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Optimum condition of membrane electrode assembly fabrication for PEM fuel cells

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Abstract−The aim of this research was to study the effect of fabrication factors on the performance of MEA of a PEM fuel cell. The MEA was prepared by using 5 cm^2 of porous electrodes with Pt loading 1 mg/cm^2 and Nafion 115 membrane from Electrochem Co. Ltd. The studied factors were temperature, pressure and time of compression in the range of 130-150 °C, 50-100 kg/cm^2 and 1-5 minutes, respectively. A 2^k factorial design was conducted in this study. The results showed that interaction between pressure and temperature and interaction between temperature and time of compression have significant effects on the performance of the MEA. With low pressure, but high temperature and long compression time, current density is increased. The results showed that the optimum condition was 65 kg/cm^2, 137 °C and 5.5 min of compression time. It was also found that the force of 69 kg-cm for assembling the single cell gave the best performance.

Key words: Membrane and Electrode Assembly, PEM Fuel Cell, Nafion

INTRODUCTION

The proton exchange membrane (PEM) fuel cell [Larminie, 2000] is one of the presently known five types of fuel cell that convert chemical energy of fuels (e.g. H_2 and O_2) directly into electricity, heat and water. The PEM fuel cell is commonly claimed to be the most promising technology due to its portable power and residential applications [Wolf et al., 2003]. The membrane electrode assembly (MEA) is often stated to be the heart of the PEM fuel cell. The MEA consists of a sheet of proton-conducting polymer electrolyte membrane with two electrodes, the negative (anode) and positive (cathode) bonded to the opposite sides of the sheet by hot-pressing method [Debe et al., 1999, 2000]. A schematic of MEA and single cell of PEM fuel cell is represented in Fig. 1. At present, the production of the MEA is still expensive. Many researchers have attempted to reduce the cost for manufacturing and to improve performance of the PEM fuel cell. Wang and Lim [2004] studied the effect of hydrophobic polymer content in gas diffusion layer (GDL) on power performance of a PEM fuel cell. They found that optimum content of fluorinated ethylene propylene in GDL giving the best performance of PEM fuel cell was at 10% by weight. Giorgi et al. [1998] reported the influence of the PTFE content in the diffusion layer of low Pt loading electrodes for PEM fuel cell. Their results indicated that at high current density, the performance of the electrodes will be decreased when the PTFE content in the catalyst layer is increased. When the PTFE content is increased then the resistance of the electrode will be increased but the porosity of the electrodes will be decreased. It showed that the porosity has an effect on the performance of the electrodes too. Cha and Lee [1999] developed a method to minimize Pt loading on catalyst layer. The loading was about 0.014 mg/cm^2. This result supported the cost reduction for manufacturing the PEM fuel cell. Yang et al. [2002] investigated five different electrodes fabricated with different procedures. They found that the electrode that was prepared by directly coating the catalyst layer on Nafion membrane using 3-methyl butanol as a solvent gives better performance of 800 mA/cm^2 at 0.6 V. In this research, we studied the effects of fabricating factors of MEA on the performance of PEM fuel cell by using design of experiment (DOE). The univariate method was also used to understand

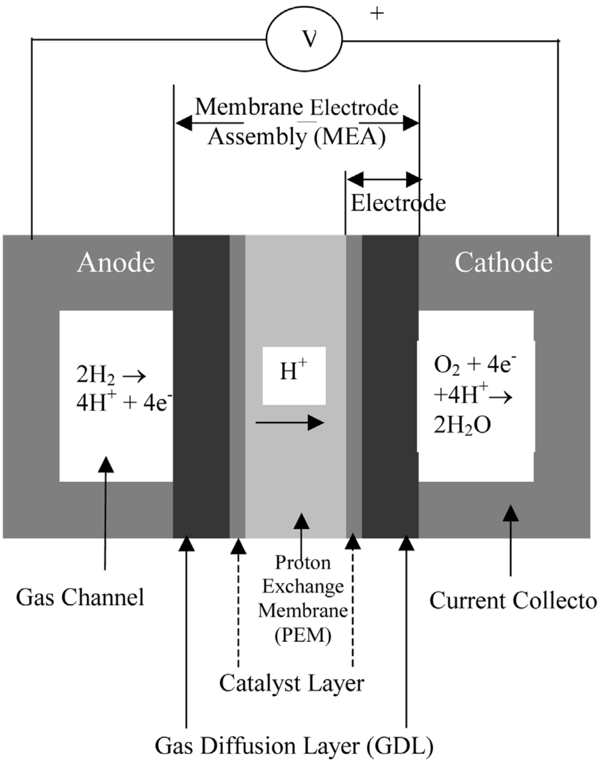

Fig. 1. Schematic of the single cell of PEM fuel cell [Litster and McLean, 2004].

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Table 1. The responses of 2^3 factorial design with center points

Run no.	Experiments	A	B	C	Current density (mA/cm^2)		Mean	%Error (abs.)
					Rep. 1	Rep. 2		
1	(1)	-	-	-	151.21	105.26	128.24	17.92
2	a	+	-	-	56.08	82.07	69.08	18.81
3	b	-	+	-	169.54	168.83	169.19	0.21
4	ab	+	+	-	206.33	213.09	209.71	1.61
5	c	-	-	+	198.32	220.33	209.33	5.26
6	ac	+	-	+	138.62	182.04	160.33	13.54
7	bc	-	+	+	123.00	106.17	114.59	7.34
8	abc	+	+	+	142.36	96.24	119.30	19.33
9	center	0	0	0	141.37			
10	center	0	0	0	124.13			
11	center	0	0	0	158.22			

the influence of each factor on the cell performance. Then, the optimum condition of MEA fabrication was determined by using response surface method (RSM).

EXPERIMENTAL

First, the Nafion membrane was treated in various solutions to remove trace organic and inorganic contaminants and to intentionally change its form. It was boiled in distilled water at 80-90 °C for 1 hr, followed by treating with 3% H_2O_2 at 70-80 °C for 1 hr to remove organic impurities. To get fully H^+ form, the membrane was boiled at 70-80 °C for 1 hr in 0.5 M H_2SO_4. After that, the membrane was rinsed repeatedly with distilled water at 80-90 °C, 1 hr for 3 times to remove the remaining H_2SO_4 on the surface of the membrane [Iyuke et al., 2003].

MEA [Pozio et al., 2002] was prepared by using 5 cm^2 commercial electrodes (Pt loading 1 mg/cm^2), Nafion 115 membrane (6×6 cm^2), and Nafion solution 5% ordered from the Electrochem Co. Ltd. Nafion solution was applied on catalyst surfaces of two electrodes by brushing procedure [Kumar et al., 1995; Wilson and Gottesfelds, 1992]. After that they were aligned with two surfaces of treated membrane. Finally, they were compressed to form an MEA by hot-pressing machine with the selected conditions. The parametric effect on MEA performance was studied by using 2^k factorial experimental design. The studied factors were pressure (A, 50-100 kg/cm^2), temperature (B, 130-150 °C) and time of compression (C, 1-5 minutes). Its performance was tested on a test station.

On the test station, hydrogen and oxygen were supplied through a humidifier with equal flow rate at 100 sccm controlled by mass flow controllers. The cell was operated under ambient pressure and at 60 °C. Potentiostat/Galvanostat type PG STATO 30 of AUTOLAB company was used to measure the values of current from the prepared MEA in a PEM fuel cell. The bonding between the electrodes and the membrane was determined by using Scanning Electron Microscopy (SEM, JSM 6400). The optimum condition of MEA fabrication was determined by conducting response surface method (RSM). Then, the effect of compression force to fabricate the single PEM fuel cell was studied with respect to the performance of MEA. To avoid the effect of MEA preparation, MEA of Electrochem Co. Ltd. was used to study this effect.

RESULTS AND DISCUSSION

All prepared MEAs were characterized in a single fuel cell test station. The cell consisted of two graphite plates with heated stainless steel endplates of Electrochem Co. Ltd. Flow field plates of parallel type gas channel, with a width and depth of 1 mm, were used. The tested MEA was mounted in the cell and the tests were conducted.

1. 2^k Factorial of Experimental Design

There are a number of factors that affect the MEA fabrication. In this research, three main factors of pressure, temperature and time of compression were chosen to study their effects on MEA fabrication and performance. The experiment was conducted by 2^k factorial design [Montgomery, 2001] with 2 replicates and 3 center points (Table 1). Results of each experiment are also shown in Table 1. The variation due to each factor was determined by using Analysis of Variance (ANOVA). The results are shown in Table 2. With 95% confidence level, the critical value of F_c ($F_{0.05, 1, 10}$) from the Appendix [Montgomery, 2001] was 4.84. Therefore, from Table 2, it was indicated that main factors alone do not have significant effects on the performance of the prepared MEA. On the contrary, the interaction between pressure and temperature and that between temperature and compression time show highly significant effects on the performance. This implies that to obtain a better performing MEA,

Table 2. ANOVA Table

Source of variation	Sum of square	Degree of freedom	Mean square	F_0
A (pressure)	989.6	1	989.6	2.26
B (temperature)	524.8	1	524.8	1.20
C (time)	186.80	1	186.8	0.43
AB	5882.5	1	5882.5	13.41
AC	164.4	1	164.4	0.37
BC	25178.5	1	25178.5	57.39
ABC	528.4	1	528.4	1.20
Pure quadratic	98.0	1	98.0	0.22
Error	4387.7	10	438.7	
Total	37940.7	18		

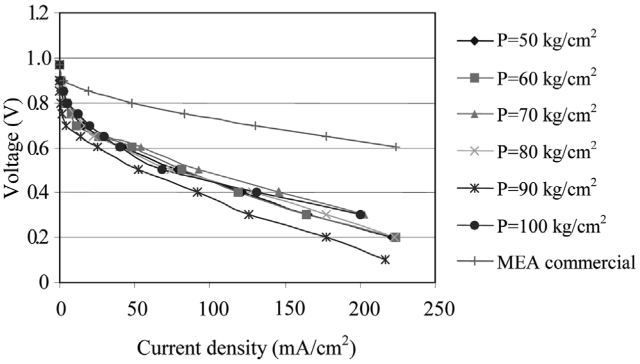

Fig. 2. Polarization curve of fabricated MEA at different pressure with temperature 150 °C and time of compression 1 min.

one has to give attention to the effect of interaction between two main factors more than on any main factor alone during MEA fabrication. After that, the univariate method was used to study the effects of each factor on the cell performance. Then, the optimum condition for MEA fabrication was determined by Response Surface Method (RSM).

2. Univariate Method

To understand the role of each main effect on the prepared MEAs, the univariate method was adopted. Each main effect was one at a time investigated for its influence on the performance of prepared MEAs with different conditions of that effect.

2-1. Effect of Pressure During MEA Fabrication

The effect of pressure on the performance of fabricated MEA is shown in Fig. 2. The current density was increased when the pressure increased from 50 to 70 kg/cm^2. Then, it was decreased when the pressure exceeded 70 kg/cm^2. The results can be explained as follows: the increase of compression pressure to a certain value can provide better contact of electrodes and membrane and, consequently, causes MEA to have low contact resistance. Therefore, the performance is improved. However, when pressure exceeded 70 kg/cm^2, the excessive force collapsed the porosity in the electrodes and membrane. This affects the mass transport of reactant gases inside the electrodes. It increases the degree of difficulty for gases to diffuse through the electrodes. Moreover, Pt on catalyst layer also penetrated in gas diffusion layer. Thus, the amount of Pt contacting both of the electrodes and membrane was decreased. Therefore, the cell performance was also deteriorated. This was observed from the voltage drop at low current density or the change of activation polarization. However, the performance of cell increased at 100 kg/cm^2, especially for the zone of activation polarization. It may be explained that the pressure of 100 kg/cm^2 gave again good contact of platinum catalyst and membrane. It can increase the degree of platinum utilization for cell reaction. By the way, the performance of ohmic drop was insignificantly different. Then, to avoid the effect of interaction between pressure and temperature, a pressure of 100 kg/cm^2 will be used to study an effect of other parameters.

2-2. Effect of Temperature During MEA Fabrication

The effect of temperature on the performance of MEA is shown in Fig. 3. It was found that the performance was improved with higher fabricating temperature. Its effect was more pronounced on resistance polarization than on activation polarization. These results may be explained by the contact resistance of MEA fabrication. When

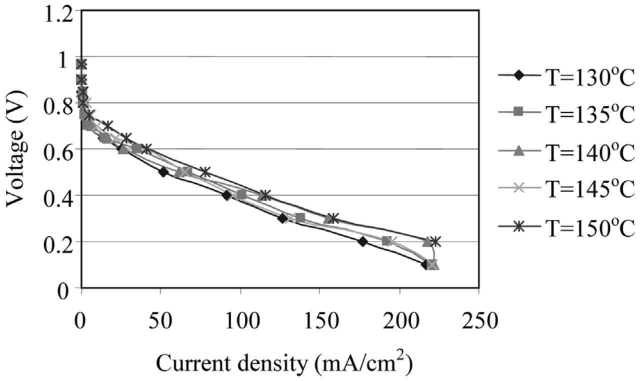

Fig. 3. Polarization curve of MEA fabrication at different temperature with pressure 100 kg/cm^2 and time of compression 1 min.

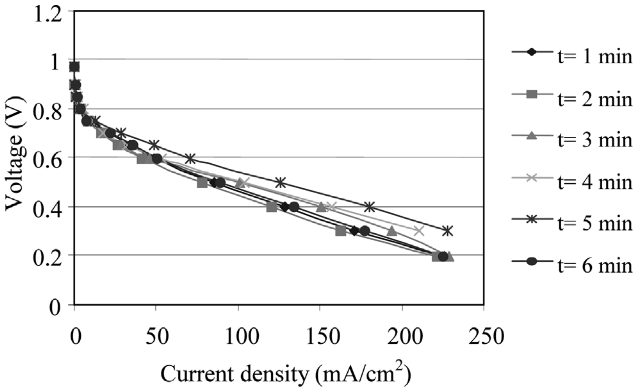

Fig. 4. Polarization curve of MEA fabrication at different time of compression with pressure 100 kg/cm^2 and temperature 150 °C.

a higher temperature was used, both of the electrodes and membrane could be well contacted, due to the softening of PTFE and membrane. Therefore, the contact resistance was lower and the performance of the PEM fuel cell became better. But it was also found that when the fabricating temperature was increased to 150 °C, the cell performance was relatively the same. Therefore, the selected temperature was 140 °C to protect the membrane from being exposed to heat exceeding its glass transition temperature of 150 °C.

2-3. Effect of Compression Time During Fabrication

Fig. 4 shows that current density is increased with increasing of compression time since the contact resistance is decreased. The obtained current density was maximum when a compression time of 5 min was used. The time of compression is the time to formulate the bonding between membrane and electrode layers under certain forcing factors. To bond these layers, the process of bonding takes a certain period of time. If the time is shorter that the period, a good bond cannot be formulated. However, using a very long compression time will not improve this layer bond as well. It was found that when compression time was increased to 6 min, current density was decreased. It can be explained by the effect of interaction of compression time and pressure effect. That is, when a porous structure is under pressure for a long time, the pore deformation could be permanent. On the other hand, with low pressure, but high temperature and long compression time of fabrication, the current density and the performance of PEM fuel cell was improved.

3. Response Surface Method (RSM) [Montgomery, 2001]

The analyses by the univariate method help to elucidate the effect of each single factor on the performance of the fuel cell. However, ANOVA also showed that the variations of the cell performance were mainly caused by the interaction of two main factors, not any single factor. Therefore, the Response Surface Method (RSM) was used to determine the optimum condition for MEA fabrication. To find the optimum point, a mathematical model is needed. The experimental results from the previous section were used to develop an empirical model to relate the fuel cell performance with the studied effects and their interaction. Linear regression was used and the obtained model is expressed as follows:

$$\hat{y} = 147.468 - 7.864x_1 + 5.727x_2 + 3.417x_3 + 19.174x_1x_2 - 39.669x_2x_3 \qquad (1)$$

by $\hat{y}$ =response (current density)

x_1 =pressure

x_2 =temperature

x_3 =time of compression

Where $x_1 = \frac{\text{Pressure} - 75}{5}$ $x_2 = \frac{\text{Temp} - 130}{5}$ $x_3 = \frac{\text{Time} - 1}{5}$

The coefficients of the model show that pressure and interaction between temperature and compression time have negative effect on current density, while temperature, compression time and interaction between pressure and temperature have a positive effect. To increase the current density of the cell, the former pair of effects should be minimized and the latter pair should be emphasized.

After that, by using RSM, the developed model was to determine the experimental conditions to be conducted in each step for finding the optimal condition. Experiments were carried out and the responses are reported in Table 3. The polarization curve for each prepared MEA with different preparation conditions was plotted. The optimum condition was observed from the results in Figs. 5 and 6. In these experiments, the condition of pressure 65 kg_f/cm^2, temperature 137 °C and compression time 5.5 minutes will be the optimum condition for the MEA fabrication.

When comparing the performance of the fabricated MEA with the commercial one (Electrochem Co. Ltd.), it was found that the performance of the fabricated one is still much lower than that of the commercial one. According to their polarization curves, one can observe that the potential of the fabricated MEA at very low current density dropped sharply. These observations might imply there was internal current loss or hydrogen-crossover taking place in the fuel cell. Another reason might be the loss of the catalyst surface during the preparation due to the brushing process when Nafion solution was applied before electrodes and membrane were assembled together. Thus, further investigation has to be carried to determine what caused the potential to drop drastically at very low current density, either crossover or catalyst loss.

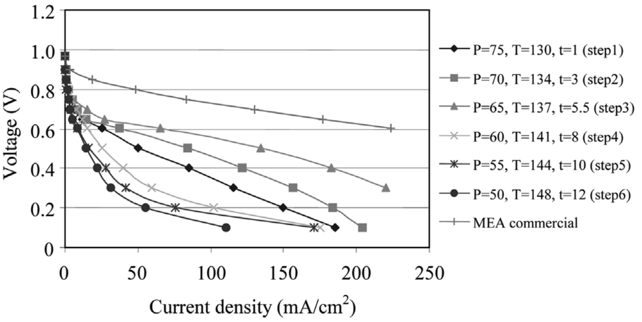

Fig. 5. Polarization curves of the PEM fuel cell which were fabricated from MEA at different condition following response surface method and compared with the commercial one.

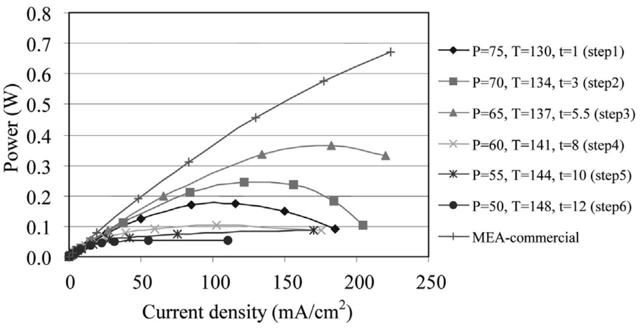

Fig. 6. Power of the PEM fuel cell which fabricate from MEA at different condition following response surface method and compared with the commercial one.

4. SEM Images of the Prepared MEAs

To understand the result of the selected fabricating condition, the physical bonding between each layer of MEA was investigated by using Scanning Electron Microscopy. Fig. 7 showx the bonding between the electrodes and membrane. The complete contacts between each layer significantly affected the performance of the PEM fuel

Table 3. experimental design following response surface method

Steps	Step	Coded variables			Natural variables			Response
		x_1	x_2	x_3	ξ_1	ξ_2	ξ_3	y
origin	0	0	0	0	75	130	1	85.37
Δ		−1	0.73	0.43	5	3.65	2.15	
Origin+Δ	1	−1	0.73	0.43	70	133.65	3.15	121.75
Origin+2Δ	2	−2	1.46	0.86	65	137.3	5.30	182.56
Origin+3Δ	3	−3	2.19	1.29	60	140.95	7.45	39.75
Origin+4Δ	4	−4	2.92	1.72	55	144.60	9.60	28.42
Origin+5Δ	5	−5	3.65	2.15	50	148.25	11.75	22.45

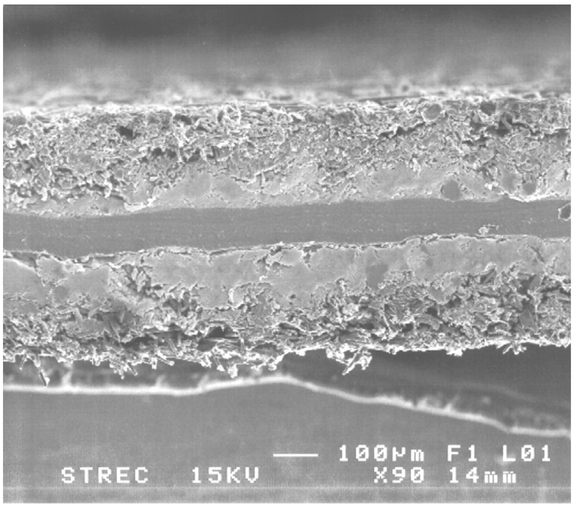

Fig. 7. SEM image of good contact between the electrodes and membrane fabricated by using the optimum condition.

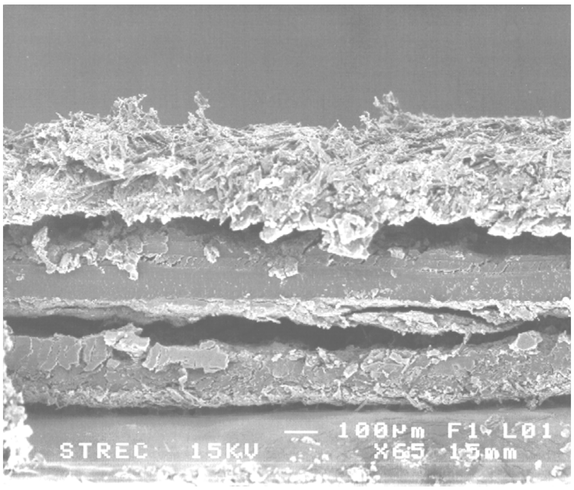

Fig. 8. SEM image of poor contact between electrode and membrane fabricated by using (at 100 kg/cm^2, 130 °C and 1 min of compression time).

cell since good contact between layers will improve conductivity and reduce contact resistance, which will decrease the ohmic loss in the cell. Consequently, the electron and proton transfers were increased. From Fig. 7, it was also found that the MEA, with good contact homogeneously throughout the cross sectional area of MEA and fabricated at the optimum condition, provided maximum power.

Fig. 8 is an example of a low performance MEA. It can be observed that the contact between each layer is poor (at 100 kg/cm^2, 130 °C and 1 min of compression time). There are gaps between each layer. These gaps increase the resistance of the MEA and deteriorate the cell performance.

5. Effect of Compression Force to Fabricate the Single PEM Fuel Cell

From Fig. 9, it was found that the current density would be increased when the force applied for mounting the MEA into a single cell test unit was increased from 23 kg-cm to 81 kg-cm. However, when the applied force was beyond 69 kg-cm, the current density was decreased. The reason is that in the beginning when more force is applied to mount the cell, it helps reduce the contact resistance between MEA with flow field plates. However, when the applied force is increased beyond a certain value, the excessive force causes the porosity of the electrodes of MEA to decrease. Therefore, the mass transport of reactant gases through the electrodes becomes more difficult, causing a reduction of electrochemical reaction. Thus, the performance of the PEM fuel cell is deteriorated.

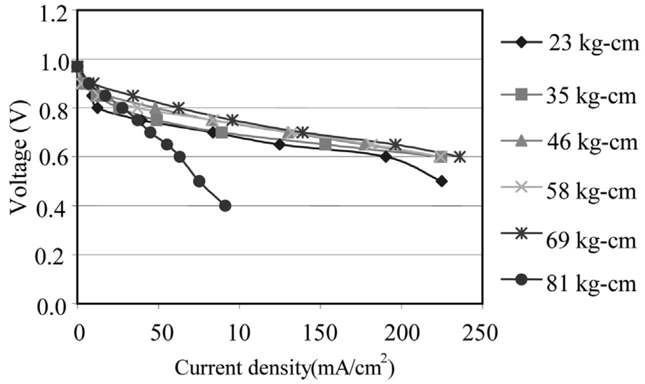

Fig. 9. Polarization curves of the single cell test unit with size of 5 cm^2 with MEA mounted at different the force.

CONCLUSION

This work aimed to study the parametric effects, such as pressure, temperature and time of compression, on the preparation of MEA for a PEM fuel cell. To determine the optimum conditions for MEA fabrication, 2^k factorial of experimental design and response surface method were used in this work. The results showed that the main effects alone were not playing an important role on MEA performance. Instead, interactions between pressure and temperature and that between temperature and time of compression have significant effects on the performance of the prepared MEA. With low pressure, but high temperature and long time of compression, current density was improved. The optimum condition for MEA fabrication was 65 kg/cm^2, 137 °C and 5.5 min of compression time. It was also found that to mount MEA into the single cell of the test unit, a force of 69 kg-cm gave the best performance. However, the obtained performance was still lower than commercial MEA. The reason might be due to the internal current loss or hydrogen crossover Thus, this developed MEA has to be improved. Future work is to investigate the potential loss in the area of open circuit and that when operating at very low current density.

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