> gas at temperature 50°C was higher than 25°C. At temperature 50°C, the purity of gas H<sub>2</sub> had been increased from 93.32% to 96.27%. Moreover, the flux of product H<sub>2</sub> that in the function of current density increased with the current. Moreover, this result had similar trend between the theoretical and experimental flux product H<sub>2</sub>. However, the highest H<sub>2</sub> flux at which 0.429 mL/min·cm<sup>2</sup> occur at temperature of 25°C instead of 50°C. The relatively simple electrochemical method in purification process had

preferred as it requires less energy and able to produce H<sub>2</sub> gas with high purity (> 90%) and recovery. Therefore, this purified H<sub>2</sub> are very important for the fuel cell application because the fuel cell required continuous supply of high purity H<sub>2</sub> to function orderly.

**Table 1.** Theoretical and experimental flux of H<sub>2</sub> gas at different current

Current (A)	Current density (A/cm <sup>2</sup> )	Theoretical Flux (mL/min·cm <sup>2</sup> )	Experimental flux (mL/min·cm <sup>2</sup> )	
			T = 25°C	T = 50°C
0.5	0.016	0.119	0.121	0.051
1	0.031	0.238	0.212	0.055
1.5	0.047	0.357	0.276	0.165
2	0.063	0.476	0.311	0.194
2.5	0.078	0.594	0.429	0.245

## ACKNOWLEDGEMENTS

This study was partially supported by the Universiti Kebangsaan Malaysia under code DIP-2017-020 and GUP-2016-043.

## REFERENCES

- [1] Yusuf, N.Y., Masdar, M.S., Isahak, W.N. R.W., Nordin, D., and Husaini, T. Challenges and Prospects of Bio-hydrogen Production for PEMFC. *International Journal of Applied Engineering Research*, 11 (19): 9960-9969
- [2] Rahman, S. N A, M. S. Masdar, M. I. Rosli, E. H. Majlan, T. Husaini, S. K. Kamarudin, and W. R W Daud (2016). Overview Biohydrogen Technologies and Application in Fuel Cell Technology. *Renewable and Sustainable Energy Reviews* 66, 62–137.
- [3] Larminie J, Dicks A. (2013). *Fuel cell systems explained*. 2nd edition. WestSussex, England: John Wiley & Sons, Ltd.
- [4] Xu, Gang, Feifei Liang, Yongping Yang, Yue Hu, Kai Zhang, and Wenyi Liu (2014). An Improved CO<sub>2</sub> Separation and Purification System Based on Cryogenic Separation and Distillation Theory. *Energies* 7 (5), 3484–3502.
- [5] Leung, Dennis Y C, Giorgio Caramanna, and M. Mercedes Maroto-Valer (2014). An Overview of Current Status of Carbon Dioxide Capture and Storage Technologies. *Renewable and Sustainable Energy Reviews* 39, 43-426.
- [6] Zaidi, S.M.J. & Rauf, M.A. (2009). Fuel cell fundamentals. *Polymer Membranes for Fuel Cells*, 1–6.
- [7] Panchenko A. (2004). *Polymer electrolyte membrane degradation and oxygen reduction in fuel cells: an EPR and DFT investigation*. Doctoral thesis, Institute für Phyzikalische Chemie der Universität, Stuttgart.
- [8] Lee, H.K. et al. (2004). Hydrogen separation using electrochemical method. *Journal of Power Sources*, 132(1-2): 92–98.
- [9] Casati, Cristina, Paolo Longhi, Luciano Zanderighi, and Fiorenzo Bianchi (2008). Some Fundamental Aspects in Electrochemical Hydrogen Purification/compression. *Journal of Power Sources* 180 (1): 103–13.
- [10] Lopes, Thiago, Valdecir A Paganin, and Ernesto R Gonzalez. (2011). The Effects of Hydrogen Sulfide on the Polymer Electrolyte Membrane Fuel Cell Anode Catalyst: H<sub>2</sub>S – Pt/C Interaction Products. *Journal of Power Sources* 196 (15).