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Performance Evaluation of a Passive Direct Methanol Fuel Cell

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Abstract: The design, fabrication and performance evaluation of a passive direct methanol fuel cell (DMFC) operated at ambient condition with an active area of 7.5 cm^2 is studied in this research. The fuel cell is air-breathing and passive without any external pumps or auxiliary devices. Oxygen is taken from the surrounding air and methanol is stored in a built-in reservoir at the anode side. It was tested with methanol of various concentrations, ranging from 1 to 5 M. It was found that cell performance improved with higher methanol concentrations. Power density of 3.5 mW cm^{-2} was achieved with 4 M methanol at a voltage of 0.2 V. This study also presents the performance of the cell tested for different types of design assemble and current collector. The main contribution of this study is the ideas and possibilities in fabrication of micro DMFC in component assemble point of view in order to enhance the power performance and all the possibilities was proofed with data from experiments.

Key words: DMFC, direct methanol fuel cell, current collector, MEA, fuel cell

INTRODUCTION

Interest in using fuel cells to power portable equipment for commercial application is relatively recent. This is perhaps partly due to the success of Li ion batteries in powering laptop computers, mobiles phones, personal digital assistants, game device and music systems. The direct hydrogen fuel cell (PEMFC) has been around for quite sometime but it is developed mainly for large-size applications and with elevated operating conditions. Direct methanol fuel cell (DMFC) has been identified as one of the most promising technologies for the niche market of portable electronics, particularly in wireless communications and computing. It offers instantaneous refuelling time, a compact and lightweight system and easy storage of liquid fuel. The need for hydrogen storage, with its inherent safety questions, can also be eliminated. The micro fuel cell will produce direct current electricity in the same manner as batteries. It can be used to power telecommunication satellites, replacing or augmenting solar panels or for biological application such as hearing aids and pacemakers. The demand is for energy storage devices that will allow these devices to operate for longer time without being plugged into an electrical outlet (Chen *et al*., 2008). Besides that fuel cell potentially offer 5-10 times greater energy densities that rechargeable batteries (Kundu *et al*., 2007).

The objectives of this research are to design, fabricate and evaluate performance of a small passive DMFC for portable application. The system fabricated in study is completely a passive operating system with no external pump used to supply neither the fuel nor oxidant and no heat control element introduced. Oxygen is taken from the surrounding air and diffusion of methanol from the built-in storage system.

MATERIALS AND METHODS

The experiments were conducted in the laboratory of Fuel Cell Institute, UKM, Malaysia. The following scope of works were carried out for this study.

Membrane electrode assembly (MEA): The MEA with an active area of 7.5 cm^2 was made in-house. Prior to fabrication, nafion 115 membrane was pre-treated via. several steps such as boiling for 1 h respectively, in 3% H_2O_2, deionised water, 0.5 M H_2SO_4 and deionised water again until the washing water was neutral. The pre-treated membrane was immersed in deionised water for further usage. The catalysts used were Pt/Ru 50% on XC-72R for anode and Pt 50% on XC-72R for cathode, both with a

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loading of 3 mg cm^{-2}. The catalyst ink consisted of catalyst, 5% Nafion solution and water was brushed onto the membrane directly. The catalyst coated membrane was then sandwiched between two gas diffusion layers, with untreated Toray carbon paper for anode and PTFE treated carbon paper treated for cathode. The membrane and gas diffusion layers were hot-pressed at 75 kgf cm^{-2}, 130°C for 2 min.

Single cell fixture: The MEA was sandwiched between two current collectors, which were made from 316 stainless steel mesh of 0.6 mm in thickness. Transparent acrylic plates and bolts were used to hold together the cell. An approximately 4 mL methanol reservoir was built at the anode side of the cell. Methanol was injected into the reservoir using syringe. Methanol diffused into the catalyst later from the built-in reservoir, while the oxygen from the surrounding air, diffused into the cathode catalyst layer through the opening of the cathode fixture.

Testing condition: MEA was hydrated before testing. All the testing of this passive DMFC was carried out at room temperature of 22-26°C. Methanol concentration was varied in the range of 1 to 5 M. Voltage-current measurements were started 20 to 30 min after the injection of methanol, so that the cell could reach stable operation. In order to obtain accurate data for polarization curve, a waiting time of approximately 1 min was employed after every change of load. After the load was removed, a few minutes have to be allocated for getting accurate open circuit voltage (Kho *et al*., 2005).

RESULTS AND DISCUSSION

Effect of methanol concentration: Figure 1 and 2 depict the effect of methanol concentration on the performance of small passive air-breathing DMFC. The methanol concentration was varied in the range of 1 to 5 M. It was found that the performance of this system could be improved by increasing the methanol concentration from 1 to 4 M. A maximum power density of 3.54 mW cm^{-2} was obtained with 4 M methanol. The methanol concentration for maximum power in a passive DMFC is much higher than that in an active cell, which has an appropriate concentration of around 1.0 M (Qi and Kaufman, 2002; Bae *et al*., 2005). In fact, it has been reported that 4 M appeared to be the optimal methanol solution in passive DMFC (Liu *et al*., 2005). The increased optimum methanol concentration in passive cell is closely related to its special feature, namely operated without any external periphery. As such, the mass transport rate of methanol in a passive cell is much slower since it only uses natural convection, compared to forced convection in an active cell.

However, when 5 M methanol is employed in the system, the performance is slightly reduced. This is probably due to an excessive methanol crossover through Nafion membrane, which is known for its high crossover rate in methanol. The permeated methanol could deteriorate cell performance through generating a mixed potential and poisoning the catalyst in the cathode (Bae *et al*., 2005; Kho *et al*., 2005; Park *et al*., 2003).

As for the increased performance achieved using 1 to 4 M methanol, it can be attributed to higher mass transfer of methanol from the reservoir to the anode catalyst layer. The enhancement in performance could also be due to the increased methanol permeation rate, which in turn increases the operating temperature and thus improves the electro-kinetics of both methanol oxidation and oxygen reduction reactions (Chen *et al*., 2006).

Various performance parameters are shown in Table 1. It could be observed that the current density at 0.15 V and the maximum power density increase with increasing methanol concentration. On the other hand, the OCV and the current density at 0.35 V decreased with increasing methanol concentration. The lower OCV and lower performance at low current densities with high concentration can be attributed to the fact that the rate of methanol crossover from anode to the cathode is higher. However, at high current densities, the mechanism leading to better performance with higher methanol concentration is more complicated. In fact, the performance behavior similar to that shown in Fig. 2-3 and Table 1 has been reported by Qi and Kaufman (2002), Chen *et al*. (2006) and Shimizu *et al*. (2004). Apart from improved mass transfer with higher methanol concentration, it is thought that the higher cell temperature is another major reason that leads to better performance in passive DMFC. As mentioned before, higher rate of methanol crossover from anode to cathode caused by high methanol concentration would in turn promote the exothermic reaction between permeated methanol and oxygen at cathode. The reaction would release more heat with higher methanol concentration, resulting in higher operating temperature. In addition, a higher operating temperature leads to lower internal resistance of the cell, which may also contributes

Table 1: Performance of passive DMFC using different methanol concentration

Methanol concentration (M)	Open circuit voltage (V)	Current density at 0.4 V (mA cm^{-2})	Current density at 0.15 V (mA cm^{-2})	Maximum power density (mW cm^{-2})
1.0	0.515	1.90	17.83	2.74
2.0	0.500	1.90	21.78	3.34
3.0	0.483	1.33	22.55	3.42
4.0	0.483	1.25	23.56	3.54
5.0	0.479	1.25	21.00	3.18

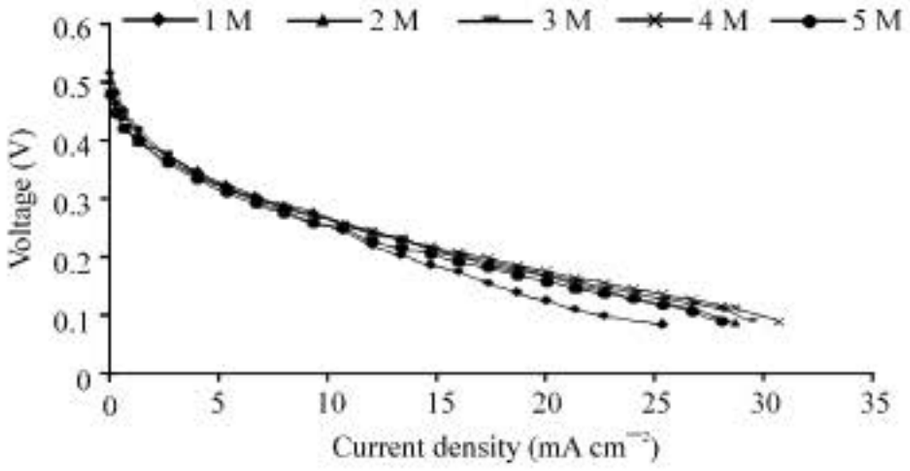

Fig. 1: Polarization curve of the small passive DMFC at different methanol concentrations

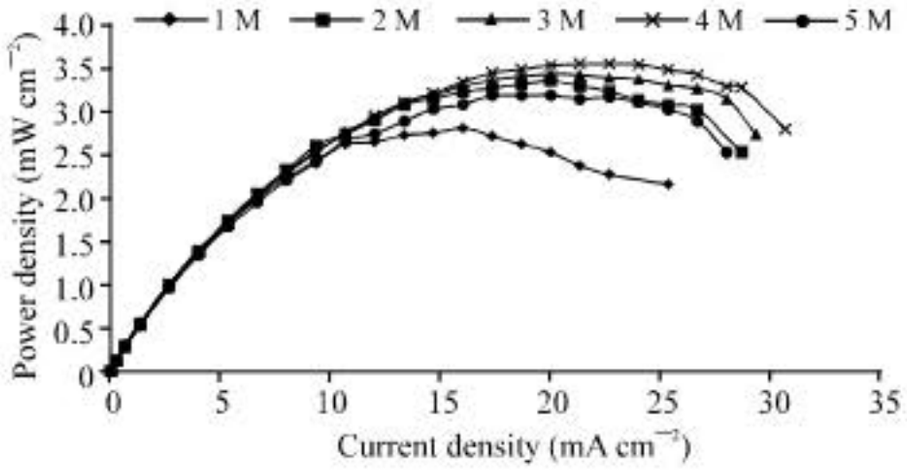

Fig. 3: Effect of methanol concentration on the performance of small passive DMFC

Fig. 2: MEA damaged by pure methanol feeding

Fig. 4: Methanol soaked in aqua gel

to the improved performance at high current densities (Chen *et al*., 2006).

Effect of high methanol concentration: It also observed that pure methanol feeding could damage the MEA (loading of 4 mg cm^{-2}) permanently as shown in Fig. 2 as compare to Fig. 14.

Effect of using aqua gel: The main obstacle in commercializing of micro DMFC is the management or carrier of in the units. Due to that this study suggested a aqua gel used as methanol carrier and observation were done by soaking the 5 M methanol in aqua gel (Fig. 4). Table 2 presents the results comparing the liquid feed methanol with methanol soaked in aqua gel. However, the results indicates that the liquid methanol perform better and logger time as compare to methanol in aqua gel.

Effect of gold coating on the surface of current collector: Current collectors which are made from stainless steel

Table 2: Performance of liquid feed methanol compare with methanol soaked in aqua gel

	Methanol in aqua gel	
Liquid methanol	Anode (mesh)	Anode (mesh with holes)
Decreasing from 210 -128 mA in less than 5 min	120 mA @ 48 mV. More stable than using liquid	Decreasing from 70 to 50 mA in less than 3 min poor performance

mesh were coated with a layer of gold. Figure 5 shows that the gold layer could improve the cell performance as much as 16% in terms of power density. Use of gold eliminates any contact resistance at the current collector-electrode interface (Liu *et al*., 2004).

Effect of assembly design

Frame design: Basically, two type of frame were fabricated and tested. Type 1 is the frame with a big square opening in the middle while Type 2 with many small holes in the middle. Both types use 3 pieces of perspex, with the outer frame being the only difference.

Due to the limitation of its passive nature, there are only a few frame designs for an air-breathing passive

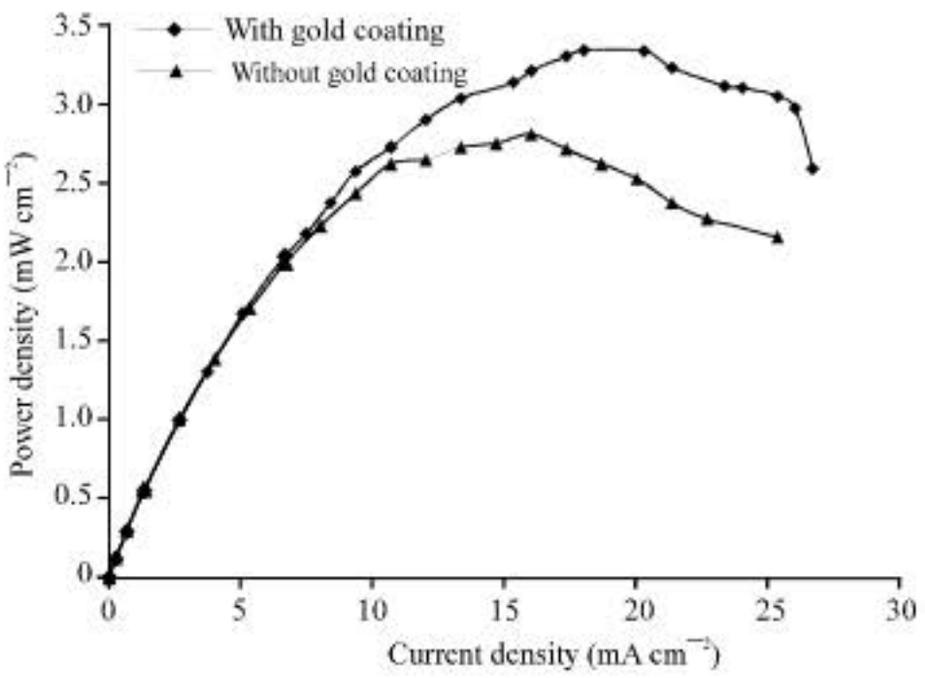

Fig. 5: Comparison in performance between gold coated and uncoated current collectors in small passive DMFC

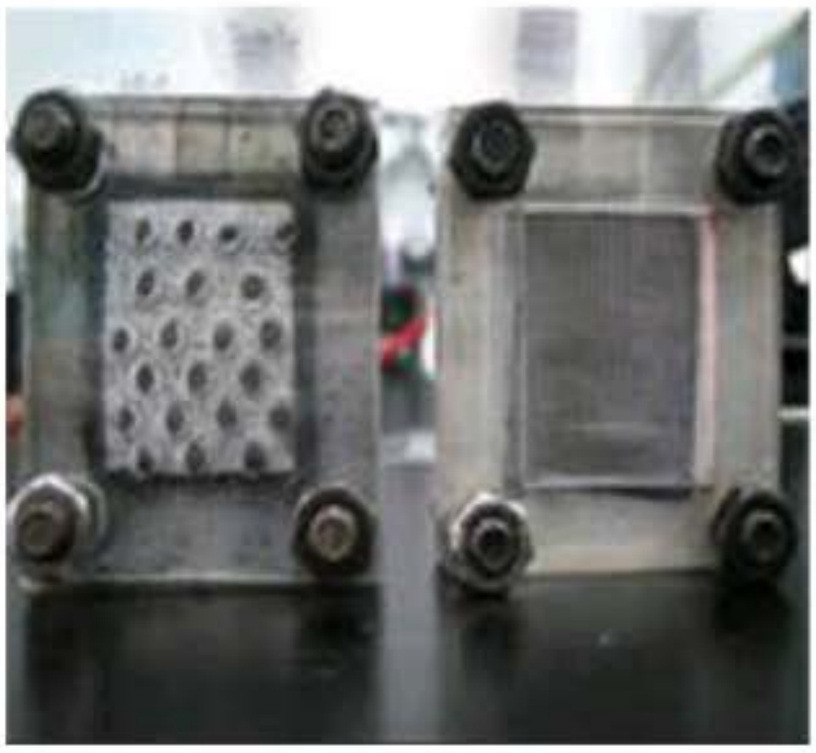

Fig. 6: Type of frame: Type 1 (right) and Type 2 (left)

Table 3: OCV and maximum current attainable for DMFC using different types of frame at cathode

	Small holes	Bar holes
OCV	339	80
Max. current	165	60

DMFC. The function of the frame is to provide structural support to the whole system. The frames at both sides will compress the structure so that current collectors are in optimum contact with MEA to ensure maximum electron flow. In designing the frame for a passive cell, there must be a compromise between the availability of fuel oxidant to anode cathode and the maximum contact between current collector and MEA. Two types of frames are compared. When Type 1 frames (as shown in Fig. 6) are used at cathode and anode, the surface of MEA that exposed to oxidant and fuel are at its maximum. However, from the experiment, it was found that Type 2 frame yielded a better result in spite of its smaller surface area exposed oxidant fuel, as shown in Fig. 7. This is due to

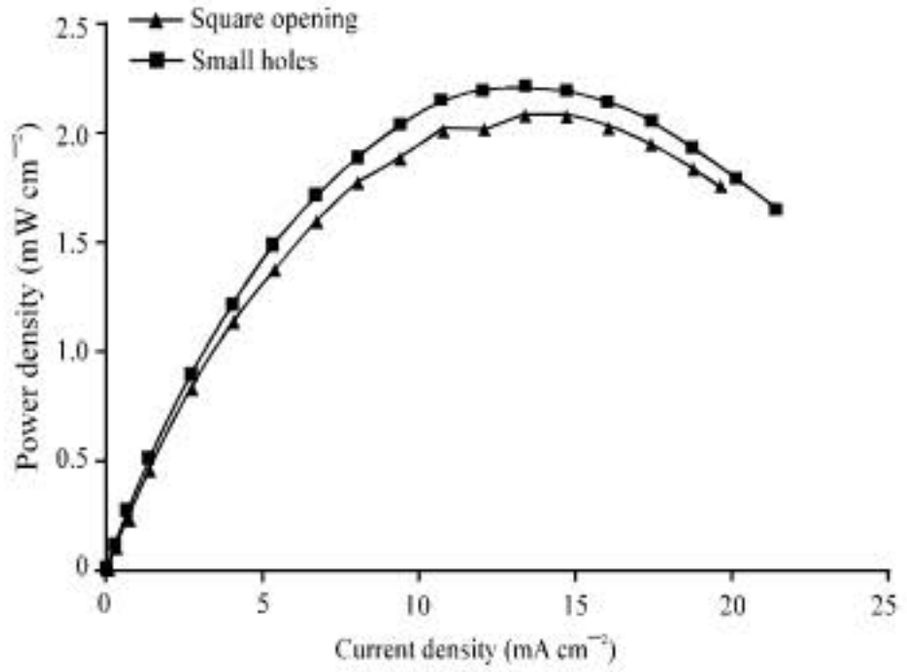

Fig. 7: Comparison between cell performance using Type 1 frame and Type 2 frame at cathode

a better contact between current collectors and MEA, which in turn ensures a higher conductivity from MEA to current collectors and thus a better performance for cell. In other words, the good contact between MEA and current collectors has more effect on performance, compared to a higher availability of oxidant. When a frame with bar holes (as shown in Fig. 15) is used, as shown in Table 3, it was found that its performance is lower than that of Type 2 frame. Apparently, it is more important to have a better contact between MEA and current collectors, than to have high supply of oxidant. This might also be due to the fact that electro-oxidation of methanol occurs at a slow rate, thus even a large amount of ambient air supply would not help to improve the performance significantly.

Current collector: Stainless steel mesh and plate are compared in terms of their ability as current collectors. Many small holes are made in both materials, as shown in Fig. 8 and 9, respectively. It was observed that better result could be achieved with mesh. In this experiment, crocodile clips were used to connect the current collectors to external load. The contact area between the clip and current collectors is a major factor that affects the performance of current collectors. Therefore, better performance achieved with mesh might be due to the better grip and thus more contact area, compared to smooth surface plate. As such, another test was carried out to investigate the effect of smooth surface of steel plate. In this experiment, instead of using clip, wire was soldered to the plate (as shown in Fig. 9) to reduce the contact resistance. However, no significant difference improvement was observed, compared to using clip. This might be due to different type stainless steel used to produce the mesh and plate.

Current collector at cathode: At the cathode, a significant Improvement could be observed in Fig. 10

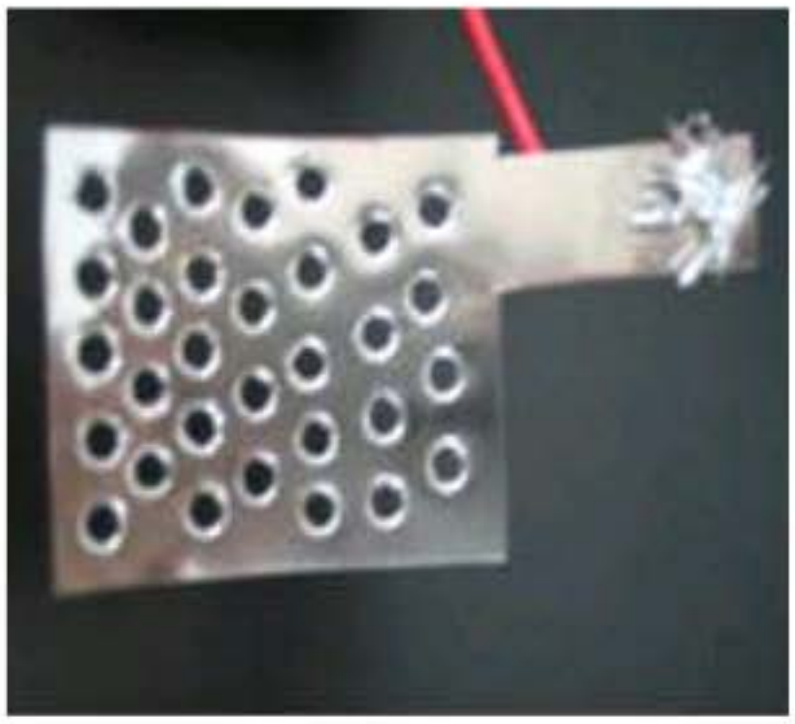

Fig. 8: Stainless steel mesh

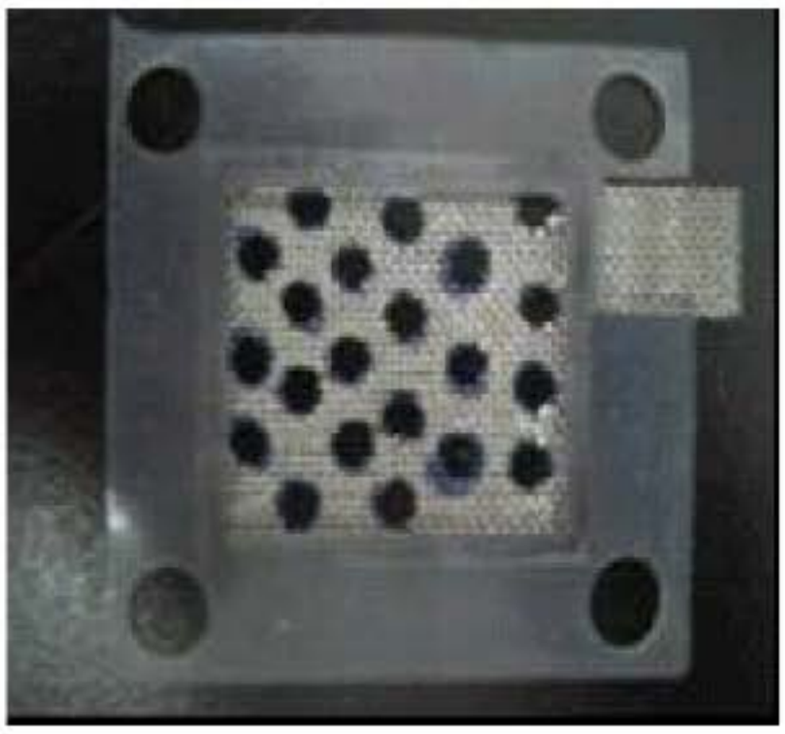

Fig. 9: Stainless steel plate

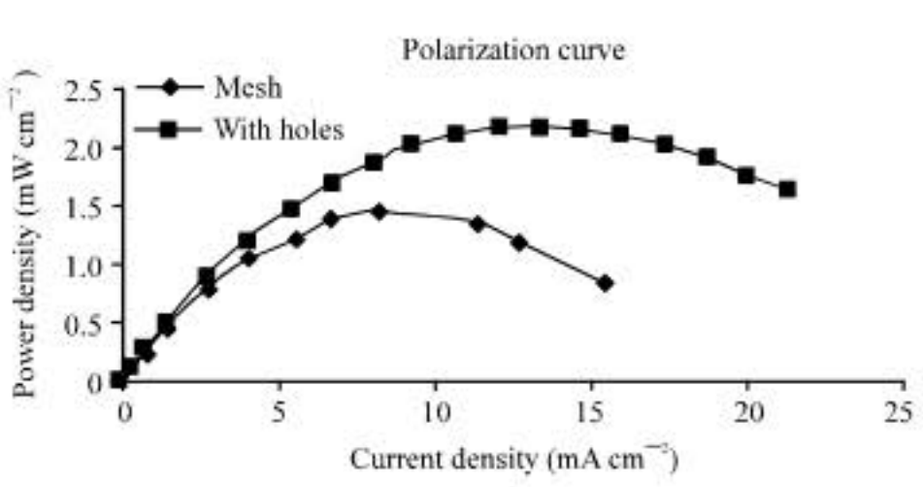

Fig. 10: Comparison between mesh and mesh with small holes as current collector at cathode

when a stainless steel mesh with small holes (as shown in the right side of Fig.11) was used as the current collector, compared with complete stainless steel mesh. The improvement is thought to be due to the better supply of oxygen from surrounding air directly to the system.

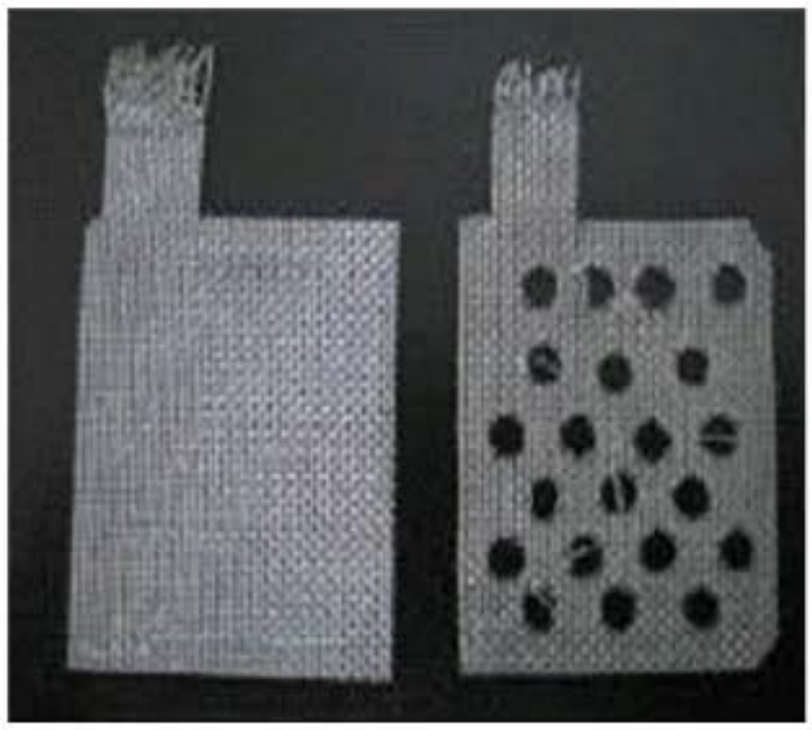

Fig. 11: (Left) Stainless steel mesh; (Right) Mesh with small holes

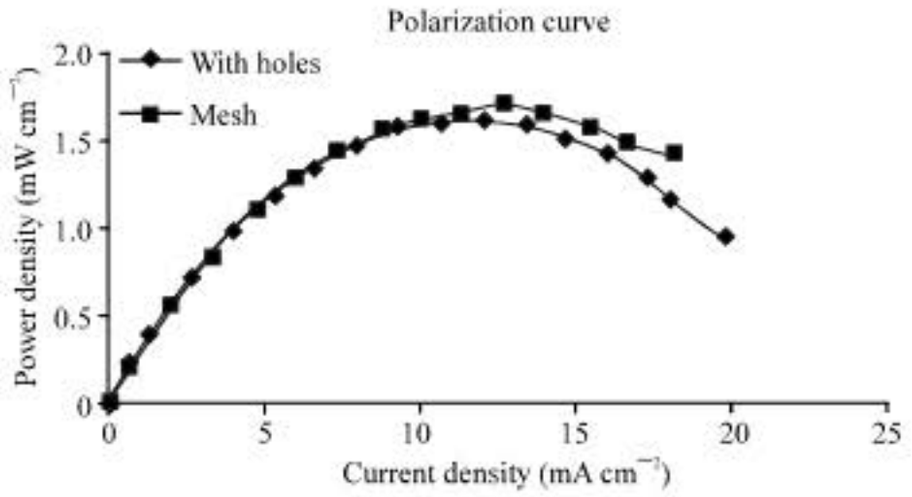

Fig. 12: Comparison between stainless steel mesh and stainless steel mesh with holes, as the current collector at anode

Current collector at anode: Unlike the trend at cathode, the holes in the stainless steel mesh did not improve the cell performance as much at the anode. With or without the holes, it seems that the supply of liquid methanol to the anode is more or less the same and the rate of reaction is also not much different, as shown in Fig. 12. It could be attributable to the slow reaction of methanol oxidation. Instead of the holes in the mesh, the level of liquid methanol would affect the performance more.

Gasket: Two types of gasket (as shown in Fig. 13) were compared. From the experiments, it was found that Type 1 gasket is easier to handle and rarely causes any leakage, even though Type 2 seems to be more leak-proof. As for Type 2, careful handling is required. Tendency of leakage is much higher.

MEA: Two types of MEA (as shown in Fig.14) were compared. It was found that the MEA with 4 holes at the peripherals yielded better result with the current assembly

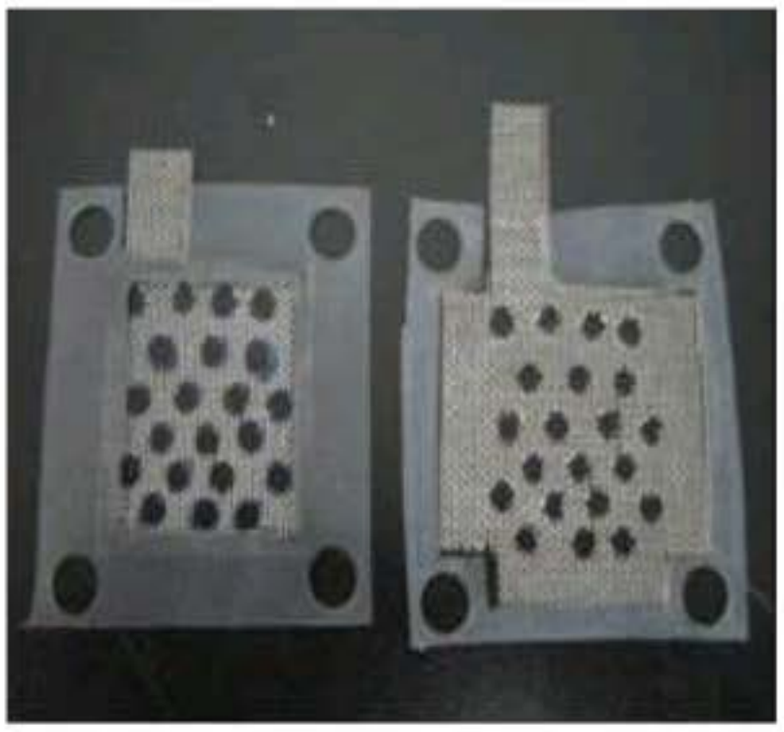

Fig. 13: Type 1(right) and Type 2 (left)

Fig. 14: (Right) MEA with holes punched at the peripherals of membrane; (Left) The membrane is just slightly bigger than the electrode

When the membrane is just slightly bigger than the electrode, leakage tends to occur.

Supporting fixture at anode: It is essential that the current collectors are in excellent contact with the MEA to ensure good performance and to reduce contact resistance. As such, it was predicted that adding a supporting fixture at the anode side to press the current collector towards the MEA might help to improve the performance. The result obtained exhibited that the supporting fixture has indeed enhance the cell performance significantly as shown in Fig. 15. Small holes are made at the fixture to allow the supply of methanol to anode (Fig. 16). Again, no inadequacy of methanol was observed, nor resistance to methanol supply that would affect the performance detrimentally. In addition to that, small holes proved

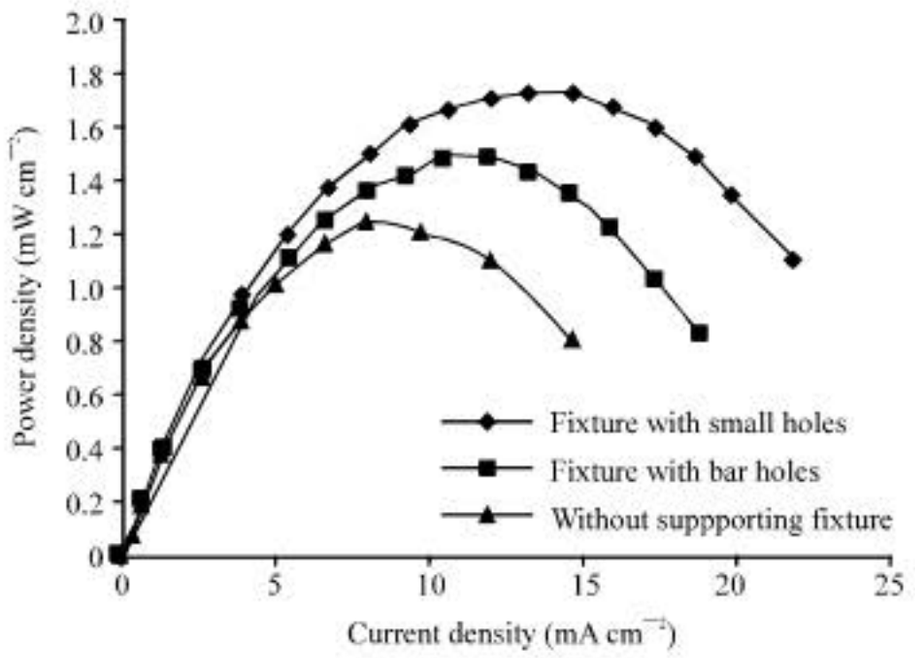

Fig. 15: Performance of DMFC with and without supporting fixture at anode

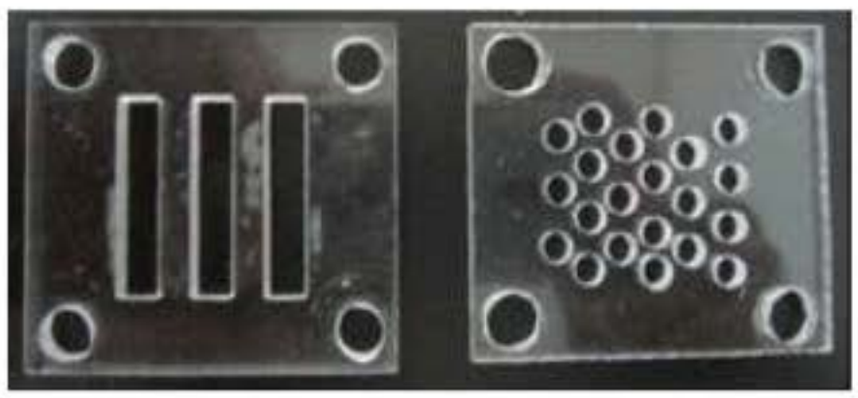

Fig. 16: (Left) Supporting fixture with bar holes; (Right) supporting fixture with small holes

to be better than the bar holes. This is similar to the observation at the cathode side as discussed earlier.

CONCLUSION

A passive air-breathing DMFC was fabricated and tested with different methanol concentrations. It was found that the power density of the cell increased with methanol concentration, until a certain limit when the performance is deteriorated excessively by methanol crossover. By using 4 M methanol, maximum power density of 3.54 mW cm^{-2} could be achieved. However, when 5 M methanol was used, the performance deteriorated. This experimental result indicates that optimum concentration in the passive cells is a result of compromise between many parameters, such as temperature, methanol transport rate and mixed potential that are influenced by methanol concentration. Besides that, this study draw some results on the type of small DMFC assemble design and type of current collector in order to improve the performance of the cell.

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