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Effect of operation parameters on performance of micro direct methanol fuel cell fabricated on printed circuit board

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Abstract

Directed methanol fuel cells (DMFCs) are fabricated on printed circuit board (PCB) substrates by means of a photolithography process. The effects of channel pattern, channel width and methanol flow rate on the performance of the fabricated DMFC are evaluated over a range of flow-channel widths from 200 to 400 μm and flow rates of methanol from 2 to 80 ml min^{-1}. A micro-DMFC with a cross-stripe channel pattern gives superior performance compared with zig-zag and serpentine type of pattern. A single cell with a 200-μm wide channel delivers a maximum power density of 33 mW cm^{-2} when using 2 M methanol feed at 80 °C. An air-breathing multi-DMFC composed of eight single unit cells gave 180 mW cm^{-2} by using a methanol reservoir. It is considered that this may be the first reported attempt to develop a multi-DMFC with micro-channels fabricated on a PCB substrate.

Keywords: Micro direct methanol fuel cell; Air breathing; Micro-channel; Power density; Printed circuit board; Channel width

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1. Introduction

The demand for portable electronics requires the development of effective power supplies. This requirement is not fully satisfied with primary and secondary batteries because the speed of technology development of these power sources has not kept pace with market demands. Accordingly, micro fuel cells are attracting much interest for such applications. The power output of a fuel cell is strongly related to the amount of fuel rather than to the volume of the system. Taking this into consideration, it is considered that a well-designed micro fuel cell can meet the power demands of portable electronics.

Most of the initial work of planar micro fuel cells has been conducted with silicon substrates [1–4]. The effects of the size and shape of the micro-channels on the power performance have been investigated and analyzed by employing computational fluid dynamics [5–7]. Although the study addressed a proton exchange membrane fuel cell (PEMFC) using pure hydrogen and air, Cha et al. [7] concluded that flooding can become a serious issue in micro-channels. In other work, O'Hayre et al. [8] developed a portable PEMFC array by using printed circuit-technology.

In order to increase the power output of a single DMFC, it is necessary to combine single cells for application in portable electronic devices. Given that a planar cell configuration offers advantages in terms of power density, manufacturability and packaging flexibility compared with conventional vertical stack designs [9], a planar flip-flop stack has been employed in this study. Further, in the absence of any reports on the effect of micro patterning on DMFC power performance, three types of channel pattern have been compared, namely zig-zag, serpentine, and cross stripes. The cells have been fabricated on a printed circuit board (PCB) substrate as these have several beneficial properties, i.e., design flexibility, facile device integration, light weight, low cost of fabrication. In addition, the effects of channel width and the methanol flow rate on micro-DMFC performance have been examined. Based on the findings from investigations a single micro-DMFC, a monopolar multi-DMFC composed of eight single cells has been fabricated and its performance evaluated.

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2. Experimental

2.1. Fabrication of micro methanol flow channel

A PCB substrate with a 70 μm-thick layer of copper was used to build a micro-DMFC channel. A high-sensitivity negative photoresist (Junsei TPR-201) was formed by hot pressing at 125 °C and 1 t for 30 s. A conventional photolithography process with a 250 nm UV lamp was used to make a pattern on the photoresist on the frontside of the PCB substrate. Also, a photolithography process was conducted on the backside of the PCB substrate to fabricate the circuit. The front and backside copper layers exposed by the photolithography process were etched with a commercial PCB copper etchant (SME Trading EP-15) for 15 min. In order to investigate the effects of flow channel width, channels of 200, 300, and 400 μm were produced. The efficacy of three types of flow pattern, namely, zig-zag, serpentine and cross stripe was employed and evaluated. A monopolar, planar, multi-cell structure was also prepared by using the best combination of flow-channel parameters was determined from single-cell experiments.

Since the exposed copper can be oxidized by methanol, the pattern requires passivation. After degreasing (ACL-009, 3 min), soft etching (Na_2O_8 and H_2SO_4, 3 min), pre-dipping (MSR-28P, 1 min) and catalyst adsorption (MSR-28A, 5 min followed by MSR-28B, 5 min) processes, nickel plating was performed at 85 °C for 20 min. Then, gold plating was performed at 50 °C. The frontside copper rib and backside copper channel were electrically connected by nickel and gold plating after a hole was made through the PCB substrate.

In order to supply the methanol and oxygen efficiently through the channel, a hole was made on the side of PCB substrate, so that a syringe needle with a 400 μm-outer diameter could be inserted and used to feed methanol and oxygen into the channel. In order to have uniformity of flow rate and easiness of supply of methanol in multi-cell operation, a reservoir was fabricated and attached underneath of PCB substrate of the anode.

2.2. Fabrication of electrode and MEA

Catalysts containing 60 wt.% of Pt–Ru or Pt on VCXC72 carbon (E-Tek) were stirred with *iso*-propyl alcohol, 5 wt% Nafion solution (DuPont), and water. Sonication and stirring were repeated five times, and finally stirring was continued for 24 h at room temperature to prepare the electrode catalyst slurry. The slurry was sprayed on the electrolyte membrane (Nafion117, DuPont) to give 4 mg cm^{-2} of metal catalyst. By using this method to fabricate an electrode, the thickness of the MEA may be as thin as 0.5 mm. The electrode was finally dried at 80 °C for 2 h. To improve the sealing, hot pressing at 125 °C and 1 t was applied for 40 s and teflon sheet of 250-μm thickness was used as a gasket. Front and back side-plates were also used to provide good sealing between the catalyst layers and the membrane.

2.3. Operation and performance test of micro-DMFC

A 2 M solution of methanol was supplied to the anode at flow rates of 2–180 ml min^{-1}. Oxygen was supplied to the cathode at a flow rate of 30 ml min^{-1}. A d.c. electronic load (Hewlett Packard 6060B) was used to measure current–voltage characteristics. The current was measured by means of a micro electronic load (Keithley 2000). Cyclic voltammetry (Autolab, Potentiostat) was used to determine the oxidation potential of methanol using a half-cell. For that measurement, hydrogen was fed into the cathode so that it became a dynamic hydrogen electrode (DHE) and served as a reference electrode. Cyclic voltammetry measurements were operated at −0.3 to 1.5 V with potential sweep speed of 20 mV s^{-1}.

Changes in membrane resistance, and interface resistance were investigated by means of a.c. impedance. The anode was used as a reference electrode and the cathode as a working electrode. In the range 100 mHz–100 kHz, the response to the a.c. amplitude of 10 mV was measured with an impedance analyzer (Autolab FRA).

3. Results and discussion

3.1. Effect of flow rate on performance of micro-DMFC

As the structure of the micro-DMFC prepared in this study has a narrow cell channel, the performance is strongly affected by the flow rate of methanol supplied to the cell [10]. Date for a change in the flow rate of 2 M methanol from 2 to 180 ml min^{-1} at 80 °C are presented in Fig. 1. A channel width of 400 μm was used for these experiments. Performance improves on increasing the flow rate up to 17 ml min^{-1}, but degrades at higher rates. A maximum power density of 23 mW cm^{-2} is obtained at 17 ml min^{-1} of methanol. Changes in the membrane resistance and interfacial resistance with increase in methanol flow rate are shown in Fig. 2. Both resistances increase with the flow rate of methanol, especially when this is above 17 ml min^{-1}.

With a very low flow rate of methanol, it is difficult to obtain good reactivity from the catalytic layers. It is suggested that non-plug flow behaviour at the higher flow rates is the reason for the degradation of fuel cell performance. An excessive flow rate may hinder the transport of protons from the catalytic layer to the membrane.

3.2. Effect of channel width on performance of micro-DMFC

It is important to analyze and optimize the transport phenomena in fuel cell systems because the transport of protons is a key factor in improving system performance. In particular, the pattern shapes of the flow channels and ribs and the diffusion layer thickness are important factors that need to be optimized. In this study, the effect of flow channel width on micro fuel cell performance is examined. The change in the fuel cell performance at 80 °C for flow channels with widths between 200 and 400 μm is shown in Fig. 3. A 200 μm-width single-cell exhibited a maximum power density of 33 mW cm^{-2} at 80 °C. As the

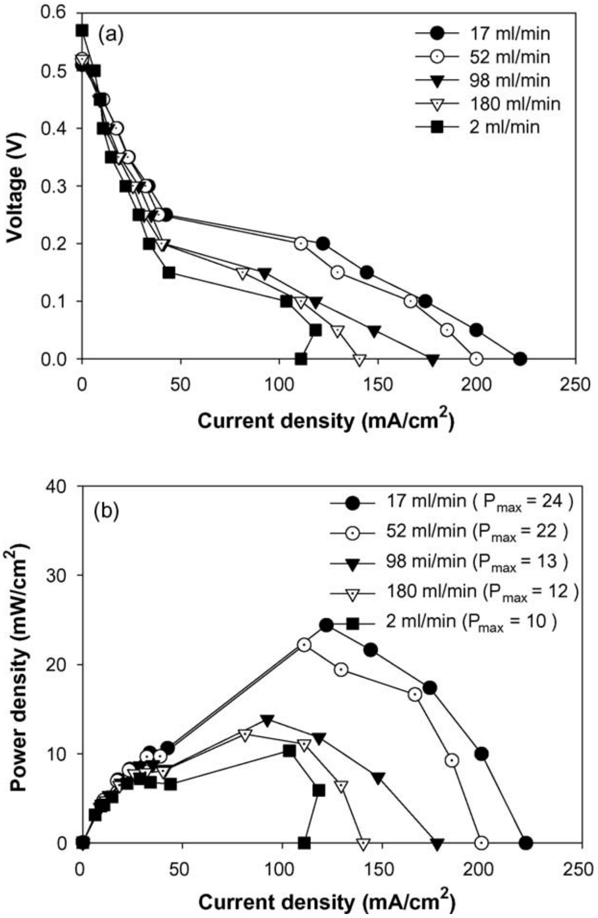

Fig. 1. Performance of micro-DMFC with various methanol flow rates: (a) *I–V* curve; and (b) power density. Insert shows maximum power density at each methanol flow rate.

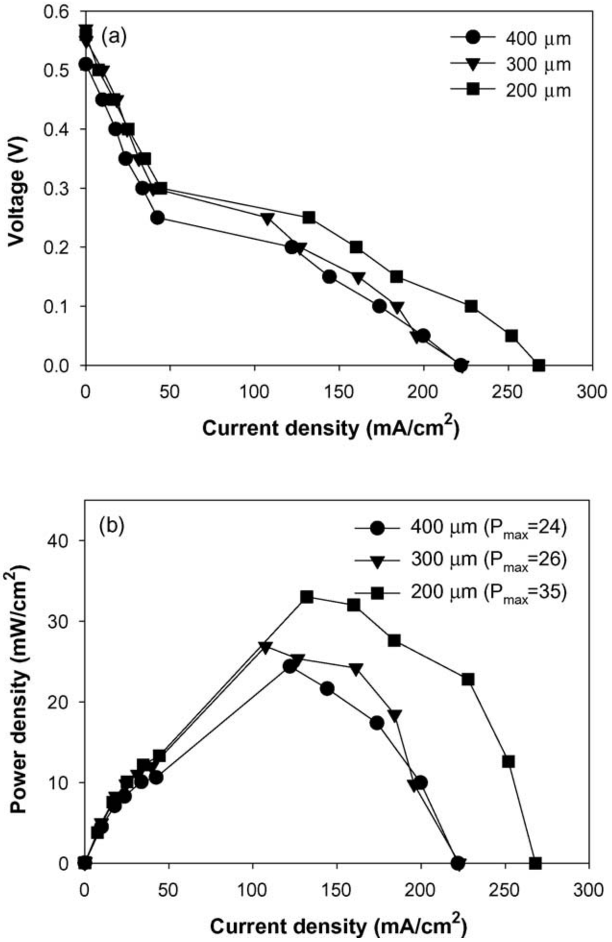

Fig. 3. Performance of micro-DMFC with various channel widths at 80 °C: (a) *I–V* curve; and (b) power density. Insert shows maximum power density at each methanol flow rate.

results show, the highest open-circuit voltage and fuel cell performance are obtained with a 200 μm-channel width, and the performance becomes degraded with increase in channel width. The same trends are observed at 40 and 60 °C.

The observed results are interpreted as follows. First, they can be explained by a dead-zone effect [9,10], which is illustrated by the oxygen concentration profiles in the diffusion layer. It is thought that the oxygen concentration is lower near the catalyst layer for a wider channel. Therefore, the performance of the micro fuel cell will be degraded with an increased channel width. In addition, a small channel has a consequent higher flow velocity, which accelerates convective mass transport. An increase in pressure loss becomes a concern as the channel size decreases. Nevertheless, the penalty encountered in terms of pressure drop is less significant than the benefits provided by enhanced flow through the micro-channels [11].

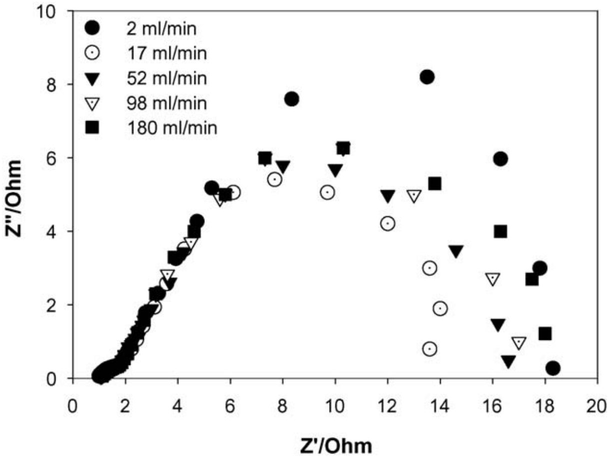

Fig. 2. Impedance plots for various methanol flow rates for a 400 μm channel width at 80 °C.

3.3. *Effect of channel pattern on micro-DMFC performance*

In order to improve the performance of micro fuel cells, a flow pattern that has a lower flow resistance has to be designed. Three distinct types of flow pattern, namely zig-zag, serpentine, and cross stripes, were fabricated, as shown in Fig. 4, and were evaluated to find a suitable pattern for micro fuel cell fabrication. The results from performance testing of the three types of flow pattern at 80 °C are shown in Fig. 5. The performance of the micro fuel cell with a cross-stripe pattern is the best, while that with a serpentine pattern is the worst. In particular, the superior

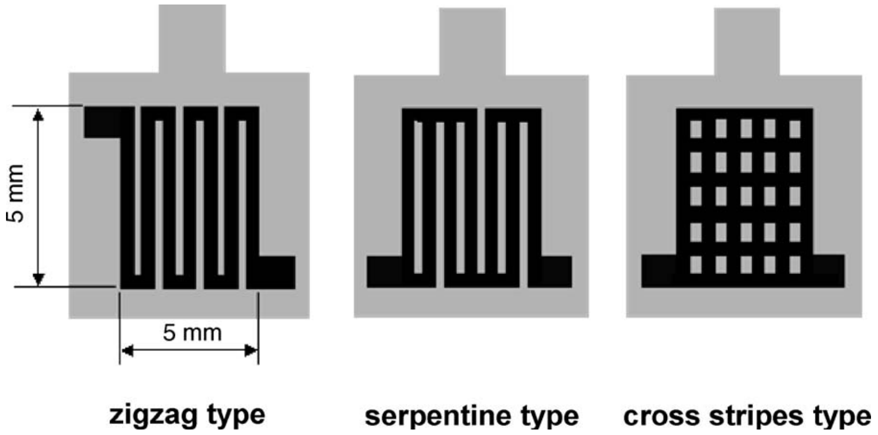

Fig. 4. Different types of channel pattern for anode and cathode.

performance with a cross-stripe pattern is obvious in the lower voltage region.

Data obtained from impedance measurements are given in Fig. 6. The lowest membrane resistance of 0.53 Ω and interface resistance of 4.22 Ω are obtained for a cross-stripe pattern. This strongly suggests that a cross-stripe pattern is favourable to obtain better transport of protons at the MEA–cell contact. A serpentine pattern has the highest interface resistance, which may be the reason for the accompanying degradation in micro fuel cell performance.

Cyclic voltammograms with different channel patterns are plotted in Fig. 7. A cross-stripe pattern has the lowest methanol oxidation and oxidation initiation potentials, while a serpentine

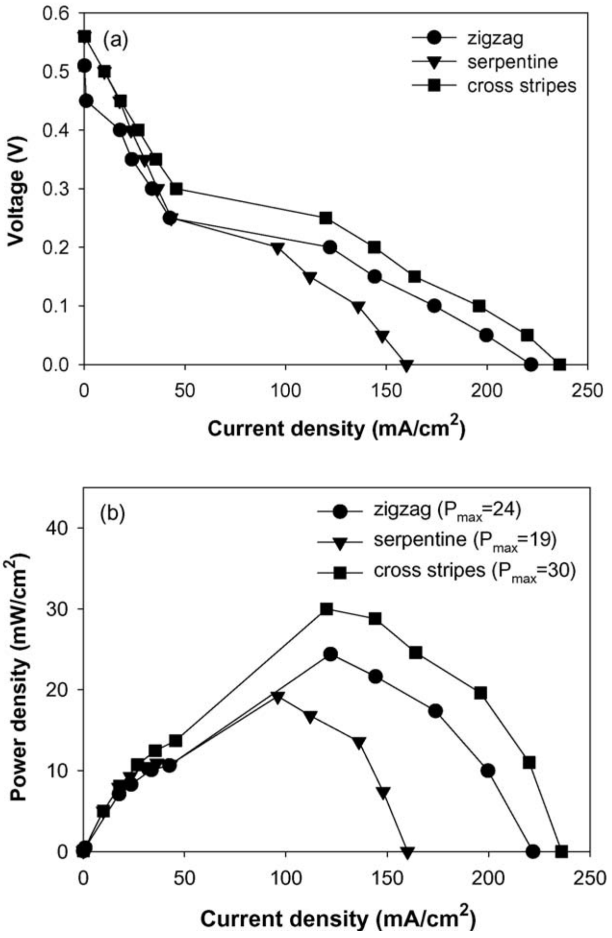

Fig. 5. Performance of micro-DMFC with various channel patterns at 80 °C: (a) *I*–*V* curve; and (b) power density. Insert shows maximum power density at each methanol flow rate.

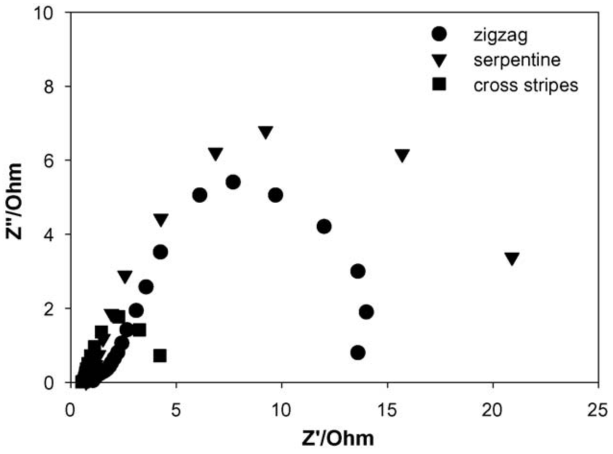

Fig. 6. Impedance plots for various channel patterns at 80 °C.

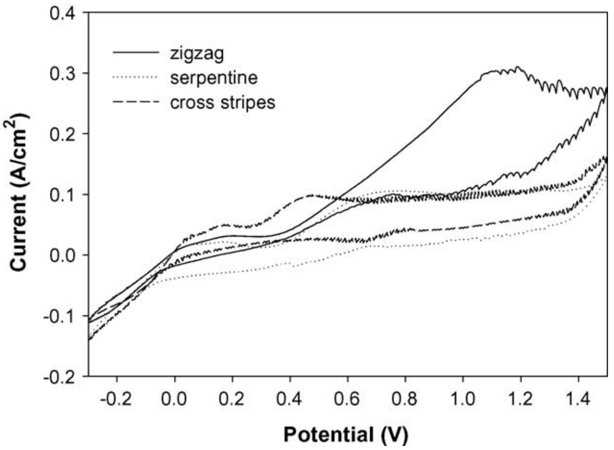

Fig. 7. Cyclic voltammetry with various flow patterns and Pt–Ru/C electrode in 2 M CH_3OH at 80 °C.

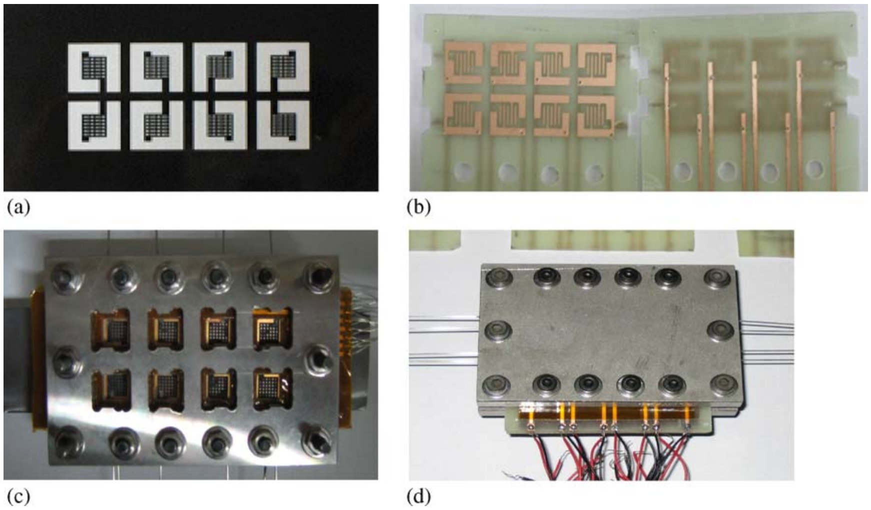

Fig. 8. Examples of multi-cell fabrication: (a) mask for photolithography; (b) front and backside patterns of multi-cell on PCB substrate; (c) fabricated air-breathing multi-cell; and (d) fabricated non-air-breathing multi-cell.

pattern has the highest oxidation potential. From the fact that the reactivity of the catalyst and the oxidation of methanol are strongly related to the oxidation and oxidation initiation potentials of methanol, the results shown in Fig. 7 suggest that not only the membrane and interface resistances, but also the oxidation potentials of methanol are affected by the type of flow pattern. It is also emphasized that channel pattern is one of the most important factors that needs to be optimized when designing a micro-DMFC.

3.4. Application to multi-cell micro-DMFC

The best combination of parameters obtained for a single micro-DMFC was used in the fabrication of a multi-cell micro-DMFC. A methanol flow rate of 17 ml min^{-1} with a cross-stripe pattern of 200 μm in width was used. A banded-structure multi-cell was fabricated to minimize the volume of the micro-DMFC because the fabrication of cells in a parallel configuration does not require an additional system for collecting the current. A monopolar design of multi-DMFC with eight single cells (four cells in each row) has been chosen to target voltage of 3.6 V for use in cellular phones. An example of the multi-cell is shown in Fig. 8. Two types of multi-micro-DMFC, namely, an air-breathing type (Fig. 8c) and a non air-breathing type (Fig. 8d), were fabricated.

A comparison of the open-circuit voltages (OCVs) of the air-breathing and non air-breathing types of monopolar multi-micro-DMFCs at the cathode side is presented in Fig. 9. The OCV of the non air-breathing DMFC falls from 3.8 to 2.2 V in 5 min. Rapid increase in crossover due to the transport of methanol through the non-catalyst layer and insufficient supply of the oxygen may be responsible for the steep degradation in performance. In order to solve these problems, an air-breathing type was introduced and a built-in methanol feed reservoir was fitted between the cell and the end-plate [11]. With these modifications, the air-breathing multi-micro-DMFC shows a marked improvement in OCV.

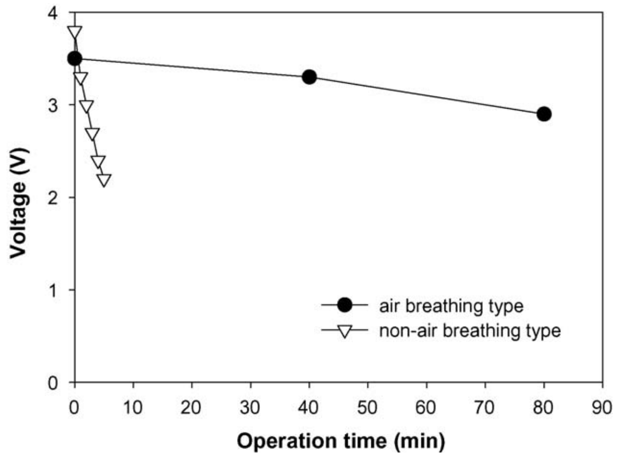

Fig. 9. Comparison of open-circuit voltages of air-breathing and non air-breathing cells at cathode side.

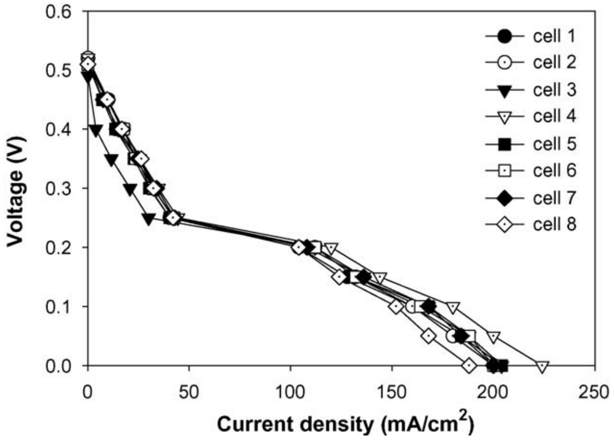

Fig. 10. Current–voltage curve of eight unit cells in air-breathing multi-cell DMFC.

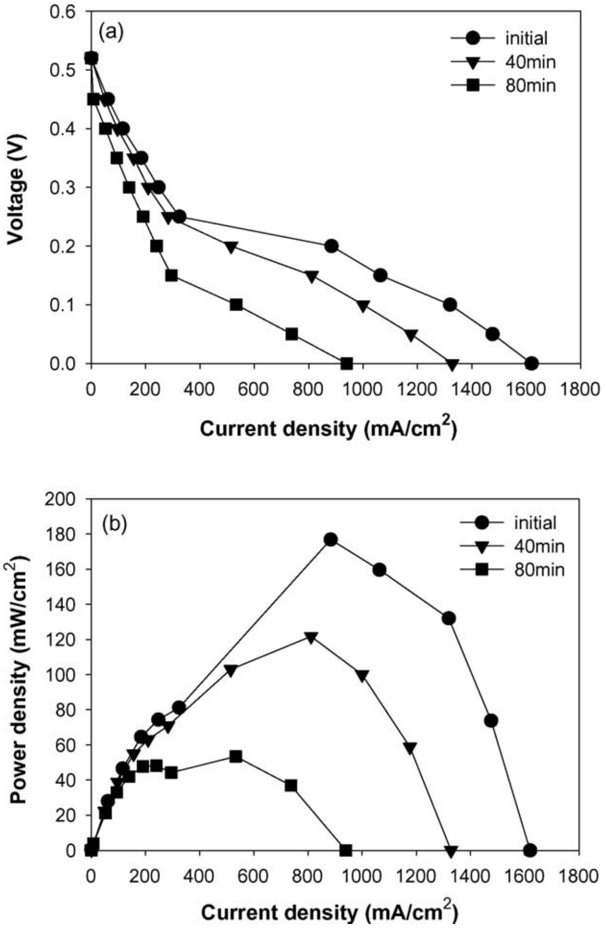

Fig. 11. Total performance of air-breathing multi-cell DMFC with operation time: (a) *I–V* curve; (b) total power density.

The performance of each cell in the air-breathing multi-cell DMFC is given in Fig. 10. The uniformity of the performance of each cell was very good in the range 0.1–0.5 V, except for cell 3. The standard deviation divided by the average of the current density data points is 0.01–0.1 over the voltage range of 0.1–0.5 V, except for cell 3.

The total performance of the air-breathing multi-cell DMFC collected from the eight unit cells is plotted in Fig. 11(a). The change in performance with operation time is also shown. The DMFC was operated for 80 min and current–voltage measurements were conducted at 0, 40 and 80 min. The results show that the performance degrades with operation of the system. It is considered that this effect is due to the oxidation of copper by methanol after lift-off of the Au–Ni layer during operation of the DMFC, which is attributed to the poor adhesion of this layer with copper on the PCB substrate. To solve this problem, thermal treatment of the Au–Ni on the copper layer is recommended, which has been limited in this study because of the use of a PCB substrate. The introduction of non-corrosive material may be also needed for the ribs of the micro pattern. In addition to the corrosion issue, it is suggested that condensation of water in the micro-channel may affect transport phenomena and the power output of the monopolar multi-DMFC.

The total power density of the air-breathing multi-cell DMFC collected from the eight unit cells is shown in Fig. 11(b). A maximum total power density of 180 mW cm^{-2} is obtained at the beginning of operation, which is slightly lower than the product of the number and the maximum power density of the unit cells in Fig. 3(b). This indicates that eight single cells do not have the same interfacial resistance, flow distribution and/or electrical resistance. The maximum total power density decreases with operation of the DMFC, as already shown in Fig. 11(a).

4. Conclusions

By using a photolithographic process on 70 μm-thick copper, micro patterns are fabricated on printed circuit boards. Direct methanol fuel cells are fabricated with a micro-patterned anode and cathode with Nafion/Pt–Ru/Pt MEA structure. The effects of channel pattern, channel width and methanol flow rate on DMFC performance have been examined. A cross-stripe patterned micro-DMFC shows the best power performance, which may be attributed to the lowest membrane resistance of 0.53 Ω and lowest interface resistance of 4.22 Ω. A methanol flow rate of 17 ml min^{-1} gives the best power performance. It is suggested that an excessive flow rate hinders the transport of protons from the catalytic layer to the membrane because of an increase in the interfacial resistance. Three widths of channel have been investigated and that with a value of 200 μm delivers the best power performance. It is considered that this is due to an improved convective mass transport coupled with the fact that wider channels experience a deleterious dead-zone effect. A single cell with a 200-μm wide channel gives a maximum power density of 33 mW cm^{-2} at 80 °C.

The performance of an air-breathing, monopolar, multi-micro-DMFC is superior to that of a non air-breathing type. The air-breathing DMFC exhibits good uniformity of performance among the eight constituent cells and maximum total power density of 180 mW cm^{-2} by using a methanol reservoir.

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