

Performance evaluation of passive DMFC single cells

Byungchan Bae, Beck Kyun Kho, Tae-Hoon Lim, In-Hwan Oh,
Seong-Ahn Hong, Heung Yong Ha*

Fuel Cell Research Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea

Received 30 August 2005; received in revised form 7 October 2005; accepted 7 October 2005

Available online 2 December 2005

Abstract

Passive direct methanol fuel cells have been extensively investigated for the effects of methanol concentration, catalyst loading of electrodes, fuel and oxidant supply modes and long-term operation on their performance. Passive cells to which the reactants, methanol and air, are supplied by natural convection flow without the help of any external devices, have shown very different behavior compared with an actively supplied cell. The optimum methanol concentration and catalyst loading in a passive cell are much higher than those of an active cell. The highest single cell performance was 45 mW cm^{-2} with a 5 M methanol feed at room temperature and ambient pressure. Forced air to a passive cell was found to have a negative effect on the performance. In addition, experiments have been conducted to find the parameters that affect the long-term operation of a passive cell.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Passive direct methanol fuel cell; Methanol concentration; Reactants supply; Catalyst loading; Continuous operation

1. Introduction

Fuel cells are considered to be promising candidates to provide power to electrical vehicles, small and large scale power stations and even portable electrical applications, such as laptop computers and mobile phones, in a manner which is more efficient and environmentally friendly than currently exist. In particular, direct methanol fuel cells (DMFC) have been considered for use in very small to mid-sized applications due to their high energy density, small volume and low toxic emissions [1–6].

For the commercialization of the DMFC as a portable power source, the balance of plants (BOP), such as methanol fuel supply devices, air blowers, heat exchangers, etc. should be minimized or eliminated in order to decrease the volume and weight and to increase energy efficiency of the DMFC. Therefore, various DMFC systems that operate under passive conditions, i.e., air breathing and passive methanol supply, have been studied [7–16].

Chen and Yang [17] reported that the hot-pressing pressure for a membrane electrode assembly (MEA) and the thickness of the electrode layer could strongly influence the performance of passive DMFCs. Guo and Cao [18] described a passive fuel delivery system using a wick material and suggested a DMFC system without the consumption of ancillary power for the fuel supply. The performance and start-up time of passive cells were also found to be significantly influenced by the pretreatment conditions of MEAs [13]. Very recently, Liu et al. [19] tested various diffusion backing materials in the anode side and found that sintered stainless steel fiber felt performed best because of its high electric conductivity. They also fabricated a 12-cell stack with a peak power of 1.8 W or 26 mW cm^{-2} to operate a mobile phone.

However, studies of passive DMFCs are relatively new, and there are only a few systematic reports on the unique features of passive cells. In our lab, we have been developing the technologies of MEAs, single cells and stacks for passive DMFCs, as described in our previous articles [12,13,15]. In this study, we present experimental results that show the characteristic behavior of passive DMFCs under various operating conditions, such as methanol concentration, catalyst loading, membrane thickness, reactant supply mode and long-term operation using single cells under ambient conditions.

* Corresponding author. Tel.: +82 2 958 5275; fax: +82 2 958 5199.

E-mail address: hyha@kist.re.kr (H.Y. Ha).

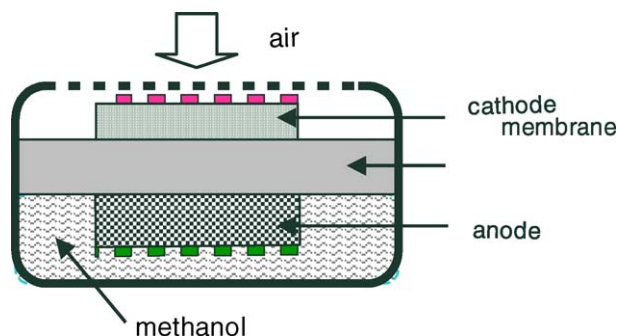


Fig. 1. Schematic diagram of a passive DMFC cell.

2. Experimental

The cathode catalyst used was an unsupported Pt black, and the anode catalyst was a Pt-Ru black (from E-Tek). The catalyst ink was prepared by dispersing an appropriate amount of catalyst in a solution of deionized water and iso-propyl alcohol (IPA) mixed with Nafion[®] solution (1100 EW, DuPont). The catalyst ink was coated on a carbon cloth (E-Tek) with an area of 6 cm² to make electrodes. The catalyst (Pt or PtRu) loading was varied from 4 to 10 mg cm⁻² in each electrode, and the total ionomer loading was 10 wt% to the catalyst for the cathode and 15 wt% to the catalyst for the anode. A pair of electrodes (a cathode and an anode) was hot-pressed on both sides of the polymer electrolyte membrane, Nafion[®] 115, at a temperature of 140 °C and with a pressure of 8 MPa for 150 s.

A schematic diagram of a passive DMFC is shown in Fig. 1, and in this study all the experiments were done in a passive mode at ambient conditions (25 °C and 1 atm) unless mentioned otherwise. A methanol solution of varying concentration was stored in a methanol reservoir attached to the anode side, and the methanol was allowed to diffuse into the anode catalyst layer driven by the concentration gradient set between the reservoir and the anode. Oxygen was supplied to the cathode from the ambient air by a kind of air-breathing action driven by the concentration gradient. The volume of the methanol reservoir in the anode compartment was 5.3 cm³, and the cathode plate had 63 holes with a diameter of 2 mm. Current–voltage curves were recorded galvanostatically by using an electronic load (EL-500P, Daegil Electronics, Korea).

3. Results and discussion

3.1. Influence of methanol concentration variation

Fig. 2 shows the performance of a passive single cell with varying methanol concentration from 2.0 to 6.0 M. The peak power density of the passive cell increased as the methanol feed concentration increased, and it reached a maximum value of 43 mW cm⁻² with a 5.0 M methanol feed. The methanol concentration for the maximum power in a passive cell is much higher than that in an active cell, which has an appropriate concentration of around 1.0 M [19,20]. This result is similar to that of Liu et al., who observed the effect of methanol concentration in a passive cell [14]. The increased optimum concentration can

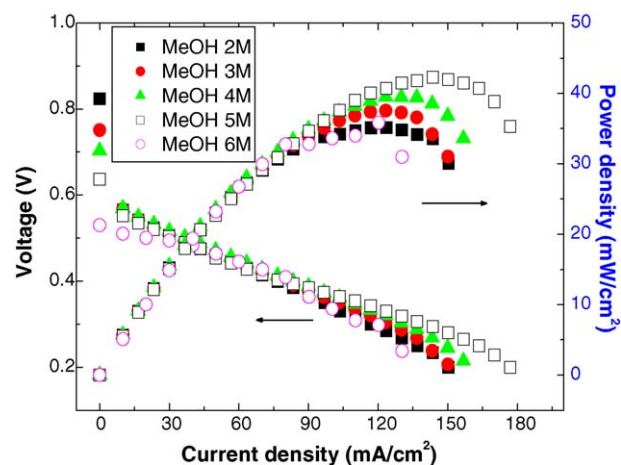


Fig. 2. Cell performance curves at different methanol concentrations: Nafion[®] 115, catalyst loading = anode/cathode = 8/8 (mg cm⁻²) based on total amount of catalyst metal.

be attributed to two factors. One is the slower mass transport rate of methanol in a passive cell featuring a natural convection when compared with a forced convection in an active cell [19]. Therefore, a higher methanol concentration is needed to compensate for the slower mass transport rate of methanol in passive cells. The other is the temperature rise in the cell due to the oxidation of crossed-over methanol at the cathode that releases a certain amount of heat. As the methanol concentration increases so does the methanol crossover rate, thus increasing the cell temperature, which eventually enhances the reaction kinetics at both the anode and cathode [14,15]. In addition to these, the crossed-over methanol could deteriorate cell performance through generating a mixed potential and poisoning the catalyst in the cathode [10,15,21,22]. Therefore, further increase of methanol concentration would result in performance decline due to the increased overpotential at the cathode. Consequently, the optimum concentration in the passive cells is a result of compromise between the temperature, methanol transport rate and mixed potential that are influenced by methanol concentration.

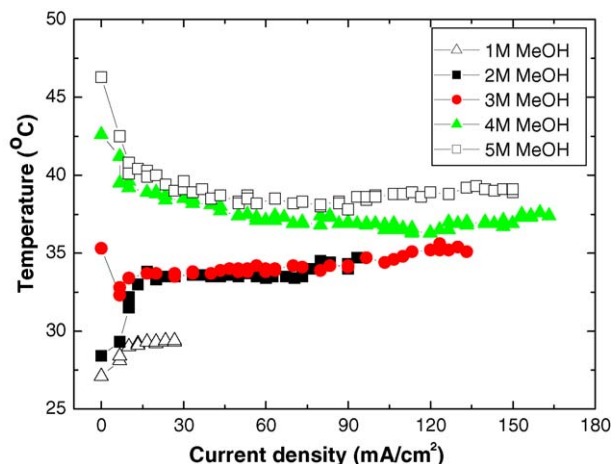


Fig. 3. Cell temperature at different methanol concentrations under passive conditions. Nafion[®] 115, catalyst loading = anode/cathode = 8/8 (mg cm⁻²).

Fig. 3 shows the temperature change of the cell with different concentrations of methanol as the electric load is increased. The cell temperature in an open circuit state (at a current density = 0) is proportional to the methanol concentration, and it reaches 46 °C with a 5.0 M feed. The pattern of temperature change upon increasing current density also varies depending on the methanol concentration used. With a methanol concentration below 3.0 M, the temperature rises as the electric load increases, similar to the case of the active cells [14,15], whereas with a methanol concentration above 3.0 M, the temperature initially declines and then maintains a nearly constant value even as the load increases. This type of temperature variation reflects the distinct feature of the passive DMFC system without a convective flow of the reactants. The heat produced in the cell can be qualitatively expressed by the following equations.

$$E_{oc}(\text{total}) = E_{oc}(\text{COM}) \quad \text{at } i = 0 \text{ (open circuit)} \quad (1)$$

$$E_i(\text{total}) = E_i(\text{COM}) + E_i(\text{ORR}) + E_i(\text{EOM}) \quad \text{at } i > 0 \quad (2)$$

(where $E_i(\text{EOM}) < 0$, endothermic)

where E_{oc} and E_i are the heat produced in an open circuit state and with a load of i , respectively, and they are calculated by multiplying the heat of reaction by the reaction rate of the species. The COM, ORR and EOM indicate the chemical oxidation of crossed-over methanol, oxygen reduction reaction at the cathode and electrochemical oxidation of methanol at the anode, respectively. Thermodynamically, the ORR and COM at the cathode are exothermic reactions, while the EOM at the anode is an endothermic one. In an open circuit state, the heat is produced by only COM (Eq. (1)), but when an electric load is applied to trigger the electrochemical reactions, the total amount of heat produced becomes the sum of the heat produced by COM and ORR at the cathode and the heat consumed by EOM at the anode (Eq. (2)). Therefore, $E_i(\text{COM})$ differs from $E_{oc}(\text{COM})$ because the rate of methanol crossover varies depending on the magnitude of the electric load imposed on the cell.

With a methanol feed below 3.0 M, the rate of methanol crossover is small, and the heat production by the ORR is larger than that by the COM, resulting in an increasing cell temperature as the load increases, as shown in Fig. 3 [2,12,15]. On the other hand, with a methanol concentration higher than 3 M, the heat production by the COM is larger than that by the ORR because of the large amount of methanol crossover. That is, when the electrochemical reaction takes place, the methanol crossover is reduced and thus the total amount of heat produced becomes less than that in the open circuit state, resulting in a temperature decline. This can be expressed as follows:

$$\Delta E_i(\text{total}) = E_i(\text{total}) - E_{oc}(\text{total}) = E_i(\text{COM}) + E_i(\text{ORR}) + E_i(\text{EOM}) - E_{oc}(\text{COM}) < 0 \quad (3)$$

(for $C_{\text{MeOH}} > 3 \text{ M}$)

However, when the electric load increases above 60 mA cm^{-2} , the cell temperature does not decrease further, but remains almost unchanged because the heat loss by the decreased methanol crossover is compensated with the heat release by the ORR.

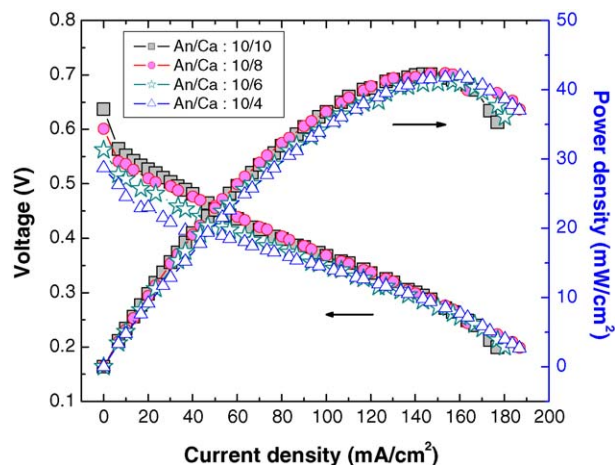


Fig. 4. Current–voltage curves for the MEAs with varying catalyst loading in the cathode at 5.0 M CH_3OH : anode catalyst loading = 10 mg cm^{-2} .

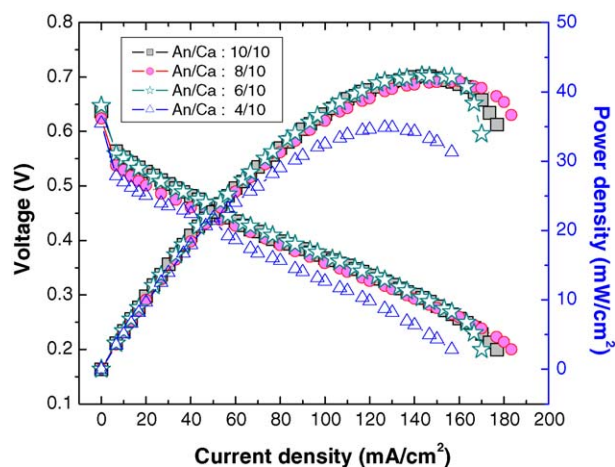


Fig. 5. Current–voltage curves for the MEAs with varying catalyst loading in the anode at 5.0 M CH_3OH : cathode catalyst loading = 10 mg cm^{-2} .

3.2. The effect of catalyst loading on cell performance

In general, DMFCs require about a 10 times larger amount of catalyst loading than the hydrogen-fueled polymer electrolyte fuel cells. In addition, the passive DMFC system requires even more catalyst loading than the active one does. Figs. 4 and 5 show the variation in cell performance as the catalyst loading is changed in the anode and the cathode, respectively. During this catalyst loading variation in one electrode, the other electrode was fixed at $10 \text{ mg-metal cm}^{-2}$. Fig. 4 shows the performance of the passive cell at various amounts of Pt varying from 4

to 10 mg cm^{-2} in the cathode. The peak powers appearing at around 150 mA cm^{-2} are almost the same for all the Pt loadings tested. However, the performance difference is rather apparent in the activation control region below 60 mA cm^{-2} , and the per-

formance increases with increasing the catalyst loading in this current region.

A variation in anode catalyst loading also exhibits results similar to the variation in the cathode catalyst loading. The peak power density is almost the same for the anode catalyst loadings higher than 4 mg cm^{-2} as shown in Fig. 5. The effect of anode catalyst loading on the performance is more apparent at low current densities than at high current densities. This is because the higher catalyst loading can cause a larger active surface area and mass transport resistance against methanol transport. However, in the mass transport controlled region or in the high current density region, the higher catalyst loading makes the thicker catalyst layer and it, in turn, could yield an excessive resistance against methanol supply to and carbon dioxide removal from the anode. Therefore, the performance is not proportional to the catalyst loading but reaches a plateau or even declines with increasing the catalyst loading [23]. The slightly lower cell performance with an anode catalyst loading of 8 mg cm^{-2} compared to 6 mg cm^{-2} in the low current region may be attributed to experimental error. Quite different from active DMFCs, the operation of passive cells is not carried out in a steady state, but the conditions, such as methanol concentration, temperature and the extent of water and CO_2 accumulation in the cell vary with time on stream, which could cause a certain degree of deviation in the experimental data. Therefore, the operation procedure and experimental conditions should be kept precisely in order to collect reliable data with passive cells.

Another set of complementary experiments has been conducted to observe the cell performance with the same amount of catalyst on both electrodes by varying the catalyst loading from 4 to 10 mg cm^{-2} in each electrode. The performance increased as the catalyst loading increased, and a maximum performance of 45 mW cm^{-2} was obtained at a loading of 8 mg cm^{-2} in both electrodes. A slightly lower performance with a 10 mg cm^{-2} loading is ascribed to the increased mass transport resistance in the electrodes as mentioned above.

Contrary to our results, Shimizu et al. observed a maximum performance with a platinum loading of 2.5 mg cm^{-2} under passive conditions [23]. This might be caused by the low methanol feed concentration of 0.5 M, where only a small amount of catalyst is needed to fully oxidize the methanol. The use of supported catalyst (53.4 wt% Pt-Ru/C) in their study must have also imparted an additional resistance to methanol transport at high catalyst loadings because a supported catalyst makes a much thicker electrode than non-supported black catalyst does.

3.3. Influence of fuel supply mode on performance

The performance of the DMFC is strongly dependent on the mode of reactants supply, and it is generally believed that active DMFCs outperform passive ones due to higher mass transport rates of the reactants in the cells; however, our research reveals that passive cells could outperform active ones under certain operating conditions. In Fig. 6 performance comparison is shown with two kinds of DMFCs: one (“passive”) was operated in a completely passive mode and the other (“active MeOH”)

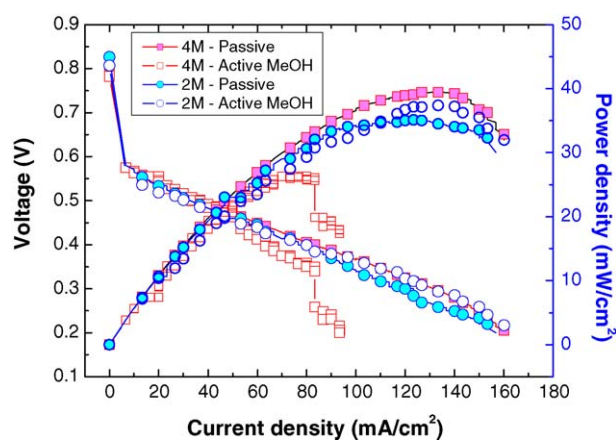


Fig. 6. Comparison of cell performance under varying methanol supplying mode: catalyst loading = anode/cathode = 8/8 (mg cm^{-2}).

was operated in an active methanol mode (1.0 mL min^{-1}) while the air supply was in a passive state.

With a 2.0 M methanol feed, the active methanol mode outperforms the completely passive one. On the other hand, with a 4.0 M methanol feed, the passive mode shows much better performance than the active methanol mode. The abrupt drop in voltage for the active methanol cell with a 4.0 M feed might be caused by accumulation of water that is produced by oxidation of crossed-over methanol as well as by the ORR in the cathode. The methanol crossover in the active methanol cell with a 4.0 M feed was the largest among others that were tested in this set of experiments. Moreover, the cathode compartment was fully open to ambient air at room temperature. Therefore, the water might not be removed effectively, but instead it could accumulate and begin flooding in the catalyst layer when an excessive amount of water is produced in the cathode [17].

Air supply is another important issue in DMFCs because the oxygen concentration in air is only 21%, and the performance of a DMFC with air is generally no higher than 60% of one operating with pure oxygen. Therefore, a much higher flow rate of air than the stoichiometric amount is generally required to enhance cell performance; however, the effect of the airflow rate could vary depending on the type of cell. In Fig. 7, passive cells are compared with active air cells in which air was blown into the cathode side using a small fan, while the methanol was supplied in a passive mode. The active air mode performed worse than the passive mode, regardless of the methanol concentration. The lower performance with the active air supply is quite inconsistent with our understanding that a faster air flow rate generally yields a higher performance due to an increased oxygen supply to the electrode. However, in the passive cell where the cathode compartment is open to the ambient air, the forced air blowing on the cell could drop the cell temperature, thus resulting in a lower performance.

In order to develop a passive DMFC for use as a portable power, the operation time of the cell with a load of methanol fuel should be longer than that of currently used power sources, such as lithium batteries. In this regard, continuous operations

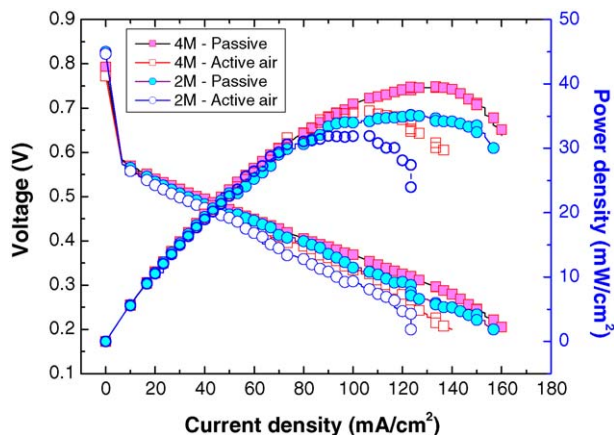


Fig. 7. Comparison of cell performance under varying air supplying mode: catalyst loading = anode/cathode = 8/8 (mg cm^{-2}).

have been tested with different modes of supply of reactants, including a completely passive, an active air, as well as an active methanol mode, respectively. Fig. 8 shows the variation in voltage over time at a load of 50 mA cm^{-2} for each feeding mode. The operation started just after injecting 5.3 mL of 4 M methanol solution into the reservoir, and there was a fluctuation in voltage in the initial stage due to methanol crossover [12]. The pattern of voltage generation varies depending on the supply mode of the reactants. The completely passive cell maintains its voltage at around 0.43 V for 80 min followed by a sharp decrease, while the active air cell lasts 90 min. However, the active methanol cell into which methanol is pumped while the air is in a passive state does not exhibit an abrupt voltage drop at least for 250 min. From these results, one can see that the voltage dropping in the completely passive and the active air cells is due to the shortage of methanol in the feed reservoir [18]. Therefore, as verified by the active methanol experiment, the DMFC could be operated for a long period of time even under passive conditions if the methanol supply is sufficient, and the air supply and water flooding may not be major problems in the low current regions. In the study by Chen and Yang [17], they observed a decrease

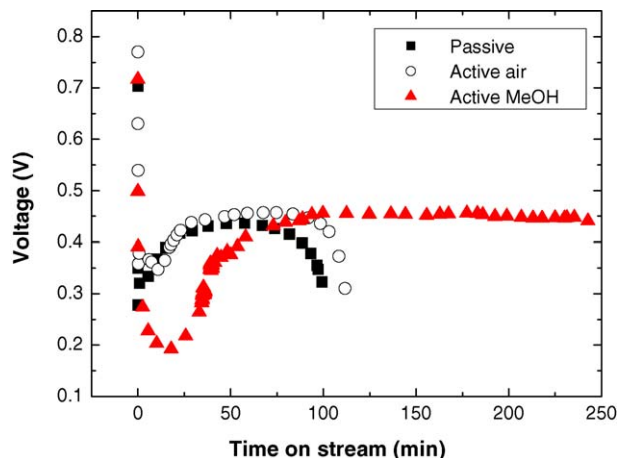


Fig. 8. Continuous operation of a passive cell at 300 mA under different operating conditions with a feed loading of 5.3 mL of 5.0 M methanol.

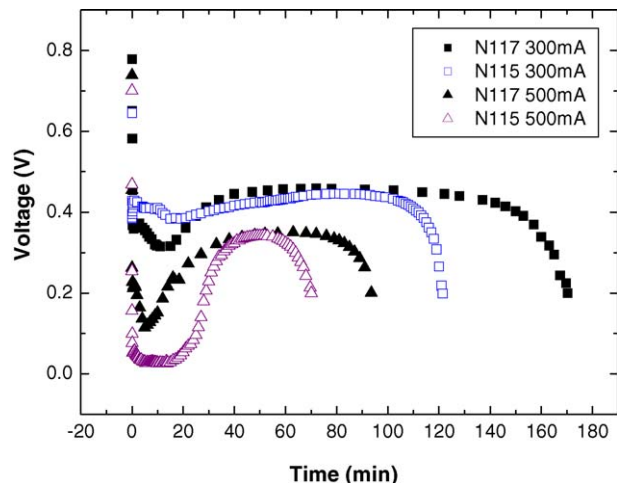


Fig. 9. Continuous operation of passive cells with Nafion® 115 and Nafion® 117, respectively, at various currents with a feed loading of 5.3 mL of 5.0 M methanol.

in voltage during continuous operation lasting 2 h under active methanol and passive air conditions. The result shows the possibility of water flooding during a continuous and prolonged operation of the air-breathing cell.

The thickness of the polymer electrolyte membrane has been confirmed to have only a slight effect on the DMFC performance from our experiments with Nafion® 115 and Nafion® 117. However, the operating time of the passive cell with a given amount of methanol loading (5.3 mL of 4 M methanol) could be affected by the membrane thickness because the rate of methanol crossover is directly proportional to the membrane thickness. Fig. 9 shows the change in cell performance over time for the two cells with different membranes, Nafion® 115 (125 μm) and Nafion® 117 (175 μm), respectively. We can see that the duration time is inversely proportional to the rate of methanol consumption, and thus, it increases as the electric load decreases and the membrane thickness increases. As mentioned previously, this is because the thicker membrane has a lower methanol loss through crossover, thereby ensuring a longer operating time. Therefore, the membrane with a lower methanol crossover should be used to increase the energy efficiency, or in other words, to increase the operating time with a given amount of methanol loading when used as a portable power source.

4. Conclusions

A passive direct methanol fuel cell was investigated to understand its behavior when varying the operating conditions, such as methanol concentration, catalyst loading in the electrodes, methanol and air supply modes under ambient conditions. Long-term operations were also conducted to observe the effects of the reactant feeding modes, membrane thickness and the magnitude of the electric load.

The passive cell showed vastly different behavior compared to the active one. Maximum performance was achieved with a 5 M methanol concentration and a catalyst loading of 8 mg cm^{-2} on both electrodes. Under ambient conditions, we achieved a

maximum power density of 45 mW cm^{-2} . Furthermore, with this particular cell configuration in which the cathode side was open to the atmosphere through holes, forced air blowing to the cell reduced cell performance due to a drop in cell temperature. Continuous operation of the passive cell was found to be significantly affected by the methanol supply rather than the air supply. Therefore, in order to increase the operating time with methanol feed, we must capture as much methanol as possible by reducing methanol crossover and by using a higher concentration of methanol feed.

Acknowledgements

This work was financially supported by the Korean Ministry of Commerce, Industry and Energy through the Institute of Industrial Technology Evaluation and Planning (ITEP) under the research program of “Development of Advanced Technologies for Next Generation”. And the authors thanks Dr. M. Aulice Scibioh for her helping in preparing this article.

References

- [1] L. Carrette, K.A. Friedrich, U. Stimming, *Fuel Cells* 1 (2001) 5–39.
- [2] K. Scott, W.M. Taama, P. Argyropoulos, K. Sundmacher, *J. Power Sources* 83 (1999) 204–216.
- [3] C.K. Dyer, *J. Power Sources* 106 (2002) 31–34.
- [4] A. Heinzl, C. Hebling, M. Muller, M. Zedda, C. Muller, *J. Power Sources* 105 (2002) 250–255.
- [5] J. Han, E.-S. Park, *J. Power Sources* 112 (2002) 477–483.
- [6] J. Pavio, J. Hallmark, J. Bostaph, A. Fisher, B. Mylan, C.G. Xie, *Fuel Cells Bull.* 2002 (2002) 8–11.
- [7] H. Chang, J.R. Kim, J.H. Cho, H.K. Kim, K.H. Choi, *Solid State Ionics* 148 (2002) 601–606.
- [8] S.C. Kelley, G.A. Deluga, W.H. Smyrl, *Electrochem. Solid State Lett.* 3 (2000) 407–409.
- [9] B. Gurau, E.S. Smotkin, *J. Power Sources* 112 (2002) 339–352.
- [10] Z. Qi, A. Kaufman, *J. Power Sources* 110 (2002) 177–185.
- [11] A. Blum, T. Duvdevani, M. Philosoph, N. Rudoy, E. Peled, *J. Power Sources* 117 (2003) 22–25.
- [12] D. Kim, E.A. Cho, S.-A. Hong, I.-H. Oh, H.Y. Ha, *J. Power Sources* 130 (2004) 172–177.
- [13] B.-K. Kho, I.-H. Oh, S.-A. Hong, H.Y. Ha, *Electrochim. Acta* 50 (2004) 777–781.
- [14] J.G. Liu, T.S. Zhao, R. Chen, C.W. Wong, *Electrochem. Commun.* 7 (2005) 288–294.
- [15] B.K. Kho, B. Bae, M.A. Scibioh, J. Lee, H.Y. Ha, *J. Power Sources* 142 (2005) 50–55.
- [16] C.Y. Chen, P. Yang, Y.S. Lee, K.F. Lin, *J. Power Sources* 141 (2005) 24–29.
- [17] C.Y. Chen, P. Yang, *J. Power Sources* 123 (2003) 37–42.
- [18] Z. Guo, Y. Cao, *J. Power Sources* 132 (2004) 86–91.
- [19] J. Liu, G. Sun, F. Zhao, G. Wang, G. Zhao, L. Chen, B. Yi, Q. Xin, *J. Power Sources* 133 (2004) 175–180.
- [20] M.K. Ravikumar, A.K. Shukla, *J. Electrochem. Soc.* 143 (1996) 2601–2606.
- [21] R. Jiang, D. Chu, *J. Electrochem. Soc.* 151 (2004) A69–A76.
- [22] J. Prabhuram, T.S. Zhao, H. Yang, *J. Electroanal. Chem.* 578 (2005) 105–112.
- [23] T. Shimizu, T. Momma, M. Mohamedi, T. Osaka, S. Sarangapani, *J. Power Sources* 137 (2004) 277–283.