

Design and fabrication of pumpless small direct methanol fuel cells for portable applications

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Abstract

This work studied the design, fabrication, and performance evaluation of a 36 cm², passive, air-breathing, room-temperature, direct methanol fuel cell (DMFC). The cell is completely passive with no external pumps or other ancillary devices. It takes oxygen from the surrounding air, and the methanol solution is stored in a built-in reservoir. The fuel cell runs successfully with methanol concentration ranging from 0.5 to 4 M. It produced a power density of 11 mW cm⁻² reached with 4 M methanol at current densities as high as 36 mA cm⁻² and at a voltage of 0.3.

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1. Introduction

Significant efforts in developing micro (sub-watt) and portable (1–20 W) direct methanol fuel cell systems are being made by several organizations around the world [1–15]. Methanol is a liquid fuel with a very high specific energy density. In addition, direct methanol fuel cells (DMFCs) can operate at ambient temperature, which significantly reduces the thermal management challenges for small systems. Furthermore, methanol is to a great extent easier to store and transport without auxiliary devices for intermediate fuel processing and fuel reforming steps which are required by hydrogen–oxygen fuel cells. The byproducts of DMFC are ecologically inoffensive CO₂ and water. These are the reasons why the DMFC system has been regarded as a potential substitution to conventional batteries for powering various low-power devices.

For many applications that have been proposed for small-scale fuel cells, it would be essential that they be stand-

alone systems with no external pumps or other ancillary devices. Therefore, air-breathing fuel cells (i.e., cells that take the oxygen directly from the surrounding air), which use a passive methanol reservoir may offer advantageous properties, because there is no need of auxiliary air or fuel circulation devices.

This work reports on some of our recent activities regarding the research and development of completely passive room temperature operation small DMFCs power sources. These systems are intended for portable electronics such as laptop computers, PDA devices, and cellular phones.

2. Experimental

Backing layers of anode and cathode consisted of a carbon paper (Toray) of 205 μm in thickness, and a carbon paper Teflon coated (Electrochem) of 240 μm in thickness, respectively. Slurry for the catalyst layer was prepared by dispersing carbon supported Pt–Ru (30.1 wt.% Pt, 23.3 wt.% Ru on Ketjen Black) for anode or carbon supported Pt (47.2 wt.% on Vulcan XC72R) for a cathode into a commercial 5 wt.% Nafion solution (Aldrich) mixed with 1,2-dimethoxyethane (Wako). The resultant slurry was spread on the carbon papers using a doctor blade. Subsequently, the coated carbon

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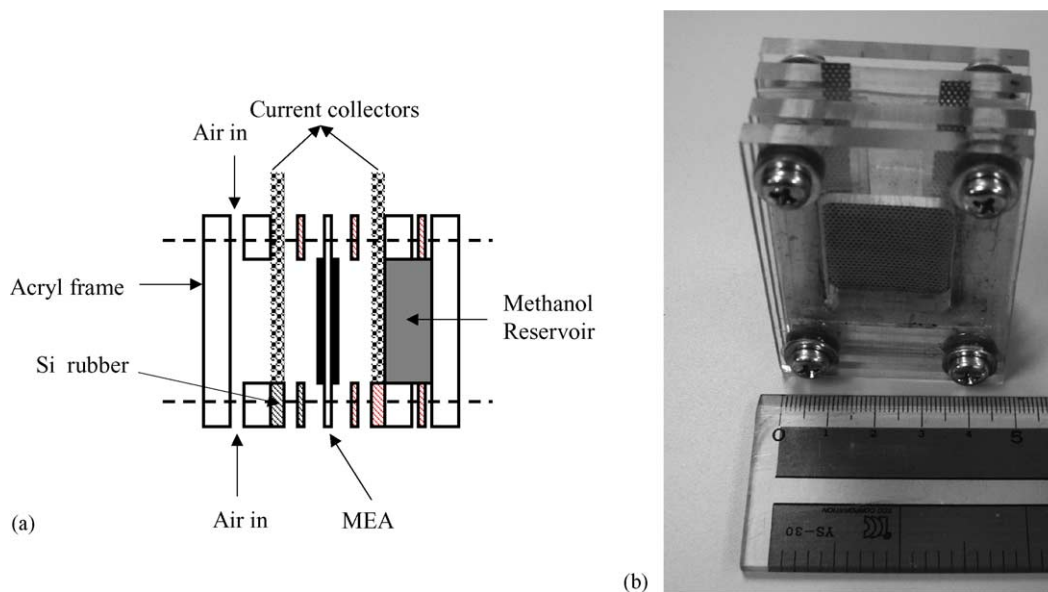


Fig. 1. The small air passive direct methanol fuel cell. (a) Design and (b) fabricated. Active area, 7.5 cm^2 .

papers were dried at 80°C for 30 min and at 140°C for 1 h in the oven.

Nafion 112 membrane (thickness: $50 \mu\text{m}$, equivalent weight 1100 meq ml^{-1} , ionic conductivity 0.083 S cm^{-1} , DuPont) was pretreated by sequential immersion in boiling solution of 3 vol.% H_2O_2 , distilled water, boiling solution of $1 \text{ M H}_2\text{SO}_4$, and distilled water, where each step lasted for 2 h.

The catalyzed electrodes for the anode and cathode respectively were positioned on both sides of the pre-treated Nafion 112 and hot pressed at 135°C and 100 kgf cm^{-2} for 5 min to form a unit of MEA.

Polarization curves were obtained by using either a Hokuto Denko Potentiostat/Galvanostat HA-501G or a Hewlett Packard 6050A DC electronic load system.

3. Results and discussion

3.1. Current collectors and optimization of catalyst

In this section, we describe the work on two design variables: (i) the current collectors and (ii) the anode catalyst loading. For these purposes, as a test vehicle, a 7.5 cm^2 active area DMFC was designed and is shown in Fig. 1a. A methanol reservoir was constructed out of Polymethyl-methacrylate (PMMA) and silicone rubber. The dimensions of the reservoir were: $25 \text{ mm} \times 6\text{--}7 \text{ mm} \times 30 \text{ mm}$ (h). Approximately 5 ml of liquid methanol solution were injected into the fuel reservoir using a syringe. The cathode was open to air as indicated in the figure, i.e., the air was supplied by natural convection. Therefore, the entire DMFC is a pump-less operation and self-activated by electrochemical reactions. All the components of the

small DMFC that are shown in Fig. 1a were machined and put together using bolts on the four corners of the cell as pictured in Fig. 1b.

Two types of current collectors (CC) were tested. The first CC was a perforated stainless steel (SUS mesh) sheet of 0.5 mm thickness with an open area of 20% was used on both anode and cathode sides. The second was the same SUS mesh but gold plated (SUS/Au) according to a reported procedure [16]. Fig. 2 shows comparative results of runs on SUS and SUS/Au current collectors. The voltage-current measurements were started after the methanol solution was poured in the cell for 10 min. Each data point represents typical steady state voltages that were taken after continuous operation for 30 s at the indicated current density. Fig. 2 demonstrates that use of the gold plated SUS on both anode and cathode sides increases the passive DMFC performance. The maximum power density nearly doubles, the maximum

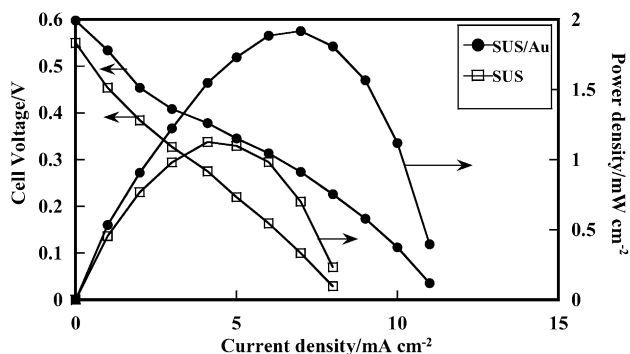


Fig. 2. Influence of current collector structure on performance and power of a 7.5 cm^2 DMFC. (SUS) stainless steel mesh, (SUS/Au) gold-plated stainless steel mesh; 0.5 M methanol solution, ambient air, room temperature, Nafion 112. Anode loading 2.5 mg cm^{-2} and cathode loading 2.5 mg cm^{-2} .

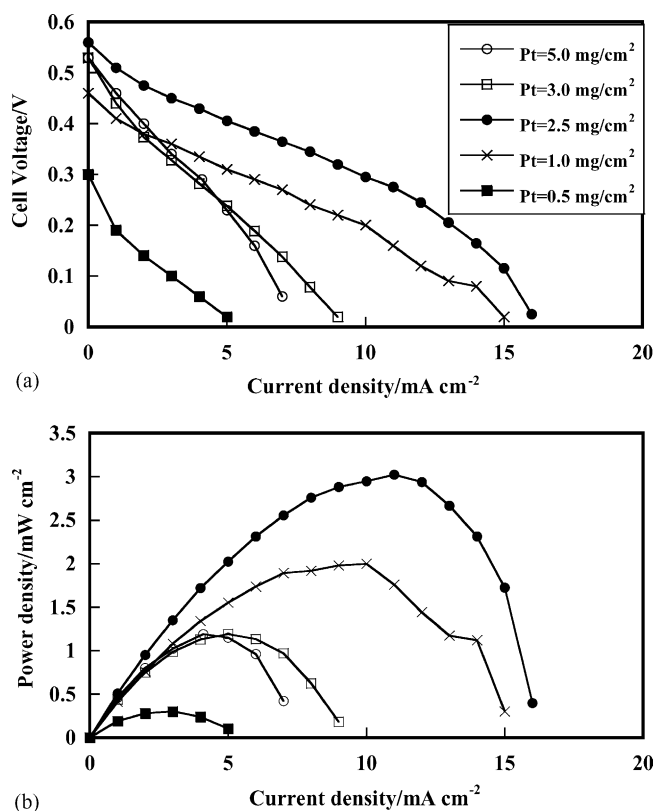


Fig. 3. Effect of platinum loading in the Pt–Ru/C anode on performance. (a) Polarization curve, and (b) power density curve in a 7.5 cm² area DMFC; 47.2 wt.% Pt (2.6 mg cm⁻²)/C cathode, current collector SUS/Au, 0.5 M methanol solution, ambient air, room temperature, Nafion 112.

usable current density increases, and the open cell voltage in the kinetics region is increased by 50 mV. Use of gold eliminates any contact resistance at the current-collector electrode interface. In subsequent experiments described below, only gold plated SUS mesh was used as the current collector.

Afterwards, we attempted to optimize the amount of Pt catalyst per unit area in the 30.1 wt.%Pt–23.3 wt.%Ru/C.

Fig. 3 shows the performance of the single cell (7.5 cm²) for various amounts of Pt varying from 0.5 to 5 mg cm⁻² in the Pt–Ru/C anode, and a 47.2 wt.% Pt (2.6 mg cm⁻²)/C cathode. The DMFC was operated at room temperature with 0.5 M methanol at anode and air at cathode. Given that DMFC performance is largely limited by charge transfer kinetics, high catalyst loadings should increase cell performance when operating in the kinetically controlled region. Large increases throughout the whole range of current densities were observed when the loading was increased from 0.5 to 2.5 mg cm⁻². When the loading was further increased, the performance started to decline. With increasing catalyst loading, the thickness of the electrode increases, and for a given structure (decided by the type of carbon and fabrication method), increasing electrode thickness results in a steeper concentration gradient for methanol. The interplay between the larger number of activation sites and the availability of adequate methanol results in the exhibition of a maximum in the loading versus performance behavior. Based on these results, an optimum of Pt–Ru loading appears to be around 2.5 mg cm⁻² when Pt–Ru/C is used to make the electrode.

3.2. Design and fabrication of a 36 cm² DMFC

3.2.1. Cell I

The initial design of our prototype DMFC was a scale-up of the 7.5 cm² laboratory cell described earlier. The active area was increased to 36 cm² and the square opening at the cathode end plate was increased to 6 cm × 6 cm for easy air access by the enlarged air cathode. The dimensions of the reservoir were: 60 mm × 8 mm × 60 mm (h). Approximately 28 ml of liquid methanol fuel were injected into the fuel reservoir using a syringe. The cell was held together with four bolts (Fig. 4).

Fig. 5, shows the results of cell polarization at three methanol concentrations. Here and below, the voltage-current

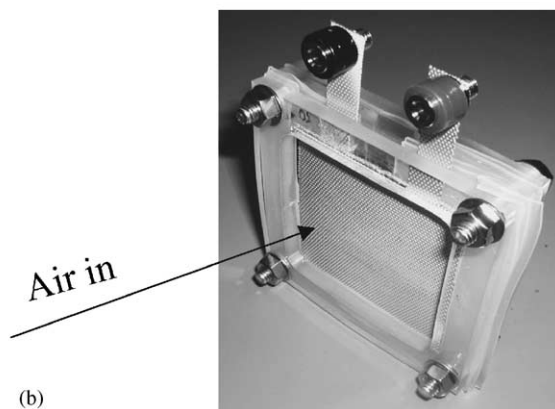
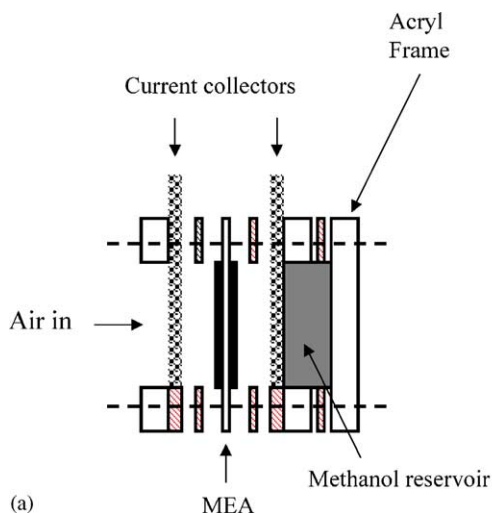


Fig. 4. The small air passive direct methanol fuel cell. (a) Design and (b) fabricated. Active area 36 cm². Cell I denoted in the text.

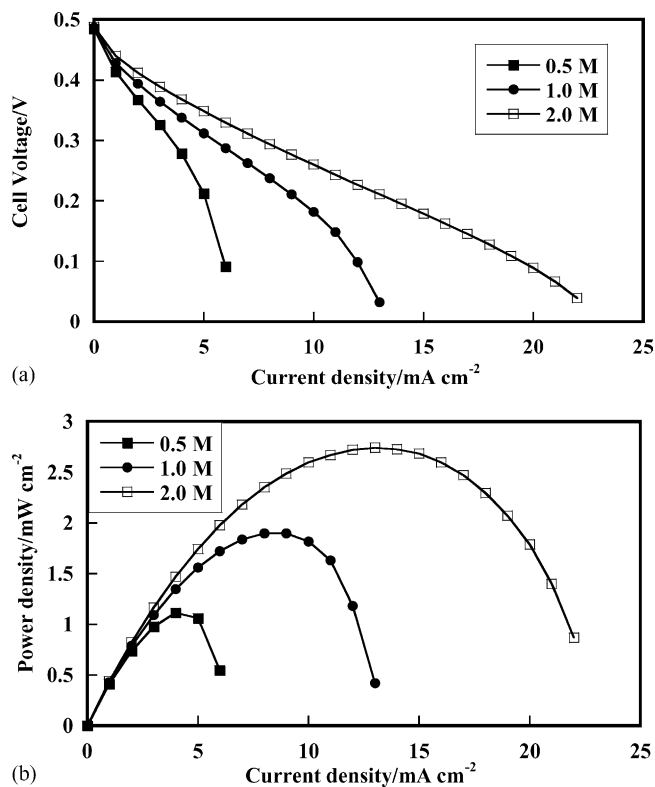


Fig. 5. Effect methanol concentration on performance of 36 cm² area DMFC (cell I in the text). (a) Polarization and (b) power density curves. Catalysts: carbon supported Pt–Ru anode (4.1 mg cm⁻² of Pt–Ru) and carbon supported Pt cathode (2.6 mg cm⁻² of Pt), current collector SUS/Au, air passive, room temperature, and Nafion 112.

measurements were started 30 min after the methanol solution was poured into the cell. Each data point represents typical steady state voltages that were taken after continuous operation for 3 min at the indicated current density.

In terms of output current, the performance at all values of cell potential increased with methanol concentration. As can be seen from Fig. 5a, the polarization curves exhibit kinetic and ohmic control, while the mass transport limitation is not apparent. The open circuit potential of ca. 0.48 V did not significantly change with methanol concentration indicating no methanol crossover effect up to 2 M methanol concentration. The maximum power density as shown in Fig. 5b is 1.15 mW cm⁻² at a voltage of 0.28 V with 0.5 M methanol, 1.9 mW cm⁻² at 0.24 V with 1.0 M methanol, and 2.74 mW cm⁻² at 0.21 V with 2.0 M methanol concentration. This trend demonstrates that the maximum power density more than doubles when the methanol concentration is increased from 0.5 to 2.0 M.

3.2.2. Cell II

The resistive behavior exhibited in Fig. 5a leads us to suspect resistance contribution to the cell arising out of either the membrane or the various contact resistances (current collector-electrode contact, and electrode-membrane interfacial contacts). To rule out the role of the membrane in the observed resistive behavior, a diagnostic experiment was conducted with the membrane (only) pressed under our MEA preparation conditions and the conductivity determined using a four-probe method. The conductivity of the non-pressed Nafion was about ca. 0.11 S cm⁻¹ and that of the pressed Nafion was of ca. 0.093 S cm⁻¹. This result is interesting, and shows that there is no significant damage done to the membrane during the pressing as practiced by us.

In order to improve the performance of cell I, some modifications were introduced. A perforated Lucite pinfield was designed, machined, and inserted to provide methanol solution for anode more smoothly (Fig. 6). A clamp was placed between outside of the Lucite end plate and current collector

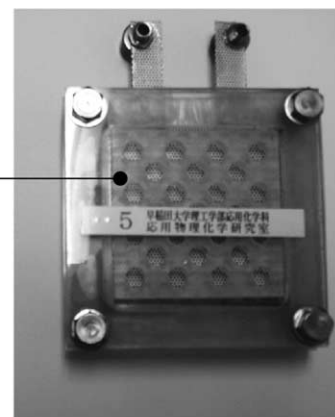
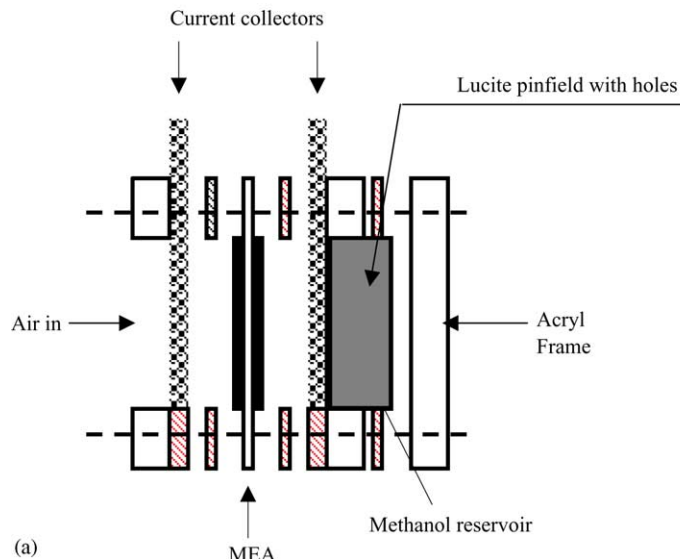


Fig. 6. The small air passive direct methanol fuel cell. (a) Design and (b) fabricated. Active area, 36 cm². Cell II denoted in the text.

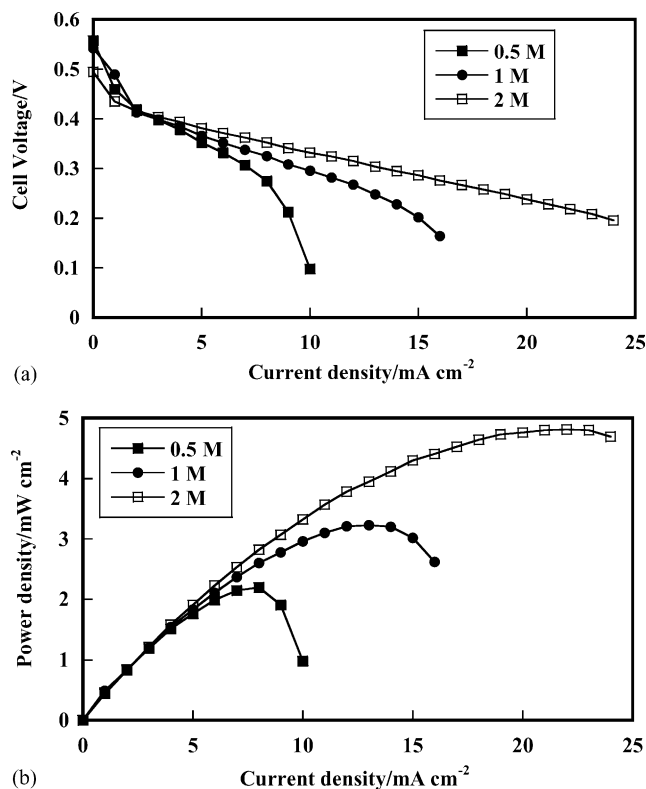


Fig. 7. Effect methanol concentration on performance of 36 cm² area DMFC (cell II in the text). (a) Polarization and (b) power density curves. Catalysts: carbon supported Pt–Ru anode (4.1 mg cm⁻² of Pt–Ru) and carbon supported Pt cathode (2.6 mg cm⁻² of Pt), current collector SUS/Au, air passive, room temperature, and Nafion 112.

of the cathode to give some compressive load to the MEA. Then the performance of this new cell denoted cell II was measured under the same experimental conditions as for cell I.

Fig. 7a shows the results of cell polarization under similar conditions as for cell I. The performance of the cell has greatly improved as a result of the design changes. In terms of output current, the performance at all values of cell potential increased with methanol concentration. Compared to the results of Fig. 5, an open circuit voltage of higher than 0.5 V is reached and the maximum power density more than doubles at all methanol concentrations considered.

3.2.3. Cell III

It was felt that the performance of the cell could be improved significantly by paying attention to the following points in the present cell design:

1. Compressive load applied to the MEA is insufficient and could lead to high resistance resulting in poor performance. Therefore, two Lucite cross bars with Ti plate 3.3 mm over were used to provide a good compressive load to the cell.
2. The methanol crossover rate is reported to be dependent on the thickness of the polymer membrane. Jung et al.

demonstrated that Nafion 112 is poor in methanol permeability and Nafion 117 is better [17]. Therefore, as the membrane thickness increases, methanol crossover decreases. However, with thick membranes, the power density of the cell will be reduced due to higher ohmic loss. This is a trade-off for the low methanol crossover. Nevertheless, for our small DMFC, at low current densities membrane resistance is not a factor; it would be desirable to use Nafion 117, which has lower permeability to methanol.

3. The catalyst used in both the electrodes for cell I and cell II were supported catalysts, not blacks (i.e., unsupported). In addition, the atomic ratio of the catalyst used is Pt:Ru = 2:3, which means platinum loading is relatively small. The optimal ratio is now considered to be Pt:Ru = 85:15 by various academics, and most of the technical data has been obtained with 50:50 of Pt/Ru. It is well established in the literature that DMFC performance is better with unsupported catalysts than with supported catalysts.

A new MEA was then prepared using Pt black and Pt–Ru black. Each MEA had 6.4 mg cm⁻² unsupported Pt–Ru anode catalyst loading with a 1:1 Pt–Ru atomic ratio and an unsupported 3.9 mg cm⁻² platinum cathode loading. Car-

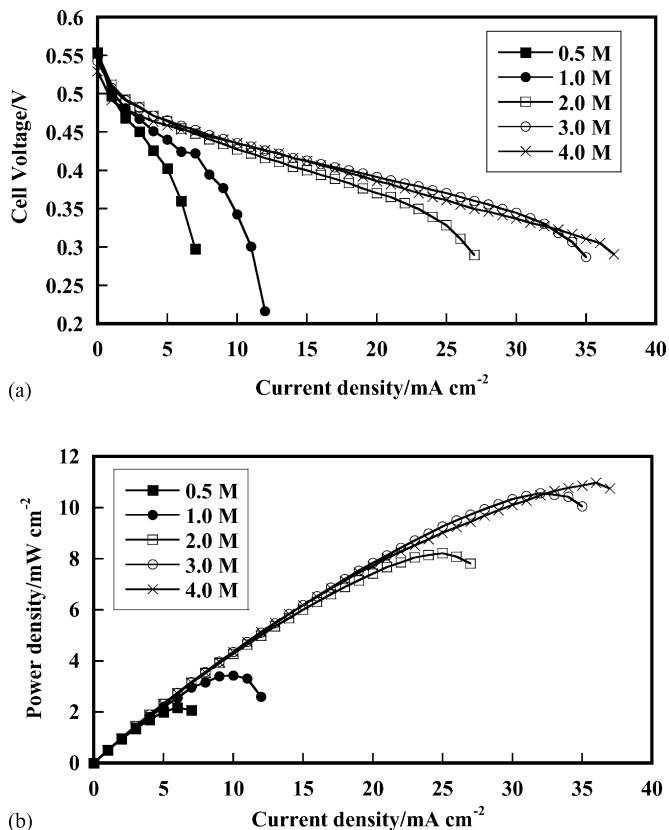


Fig. 8. Effect methanol concentration on performance of 36 cm² area DMFC (Cell III in the text). (a) Polarization and (b) power density curves. Catalysts: unsupported Pt–Ru anode (6.4 mg cm⁻² of Pt–Ru) and unsupported Pt cathode (3.9 mg cm⁻² of Pt), current collector SUS/Au, air passive, room temperature, and Nafion 117.

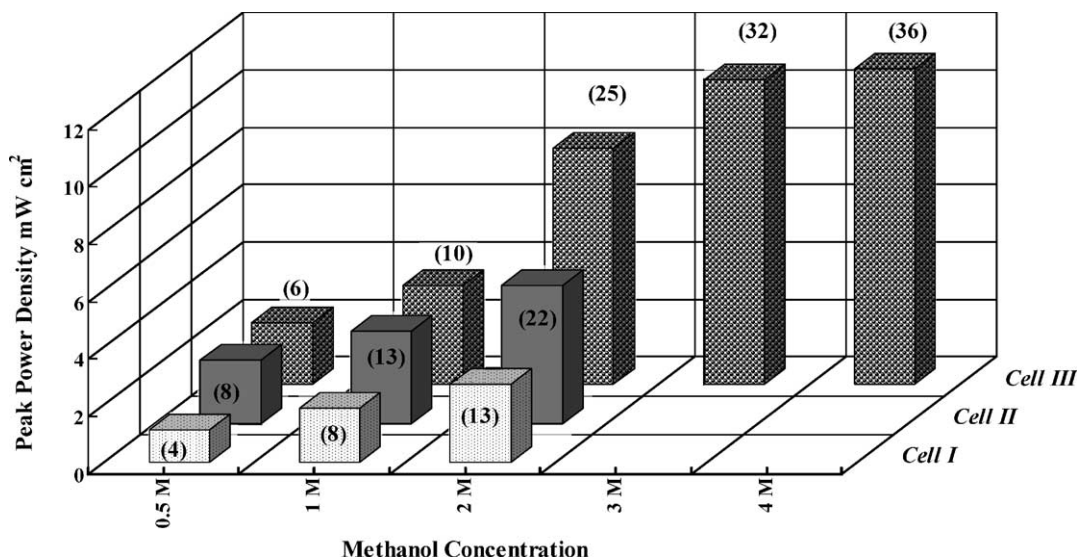


Fig. 9. Summary of performance of various cells tested in terms of peak power density vs. methanol concentration obtained in this work with various cells fabrications. Numbers between brackets represent the maximum current densities at the corresponding maximum power densities.

bon paper (Toray) was used for the anode and Teflon-coated carbon paper for the cathode. A Nafion 117 was used as the membrane electrolyte. The membrane electrolyte was sandwiched between the sheets of the anode and cathode, and then hot-pressed at 135 °C, 100 kgf cm⁻² for 10 min to assemble the MEA. This new MEA was tested with five different methanol concentrations and the cell polarization curves are shown in Fig. 8. Cell voltage versus current density is displayed in Fig. 8a whereas Fig. 8b shows the dependence of power density on current density. 3 M methanol gave the best performance, with 4 M yielding almost comparable results. Of particular interest, the OCV for this MEA was almost stable and higher than 0.53 V for all methanol concentrations. It clearly demonstrates the better performance of Nafion 117 against Nafion 112 with respect to methanol crossover and the superiority of unsupported catalysts over the supported ones.

Compared to results in Fig. 7, with 2 M methanol, the performance was greatly improved, i.e., more than 100% improvement in the cell voltage (at c.d.s near 20 mA cm⁻²); the maximum achievable power density is increased by 80–90%.

4. Summary and conclusions

The small direct methanol fuel cell intended for room temperature operation was designed, constructed and tested for performance. The cell is a stand-alone system with no external pumps or other ancillary devices. A number of technical issues such as the type of current collector, the anode catalyst, the membrane electrolyte, and fuel delivery were addressed in this work.

Fig. 9 shows three-dimensional (3-D) plots of different performance versus methanol concentration obtained in this work with various cells fabrications. As can be seen the

maximum peak power density as high as 11 mW cm⁻² was reached with 4 M methanol at current densities higher than 30 mA cm⁻² and at a voltage of 0.3 V.

By comparison, Chang et al. [18] reported a passive DMFC producing about 10 mW cm⁻² at 0.3 V of power density. Blum et al. [19] reported that their passive DMFC delivered 12.5 mW cm⁻² with continuous recharge. Furthermore, the performance is good and comparable to the JPL data up to 40 mA cm⁻² for a five flat pack stack DMFC with which a peak power of 12 mW cm⁻² was reached at an average voltage of 0.2 V [14]. Clearly, our passive DMFC competes quite well with other's passive DMFC in terms of power output.

Consequently the present prototype of 36 cm² passive DMFC and its stack can be applied to portable communication systems such as cellular phones. A stack design is under study with the ultimate target of 1–2 W class of power delivery.

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