

Short communication

Performance of an air-breathing direct methanol fuel cell

C.Y. Chen*, P. Yang

Institute of Nuclear Energy Research (INER), 1000 Wenhua Rd., Chiaan Village, P.O. Box 3-14, Lungtan, Taiwan

Received 23 December 2002; received in revised form 26 February 2003; accepted 6 March 2003

Abstract

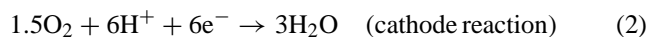
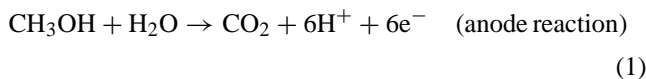
An air-breathing direct methanol fuel cell (DMFC) is attractive for portable-power applications. There are, however, several barriers that must be overcome before DMFCs reach commercial viability. This study shows that the cell power density is strongly affected by the fabrication conditions of the membrane electrode assembly (MEA) and by the technique used for assembly of the cell components. The results indicate that reducing the pressure and the thickness of catalyst layer in the MEA fabrication process can significantly improve power density. The production of water at the cathode, especially at a high power density, is shown to have a strong impact on the operation of an air-breathing DMFC since water blocks the feeding of air to the cathode. The power density ($\geq 20 \text{ mW cm}^{-2}$) of an air-breathing DMFC is found to drop to nearly half of its initial value after 30–40 min of operation in a short-term stability test. This appears to be one of the major limitations for portable electronic applications. Despite the many practical difficulties associated with an air-breathing DMFC, an attempt is also made to highlight the importance of the component assembly technique using a small cell pack with four integrated unit cells. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Direct methanol fuel cell; Membrane electrode assembly; Air-breathing; Catalyst layer; Mobile phone

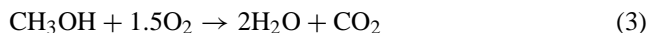
1. Introduction

Fuel cell technology has been generally recognized as a key 21st-century energy source with a wide variety of application that include power stations, road transportation, and small power-supply units [1–4]. This is because fuel cells have a higher efficiency of fuel utilization and are more environmentally clean than combustion engines. In small power-supply units, a direct methanol fuel cell (DMFC) that uses liquid methanol directly without a reformer is considered to be a promising candidate for portable power sources because methanol has a higher specific energy (about 3000 Wh kg^{-1}) than lithium-ion batteries (approximately 200 Wh kg^{-1}) [5] and can be operated at ambient conditions. These advantages are important for portable electronic applications such as mobile phones, notebooks, and other advanced mobile electronic devices, whose power requirement is increasing as the battery market grows.

A DMFC has an anode at which methanol is electrochemically oxidized to CO_2 and a cathode at which oxygen is reduced to water. The cell reactions are:



which can be combined as the overall reaction:



Thus, the overall cell reaction is the electro-oxidation of methanol to carbon dioxide and water.

The thermodynamic reversible potential (298°K) of the overall reaction is 1.21 V, which is close to 1.23 V for the hydrogen–oxygen fuel cell [6]. Furthermore, DMFCs do not require any fuel-processing equipment and can be operated at ambient temperature and pressure. Air-breathing DMFCs have thus attracted interest as alternative power sources for next-generation power units for portable electronics since the air compressors can be simply removed, which reduces the volume, costs and energy consumption of the system. Nevertheless, investigations of this type of DMFC in ambient environments are few [5,7]. Thus, whether an air-breathing DMFC is a practical device remains undetermined. While some technical barriers exist such as poor methanol oxidation kinetics, methanol cross-over in the electrolyte [6], and there are other engineering issues concerning peripherals such as fuel-storage tanks, power conditioning devices, and fuel circulation system that have to be miniaturized, work reported here concerns a series of tests on an air-breathing DMFC. The effect of operating conditions on the power density of an air-breathing DMFC is examined. This investigation includes stability tests for assessing the effects of

* Corresponding author. Fax: +886-3-4711409.
E-mail address: cychen@iner.gov.tw (C.Y. Chen).

the ambient air supply on the performance of a cell over a short life-time. MEA fabrication process parameters, which include the hot pressure, the thickness of the electrode layer and the amount of Pt catalyst, as well as the performance of a small pack of four cells are also evaluated.

2. Experimental

2.1. Catalyst preparation and characterization

40 wt.% Pt-20 wt.% Ru and 50 wt.% Pt catalysts both supported on a conductive carbon black with a high surface area, together with 60 wt.% Pt-30 wt.% Ru and 100 wt.% Pt catalysts were obtained from Johnson Matthey Inc. The mean particle sizes of the catalysts range between 2.5 and 4 nm. The anode catalyst was prepared from a mixture of 40 wt.% Pt-20 wt.% Ru, 60 wt.% Pt-30 wt.% Ru and 5% Nafion solution (DuPont) to enable the electrodes of the MEA to be fabricated at various Pt concentrations. The cathode catalyst was prepared from a mixture of 50 wt.% Pt, 100 wt.% Pt and 5% Nafion solution. The catalysts were rigorously stirred until the mixture became a smooth paste. The microstructures of the as-received Pt catalysts and of the Pt catalysts on MEAs were examined by means of a JOEL 2000FX transmission electron microscope (TEM).

2.2. Fabrication of the membrane electrode assembly

Nafion 117 membranes (DuPont) were cleansed by boiling in deionized water, 3 wt.% H_2O_2 , 3 wt.% H_2SO_4 , deionized water and deionized water again for 1 h in each step. A thin layer of electrode was then coated on each surface of the membrane by screen printing with the prepared catalysts. The MEA was obtained by hot pressing at 120°C and $5\text{--}100\text{ kg cm}^{-2}$ for 1–2 min. The active area of the MEA was 4 cm^2 with a Pt loading of $0.7\text{--}6\text{ mg cm}^{-2}$ in each electrode. Here, the screen printing process was adopted to achieve a high performance, low cost, effective manufacturing process suitable for mass production.

2.3. Single-cell testing

The MEA was sandwiched between carbon cloths (purchased from ElectroChem. Inc. and used as diffusion layers) and then installed in a single-cell test with two current-collectors. The current-collectors were made from 1.2 mm stainless-steel plates which had a series of 3 mm diameter holes to allow the passage of fuel or ambient air. The cell was held together between acrylic plates by means of a set of four retaining bolts positioned at the periphery of the cell.

The peak power density was determined from voltage–current (polarization) curves. When the cell was operated over an extended period (2 h in the stability test), the power density was obtained at a constant voltage from the peak

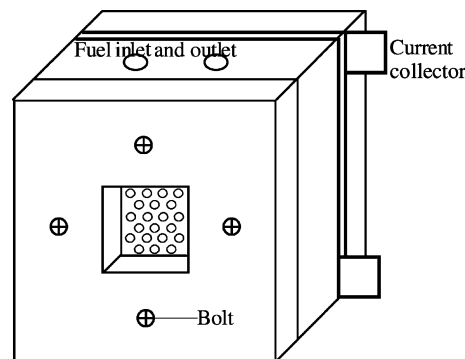


Fig. 1. Schematic diagram of experimental DMFC.

power density in the polarization curves. In the stability test, the cell was connected to a simple flow rig, which consisted of a Eyela MP-3N peristaltic pump, to supply the aqueous methanol solution from a reservoir ($\sim 50\text{ cm}^3$) at a rate of 10 ml min^{-1} . This process eliminated the influence of changes and heterogeneity in the methanol concentration. A schematic diagram of the experimental DMFC is shown in Fig. 1. Tests on air-breathing and air-blown DMFCs were carried out at various temperatures by a test station equipped with a Chroma 63030 electronic load.

3. Results and discussion

A preliminary study of the effects of MEA fabrication process conditions, operating conditions (including cathode-side air flow, methanol concentration, temperature), and the component assembly technique on the power density of a DMFC is described as follows.

3.1. Effect of MEA fabrication process conditions

The variation of the peak power density with time for air-breathing DMFCs with various amounts of Pt at room temperature (23°C) and ambient pressure is shown in Fig. 2. The peak power density of each MEA was determined from the fifth cycle of the polarization curves to avoid the instability of the first few cycles. Each MEA was tested over several days (1–2 tests per day) to assess the effects of time and environment on cell performance. The data indicate that the standard errors of the power densities for air-breathing DMFCs at 23°C range from ~ 8 to $\sim 14\%$. For changes in the fabrication process conditions such as the hot pressure, the thickness of the electrode layer, Pt and Pt-Ru concentrations, the power densities of the MEAs were evaluated to determine how the MEA manufacturing process could be improved to increase the power density and optimize the utilization of the catalyst. The variation of peak power density with Pt loading on fuel electrodes under different fabrication process conditions is shown in Fig. 3. The power density increases with increasing Pt concentrations for a given electrode thickness, as shown by each line (L1–L4). By contrast, the power density

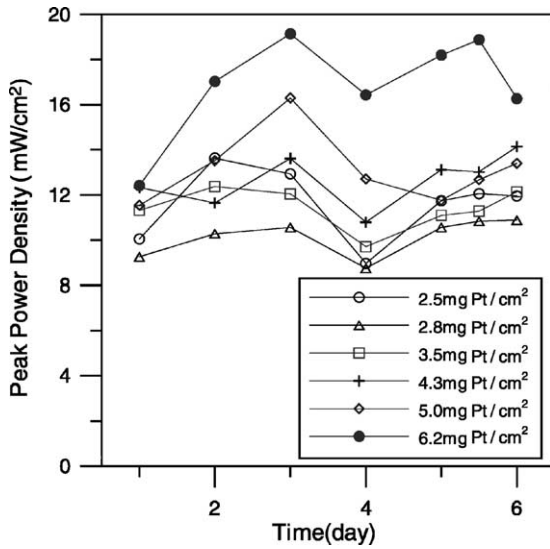


Fig. 2. Variation of peak power density with time for air-breathing DMFCs with various amounts of Pt at room temperature (23 °C) and ambient pressure.

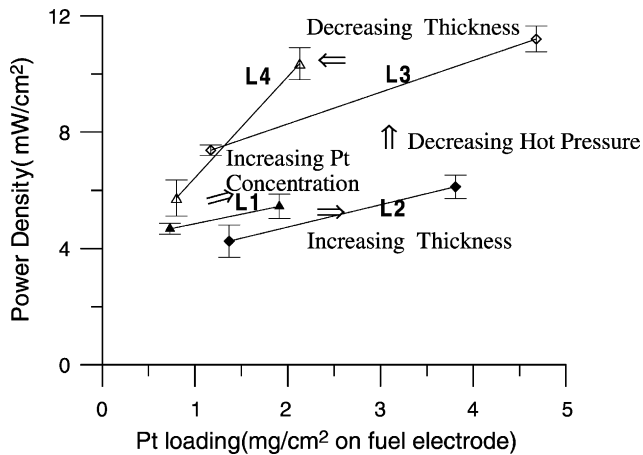


Fig. 3. Variation of peak power density with amount of Pt on fuel electrodes under various manufacturing process conditions.

decreases from line L1 to L2 as the electrode layer thickness increases for the same Pt loading. Notably, the power density increases as the hot pressure is decreased from L2 to L3. Finally, the power density with optimum catalyst utilization is obtained by reducing electrode layer thickness from L3 to L4. Apparently, the power density depends not only on the amount of Pt catalyst but also on the pressure applied.

The above findings have shown that reducing the pressure and the thickness of the electrode layer in the MEA fabrication can significantly increase the power density. Consequently, if the pressure is excessive or the electrode thickness is too thick, the power density is suppressed even at a higher Pt loading. This phenomenon may be associated with Pt aggregation, grain growth, or other effects such as the porosity of electrodes. TEM results indicate no appreciable difference between the microstructures of the as-received catalysts and those on MEAs made with a low or a high hot pressure, as shown in Fig. 4. Clearly, no discernible changes of Pt morphology can be identified from the TEM images. Thus, the improved MEA performance at a lower hot pressure can be attributed to the higher porosity of carbon.

3.2. Effect of cathode-side air flow

A short-term stability test on an air-breathing DMFC with 3 wt.% MeOH was conducted at 0.23 V and room temperature (22 °C) and the results compared with those of a test on an air-blown DMFC, as shown in Fig. 5, to understand whether oxygen supplied by the natural convection of the atmospheric air is sufficient for operation over long periods. The test results indicate that the power density declines rapidly because water blocks almost entirely the air fed into cathode side. Surprisingly, after 40 min, the power density falls to a constant value (10 mW cm⁻²) at which the diffusion of air through water reaches a steady state. If most of water is removed by supplying sufficient air to the cathode side using a blower at 30 °C, then the power density can be maintained at a high level and declines only slowly.

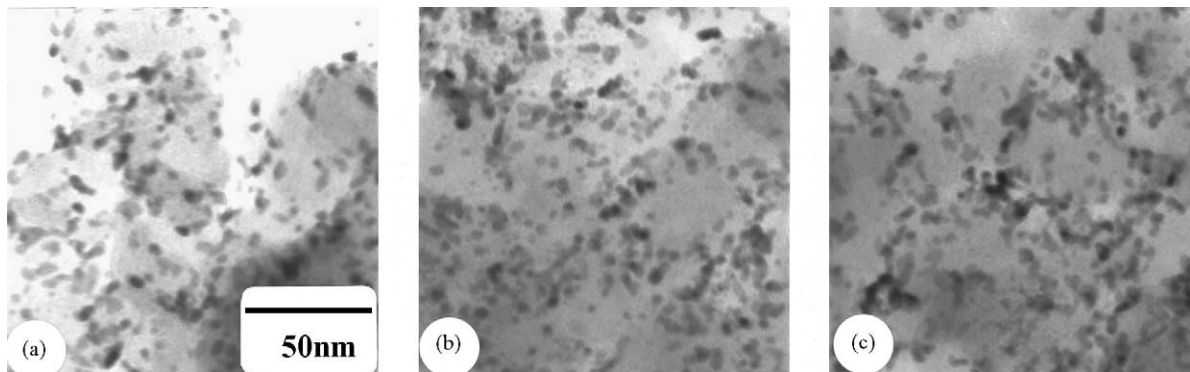


Fig. 4. TEM images of Pt catalysts: (a) as-received catalysts; (b) catalysts on MEA with a low hot pressure; (c) catalysts on MEA with a high hot pressure. The scale bar in (a) refers to all images.

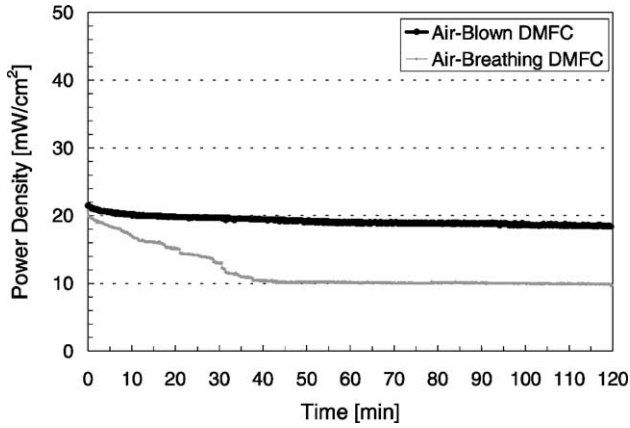


Fig. 5. Two-hour stability test at 0.23 V and room temperature (22 °C) for air-breathing and air-blown DMFCs tested with 3 wt.% MeOH.

This decline in power density during the test may be due to methanol cross-over and the gradual accumulation of water at the cathode sites. This observation demonstrates that insufficient removal of the cathode reaction product (water) will degrade the power density of the cell. The data in Fig. 5 also indicate that, at room temperature, operation of an air-breathing DMFC above 10 mW cm⁻² is hard to sustain; the magnitude of this power density depends on the design of the flow field, the characteristics of the gas diffusion layer and the environmental conditions such as temperature, humidity and ventilation.

3.3. Effect of methanol concentration

DMFCs with five different methanol concentrations (0.5, 1.5, 3.0, 6.0, 9.0 wt.%) were subjected to stability tests at 30 °C. In each case, the power density was determined with flowing air at the same temperature as the methanol solution. The typical variation of power density with methanol concentrations at 30 °C is presented in Fig. 6. Notably, the peak power density increases until the methanol concentration reaches about 3.0 wt.%. Then, the power density declines as the methanol concentration is increased from 3 to 9 wt.%. The problem of the high methanol concentration is

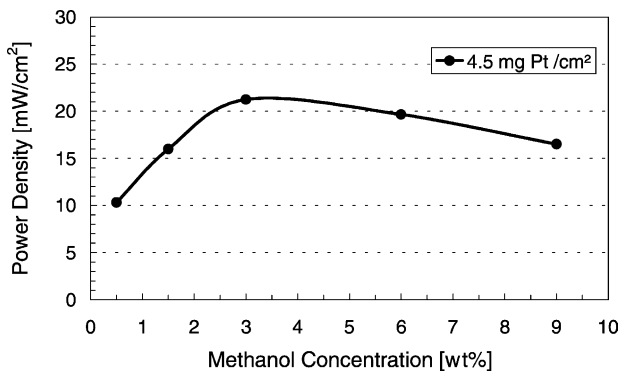


Fig. 6. Variation of power density with methanol concentration at 30 °C.

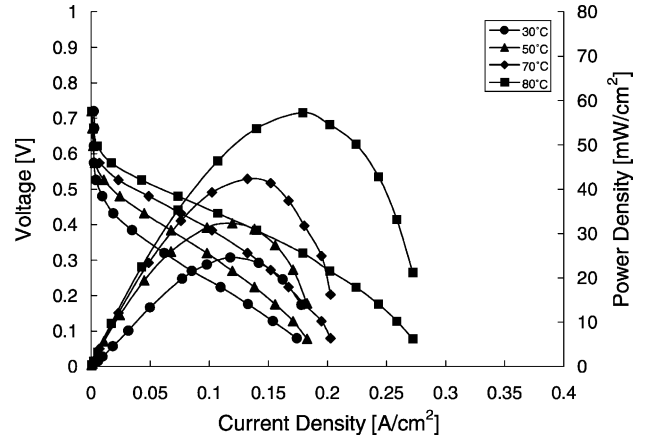


Fig. 7. Performance of air-breathing DMFC at various methanol solution temperatures tested with 3 wt.% MeOH.

explained by an increase of methanol cross-over through the membrane [8] and an increase in the coverage of the poisoning methanolic residues on the anode surface [9,10]. The results indicate that 3–4 wt.% methanol yields the best compromise between power density and energy efficiency for the Pt and Pt-Ru catalysts used in this study.

3.4. Effect of temperature of methanol solution and air

The temperature of methanol on the anode side also affects the cell performance of an air-breathing DMFC, as can be observed from the typical polarization curves in Fig. 7. The effect of methanol solution temperature on the peak power density as determined from the polarization curves in Fig. 7 is given in Fig. 8. Although methanol transport to the cathode side may increase with temperature, and thereby significantly reduce cell performance, the power density increases with temperature because the methanol oxidation rate increases with temperature. When a blower is used to supply air to the cathode side at the same temperature as that supplied to the anode side, a higher power density is obtained.

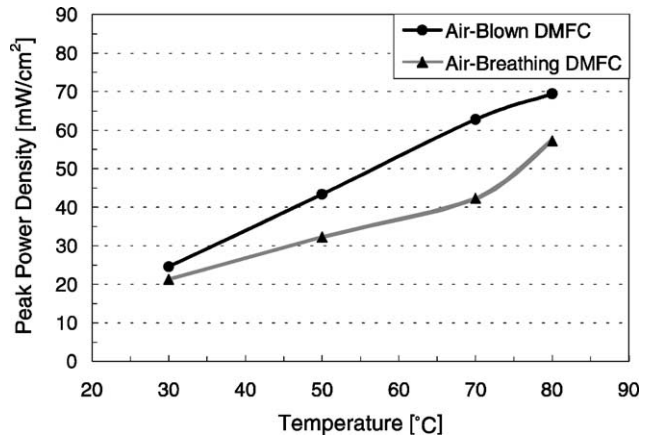


Fig. 8. Effect of methanol solution temperature on peak power density for air-breathing and air-blown DMFCs tested with 3 wt.% MeOH.

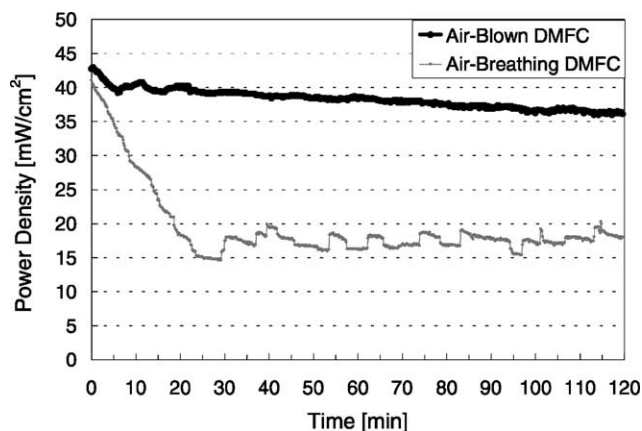


Fig. 9. Two-hour stability test at 0.28 V and 50 °C for air-breathing and air-blown DMFCs tested with 3 wt.% MeOH.

This is because the oxygen reduction rate increases with temperature at the cathode side.

A short-term stability test of a DMFC with 3 wt.% MeOH was also conducted at 0.28 V and at an elevated temperature of 50 °C, as shown in Fig. 9. Again, without air blown into the cathode side, the power density declines dramatically to 15–20 mW cm⁻² in the presence of water at the cathode, even when the methanol solution is at an elevated temperature of 50 °C. The fluctuation of power density between 15 and 20 mW cm⁻² is caused by the intermittent falling of water from the cathode side, which disturbs the natural convection of the atmospheric air at that side. As would be expected from the previous results at 30 °C, removing most of the water by blowing sufficient air toward the cathode side at 50 °C can sustain a high power density. Notably, after 30–40 min of operation at either 30 or 50 °C, the power density drops to almost half its initial value (i.e. from ~40 mW cm⁻² falls to 15–20 mW cm⁻² at 50 °C, and ~20 mW cm⁻² falls to ~10 mW cm⁻² at 20 °C). Based on all of these facts, the flooding of water at the cathode appears to be a main weakness of an air-breathing DMFC.

The effect of methanol concentration on cell power density at various temperatures is shown in Fig. 10. The power densities at three different methanol concentrations (3.0, 6.0, 9.0 wt.%) were obtained from stability tests at a constant voltage with flowing air at the same temperature as the methanol solution. The variation of power density with methanol concentration changes little with temperature. At an elevated temperature of 50 °C, the power density is decreased more at a high methanol concentration (9 wt.%) due to the methanol cross-over effect. Although methanol cross-over at 20 and 30 °C is less significant than that at 50 °C for 9 wt.% MeOH, the power density using a high methanol concentration must still be improved.

3.5. Effect of cell component assembly

Despite the problems encountered in the evaluation of the cell performance of an air-breathing DMFC, an attempt

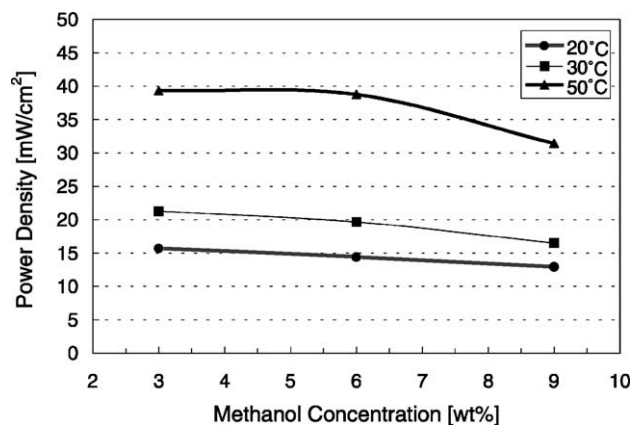


Fig. 10. Effect of methanol concentration on power density at various temperatures.

was made to evaluate the performance of a small pack of four unit cells, which were electrically connected in series to meet the voltage requirement of power conditioning for mobile phones. A small air-breathing DMFC cell pack is shown in Fig. 11. The outer dimensions of the pack are only 50 mm × 70 mm × 14 mm. The cathodes are on both sides of the pack and are simply exposed to ambient air at room temperature (21 °C). The 3.0 wt.% methanol solution is stored between the two sub-modules. Each sub-module consists of two unit cells and each cell has an active area of 8 cm². The power performance of this pack with a 3.0 wt.% methanol concentration at 30 °C is shown in Fig. 12. The maximum power output is 342 mW at 1.0 V and the power density is 10.7 mW cm⁻², which is lower than the single-cell test result of 21.3 mW cm⁻² obtained under the same MEA fabrication process conditions. This observation implies that a small cell tends to suffer from loss of power density due to component assembly problems such as contact resistance loss. Accordingly, in addition to other engineering problems associated with the reduced volume and weight required for portable-power applications, a proper cell design for a component assembly that does not reduce the power density is an important issue for DMFC systems.



Fig. 11. Small air-breathing DMFC cell pack with four unit cells.

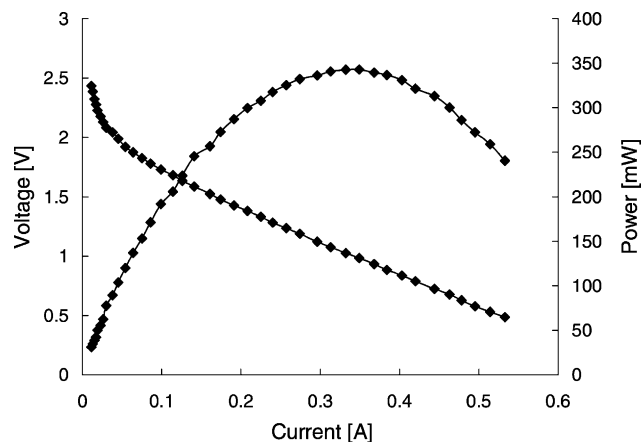


Fig. 12. Power performance of cell pack with 3.0 wt.% MeOH at 30 °C and in ambient air at 21 °C.

4. Conclusions

This study has shown that the cell performance of a DMFC is significantly affected by MEA fabrication process conditions, air flow, methanol concentration, fuel and oxidant temperatures, and the cell assembly technique. The results indicate that the power density can be improved by reducing the hot pressure and the thickness of the electrode layer in the MEA fabrication process. This work has focused on tests of the influence of air flow on cell performance, to compare an air-breathing DMFC with an air-blown DMFC. The production of water at the cathode, especially at a high power density, is found to impact strongly on the performance of an air-breathing DMFC, since the water blocks almost all of the air fed into the cathode. Based on the experimental observations, the power density drops markedly to nearly half of its initial value even after it is increased up to 40 mW cm⁻², as required for mobile phones. The flooding of cathode by water must be prevented, or at least reduced, to overcome this main drawback. The problem can be alleviated to a great extent by blowing air toward the cathode and

operating the cell at an elevated temperature. On the other hand, applying an air compressor (or mini-fan) and a heater to a small DMFC would increase cost, volume and weight, which restricts commercial viability. Alternatively, a breakthrough in airflow field design may remove most of water at the cathode side, but this is a challenging task. Testing a small air-breathing cell pack has also revealed that proper cell design in a component assembly is important when the volume and weight of the cell pack are substantially reduced. Overall, in addition to many technical considerations, water management appears to be one of the major limitations of air-breathing DMFCs which must be overcome before such devices can become the next-generation power units for portable electronic devices.

Acknowledgements

The authors would like to thank the Institute of Nuclear Energy Research (INER) for financially supporting this research.

References

- [1] A.J. Appleby, R.B. Foulkes, Fuel Cell Handbook, Nostrand Reinhold (Van), New York, 1989.
- [2] J.M. Ogden, M.M. Steinbugler, T.G. Kreutz, J. Power Sources 79 (1999) 143.
- [3] H. Chang, J.R. Kim, J.H. Cho, H.K. Kim, K.H. Choi, Solid State Ion. 148 (2002) 601.
- [4] K. Scott, W.M. Taama, P. Argyropoulos, J. Power Sources 79 (1999) 43.
- [5] J. Han, E.-S. Park, J. Power Sources 112 (2002) 477.
- [6] K. Scott, W.M. Taama, P. Argyropoulos, K. Sundmacher, J. Power Sources 83 (1999) 204.
- [7] A.K. Shukla, P.A. Christensen, A.J. Dickinson, A. Hamnett, J. Power Sources 76 (1984) 54.
- [8] A. Heinzl, V.M. Barragan, J. Power Sources 84 (1999) 70.
- [9] H. Dohle, J. Divisek, R. Jung, J. Power Sources 86 (2000) 469.
- [10] A.S. Arico, P. Creti, P.L. Antonucci, J. Cho, H. Kim, V. Antonucci, Electrochim. Acta 43 (1998) 3719.