

Effect of oxygen and methanol supply modes on the performance of a DMFC employing a porous plate

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Abstract

The effect of oxygen and methanol supply modes on the performance and the fluxes of methanol and water through the membrane electrode assembly, MEA, of a DMFC with and without a porous plate was investigated. For the conventional MEA, MEA_C, flowing oxygen and methanol were essential to stabilize the cell performance, avoiding flooding at the cathode and depletion of methanol at the anode. As a result of flowing oxygen, methanol and water fluxes through the MEA_C increased by more than twice that for the air-breathing cell. For the MEA with a porous plate, MEA/PCP, the flow of oxygen and methanol had no significant effect on the cell performance, where the porous carbon plate, PCP, prevented the cathode from flooding by reducing the mass transport through the MEA. Methanol and water fluxes through the MEA/PCP were not affected by flowing oxygen at 0.1 l min⁻¹. However, the increase in oxygen flow rate from 0.1 l min⁻¹ to 1 l min⁻¹ had a negative effect on the cell performance either in the MEA_C or in the MEA/PCP. This would be due to the cooling effect for MEA_C and the drying effect for the MEA/PCP. A moderate supply of oxygen to the cathode, like air-breathing, was appropriate for the DMFC with a PCP.

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1. Introduction

There has been an increasing demand for the development of direct methanol fuel cells (DMFCs) because of their high energy densities that are suitable for mobile electric devices and automobiles. However, the energy density of the DMFCs currently under development is still far from that expected due to the methanol crossover and the high over voltage at the electrodes [1–4]. Due to the methanol crossover, the DMFC usually shows the highest performance at low concentrations of methanol from 2 to 3 M [5,6] under active conditions and about 5 M [7–9] under passive conditions. To overcome the methanol crossover, a large number of studies [10–14] were carried out for developing a new proton-conducting membrane with a low methanol permeability and high proton conductivity. Modification of the existing membranes like Nafion has also been conducted by conversion to a composite membrane [15–17] with inorganic or organic materials, surface modification by physical treatment [18] or by

coating the surface with a thin film [19,20]. Only a few papers have considered reducing the ability for methanol crossover by mass transport control in the backing layer [21–24].

The authors have demonstrated, in recent reports [21–23], that a passive DMFC with a porous carbon plate significantly reduced the methanol crossover, MCO, and constantly controlled the cell temperature. The separation of methanol through this type of passive DMFC under open circuit conditions was explained by diffusion control of the methanol by the PCP depending on the properties of the porous material, i.e., thickness, porosity and water absorptivity of the porous material [22]. Under closed circuit conditions, the PCP and the CO₂ gas layer that formed between the anode and the porous plate stably controlled the mass transport of methanol and water from the reservoir to the anode, and this facilitated operation with very high concentrations of methanol, even neat methanol [23]. When high concentrations of methanol were used with the porous plate, the Faraday efficiency was kept high and back diffusion of water from the cathode to the anode through the membrane occurred, resulting in no flooding at the cathode. The objective of this paper is to clarify the effects of oxygen and methanol supply modes that affect the mass transfer rate between the MEA and outside

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of it on the type of DMFC using a PCP. Another objective is to show the superior characteristics of this type of DMFC.

The flooding, which is a well-known problem in the passive DMFCs [25,26], causes blocking of the oxygen supply to the cathode resulting in a decrease in the power density as a result of water accumulation at the cathode. This occurs when the rate of water production is *faster* than the rate of water removal at the cathode. Hence, the flooding relates to the methanol and water fluxes through the membrane and the rate of the oxygen reduction reaction, i.e., current density, and the rate of water evaporation at the cathode, i.e., flow rate, temperature and humidity of the cathode gas. The evaporation of water from the cathode under air-breathing condition is usually very small, so flooding easily takes place. Flooding can be avoided by blowing air or oxygen to the cathode where the rate of evaporation is greatly increased [26,22]. Another main problem encountered in a passive DMFC is the depletion of methanol at the anode by the methanol crossover; the long-time operation of a passive DMFC was affected by the methanol supply rather than the air supply [9]. To avoid this problem, fresh methanol must be allowed to flow continuously at the anode side.

In this paper, the effects of the oxygen and methanol supply modes on the current density, temperature and the fluxes of methanol and water through the MEA were investigated for DMFCs with and without the PCP. The differences in those variables at different supply modes were discussed from the viewpoints of occurrence of flooding and methanol depletion.

2. Experimental

2.1. MEA preparation

The conventional MEA, which uses carbon cloth (35% Teflonized, ElectroChem Inc.) as the anode and cathode backing layers, was prepared in the following manner. Pt black (HiSPEC 1000, Johnson Matthey Fuel Cells Co. Ltd.) and Pt–Ru black (HiSPEC 6000, Johnson Matthey Fuel Cells Co. Ltd.) were used as the catalyst for the cathode and anode, respectively. Catalyst ink was prepared by dispersing an appropriate amount of the catalyst in a solution of de-ionized water, isopropyl alcohol, and 5 wt% Nafion solution (Wako Inc.). The ink was then coated on carbon cloth to form the electrodes. The catalyst loading was 12 mg cm^{-2} and 9 mg cm^{-2} for the anode and cathode, respectively, and the ionomer loading on the catalyst was 10 wt% for the cathode and 15 wt% on the anode. Nafion 112 was used as the electrolyte membrane. The MEA was then fabricated by sandwiching the membrane between the anode and the cathode and hot pressing them at 408 K and 5 MPa for 3 min.

2.2. Porous carbon plate (PCP)

A porous carbon plate made of a composite of carbon nanotubes and amorphous carbon, supplied from Mitsubishi Pencil Co. Ltd., with 1.0 mm thickness was used in this study. The microstructure of the PCP analyzed by a mercury porosimeter (Pascal 140+440, Thermo Finnigan Inc.) revealed that it had $0.713 \text{ cm}^3 \text{ g}^{-1}$ in total cumulative pore volume, $1.49 \mu\text{m}$ in

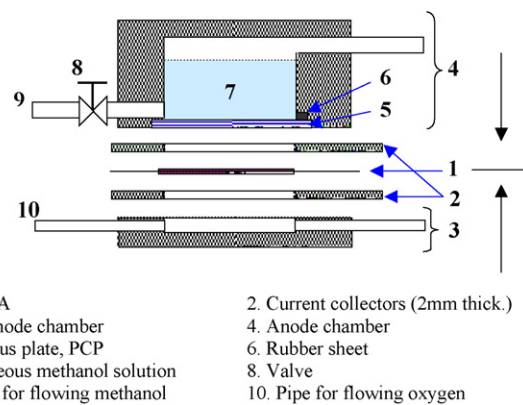


Fig. 1. Schematic diagram of a DMFC with or without porous plate.

average pore diameter, and 0.514 in total porosity. The PCP was hydrophobic and its water absorptivity as defined in our previous paper [22] was nearly zero. The PCP was placed on an anode current collector and used as mentioned below.

2.3. Cell structures with and without a PCP and oxygen/methanol supply modes

Fig. 1 shows a DMFC, used in this experiment, with the porous carbon plate. In the anode compartment, a methanol reservoir, 12 dm^3 , with two stainless steel pipes for flowing methanol was prepared. On the cathode side, there was a cathode chamber with two stainless steel pipes for flowing O_2 . This chamber was removed in the air-breathing mode. The MEA was sandwiched between two current collectors, which were plates of stainless steel of 2 mm thickness and open holes with a 73% open ratio. The MEA with the plates was fixed with the anode chamber in the air-breathing mode and was fixed between the anode and cathode chambers in the other operation modes.

When a PCP was used, the PCP was placed on the anode current collector by exposing the upper surface in the methanol solution. This configuration forced the methanol to pass through the porous plate then through the openings in the anode current collector to reach the anode catalyst layer. Under closed circuit conditions, the openings of the anode current collector and a part of the pores of the PCP would be filled with CO_2 produced at the anode, and hence, a CO_2 gas layer would be formed between the anode and the methanol solution. In this case, both the PCP and the CO_2 gas layer obstruct methanol transport from the reservoir to the anode. Without the PCP, the CO_2 gas layer is not formed, and CO_2 easily escapes through the openings of the current collector to the reservoir in a form of bubbles. This situation allows direct contact with the anode for the solution and then a high methanol transport.

The cell was arranged horizontally keeping the reservoir upside to ensure a constant contact between the solution and the PCP and/or anode.

The methanol solution was supplied either in a passive mode or an active mode. The passive mode was defined as no flow of methanol to the anode and was realized by an injection of 6–7 cc of methanol solution into the reservoir. In the active

mode, methanol solution was introduced to the reservoir through the lower tube at a rate of 1.5 ml min^{-1} using a pump (Iwaki, SDK-081). On the other hand, as a mode of oxygen supply, air-breathing was defined as just exposing the cathode to ambient air without the cathode chamber. By using the cathode chamber for the oxygen flow, oxygen was supplied at different flow rates, 0.1 l min^{-1} and 1 l min^{-1} .

The methanol concentrations used in this study were chosen to be 2 M (mol l^{-1}) for the MEA without PCP, MEA_C , and 16 M for the MEA with PCP, MEA/PCP , where the DMFC power output became a maximum for each type of MEA [23].

2.4. Measurement of the cell performance

In this study, all the experiments were conducted under ambient conditions (293 K and 1 atm), methanol solution at a certain concentration was fed into the reservoir, and left in the cell for a few minutes until the PCP became saturated with methanol. The time progress of the current density, i - t characteristics, at 0.1 V was measured using an electrochemical measurement system (HAG-5010, Hokuto Denko Co. Ltd.). 0.1 V was selected because both of flooding at the cathode and depletion of methanol at the anode were enhanced at high current densities under this cell voltage. The temperature of the cell was also measured using a thermocouple placed between the surface of anode current collector and the porous plate. The methanol and water fluxes during the i - t experiments were evaluated by measuring the weight and concentration of the methanol solution before and at the end of the i - t experiments [23].

3. Results and discussion

3.1. Influence of methanol/oxygen supply modes on the performance of the conventional MEA, MEA_C

3.1.1. Performance with a passive methanol supply with different oxygen supplies

Fig. 2 shows the time progress of the current density, i - t curves, for the DMFC without the PCP with a passive methanol supply and different oxygen supply modes; air-breathing, oxygen flow at 0.1 l min^{-1} and 1 l min^{-1} . As shown in the figure, under the air-breathing conditions, the current density was initially as high as 160 mA cm^{-2} but it rapidly decreased to about 40 mA cm^{-2} within 1 h . For the oxygen flow at 0.1 l min^{-1} and 1 l min^{-1} , the current density remained constant around 140 mA cm^{-2} and 110 mA cm^{-2} , respectively, for about 2 h , then decreased to a value similar to that for the air-breathing condition. The rapid reduction of the current density during the air-breathing would be related to the flooding at the cathode as reported [25,26]. Water produced at the cathode would block the feeding of air at the cathode. Under the O_2 flow modes, water removal from the cathode by evaporation would be enhanced and so the current density remained at a high value [26].

The decrease in current density with time was also affected by the depletion of methanol at the anode. For the air-breathing, the volume and concentration of the methanol solution initially were 6.2 cm^3 and 2.1 mol l^{-1} , respectively, and these values

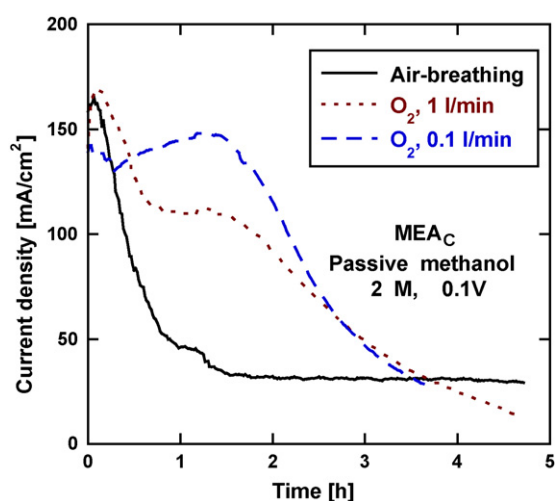


Fig. 2. Current profile during continuous operation of a DMFC without porous plate, MEA_C , operated with different oxygen supplying modes under cell voltage 0.1 V and 2 M .

were finally reduced to 3.9 cm^3 and 0.2 mol l^{-1} , respectively. The percent of methanol consumed during the experiment was calculated to be 95%. This was calculated to be 85% and 90% for the oxygen flow at 0.1 l min^{-1} and 1 l min^{-1} , respectively.

The current density decreased with the increasing oxygen flow from 0.1 l min^{-1} to 1 l min^{-1} may be related to a cooling effect [9] as shown below.

Fig. 3 shows the cell temperature in the experiment shown in Fig. 2. The highest cell temperature was obtained for the oxygen flowing at 0.1 l min^{-1} , where it increased to 307 K and was about 5 K higher than those in the other supply modes. The lower temperature for the oxygen flow at 1 l min^{-1} was considered a reason for the smaller current density compared with that at 0.1 l min^{-1} , suggesting a cooling effect. The cell temperature was related to the rate of methanol crossover that induced an increase in the cell temperature by the exothermic oxidation reaction of the permeated methanol [25,27,28]. The

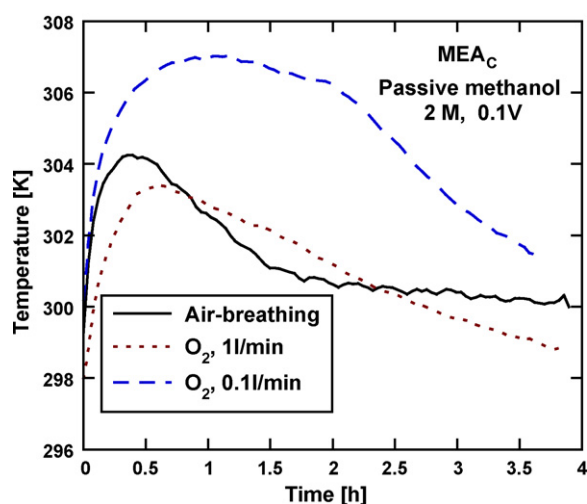


Fig. 3. Variations in operating cell temperature of a DMFC without porous plate, MEA_C , operated with different oxygen supplying modes under cell voltage 0.1 V and 2 M .

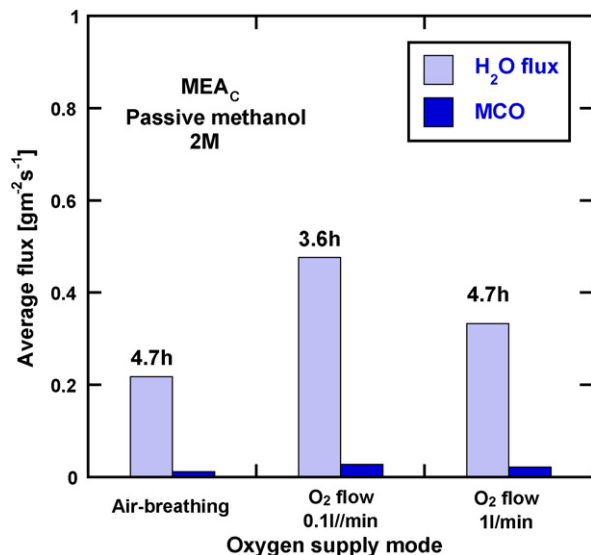


Fig. 4. Effect of oxygen supplying mode on methanol and water fluxes of a DMFC without porous plate, MEA_C, under cell voltage 0.1 V and 2 M.

low temperature for the air-breathing mode may be attributed to the lower methanol crossover as shown below.

Fig. 4 shows the effect of different oxygen supply modes on the methanol and water fluxes through the MEA during the $i-t$ experiments shown in Fig. 2. As a result of the oxygen flowing, both the methanol and water fluxes through the MEA increased to one and a half or twice the value under the air-breathing mode. This should be due to the increased rate of evaporation of the solution at the cathode by the flowing oxygen, which in turn enhanced the driving force for mass transfer through the MEA_C [26]. The average values of the methanol and water fluxes for 0.11 min⁻¹ were higher than that at 11 min⁻¹, and this can be explained based on two reasons. First the higher temperature for 0.11 min⁻¹ than that for 11 min⁻¹ enhanced the mass transfer of methanol and water through the MEA; the second reason is that the higher current density induced a larger water transport from the anode to cathode by the electro osmosis [29].

3.1.2. Performance with an active methanol supply with different oxygen supplies

Fig. 5 shows the $i-t$ curves for the DMFC without the PCP with flowing methanol and different oxygen supply modes. In the case of air-breathing, the current density was much lower than those with the oxygen flows through the operating time, and this decreased with time to less than 30 mA cm⁻² which is slightly lower than that in the case of air-breathing and passive methanol shown in Fig. 2. Reduction in the current density under the air-breathing mode would be related to the flooding at the cathode. The methanol crossover might be increased resulting from no depletion of the methanol under this condition. On the other hand, with the oxygen flows, the current density was highly constant and similar in each case unrelated to the flow rates except for the initial period within 0.75 h. The initial period would be needed to reach the steady state. The flow of both methanol and

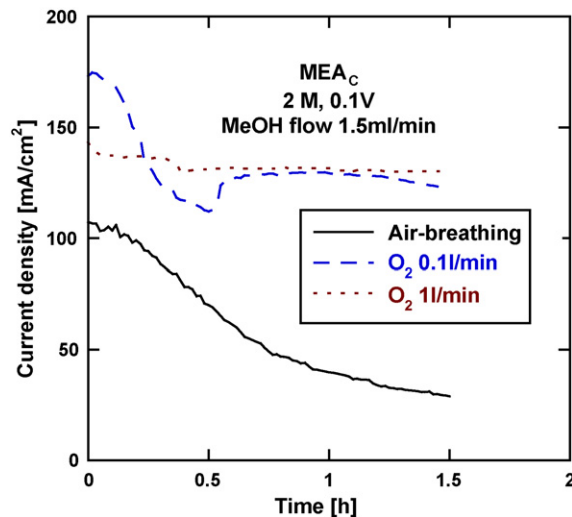


Fig. 5. Current profile during continuous operation of a DMFC without porous plate, MEA_C, operated with different oxygen supplying modes under cell voltage 0.1 V and flowing methanol 2 M.

oxygen stabilized the current density because the flowing oxygen prevents flooding at cathode [22,26] by increasing the rate of water removal by evaporation, and flowing methanol prevents the depletion of methanol at the anode [9].

The negative effect of the increasing O₂ flow from 0.1 l min⁻¹ to 1 l min⁻¹, observed in the passive methanol feeding, did not appear. This might be related to the high reaction rate, resulting from the water removal by the oxygen supply at the cathode, which reduced the effect of the methanol crossover by consuming the methanol at the anode.

Fig. 6 shows the cell temperature in the $i-t$ experiment shown in Fig. 5. The cell temperature was the lowest in the case of air-breathing, and this might be related to the excessive flooding due to the methanol flow at the anode.

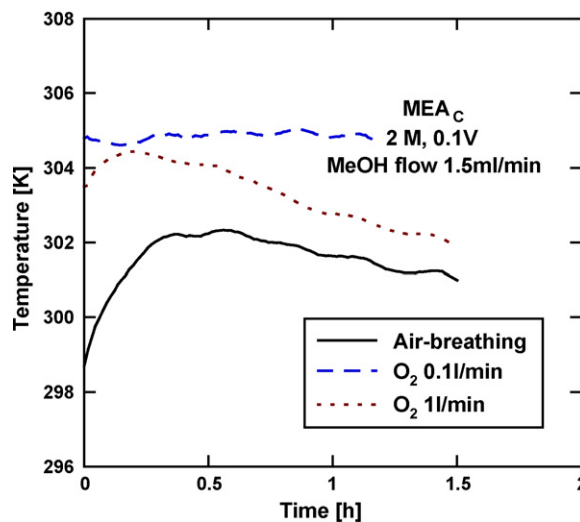


Fig. 6. Variations in operating cell temperature of a DMFC without porous plate, MEA_C, operated with different oxygen supplying modes under cell voltage 0.1 V and flowing methanol 2 M.

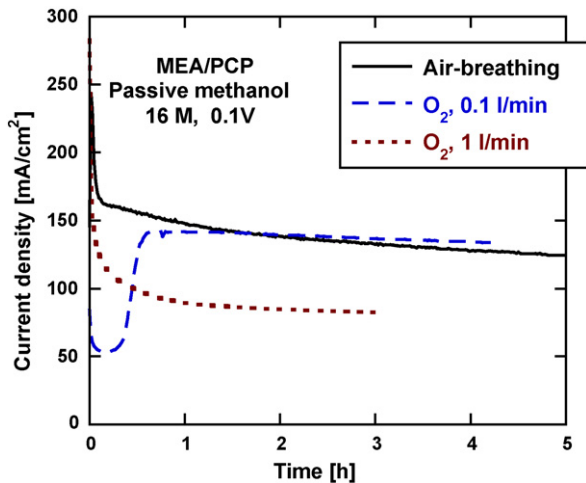


Fig. 7. Current profile during continuous operation of a DMFC with porous plate, MEA/PCP, operated with different oxygen supplying modes under cell voltage 0.1 V and 16 M.

3.2. Influence of methanol/oxygen supply modes on the performance of MEA with PCP, MEA/PCP

3.2.1. Performance with the passive methanol supply with different oxygen supplies

Fig. 7 shows the i - t curves for the DMFC with PCP, MEA/PCP, with the passive methanol supply and different oxygen supply modes. The flowing of oxygen for the MEA/PCP did not have a positive effect on the current density, in contrast to the conventional MEA as shown in Fig. 2. The current density with the air-breathing remained high and almost similar to that with an oxygen flow of 0.11 min^{-1} . The current densities for all of the oxygen supply modes slightly decreased with time due to the weak decrease in the methanol concentration during that time. PCP prevented the methanol crossover and water flux through the MEA [23] resulting in a small methanol consumption during the experiment, i.e., 20% (during the 4.2 h experiment) for the oxygen flow at 0.11 min^{-1} and 18% (3 h) for the oxygen flow at 11 min^{-1} . Hence, the flowing of O_2 did not have a positive effect on the performance where the flooding was prevented. For the oxygen flow at 0.11 min^{-1} , although the current density was initially low which was affected by the initial condition, it increased and became almost constant after 0.7 h. The current density decreased with the increase in oxygen flow rate from 0.11 min^{-1} to 11 min^{-1} . This reduction in current density would be related to a change in the mass transport through the membrane. In fact, the methanol flux and the water flux with oxygen flowing at 11 min^{-1} were different from that at 0.11 min^{-1} and air-breathing as shown in Fig. 8. The rate of water removal at the cathode by evaporation was increased substantially and was calculated to be almost six times that at 0.11 min^{-1} based on the dependency of the mass transfer coefficient on the gas flow rate, by the increase in the oxygen flow to 11 min^{-1} . This would cause a larger methanol flux and a low back diffusion of water. Methanol concentration at the anode/electrolyte interface must be higher than that at the cathode/electrolyte interface, because crossover methanol was

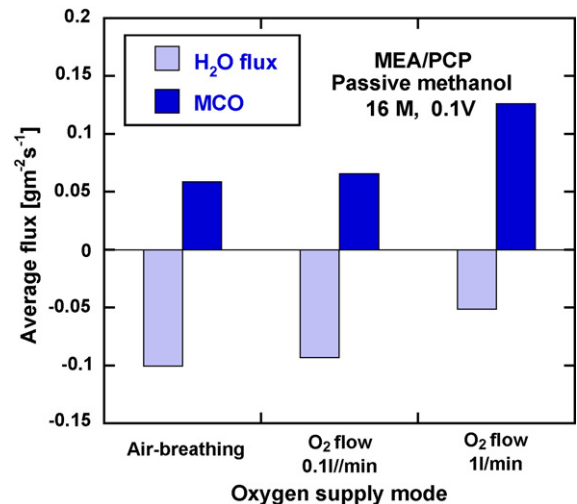


Fig. 8. Effect of oxygen supplying mode on methanol and water fluxes of a DMFC with porous plate, MEA/PCP, under cell voltage 0.1 V and 16 M.

oxidized to water at the cathode. Then, methanol was transported from the anode to the cathode by diffusion as well as by electro osmotic action. On the other hand, the concentration of water at the cathode/electrolyte was higher than that at anode/electrolyte at high methanol concentrations, because water was consumed by the anode reaction and produced at the cathode by the oxidation of crossover methanol. Then, back diffusion of water took place from the cathode to the anode based on the difference of water concentration between them. Fig. 8 shows that the increased oxygen flow from 0.11 min^{-1} to 11 min^{-1} reduced the back diffusion of water to half while the methanol flux was nearly doubled. In contrast, there was no big difference in the value of fluxes between air-breathing and the oxygen flow at 0.11 min^{-1} .

Fig. 9 shows the cell temperature in the experiment shown in Fig. 7. The flowing of oxygen and the oxygen supply modes did not affect the cell temperature where the PCP controlled the mass transport through the MEA.

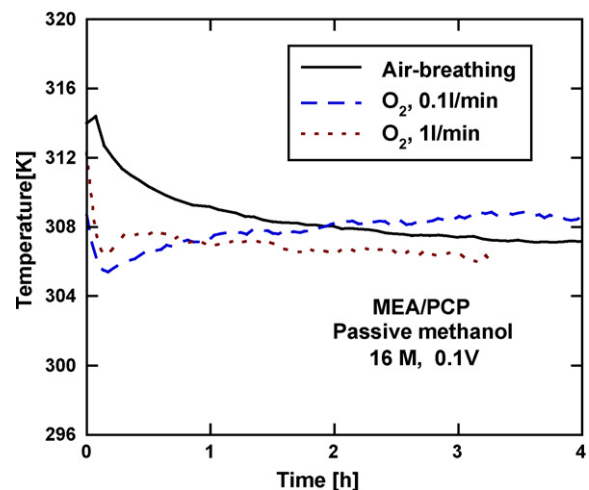


Fig. 9. Variations in operating cell temperature of a DMFC with porous plate, MEA/PCP, with different oxygen supplying modes under cell voltage 0.1 V and 16 M.

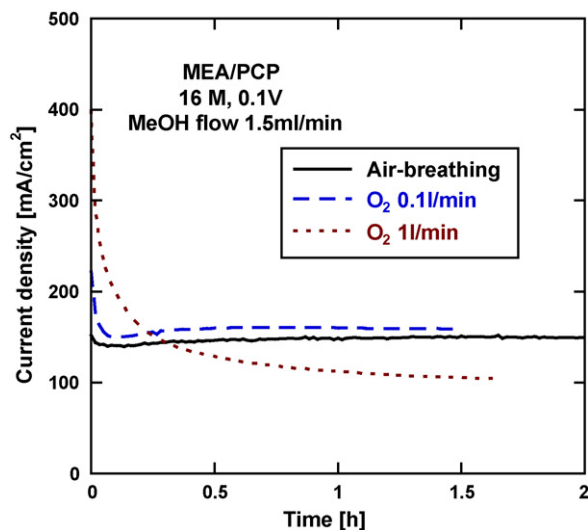


Fig. 10. Current profile during continuous operation of a DMFC with porous plate, MEA/PCP, with different oxygen supplying modes under cell voltage 0.1 V and flowing methanol 16 M.

3.2.2. Performance with the active methanol supply with different oxygen supplies

Fig. 10 shows the i - t curves for the DMFC with PCP, MEA/PCP, with the active methanol supply and the different oxygen supply modes. There was no big difference in the performance with the air-breathing and the oxygen flow at 0.1 l min^{-1} .

The performance between the passive methanol supply, shown in Fig. 7, and the active methanol, shown in Fig. 10, was quite similar in each case. Because the methanol transport from the reservoir to the anode was strongly controlled by the PCP in these experiments, the effect of the flow rate on the performance would be small. Strictly speaking, we understood that the current density for the air-breathing and the oxygen flow at 0.1 l min^{-1} became constant during the experiment, and a decrease in the current density with time as shown in Fig. 7 was not observed in Fig. 10. This is because the depletion of the methanol in the reservoir did not occur under the active methanol conditions.

In the case of the flowing oxygen at 1 l min^{-1} , the current density was initially high, about 400 mA cm^{-2} , but rapidly decreased. This high initial current density was related to the cell temperature which was about 320 K, almost 10 K higher than those in the other cases as shown in Fig. 11. The heat production by the oxidation of the initially accumulated methanol at the cathode under open circuit would be accelerated by the oxygen flow.

The above comparison in the DMFC performance between the MEA with and without the PCP made it clear that a very moderate supply of oxygen to the cathode, as with air-breathing, was appropriate for the MEA with the PCP. The employment of the PCP reduced the methanol crossover and prevented the MEA from flooding by controlling the mass transport of methanol and water by the PCP. Also the effect of the methanol flow rate on the cell performance was small compared with that of the MEA without the PCP. Such moderate methanol and water supplies would be desired for a practical DMFC system, because the

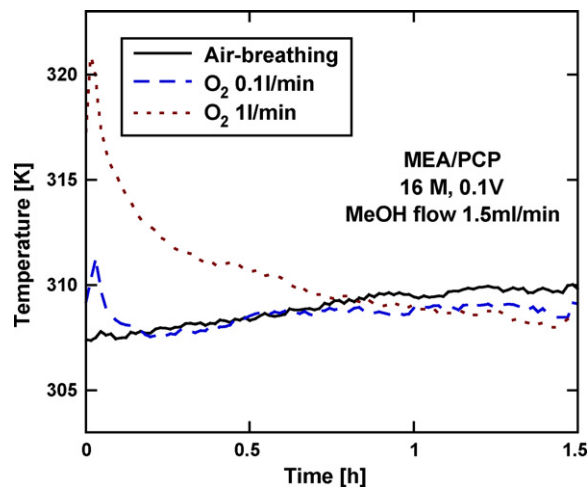


Fig. 11. Variations in operating cell temperature of a DMFC with porous plate, MEA/PCP, operated with different oxygen supplying modes under cell voltage 0.1 V and flowing methanol 16 M.

excess power needed for the flow of oxygen and/or methanol can be minimized.

4. Conclusions

The performance of a DMFC with and without a PCP was investigated under different methanol/oxygen supply modes, passive and active supplies of methanol, and air-breathing and flowing supplies of oxygen, under ambient conditions using methanol concentrations of 2 M for MEA without the PCP and 16 M for that with the PCP. The following conclusions were drawn.

- (1) Both flooding at the cathode and depletion of methanol at the anode decreased the cell performance of the DMFC without the PCP. The flow of both oxygen and methanol increased the current density.
- (2) The performance of the DMFC with a PCP was hardly affected by the flow either methanol or oxygen, due to the mass transport control by the PCP.
- (3) A moderate supply of oxygen to the cathode, such as air-breathing, was appropriate for the DMFC with a PCP.
- (4) Increasing the O_2 flow rate from 0.1 l min^{-1} to 1 l min^{-1} had a negative effect on cell performance both with and without a PCP, due to a cooling effect or a drying effect on the MEA.

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References

- [1] A.S. Arico, S. Srinivasan, V. Antonucci, Fuel Cell 1 (2001) 133–161.
- [2] T. Schultz, K. Su Zhou, Sundmacher, Chem. Eng. Technol. 24 (2001) 1223–1233.

- [3] J.G. Liu, T.S. Zhao, R. Chen, C.W. Wong, *Electrochem. Commun.* 7 (2005) 288.
- [4] J.G. Liu, T.S. Zhao, Z.X. Liang, R. Chen, *J. Power Sources* 153 (2006) 61–67.
- [5] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K. Surya Prakash, G.A. Olah, *J. Power Sources* 47 (1994) 377–385.
- [6] M.K. Ravikumar, A.K. Shukla, *J. Electrochem. Soc.* 143 (1996) 2601–2606.
- [7] S.R. Yoon, G.H. Hwang, W.I. Cho, I.-H. Oh, S.-A. Hong, H.Y. Ha, *J. Power Sources* 106 (2002) 215–223.
- [8] R. Chen, T.S. Zhao, *J. Power Sources* 152 (2005) 122–130.
- [9] B. Bae, B.K. Kho, T. Lim, I. Oh, S. Hong, H.Y. Ha, *J. Power Sources* 158 (2006) 1256–12261.
- [10] J.T. Wang, S. Wasmus, R.F. Savinell, *J. Electrochem. Soc.* 143 (1996) 1233–1239.
- [11] E. Peled, T. Duvdevani, A. Aharon, A. Melman, *Electrochem. Solid State Lett.* 3 (2000) 525–528.
- [12] M.V. Fedkin, X. Zhou, M.A. Hofmann, E. Chalkova, J.A. Weston, H.R. Allcock, S.N. Lvov, *Mater. Lett.* 52 (2002) 192–196.
- [13] T. Yamaguchi, M. Ibe, B.N. Nair, S. Nakao, *J. Electrochem. Soc.* 149 (2002) A1448–A1453.
- [14] M.L. Ponce, L. Prado, B. Ruffmann, K. Richau, R. Mohr, S.P. Nunes, *J. Membr. Sci.* 217 (2003) 5–15.
- [15] A.S. Arico, P. Creti, P.L. Antonucci, V. Antonucci, *Electrochem. Solid State Lett.* 1 (1998) 66–68.
- [16] C. Yang, S. Srinivasan, A.S. Arico, P. Creti, V. Baglio, V. Antonucci, *Electrochem. Solid State Lett.* 4 (2001) A31–A34.
- [17] N. Jia, M.C. Lefevre, J. Halfyard, S. Qi, P.G. Pickup, *Electrochem. Solid State Lett.* 3 (2000) 529–531.
- [18] I.J. Hobson, H. Ozu, M. Yamaguchi, M. Muramatsu, S. Hayase, *J. Mater. Chem.* 12 (2002) 1650–1656.
- [19] W.C. Choi, J.D. Kim, S.I. Woo, *J. Power Sources* 96 (2001) 411–414.
- [20] Y.K. Xiu, K. Kamata, T. Ono, K. Kobayashi, T. Nakazato, N. Nakagawa, *Electrochemistry* 73 (2005) 67–70.
- [21] N. Nakagawa, K. Kamata, A. Nakazawa, M. Ali Abdelkareem, K. Sekimoto, *Electrochemistry* 74 (2006) 221–225.
- [22] N. Nakagawa, M. Ali Abdelkareem, K. Sekimoto, *J. Power Sources* 160 (2006) 105–115.
- [23] M. Ali Abdelkareem, N. Nakagawa, *J. Power Sources* 162 (2006) 114–123.
- [24] G.Q. Lu, C.Y. Wang, T.J. Yen, X. Zhang, *Electrochim. Acta* 49 (2004) 821.
- [25] R. Chen, T.S. Zaho, J.G. Liu, *J. Power Sources*, *J. Power Sources* 157 (2006) 351–357.
- [26] C.Y. Chen, P. Yang, *J. Power Sources* 123 (2003) 37–41.
- [27] J.G. Liu, T.S. Zaho, Z.X. Liang, R. Chen, *J. Power Sources* 153 (2006) 61–67.
- [28] J. Liu, G. Sun, F. Zhao, G. Wang, G. Zhao, L. Chen, B. Yi, Q. Xin, *J. Power Sources* 133 (2004) 175–180.
- [29] S. Yao, X. Tang, C. Hsieh, Y. Alyousef, M. Vladimer, G. Fedder, C. Amon, *Energy* 31 (2006) 636–649.