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*by* Dedikarni Panuh

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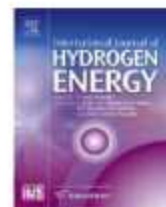
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## Performance and stability of single and 6-cell stack passive direct methanol fuel cell (DMFC) for long-term operation



Mohd Shahbudin Masdar<sup>a,b,\*</sup>, Dedikarni<sup>a,c</sup>, Azran Mohd Zainoodin<sup>a</sup>,  
Masli Irwan Rosli<sup>a,b</sup>, Siti Kartom Kamarudin<sup>a,b</sup>, Wan Ramli Wan Daud<sup>a,b</sup>

<sup>a</sup> Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600, UKM, Bangi, Selangor, Malaysia

<sup>b</sup> Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600, UKM, Bangi, Selangor, Malaysia

<sup>c</sup> Department of Mechanical Engineering, Faculty of Engineering, Islamic University of Riau, Pekanbaru, Riau, 28284, Indonesia

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### ABSTRACT

A passive, air-breathing, 6-cell direct methanol fuel cell (DMFC) stack is designed, fabricated and tested based on the performance of a passive single-cell DMFC. A large methanol reservoir in a hexagonal shape is considered in designing the stack in order to increase the DMFC operation time without any interruption, i.e., to refill the methanol solution. Hence, the ratio of methanol solution volume in the reservoir for the single cell, i.e., 8 ml, and hexagonal stack, i.e., 240 ml, is 1:30. The power output of 500 mW is achieved at 1.5 V using a 5 M methanol solution at room temperature. With a large volume of methanol, i.e., 240 ml of 5 M methanol in the hexagonal stack, it can be operated continuously at 1.5 V for more than 40 h, whereas for a small volume, i.e., 8 ml in a single cell, the operation can reach only 3 h–4 h with a similar reduction of 25% from the initial power output. Moreover, the DMFC stack is used for long-term operation more than 3000 h, and the morphology of MEA is analyzed.

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## Introduction

Recently, there has been considerable interest in the use of direct methanol fuel cells (DMFCs) to replace conventional batteries for powering portable electronic devices [1–4]. Over the past decade, in many published reports, much effort by researchers has been devoted toward the development of new electro catalysts [5–7] and electrolyte membranes [8,9] to

overcome the persistent technical barriers of DMFCs. These barriers include the slow kinetics of methanol oxidation and oxygen reduction reactions, cathode catalyst poisoning, and high methanol crossover (MCO) through the electrolyte membrane. Methanol crossover occurs when the methanol feed to the anode compartment diffuses through the separating membrane into the cathode compartment, which is a significant problem that limits the performance of DMFCs. However, most of this research has focused only on the behavior of the

\* Corresponding author. Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600, UKM, Bangi, Selangor, Malaysia. Fax: +60 389118345. E-mail address: [shahbud@ukm.edu.my](mailto:shahbud@ukm.edu.my) (M.S. Masdar).

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DMFC performance in a half-cell or single-cell configuration. Furthermore, compared with single cells, the development of a fuel cell stack system is more challenging because of power fluctuations that occur during the integration of single cells into the stack [10]. In order to have high efficiency of the system, the crucial design parameter is to develop the DMFC stack, i.e., including cell components such as the membrane electrode assembly (MEA), to produce high methanol utilization efficiency with sufficient power to operate the system [11].

Based on a literature review, several studies on the development of DMFC stacks are reported with different system designs and materials used. For instance, Cao et al. fabricated two mono-polar 6-cell DMFC stacks with two different anode flow fields on silicon substrates [12]. Each single cell had an active area of  $1.4 \times 1.4 \text{ cm}^2$ . The volume and weight of the stack were only  $5.3 \text{ cm}^3$  and  $10.7 \text{ g}$ , respectively. Based on their experiment, the results showed that the stack with double serpentine-type flow fields could generate better performance, with maximum output power reaching  $351 \text{ mW}$  at a voltage of  $1.5 \text{ V}$  [12]. Moreover, Guo et al. developed a 4-cell DMFC stack on a printed circuit board (PCB) with a total active area of  $76.6 \text{ cm}^2$  and obtained a maximum power output of  $320 \text{ mW}$  at  $0.35 \text{ A}$  using a  $50 \text{ cm}^3$  methanol solution [13]. In addition, Zhu et al. developed a twin stack containing planar 8-cell DMFCs with stack dimensions of  $13 \text{ cm} \times 2 \text{ cm} \times 10 \text{ cm}$ . The stack, equipped with a fuel feed device, successfully powered a sensor node for 39 h while consuming 80 ml of 4 M methanol. A peak power density of  $16.9 \text{ mW cm}^{-2}$  was achieved, and the power output of  $540 \text{ mW}$  at  $1.8 \text{ V}$  was obtained [14].

In all of the above and other published [15,16] reports on the development of DMFC stacks, the stack performance and efficiency were dependent on the 1) Design of the stack, i.e., MEA properties such as catalyst loading; 2) Stack configuration, i.e., stack design and materials used; and 3) The operating parameters, i.e., methanol concentration, temperature, flowrate; and system operating mode, i.e., active, semi-passive or passive. For instance, Baglio et al. studied the effect of catalyst loading in the MEA and methanol concentration in their DMFC stack. They found that the maximum power was obtained at an ambient temperature with  $4 \text{ mg cm}^{-2}$  Pt loading (varied from 1.5 to  $6.0 \text{ mg cm}^{-2}$ ) using 5 M methanol concentration (varied from 1 to 10 M) [17].

In the case of the stack configuration, most researchers have concentrated on a compact stack design that is lighter, is easier to handle and saves space. However, the compact stack design has drawbacks, such as limits on the methanol fuel volume in one-time operation for the passive system DMFC. This would affect the operation time of the DMFC stack because methanol acts as a reactant for the anode reaction and hence affects the time management in order to refill the methanol fuel. However, several papers reported and considered a large methanol reservoir or tank for the passive system DMFC stack [14,15]. For instance, Guo and Faghri developed a 1 W passive DMFC stack with a total active area of  $72.0 \text{ cm}^2$ . The stack could be filled with 500 g (approximately 500 ml) of 3 M methanol solution at a time, and a power output of  $1.5 \text{ W}$  was achieved at  $2.4 \text{ V}$  at room temperature. Moreover, the stack continuously ran at  $33 \text{ mA cm}^{-2}$  for 57 h and generated total electrical energy of  $26.1 \text{ Wh}$  [18].

Nevertheless, improving performance and long-term stability are key factors for the success of DMFCs in the market. Because different phenomena are involved in the current generation of DMFCs, i.e., charge transfer reaction, mass transport, adsorption processes, etc., the measured performance loss due to degradation of the MEA can be the result of various causes [19]. For instance, Cheng et al. revealed that there was significant performance degradation after 1002 h of operation. Increases in the catalyst particle size from both the anode and cathode catalysts were observed after the DMFC lifetime test. Changes in the microstructure, surface composition, interfacial structure of the MEA, and aging of Nafion® under the DMFC lifetime tests were also observed [20].

In this work, a passive system DMFC stack was designed, fabricated and evaluated based on the performance of a single-cell DMFC. A large fuel reservoir was considered in the stack design in order to increase the operation time of the DMFC stack. However, the geometric shape and size of the DMFC stack were different from those of Guo and Faghri's DMFC stack [18], i.e., hexagonal and rectangular geometric shapes and the approximate maximum methanol solution used 280 ml and 500 ml for this study and Guo and Faghri's work, respectively. A detailed explanation of the advantages of the hexagonal shape used in this study will be discussed in the experimental section. Moreover, the passive single cell and the stack of DMFCs were operated with dilute methanol solutions with concentrations varying from 2 to 6 M. The power output and stability performance of the stack were measured for long-term operation. The effects of the methanol concentrations and operation time will be discussed based on stack power, stability and degradation of stack performance.

## Experimental

### MEA fabrication for single cell and DMFC stack

Nafion 117 electrolyte membrane (DuPont™) was used as an electrolyte membrane. Platinum (Pt)/Ruthenium (Ru)-black (HiSPEC 6000, Alfa Aesar, USA) and Pt-black (HiSPEC 1000, Alfa Aesar, USA) were used as catalysts for the anode and cathode, respectively. Commercial carbon cloth (E-TEK, USA) was used as a backing layer with  $2.0 \text{ mg cm}^{-2}$  of carbon black loading with 5 wt% polytetrafluoroethylene (PTFE) serving as a diffusion layer at the anode and cathode. The catalyst inks were prepared by dispersing an appropriate amount of the catalyst in a solution of deionized water, isopropyl alcohol, and 5 wt% Nafion® solution (Wako Pure Chemical Industries, Ltd.). For the anode, Pt–Ru ink and Pt ink were coated on the diffusion layer for the anode and cathode, respectively. Catalyst loading on both the anode and cathode is  $8.0 \text{ mg cm}^{-2}$ . The MEAs with  $4 \text{ cm}^2$  active areas were then fabricated by sandwiching the membrane between the anode and cathode and hot pressing them at  $135 \text{ }^\circ\text{C}$  and 5 MPa for 3 min.

### Passive DMFC stack design

In this study, a passive single cell and stack were operated to compare the performance of each unit. For the single cell of



the DMFC, the cell was designed and fabricated similar to that our previous report [21] as shown in Fig. 1. Polycarbonate was chosen for the plate material for the transparent methanol reservoir with rectangular geometry. No more than 10 ml of the methanol fuel could be filled in the reservoir in a one-time operation for the single-cell DMFC.

Meanwhile, for the stack, a complete passive DMFC stack was designed and proposed for a 500 mW power output. Therefore, on our basis calculation by referring to the single cell performance, the passive DMFC stack was designed comprising six cells with a total active area of  $24 \text{ cm}^2$  ( $4 \text{ cm}^2$  per cell). The cells were fixed on the hexagonal shape of the methanol reservoir with the anodic side facing the fuel tank, which allowed the methanol fuel to be supplied passively to each cell. Each cell consisted of two current collector plates, four gaskets, the membrane electrode assembly (MEA) and the cathode cover as the end plate, as shown in Fig. 2.

From the design aspect, we assume that by designing the stack with a hexagonal shape in passive operation, the methanol fuel distribution in the reservoir will be uniform, and hence the limiting mass transport of fuel to the anode can

be reduced. This limiting fuel transport would be affected to reduce the performance of DMFC. For instance, Fig. 3 shows the comparison of the mass transport distribution (by referring to the distance) in the reservoir between two shapes of stack: hexagonal and rectangular with 6 cells. It was easily understood by referring to Fick's Law that the distance from the center point of the geometry to the anode surface,  $\Delta x_i$ , would affect the flux or mass transport in the reservoir. In the case of a hexagonal shape, because all  $\Delta x_i$  values are similar, we can assume that the concentration of fuel at the anode surface is similar, hence the performance of each cell in the stack will be similar (considering that the performance of MEAs is similar). However, for the rectangular shape, limiting mass transport could occur, especially for cells 1 and 4 as shown in Fig. 3(b), hence the performance of each cell would be varied and affect the stack performance. This mass transport phenomenon, i.e., methanol distribution inside the reservoir, could be one of the advantages of using a hexagonal shape rather than rectangular, which has been used by other researchers.

#### a) Fuel reservoir as stack holder

To maintain design flexibility, polycarbonate was chosen for the plate material for the transparent methanol reservoir. Similar polycarbonate material was used by Feng et al. [1] and Yuan et al. [16] to fabricate DMFC stacks. They stated that they can provide sufficient rigidity to support the unit cells in the stack [1,16]. The dimensions of the methanol reservoir as a stack holder were  $143 \text{ mm} \times 124 \text{ mm} \times 30 \text{ mm}$ , as shown in Fig. 4(a). One can see that this stack holder was large, and the design did not meet the compact passive DMFC system and contributed to increasing the total weight of the passive DMFC stack. With these dimensions, approximately 280 ml of the methanol fuel could be filled into the reservoir in a one-time operation instead of less than 100 ml, which has been reported in most previous literature [13,14,22]. Therefore, we assume that with this large amount of fuel, the passive DMFC stack could operate for a very long time without any addition or refilling of fresh methanol fuel. This would therefore be of benefit in any electronic devices that require long-term operation, and it would save time for the user in terms of the frequency of refilling the reservoir with fresh methanol. For comparison, the performance and operation time using a single-cell DMFC with 8 ml of fuel were compared to this hexagonal stack with 240 ml of methanol.

#### b) Current collector

The current collector is one of the key components of the unit cell that serves to conduct the electricity. In this work, a 316L stainless steel plate with a thickness of 1.0 mm was used, which provides not only sufficient stiffness but also high electrical conductivity and corrosive resistance at a cheaper price.

A parallel flow-field design was machined on both the anode and cathode current collectors as shown in Fig. 4(b), providing the passage of fuel and oxidant, which resulted in an open ratio of 50% (total area of holes in current collector to total area of the MEA active area). Meanwhile, by designing

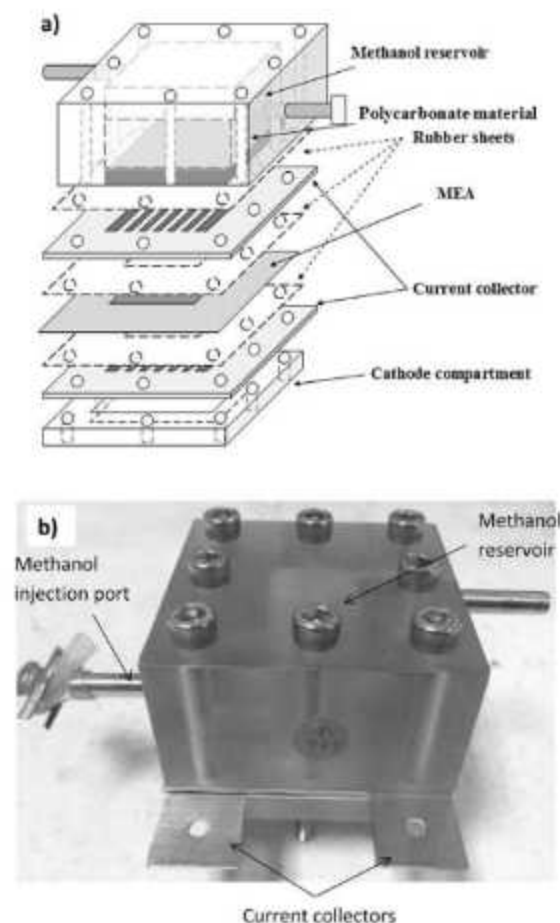


Fig. 1 – A single-cell DMFC used in this study: a) schematic cell components, b) actual photo.

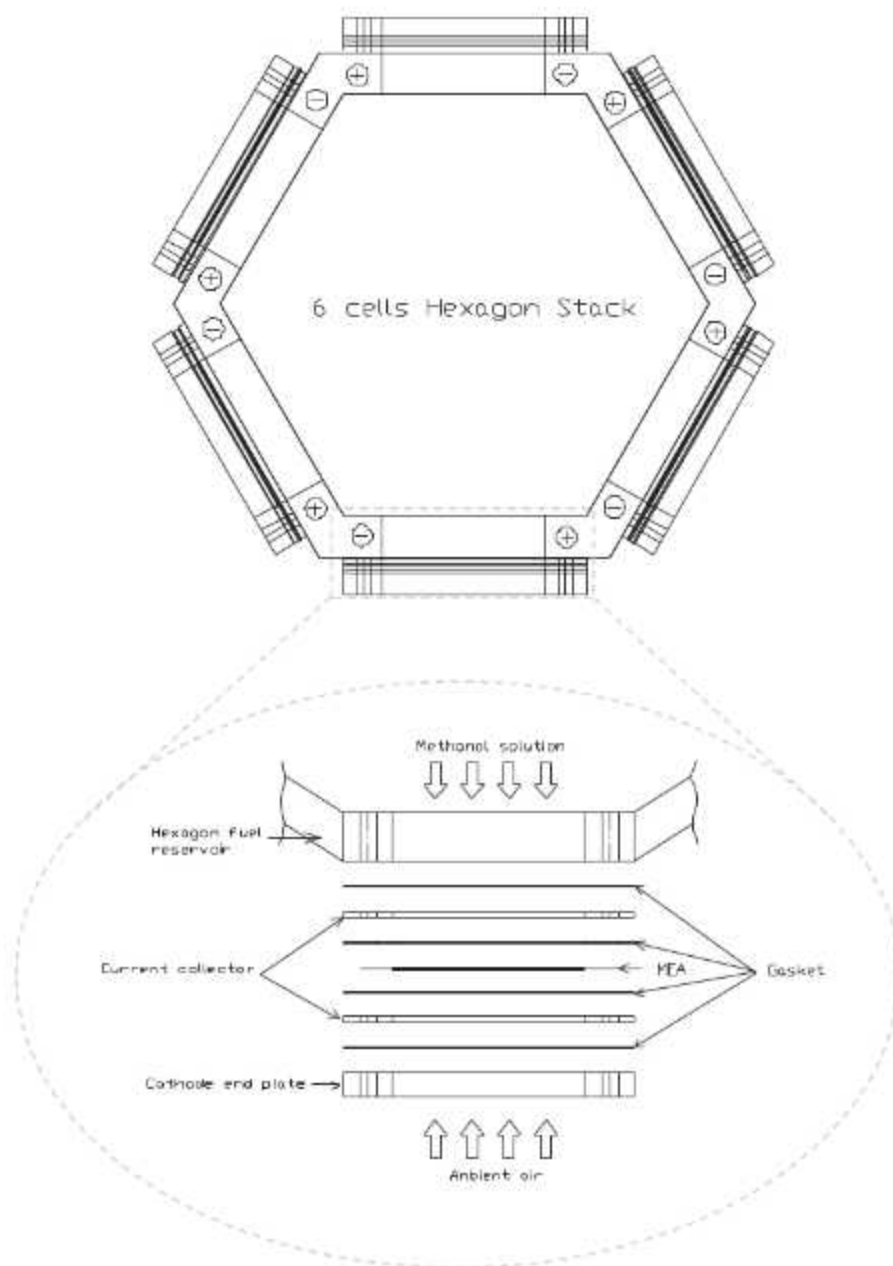
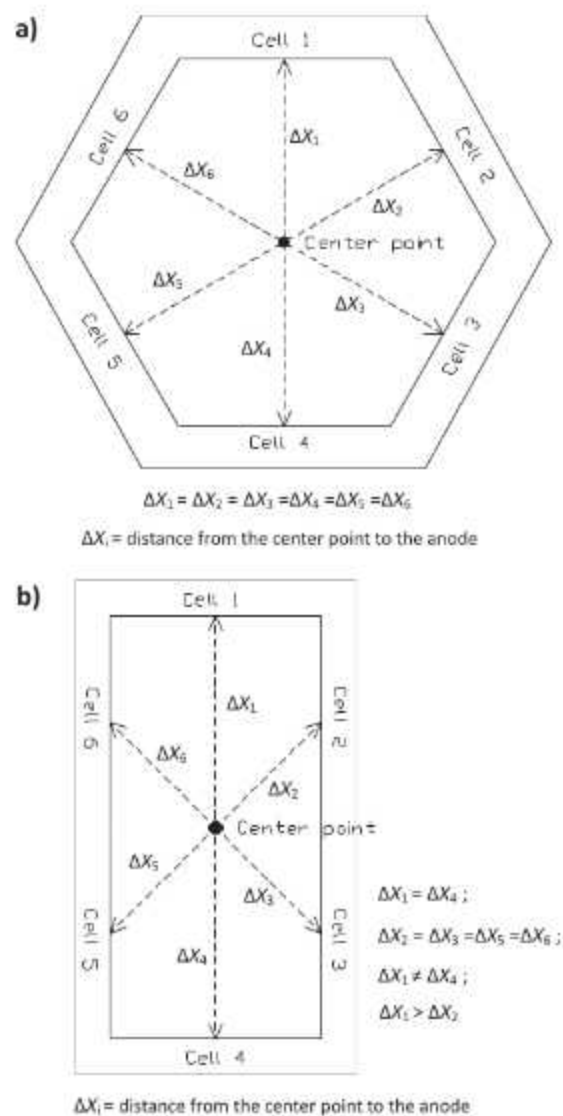


Fig. 2 – Schematic drawing of a 6-cell DMFC stack in hexagonal stack and stack components.

two terminals for each current collector plate, it was possible to test the passive DMFC in different electrical cell configurations (single cell, multiple cells connected in series or in parallel). In the passive DMFC of the hexagonal stack, the cell is placed side by side with the same polarity on the same side of the MEA and with the anodes and cathodes connected in series using a 50  $\mu\text{m}$  thick stainless steel sheet, as shown in Fig. 5.

#### c) Gasket

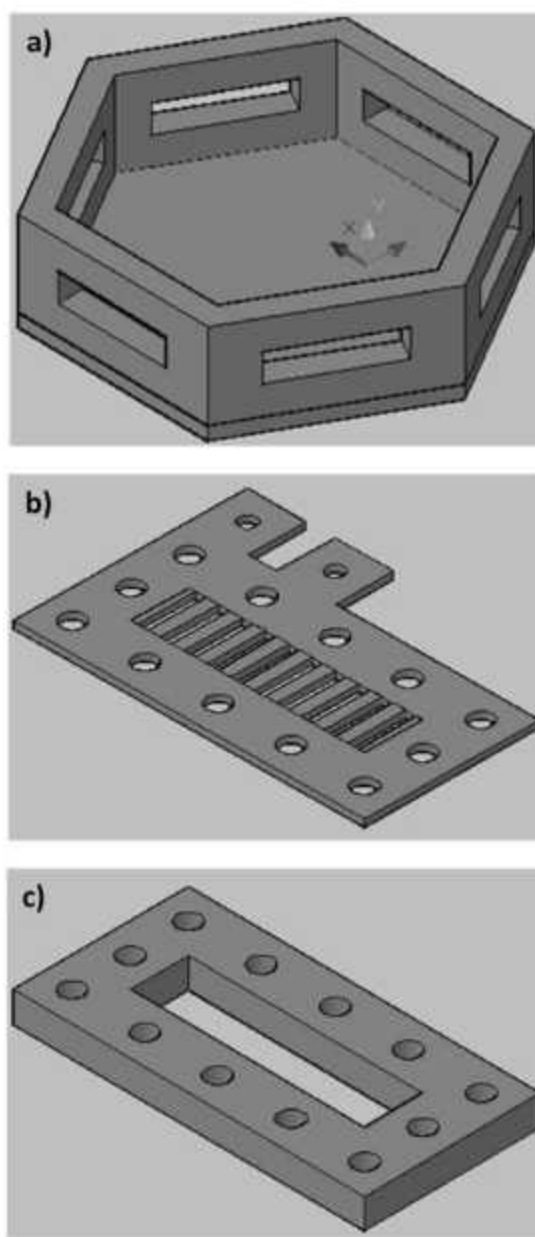
In order to prevent the leakage of methanol from the anode to the cathode, gaskets were added between the current collectors and the edged membrane of each MEA, as shown in Fig. 2. Because of the properties of polycarbonate, acrylic (cathode cover) and stainless steel, the seal design was based on the assumption that compressibility of the seal was one of



**Fig. 3 – Comparison of the distance from the center point to the anode in the reservoir between two shapes of stacks with 6 cells: a) hexagonal, b) rectangular.**

the most important parameters. For a given pressure, i.e., tightened nuts, the use of a thinner gasket usually results in a larger gap between the current collector and gasket, which tends to increase the leakage of methanol solution [23].

However, the use of excessively thick gaskets will cause poor contact between an electrode and a current collector, which increases contact resistance. To this end, silicon rubber was selected on the anode and cathode sides. The high compressibility of the silicon rubber provided good contact between the edged membrane and current collector, which resulted in a good seal to prevent the leakage of methanol solution. By selecting the proper thickness of the gasket, the compression of the silicon rubber can be controlled to achieve



**Fig. 4 – Design of a 6-cell stack: a) methanol reservoir (polycarbonate), b) anode and cathode current collectors (stainless steel), c) cathode cover/end plate (acrylic).**

sufficient sealing and good contact between the electrodes and current collectors. In this work, a 0.3 mm thick silicon rubber sheet was chosen for the gaskets on the anode and cathode.

Furthermore, acrylic material 5 mm thick was used as the cathode cover and as the end plate for each cell, as shown in Fig. 4(c). At the top of the stack, the cover and holder were constructed from acrylic material (3 mm thick), and two



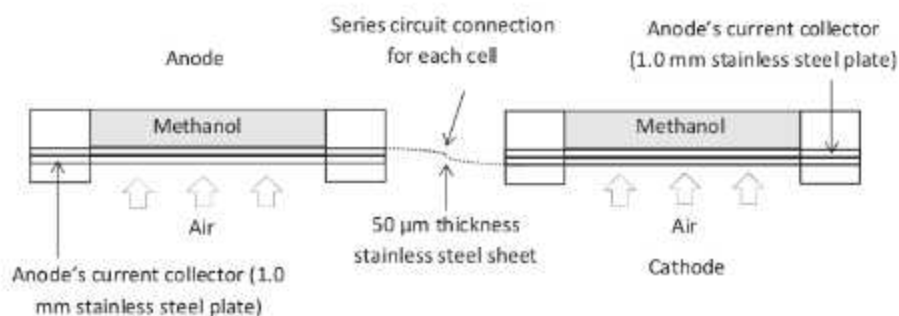


Fig. 5 – Series circuit connection between cells in the hexagonal DMFC stack.

3.0 mm circular holes were located in the cover to release any  $\text{CO}_2$  formed by the anode reaction and fill with methanol fuel, respectively. During the stack assembly process, twelve bolts along the perimeter of the cells with M4 size were used to hold the cell components together and provided the contact pressure and gasket compression. Meanwhile, the overall weight of the stack was 510 g, without methanol fuel. Actual photos of the 6-cell hexagonal stack used for this study are shown in Fig. 6.

#### DMFC stack operation and long-term performance

The single cell and 6-cell stacks were operated in passive mode in ambient air conditions at a constant voltage. This voltage was referred to the optimal voltage at maximum power output, i.e., constant 0.2 V and 1.5 V for the single cell and stack DMFC, respectively. The experiment was started by varying the methanol concentration from 2 M to 6 M for the single cell and the stack to establish the optimal concentration based on the maximum power density obtained. The methanol fuel was injected at 8 ml and 240 ml (including 93 ml of fuel at the bottom level of the effective electrode area) for the single cell and stack, respectively. Fig. 7 shows the difference in methanol volume based on the level of fuel in the hexagonal methanol reservoir: a) the maximum fuel volume that could be filled at one time and b) the fuel volume used in this study. The performance of the cell (current–voltage,  $I$ – $V$ ) for all methanol concentrations was measured using linear sweep voltammetry (LSV) mode in a Potentiostat/Galvanostat WMPG1000 model (WonATech, Korea). The temperature was measured at the surface of the cathode by a thermocouple for the single cell and the stack.

To study the performance of the MEA and the degradation effect on performance for long-term operation, the stack was operated continuously for more than 3000 h (approximately four months). Initially, the stack was operated for approximately 60 h, and then the remaining solution in the reservoir was replaced with fresh fuel. This procedure was repeated every 60 h. The 60 h duration operation was considered as one cycle, and the stack was operated for 50 cycles using similar optimal methanol concentrations. Meanwhile, the level or height of fuel and the methanol concentration in the reservoir were measured at the initial operation and after 60 h of stack operation (remaining solution). The concentration of

methanol was measured using a density meter (Anton Paar Model DMA 35).

For a comparison in terms of the methanol reservoir design as well as the effect of the methanol volume on performance, i.e., of the single cell and hexagonal stack, the approximate energy density,  $E$ , in  $\text{Wh L}^{-1}$  was calculated based on experimental data and the following equation (Eq. (1))

$$E = \frac{P_{\text{avg}} \cdot t_{25}}{V_{\text{fuel}}} \quad (1)$$

where  $P_{\text{avg}}$  is the average power from the initial operation until the power decreases to 25% in milliwatts (mW),  $t_{25}$  is the time

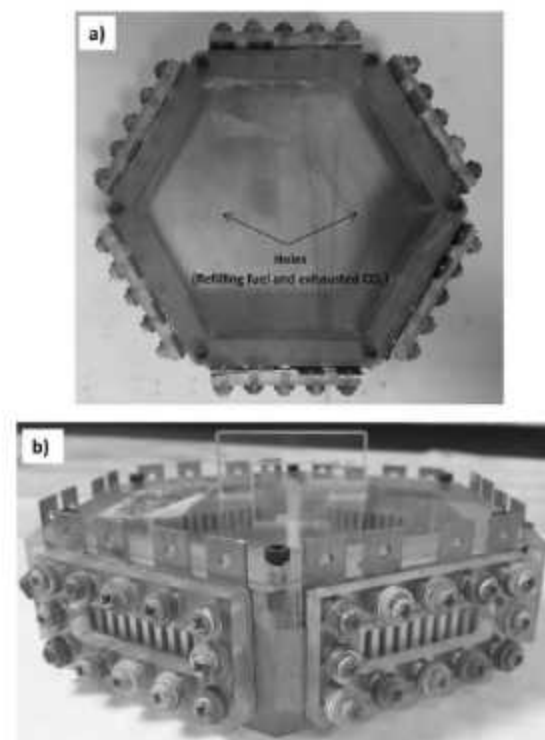
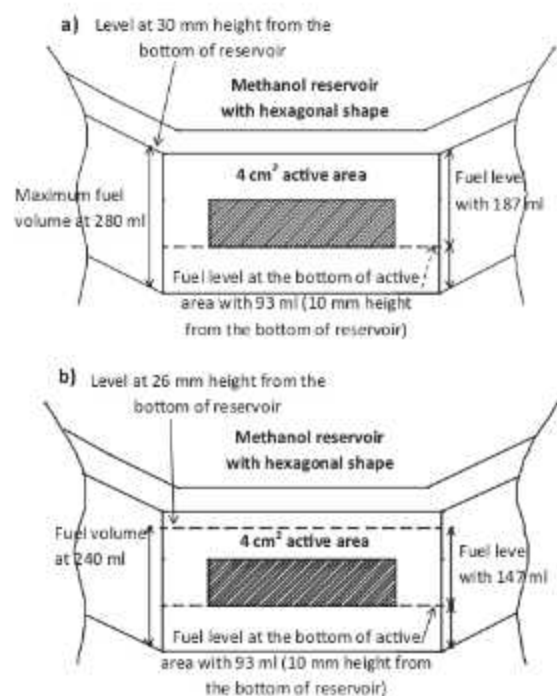


Fig. 6 – Photo of a 6-cell DMFC stack: a) top view with top cover, b) side view of hexagonal stack.



**Fig. 7** – Methanol volume based on the level/height of fuel in the hexagon reservoir; a) the maximum fuel volume that could be filled at one time; b) fuel volume used in this study.

required for the performance to decrease to 25% in hours (h), and  $V_{fuel}$  is the actual volume of methanol for anode reaction in the reservoir in ml.

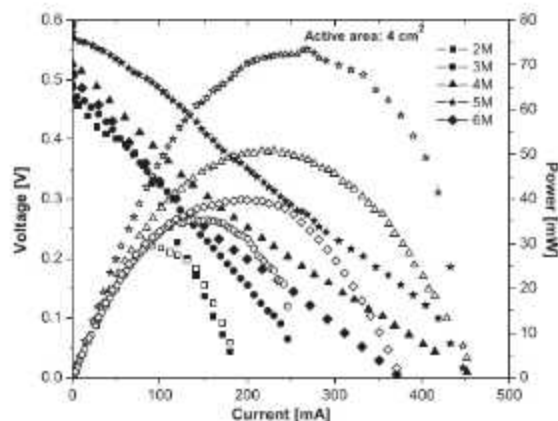
#### Morphology of MEA

The cross sections of MEA were observed for morphological analysis. The morphology for unused MEA and the selected MEA used for long-term operation, i.e., over 3000 h, were compared. This technique provided information about the degradation of the catalyst layer on the electrolyte membrane. Therefore, field emission scanning electron microscopy (FESEM) ZEISS Supra-55VP model (Carl Zeiss AG, Germany) was used for this morphological analysis.

## Results and discussion

#### Performance of passive single cell

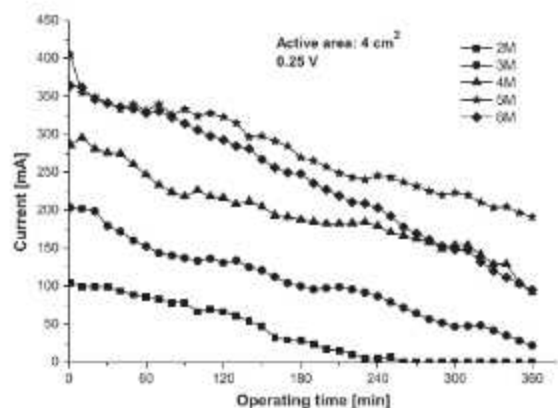
Fig. 8 shows the I–V curve for the single-cell DMFC with different methanol concentrations from 2 M to 6 M. As noted in the figure, the open-circuit voltage (OCV) was obtained in the range of 0.49 V–0.56 V. The OCVs decreased with increasing methanol concentrations from 2 M to 6 M; i.e., the OCVs at 2 M and 6 M were obtained at 0.56 V and 0.49 V, respectively. This tendency was similar to those of previous



**Fig. 8** – Single cell performance (current–voltage–power) of a 4 cm<sup>2</sup> active area for different methanol concentrations from 2 M to 6 M in ambient air conditions.

studies by Liu et al. [24] and Kulikovskiy [25]. It was suggested that the decrease in OCVs with increasing methanol concentrations was due to the mixed potential caused by methanol crossover (MCO). We understood that the flux of methanol crossover would increase with increasing methanol concentrations and hence reduced the OCVs. However, the maximum power increased with increasing methanol concentration from 2 M to 5 M before it decreased at 6 M. The maximum power output for the single-cell DMFC can be up to 89.2 mW, whereas the limiting current was obtained at 557 mA using 5 M concentration.

Fig. 9 shows the profiles of the current with time for the single-cell DMFC using different methanol concentrations at 8 ml in the reservoir. For all the cases in this figure, the current decreased with time during 6 h of operation. For low concentrations i.e., 2 M and 3 M, the current profiles show a rapid decrease up to 80% compared with their initial and final current at 6 h. Furthermore, by using 2 M, all methanol in the reservoir was consumed in the anode reaction as shown by



**Fig. 9** – Profiles of current output during 6 h (360 min) of operation for single-cell DMFC at 0.25 V with different methanol concentrations from 2 M to 6 M.



the very small current produced or zero current after 6 h of operation. Meanwhile, at 4 M and 5 M, the performance decreased in the range from 50% to 60% and at 6 M was nearly 70%. It was easily understood that the percentage of the decrease from initiation to 6 h of operation was due to the amount of methanol or the concentration at 8 ml in the reservoir. With similar volumes of methanol solution, the operating time would increase with increasing methanol concentration. However, for 6 M, the rapid decrease could be affected by other factors such as high methanol crossover.

The current densities at 2 h in the measurement of Fig. 9 are summarized in Fig. 10 with additional data for cell temperature at the cathode during 2 h of operation. As is clear from Fig. 10, there was a linear dependence of current density on methanol concentration, up to 5 M, before decreased at 6 M, i.e., from 323 mA to 293 mA for 5 M and 6 M, respectively. The linear dependence of the current on the concentration suggested that the cell operation was under the rate controlled by the methanol transport. By increasing the methanol transport, increasing the methanol concentration, the anode reaction rate would be increased and hence increase the current. When the current densities, i.e., at 2 h operation, proportionally increase with increasing methanol concentration, the current density must be determined by the rate of methanol transport to the anode [26]. This tendency is similar to that of our previous reports in the rate of the determining step in DMFC [26] and DFAFC [21].

For the operation above 5 M, the bend of the line indicates a change in the rate controlling step by methanol transport. In this region (negative slope in Fig. 10), the electrode reaction, at both the anode and cathode or the MCO, would be the rate determining step at high concentrations instead of the methanol supply. This trend is similar to that of our previous reports for the negative slope in DMFC [26] and DFAFC [21]. In this study, when methanol concentration increases beyond 5 M and becomes too high, the MCO flux dominates the performance gained from the improved fuel transport rate. Hence, the overall cell performance decreases with methanol concentrations of 6 M. In high concentration ranges (above

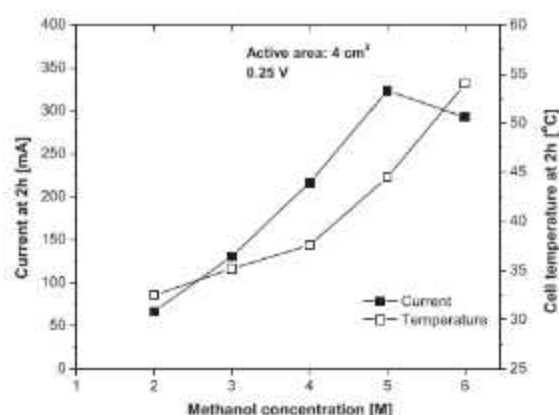


Fig. 10 – Current and temperature profiles at a 2 h steady-state condition for single-cell DMFC at 0.25 V with different methanol concentrations from 2 M to 6 M.

5 M), cell performance is hindered by the increase in fuel crossover flux. Higher concentrations of methanol result in higher fuel supply rates, which cause higher fuel crossover because of the diffusion force generated, so the overall cell performance is reduced.

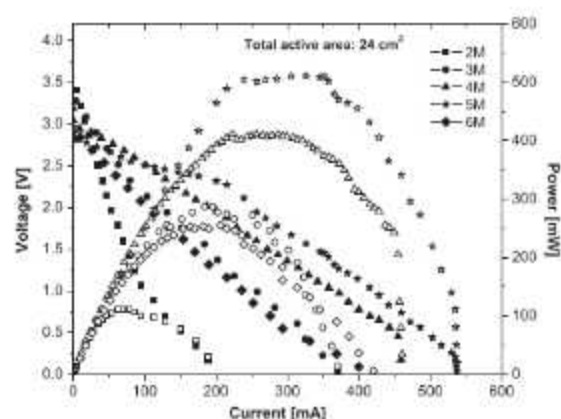
By increasing the methanol concentration, i.e., from 2 M to 6 M, it can increase the mass transport rate of methanol to the anode while simultaneously increasing the MCO rate and thus raising the mixed potential at the cathode. Therefore, the main reason of decreased DMFC performance at higher methanol concentrations, i.e., 6 M, is due to increased MCO that causes an excessive mixed potential at the cathode and thus deteriorates the cathode activity. Ha et al. were mentioned that the MCO could deteriorate the cell performance by generating a mixed potential and poisoning the catalyst in the cathode. Therefore, a further increase in methanol concentration would result in a performance decline due to the increased over-potential at the cathode [27]. Furthermore, a high MCO leads to water flooding and reduces the access of oxygen to the catalyst [28]. Hence, these phenomena could affect the electrochemical reaction in the cell, as shown by the decreasing current at 6 M.

Furthermore, the operation using different concentrations would affect the cell temperature. Fig. 10 shows the cell temperature obtained at the cathode surface at different methanol concentrations. The cell temperature varies under a load application at 0.25 V, and the value increased with increasing methanol concentration up to 54.2 °C at 6 M, as shown in Fig. 10. It increases with increasing methanol concentration from 32.4 °C at 2 M to 54.2 °C at 6 M. One can infer from Fig. 10 that the heat contribution by oxidation of the crossover methanol is higher than that released by oxygen reduction at the cathode. Therefore, at a high MCO, higher heat contributed to increasing the cell temperature, i.e., the higher cell temperature obtained at 6 M. Similarly, Ha et al. mentioned that the increase in methanol concentration would increase the MCO and hence increase the cell temperature [27].

#### Performance of 6-cell stack

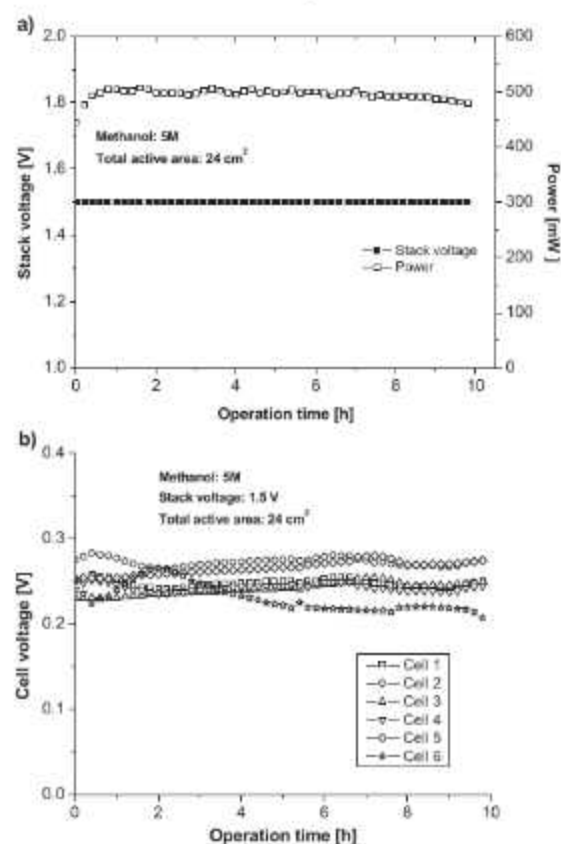
Fig. 11 shows the I–V curves for a passive 6-cell stack with different concentrations from 2 M to 6 M. The results show a similar trend to that of the single-cell performance as shown in Fig. 8. As seen in Fig. 11, the OCVs were obtained in the range of 2.4 V–3.41 V, and the values decreased with increasing methanol concentrations from 2 M to 6 M. It was confirmed again that 5 M was the optimal methanol concentration for the hexagonal stack, and the peak power output of 514 mW was obtained at 338 mA and 1.5 V. Therefore, for the performance test of the stack, the methanol concentration and the voltage were fixed at 5 M and 1.5 V, respectively.

Fig. 12 shows the profiles of the a) power and b) cell voltage for the 6-cell hexagonal stack at 5 M and constant 1.5 V with 240 ml of methanol solution during 10 h of operation. At the beginning of the cell operation, the power was observed to be unstable, largely increasing before becoming stable with time. The unstable power was related to the unstable initial methanol transport to the electrode. From the figure, stable power was obtained at nearly 500 mW and was constant throughout



**Fig. 11** – Performance of a 6-cell DMFC stack with a 24 cm<sup>2</sup> active area for different methanol concentrations from 2 M to 6 M in ambient air conditions.

10 h of operation. For each cell in the passive stack, as shown in Fig. 12(b), the voltage profiles showed unstable values, decreasing or sometimes increasing with time in the range of 0.2 V–0.3 V. These differences in profiles were due to the non-



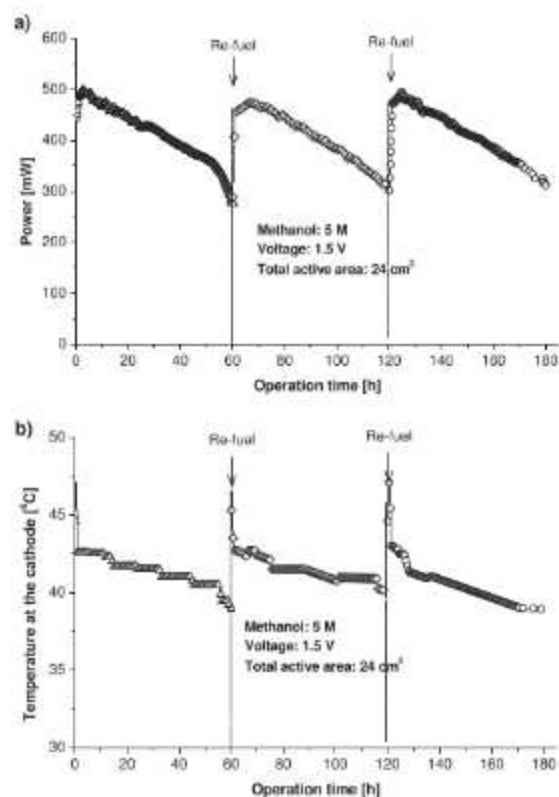
**Fig. 12** – Performance profiles with operation time at 1.5 V and 5 M methanol concentration: a) voltage and power output of DMFC stack, b) voltage for each cell in the stack.

uniform mass transport rates of reactants, i.e., methanol and O<sub>2</sub>, toward the electrodes as well as the insufficient removal of the reaction products, i.e., CO<sub>2</sub> and water, from the electrodes. However, the differences in cell voltages or cell performance for each cell in the stack were small and could be neglected.

#### Long-term operation of stack

To determine the DMFC stack performance over an extended period of time, a long-term test of the stack with 240 ml of 5 M methanol was performed, as illustrated in Fig. 13 (a). Similarly, the stack was operated under a constant voltage of 1.5 V. At the beginning of stack operation, unstable performance was observed, largely increasing before becoming stable after 1 h of operation. This profile was similar to that shown in Fig. 9 owing to the mass transport of methanol. In Fig. 13, it can be seen that the stack power output was nearly stable and gradually decreased with almost 45% reduction from the initial power after 60 h of operation. The remaining solution in the reservoir was then removed and replaced with a new 5 M methanol solution, as shown by the arrow in Fig. 13.

In the second cycle of the next 60 h of operation, a similar performance profile was obtained to that observed in the first 60 h, and the stable power reached was very similar to that of the previous 60 h, i.e., at almost 505 mW. Again, the power



**Fig. 13** – Stack operation during 180 h of operation at 1.5 V and 5 M methanol concentration: a) power output profiles, b) temperature profiles.



decreased gradually with time during 60 h of operation (120 h of total operation), and the reservoir was filled with fresh 5 M methanol for the third cycle of stack operation. It seemed that the performance fell back to 510 mW after 2 h and was then stable and gradually decreased for the next 60 h of operation. It was easily understood that the decreased performance of the stack during 60 h for each cycle (as shown in Fig. 13) was due to diluted methanol in the reservoir as a result of methanol consumption in the anode reaction. This was confirmed by methanol concentration measurement in the reservoir at the beginning (fresh), 5.0 M, and end (remaining),  $2.8 \pm 0.1$  M, of 60 h of stack operation.

For long-term operation after 60 h, the remaining solution and the level of fuel from the bottom of the reservoir were measured as 117 ml on average and as  $13 \pm 1$  mm in height, as seen in Fig. 7. It is easily understood that the decreases in volume, i.e., from 240 ml to 117 ml, and fuel level, i.e., from 26 mm to 13 mm in height, are due to the consumption of the methanol. From the other point of view, the decrease in the fuel level causes a decrease in the contact area between the effective electrode and the fuel due to the vertical orientation operation. Based on our result (as shown in Fig. 13(a)), the profiles of power show a gradual or linear decrease with time during 60 h of operation. We believed that the decreases in the performance of the DMFC stack were mainly due to methanol consumption in the anode reaction, so the remaining methanol in the reservoir would be diluted. Moreover, it is suggested that the anode diffusion layer plays an important role to distribute the methanol fuel at the effective electrode even if the contact area decreases between the electrode and the fuel. Therefore, the decrease in performance due to the contact area factor is very small and can be negligible, as illustrated by the lack of a rapid drop in the power profile in Fig. 13(a). Meanwhile, Nakagawa et al. studied the orientation of cells either vertical or horizontal [29]. They also found that the orientation did not affect the cell performance when the cell was operated under the rate determining step and was controlled by the methanol transport as mentioned previously.

Fig. 13(b) shows the measured temperature at the cathode surface during the stack performance test as shown in Fig. 13(b). For the temperature measurement, we measured the temperature for only one cell (cell 1) to represent the temperature during stack operation (assuming a similar temperature value and profile for each cell). At the beginning of the operation, the high initial temperature in the range of  $47^\circ\text{C}$ – $48^\circ\text{C}$  could be due to higher MCO as mentioned previously. For all cases, i.e., after refueling, the temperature was stable and gradually decreased with time from  $43.5^\circ\text{C}$  to  $39.2^\circ\text{C}$ . This temperature profile was related to the output electric current as shown in Fig. 13(a) and the degree of MCO. For instance, at high MCO, higher heat contributed (due to methanol oxidation at cathode) to increasing the cell temperature, i.e., the higher cell temperature obtained in Fig. 13(b).

#### Performance stability and degradation

In Fig. 13(a), it can be seen that with a large volume, i.e., 240 ml of solution at 5 M, the stack can be operated for 40 h with a 25%

reduction from the initial performance, and its performance then decreases to 45% after approximately 58 h–60 h of operation. It was clear that with a small volume such as 8 ml of solution in the reservoir for a single-cell DMFC, the operation could last for only 3 h–4 h with a similar reduction of 25%.

The DMFC stack performance over an extended period of time was continued for several cycles (60 h per cycle) to monitor the degradation of the stack performance. Fig. 14 shows the stack performance from cycles 1 to 50 using 240 ml of 5 M methanol solution in the reservoir. For all cycles, unstable performance was obtained in the first 1–2 h with large increases and decreases with time. In the figure, it is easily seen that the degradation of the DMFC stack increased with increasing operating cycle. For instance, after 30 h of operation, the percentage of degradation (compared with that of a single cycle) increased by 8.5%, 19.4%, 25.9%, 29.8% and 38.1% in the 10th cycle, 20th cycle, 30th cycle, 40th cycle and 50th cycle, respectively.

To compare the stability of power output between the single cell and the stack, the energy density,  $\bar{E}$ , in  $\text{Wh L}^{-1}$  was calculated based on the methanol solution volume and the operating time. Although this parameter does not show the exact energy density and the amount of fuel consumption for the reaction, it can be a parameter to compare the stability of the power output of the single cell and stack.

Fig. 15 shows the calculated  $\bar{E}$  and power density during long-term operation from 1 to 50 cycles (~3000 h). For the single cell operation with 8 ml of fuel,  $\bar{E}$  was calculated to be  $36.9 \text{ Wh L}^{-1}$ . This value was similar to that obtained by Nakagawa et al. at nearly  $35 \text{ Wh L}^{-1}$  with 8 ml of fuel in the passive condition [30]. As is clear in Fig. 15, by comparing the 1st cycle for both the single cell, i.e., 3 h of operation, and stack, i.e., 40 h of operation, the calculated  $\bar{E}$  for the stack was almost 4 times higher than the single cell at  $142.5 \text{ Wh L}^{-1}$ , even at a similar power density of  $21 \text{ mW cm}^{-2}$ . It can be easily seen that with the large methanol reservoir—i.e., the hexagonal stack—the energy density of DMFC would increase as

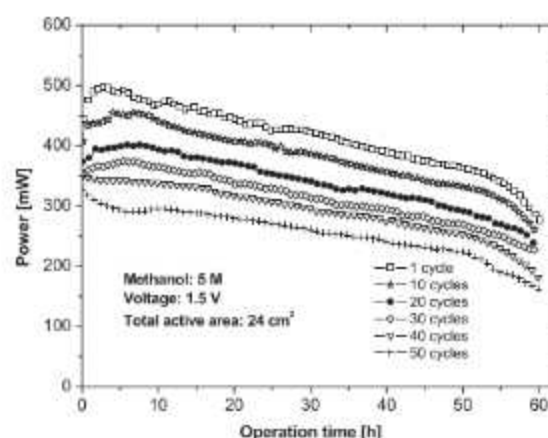


Fig. 14 – Profiles of stack power output during long-term operation of a DMFC stack at 1.5 V and 5 M from 1st cycle until 50th cycle.

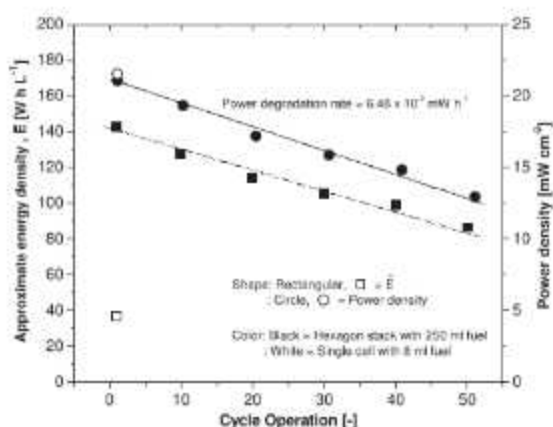


Fig. 15 – Approximate energy density and degradation rate of stack performance from the 1st to the 50th cycle of operation.

result of increasing operation time. The calculated energy density in this study was slightly higher than that obtained from previous work by Kim at  $95 \text{ Wh L}^{-1}$  [31] and similar to that of EFOY 1600-M5 from the Smart Fuel Cell company at  $141.5 \text{ Wh L}^{-1}$  [32]. However, it was lower than previous studies using high methanol concentrations or neat methanol such as  $600 \text{ Wh L}^{-1}$  [30] and  $800 \text{ Wh L}^{-1}$  [33].

Meanwhile, the performance of the 6-cell stack decreased with time as shown by the linear decrease of E and power density with increasing cycles seen in Fig. 15. For instance, the power density decreased from  $21.5 \text{ mW cm}^{-2}$  to  $13.0 \text{ mW cm}^{-2}$  for the 1st cycle and 50th cycle of operation, respectively. The calculated rate of degradation of the power output was  $6.48 \times 10^{-2} \text{ mW h}^{-1}$ . This value was lower than that reported by Cheng et al. of  $8.73 \times 10^{-2} \text{ mW h}^{-1}$  after 1002 h of operation [20], which could be due to the MEA preparation. Therefore, it was suggested that the MEA preparation, i.e., types of material, technique used, and difference in loading, could be the main factor in the performance degradation.

This degradation could result from the degradation of each MEA in the stack. Two possible reasons have been suggested for the reduced MEA performance due to a decrease in the

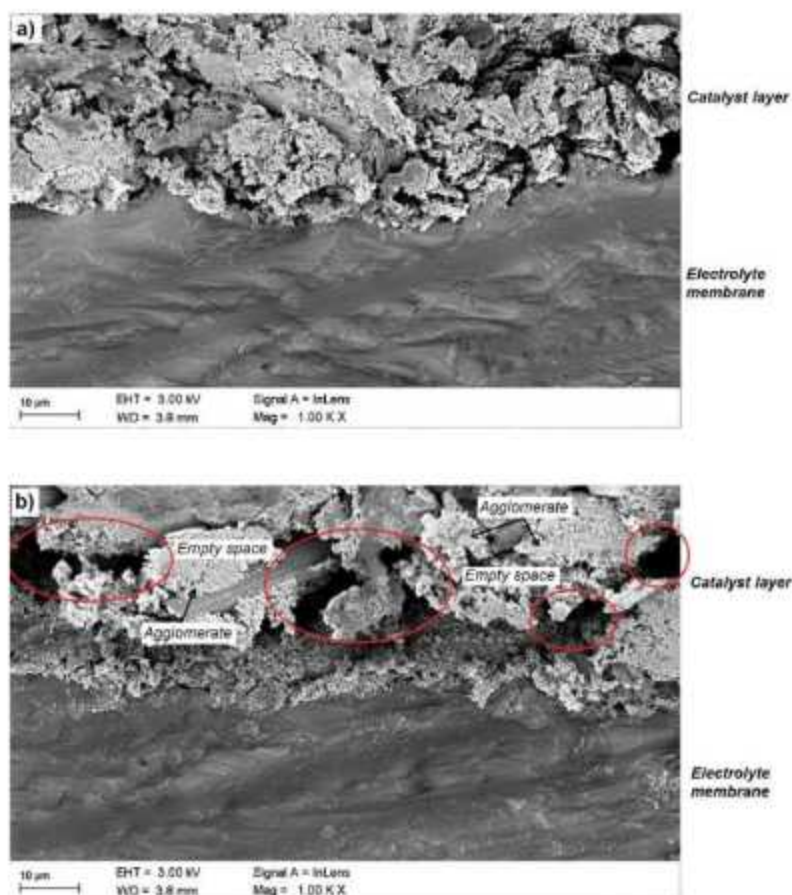


Fig. 16 – A cross-sectional FESEM view of the MEA; a) unused MEA, b) MEA of cell 1 after 3000 h of stack operation.



activity of electrochemical reaction. The first is the contribution of the catalyst detached from the catalyst layer or from the carbon supporting surface mostly at the anode electrode. This condition occurred in this study as shown in Fig. 16(a).

Fig. 16 shows the cross-section morphology of a) the unused MEA and b) the MEA of cell 1 after 3000 h of operation. By comparing these two images, it is clearly seen that an empty space presence between the catalyst layer and the electrolyte membrane and agglomeration of catalyst occurred in the used MEA. The particles of the catalyst agglomerated after prolonged operation and led to a gradual decrease in the electrochemically active surface area. Hence, it would decrease and degrade the stack performance in long-term operation as shown in Figs. 14 and 15. Cheng et al. [20] found that the surface areas of catalysts and atomic %Ru of PtRu black noticeably decreased after the lifetime operations, which led to decreased activity of catalysts. They suggested that the formation of ruthenium oxide occurred and could also result in the reduction of atomic % Ru in PtRu black. Therefore, it was easily understood that with higher catalyst loading of PtRu used in this study, i.e.,  $8 \text{ mg cm}^{-2}$  compared with  $2 \text{ mg cm}^{-2}$  used by Cheng et al., it could reduce the degradation of PtRu at the anode. Hence, the degradation rate of DMFC performance could be reduced as result of a lower degradation rate than that in the work by Cheng et al. [20] as mentioned previously.

Moreover, in investigating the degradation of a DMFC, Lai et al. concluded that the catalysts in both the anode and cathode aggregated to decrease the catalytic activity in the degradation process by XRD and TEM [34]. Moreover, Silva et al. identified morphological changes in the catalyst surfaces, such as loss of porosity and platinum aggregation, and deformation on the MEA components (anode, cathode and membrane) [35]. These morphologies were identified using the SEM and TEM study when the cell was operated long-term for more than 1500 h.

Meanwhile, a second contribution could be chemical aging of the electrolyte membrane [35], which would have the effect of reducing the transportation of protons ( $\text{H}^+$ ) from anode to cathode, thus slowing the reduction reaction at the cathode. Based on physical observation during this study, the color of electrolyte membrane changed from transparent-white to yellow-brown after a long-term stack operation. This change in color could be affected by chemical aging or changing chemical composition in electrolyte membrane. Moreover, this chemical aging would increase the cell resistance, leading to lower ionic conductivity of the electrolyte membrane and hence, to lower voltage and performance [35].

## Conclusion

A passive 6-cell DMFC stack was designed, fabricated and tested based on single-cell performance. The performance of the single cell and stack were tested with different methanol concentrations ranging from 2.0 M to 6.0 M, and the optimal performance was achieved by using methanol at a concentration of 5.0 M. The power densities obtained for the single cell and 6-cell stack were very similar at  $21 \text{ mW cm}^{-2}$  using 5 M concentration at ambient temperature. A power output of the stack of 505 mW could be reached at 1.5 V. The rate of

reduction and degradation of performance were also measured for both the single cell and the 6-cell stack DMFC. The stack with a huge reservoir could run for more than 40 h of operation without adding or refilling the methanol solution but for only 3–4 h for single cell operation, with similar reductions of 25% from the initial power output. Therefore, a large reservoir would benefit any electronic devices that require long-term operation i.e., without any addition or refilling of fresh methanol fuel, and this would save time for the user in terms of the frequency of refilling the reservoir. Hence, DMFC technologies are a suitable candidate and will be a more attractive option for powering advanced electronic devices in the future.

## Acknowledgments

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