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Vertical operation of passive direct methanol fuel cell employing a porous carbon plate

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ABSTRACT

Vertical operation of a passive DMFC employing a porous carbon plate, PCP, with different resistances for fluid flow and bubble point pressure was investigated to clarify the properties required for the PCP for vertical operation. Moreover, the cell performance was investigated under different solution head pressures within 22 mm height and was discussed based on the methanol transport through the PCP. In contrast to the horizontal orientation, the static pressure of the liquid as a function of its height on the vertical axis *h* along the PCP surface, in the vertical orientation, enhanced the convective methanol flux through the PCP and affected the DMFC performance depending on the properties of the PCP and the methanol concentration used. The effect of the solution head pressure on the DMFC performance in the vertical orientation could be controlled by using PCP with high bubble point pressures. The DMFC could attain stable performance under both horizontal and vertical cell orientations and different solution head pressures even with 100% methanol by using a PCP with the proper resistance for the methanol transport and bubble point pressure. A thin PCP of 0.5 mm thickness with the proper resistance enabled the vertical operation producing a constant power density over 40 mW/cm^2 using 100% methanol at 0.25 V.

1. Introduction

The explosive growth of portable and wireless consumer electronics over the past few years has spurred the development of new power source technologies having increased power and energy density to meet the demands for these new products. Because even the best battery technology no longer meets the energy demand of the modern electronic products, scientists are searching for innovative, miniaturized power systems that can significantly prolong the operation time of the portable device [1]. There is great interest in the development of direct methanol fuel cells (DMFCs) because of their high theoretical energy densities that are suitable for mobile electrical devices and automobiles. However, the energy density of the DMFCs currently under development is still far from that expected due to the methanol crossover, MCO, and the high overvoltage at the electrodes [2–5]. To overcome the methanol crossover, a large number of studies [6–10] were carried out for developing a new proton-conducting membrane with a low methanol permeability and high proton conductivity. Some papers have considered reducing methanol crossover by mass transport control in the backing layer or by adding a porous material in front of the anode surface [11–19].

The authors have demonstrated, in recent reports [12–17], that a passive DMFC with a porous carbon plate, PCP, significantly reduced the methanol transport from the methanol reservoir to the anode surface. The PCP and the CO_2 gas layer that formed between the anode and the porous plate stably controlled methanol and water fluxes from the reservoir to the anode, and they allowed operation with very high concentrations of methanol, even 100% methanol. At such high methanol concentrations, water produced at the cathode back diffused from cathode to anode through the membrane and used for the anodic reaction [12]. The resistance to methanol transport could be increased by increasing the PCP thickness, decreasing its pore size or by increasing the thickness of the CO_2 gas layer [16].

We have already confirmed the efficient operation of a passive DMFC with PCP in the horizontal orientation [14–17]. In the actual application of a passive DMFC, the cell could be operated in different cell orientations. Some researchers have studied the effect of cell orientation on the performance of the passive DMFC and they found that vertically oriented cells produced a better performance than horizontally oriented ones at middle and high current densities. The improved performance was related to the increased operating temperature as a result of the high MCO which in turn reduced fuel utilization [20,21]. Others showed that vertical orientation showed lower performance than the horizontal one, and they related this

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to the large amount of water which flowed down along the surface of the cathode in the vertical case [22]. These studies revealed that the uncontrollable MCO was the main reason for these variations. Without solving this problem, performance will be affected by cell orientation.

An ideal DMFC should have a low MCO and stable operation under different cell orientations. By placing a PCP on the anode, MCO can be controlled; thereby the DMFC can avoid an uncontrollable increase in temperature and cathode flooding [14]. In this study, theoretical consideration of the effect of cell orientation and solution head pressure at the fuel reservoir on the performance was conducted. Experiments were also carried out to investigate vertical operation of the passive DMFC using different PCPs with different resistances to methanol transport at different methanol concentrations. Results were discussed on the basis of the effect of solution head pressure on the convective solution flow, which significantly affects the MCO, and therefore cell performance, through the PCP and the CO_2 gas layer.

2. Theoretical consideration

2.1. Mass transport through the porous plate

2.1.1. Effect of orientation

In a passive DMFC with a PCP placed between the anode and the methanol reservoir as shown in Fig. 1, methanol is transported through the pores of the PCP, reaches the anode surface, and then reacts with water producing CO_2 under closed circuit conditions. After closing the circuit, CO_2 gas is accumulated in the space between the PCP and the anode surface, and, in a short time, CO_2 bubbles are generated from the PCP into the reservoir through some of the pores of the PCP after its pressure reaches the bubble generation point, P_{bgp}. In this case, a gas/liquid interface is formed inside the pores of the PCP or on the surface of the PCP, and hence, methanol is vaporized at the interface and transported as a vapor from the interface to the anode according to the gradient of the methanol concentration in the gas layer. The pressure of the gas layer is determined to be a certain value by the balance between the CO_2 production rate at the anode and the pressure drop through the PCP for the CO_2 gas flow. In the horizontal orientation as shown in Fig. 1, we have confirmed that methanol crossover can be significantly controlled by the electrode structure with PCP under closed circuit condition and that high concentrations of methanol up to 100% can be used in the DMFC. For utilization of the high concentrations of methanol using MEA consisting of a conventional membrane like Nafion, this vapor feeding of methanol to the anode is essential, and we should prevent the membrane from direct contact with methanol solution with high concentrations because this will cause serious damage to the membrane [23].

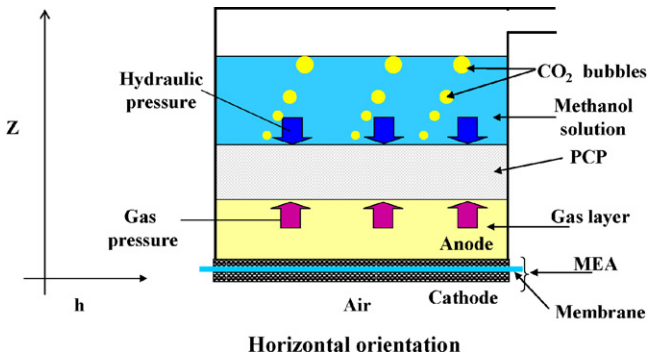

Fig. 1. Schematic diagram of a passive DMFC with a porous plate in horizontal orientation.

In the horizontal orientation as shown in Fig. 1, the bubble generation point P_{bgp} is uniform over the surface of the PCP as long as the pore structure of the PCP is uniform and is expressed as the summation of the bubble point pressure of the PCP, $P_{bp.PCP}$, and the hydrostatic pressure of the solution, $P_{liq.(Z)}$, when both of them are uniform over the PCP in the horizontal orientation.

$$P_{bgp} = P_{bp.PCP} + P_{liq.(Z)} \quad (1)$$

When the pressure of the gas layer, $P_{gas(i)}$ which is a function of current density in the operation, is over the bubble generation point P_{bgp},

$$P_{bgp} < P_{gas(i)} \quad (2)$$

$$P_{bp.PCP} + P_{liq.(Z)} < P_{gas(i)} \quad (3)$$

The position of the gas/liquid interface is kept inside the pores or on the surface of the PCP. Hence, the gas layer can avoid inrushing methanol solution through the pores, as long as the pressure of the

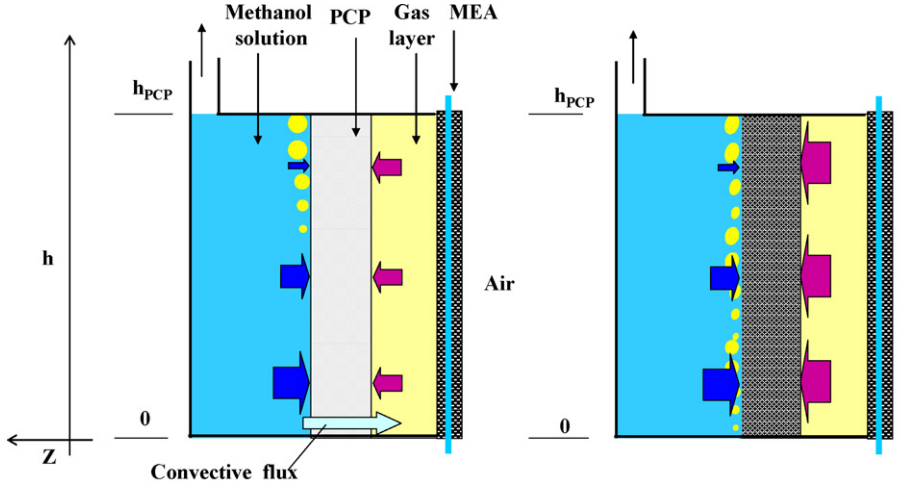

Fig. 2. Schematic diagram of a passive DMFC with a porous plate in vertical orientation in the case of the solution covers the whole surface of the PCP.

gas space is kept at P_{bgp} or higher by a certain production rate of CO_2, i.e., a certain current density, at the anode. In this case, the MEA can be prevented from direct contact of the membrane with the solution.

In the vertical orientation as shown in Fig. 2 where we considered a case in which the reservoir is fully filled with methanol solution, the bubble generation point P_{bgp} increased with the increasing height h of the PCP, because the hydrostatic pressure of the solution decreased with the increase in h defined in Fig. 2. Hence, a pressure difference in the local bubble generation point is produced between the different positions at different h values, e.g., h_1 and h_2 ($h_2 > h_1$) resulting in different P_{bgp}, e.g., $P_{bgp(h_1)} > P_{bgp(h_2)}$. On the other hand, the pressure of the gas layer is almost constant irrespective of the height h because of the negligibly small density of gas compared to that of liquid. If a local area on the PCP shows $P_{bgp} > P_{gas(i)}$, methanol solution flows into the gas layer through the PCP based on the pressure drop ΔP ($=P_{liq.(h)} - P_{gas(i)}$), and the flow through the PCP can be expressed by Darcy's equation as follows:

$$F = \frac{KA\Delta P}{\mu l} \tag{4}$$

where F is the volume flow rate of the fluid, μ is the viscosity of the fluid, l is the thickness of the PCP, ΔP is the pressure drop across the PCP, A is the cross sectional area of the PCP, and K is the permeability known as Darcy's constant for laminar flow. The flow of the methanol solution causes a large MCO and would pose damage to the MEA. To avoid this in the DMFC in the vertical orientation, the bubble point pressure of the PCP has to be extensively higher than the maximum static head pressure at $h = 0$, i.e., $P_{bp.PCP} \gg P_{liq(0)} = (\rho g h_{PCP})$, where ρ is the density of the solution, g is the acceleration of gravity and h_{PCP} is the height of the PCP. For the bubble point of the porous plate and the flow rate of the methanol permeating through the PCP, the pore size, porosity, and also the thickness of the plate, as well as the viscosity of the fluid, must be important.

2.1.2. Effect of solution levels in the reservoir

In the actual operation of a DMFC, the level of the solution in the reservoir would change with operation time. It decreases or increases depending on methanol consumption or refilling. In the horizontal orientation, methanol solution covers the entire surface of the PCP with a constant height irrespective of the solution. On the other hand, in the vertical orientation, decreasing the solution level may result in the appearance of an area of the PCP where the methanol solution could not be sucked into the pores of the PCP as shown in Fig. 3b.

Maximum sucking height of the solution, h_{max}, for a capillary tube with radius r is simply given by the following equation:

$$h_{max} = \frac{2\gamma \cos\theta}{\rho g r} \tag{5}$$

where γ is the surface tension of the solution and θ is the contact angle. According to Eq. (5), h_{max} can be increased by decreasing the PCP pore diameter, increasing the surface tension of the methanol solution or/and changing the surface property of the PCP to hydrophilic.

Fig. 3a shows an ideal case where the PCP sucks the solution to the top of the PCP, h_{PCP}, by osmotic action and the gas pressure in the gas layer can be kept higher than that of the bubble point at all positions along the height, i.e.,

$$\text{for } h = 0 \text{ to } h_{PCP}, \quad P_{bgp} < P_{gas(i)} \quad \text{and} \quad h_{max} > h_{PCP} \tag{6}$$

We can expect operation with a low and constant MCO in this case. However, when the sucking ability of the PCP is not high enough to fill the pores at the top of the PCP with the methanol solution, methanol solution will flow into the gas space from the bottom of the PCP, as shown in Fig. 3b, because the dry area of the PCP does not have a sufficient pressure drop for the CO_2 gas flow, and CO_2 easily escapes through this area so that the gas space can not be kept at a certain high pressure, resulting in $P_{bgp} > P_{gas(i)}$. A proper PCP for vertical orientation should provide $h_{max} \geq h_{PCP}$, where h_{PCP} is the height of the PCP. If not, the solution level in the reservoir, h_l, must be increased to maintain $(h_{max} + h_l) \geq h_{PCP}$.

As mentioned above, the power generation of the DMFC vertically arranged would be affected by the properties of the PCP and the solution. Those properties need to satisfy Eq. (6) for a DMFC the performance of which is not affected by the solution level.

3. Experimental

3.1. MEA preparation

The conventional MEA, which uses carbon cloth (35% Teflonized, ElectroChem, Inc.) as the anode and cathode backing layers, was

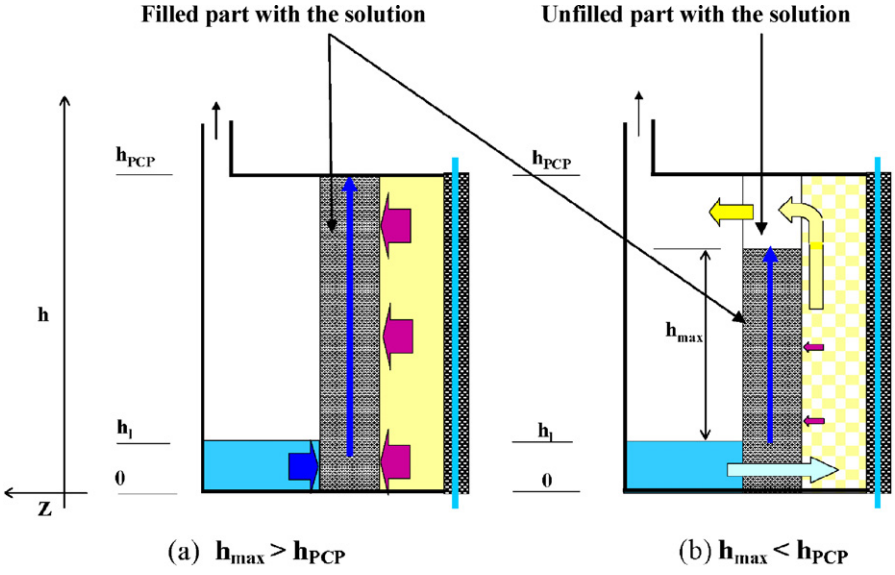

Fig. 3. Schematic diagram of a passive DMFC with a porous plate in the vertical orientation in the case of the solution did not cover the whole surface of the PCP.

Table 1
Properties of the porous carbon plates (PCPs) used.

PCP	Thickness, L [mm]	Bubble point pressure, P_{bp} [kPa]	Darcy constant, K [m^2]	Resistance (L/K), R [m^{-1}]
α	2.0	1.1	1.7E−12	1.2E+9
β	1.0	12.2	1.8E−14	5.5E+10
γ1	0.5	91.9	6.0E−14	8.3E+9
γ2	0.5	5.4	2.4E−13	2.1E+9
γ3	0.5	3.2	2.7E−13	1.8E+9

prepared in the following manner. 3–4 mg cm^{-2} of carbon black containing 10% Nafion was prepared on the surface of the carbon cloth. 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 catalyst for the cathode and anode, respectively. The catalyst loading was 10–12 mg cm^{-2} in each electrode, and the ionomer loading to the catalyst was 10 wt% for the cathode and 15 wt% to the anode. Nafion 112 was used as the electrolyte membrane. Then, the MEA was fabricated by sandwiching the membrane between the anode and the cathode and hot pressing them at 408 K and 5 MPa for 3 min.

3.2. Porous carbon plates, PCPs

Three different types of PCPs, α, β and γ, made of different raw materials and prepared by different procedures, were used in this study. These porous carbon plates were supplied from Mitsubishi Pencil Co., Ltd., Perm-porometer (Porous Materials, Inc.) was used to evaluate the permeability of air according to Darcy's constant and to measure the bubble point pressure of the PCP using Galwick solution having a surface tension of 15.7×10^{-3} N m^{-1}, which is close to that of pure methanol, 22.5×10^{-3} N m^{-1}. Although the measured bubble point pressures were not the actual ones for the methanol solutions, we referred to these measured values as similar to those for the actual methanol solutions. Based on Dracy's constant K, defined in Eq. (5), a resistance R (=L/K, where L is the thickness) was calculated and used as an indicator of the resistance of the PCP to methanol transport. Although the resistance, R, is not the actual resistance for the methanol transport through the PCP, it can be used as a qualitative indicator of the actual resistance among the PCPs. Those properties of the porous carbon plates used in this experiment are listed in Table 1.

3.3. Passive DMFC with PCP

MEA with the PCP was set in a plastic holder as shown in Fig. 4. In the anode compartment, a methanol reservoir, 22 mm wide, 22 mm long and 25 mm deep was prepared. The MEA was sandwiched between two current collectors, which were stainless steel plates of 2 mm thickness with open channels for the passages of fuel and oxidant. The open ratio of the area for the active electrode was 73%.

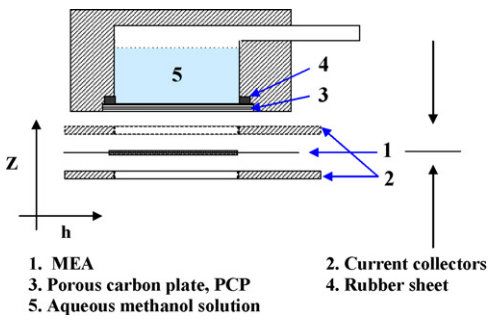

Fig. 4. Schematic diagram of the structure a passive DMFC with a porous plate.

Under this configuration, methanol had to pass through the porous plate then through the openings of the anode current collector. Under closed circuit conditions, the openings of the anode current collector were filled with CO_2 gas which is enclosed between the porous plate and the anode. Therefore, a layer of CO_2 gas was formed between the porous plate and the anode, and this gas layer prevented methanol transport from the reservoir to the anode; methanol must be transported through the gas layer as a vapor.

3.4. Operation under different cell orientation

As a comparison of the cell performance between different cell orientations, horizontal and vertical, the same DMFC was operated in the different orientations as follows. In the horizontal orientation, the cell was placed horizontally by setting the Z-axis vertical as shown in Fig. 1, and the operation was started by injecting 7 ml of methanol solution into the reservoir where the solution level in the reservoir was 1.4 cm. In the vertical orientation, the cell was placed vertically by setting the h axis vertical as shown in Fig. 2, and solution level was set at h = 2.2 cm (=h_{PCP}) in order to ensure covering the entire PCP surface with the solution.

3.5. Operation under different methanol solution head pressures

The effect of the solution head height, i.e., solution head pressure, on the cell performance in the vertical orientation was investigated by placing a cell vertically as shown in Fig. 2, and by changing the solution level in the reservoir using a syringe, from 2.2 cm, i.e., full level, to 0.6 cm. At each solution level, the cell was operated at a constant voltage for 1 h or 1.5 h.

3.6. Measurement of the cell performance

In this study, all the experiments were conducted in a complete passive mode with the surrounding air under ambient conditions of 297 K and 1 atm. Methanol solutions of different concentrations were fed into the reservoir by a syringe through the open tube. Within several minutes of injecting methanol into the solution reservoir under open circuit conditions, circuit was closed and the time progress of the current density, i–t characteristics, at 0.25 V cell voltage was measured for about 1–5 h. These measurements were conducted using an electrochemical measurement system (HAG-5010, Hokuto Denko, Co., Ltd.). The temperature of the cell was also measured using a thermocouple placed on the cathode surface.

4. Results and discussion

4.1. Effect of cell orientation on cell performance

Fig. 5 shows the effect of the cell orientation, horizontal and vertical, on the cell performance for PCP-α operated with 40 wt%, 50 wt%, 60 wt% and 70 wt% methanol at 0.25 V. In the vertical operation, the reservoir was filled with methanol solution as shown in Fig. 2. As shown in Fig. 5a, the stable power output after 1 h was about 21.5 mW cm^{-2} and it was not affected by cell orientation, with increasing concentration to 50%, Fig. 5b, the performance increased to 23 mW cm^{-2}, and also it was not affected by cell orientation. At the initial operations within 1 h, a small difference can be seen in the power density in Fig. 5a and b. The difference in the performance at different cell orientations would be due to a difference in an initial situation for forming the gas layer on the anode [14]. When the concentration increased to 60%, Fig. 5c, the performance decreased to 20 mW cm^{-2} in the horizontal case and to 17 mW cm^{-2} in the vertical case. A further increase in concentra-

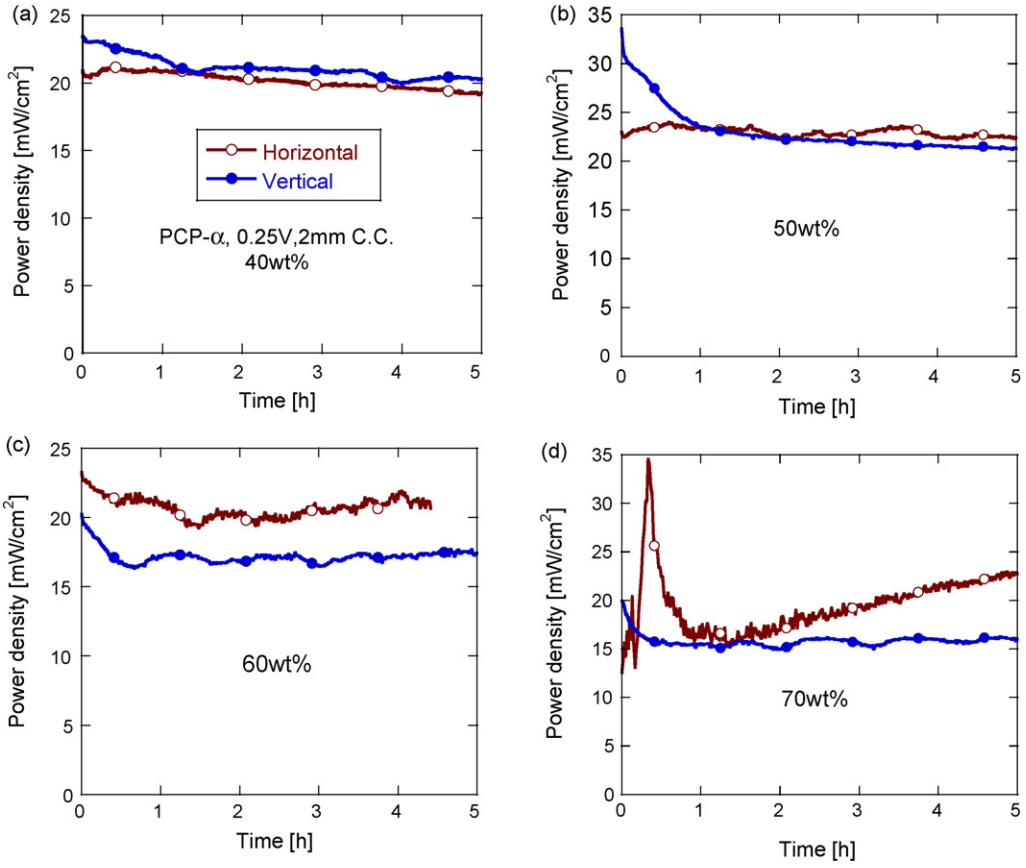

Fig. 5. Effect of cell orientation on the power density profile during the continuous operation of the passive DMFC in the case of using PCP-α operated with a) 40wt%, b) 50wt%, c) 60wt% and d) 70wt% methanol at cell voltage of 0.25V.

tion to 70%, Fig. 5d, resulted in a further decrease in performance, 15.5 mW cm^{-2}, in the vertical orientation.

The power density at 4 h of operation in Fig. 5 was plotted against the concentration in the different cell orientations in Fig. 6. The power density increased with increasing methanol concentration up to 22 mW cm^{-2}; it was nearly the same in the horizontal and vertical orientation, and there is a linear dependency of power density on the methanol concentration in this range. With increasing concentration from 50 wt% to 60 wt%, the power density decreased and it further decreased by increasing the concentration to 70 wt%. Vertical orientation exhibited a lower performance than the horizontal one in the higher range, 60 wt% and 70 wt%. The linear dependency of the performance up to 50 wt% suggested that the DMFC was operating under a limiting current situation where the MCO was kept at a very low level [14,16]. Beyond this range, i.e., above 50 wt%, a higher MCO occurs, and therefore performance decreased. The lower performance of the vertical orientation shown in the range above 50 wt% suggested that a higher MCO occurred in the vertical orientation than in the horizontal.

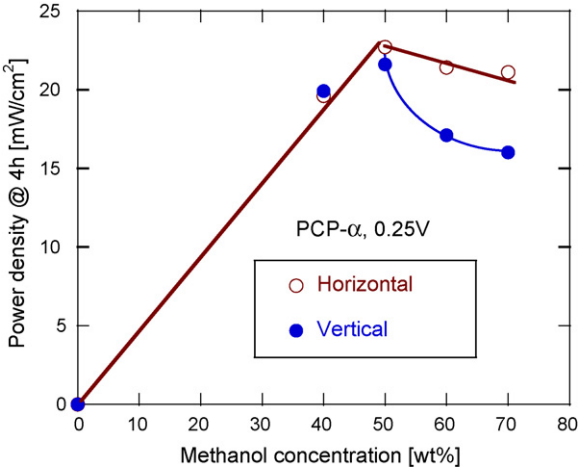

Fig. 6. Effect of cell orientation on the power density at 4 hours of the cell operation conducted in Figure 5 at different methanol concentrations.

As a result of applying the PCP at the anode, we could operate the DMFC with a high methanol concentration [12–17]. PCP-α has the lowest resistance among the PCPs, as shown in Table 1, 1.2×10^9 m^{-1}; therefore, the cell was operated under limiting current situation only up to 50 wt%. In the horizontal orientation, the pressure drop through the PCP was uniform along the PCP surface, 1.4 cm solution head, calculated to be 0.137 kPa. While in the vertical orientation, there is a variation in the liquid solution head pressure along the PCP, from 0 cm to 2.2 cm, i.e., 0–0.216 kPa, at the top and the bottom of the PCP, respectively. Where the bubble point pressure of this PCP (1.1 kPa), noting that this value was obtained with Galwick solution, not with the methanol solution, is not too high in comparison to the variation in the liquid solution head pressure along the PCP, 0.216 kPa, this variation might enhance the convective solution flow through the PCP at the bottom and thereby increase the MCO thus, it reduced the power density in the vertical orientation. Because the bubble point pressure of the PCP-α was quite low, 1.1 kPa, and was relatively close to the static pressure 0.216 kPa at the bottom, this suggested that a low pressure of the CO_2 gas layer was critical to resist this small variation in the solution head pressure. On the other hand, the viscosity of the methanol solution largely decreased with increasing concen-

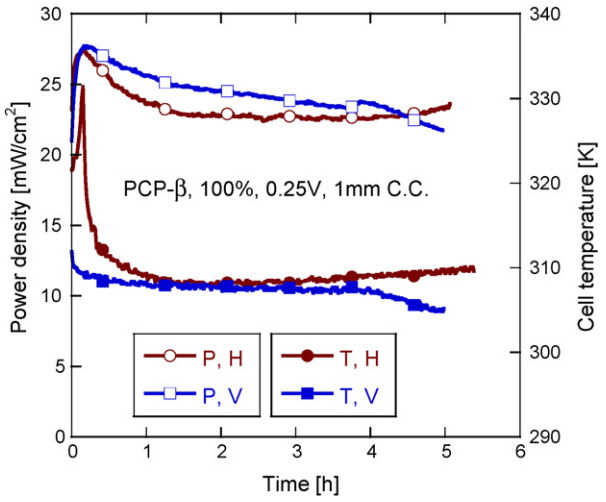

Fig. 7. Effect of cell orientation on the power density and cell temperature of the passive DMFC in the case of using PCP-β operated with 100% methanol at cell voltage of 0.25 V.

tration in the range over 50 wt%, 1.6×10^{-3} kg m^{-1} s^{-1} at 40 wt% to 1.2×10^{-3} kg m^{-1} s^{-1} at 70 wt% [24]. This relatively large decrease in the viscosity of the methanol solution from 50 wt% to 70 wt% may also enhance the solution flow, depending on Eq. (4), through the PCP at the critical pressure condition mentioned above, hence, cause the lower performance in the vertical orientation than that of the horizontal.

Fig. 7 shows the effect of the cell orientation on power density and cell temperature in the case of using PCP-β, which has the highest resistance ($R = 5.5 \times 10^{10}$ m^{-1}) in this experiment as shown in Table 1, using 100% methanol at 0.25 V, and using a 1 mm current collector. As shown in the figure, both power density and temperature were not affected by cell orientation; they were 24 mW cm^{-2} and 309 K for a stable operation over 1 h. The operation enabled with 100% methanol would be due to the high resistance of the PCP to methanol transport. The performance was not affected by the cell orientation, and this would be related to the high bubble point pressure of this PCP, 14.3 kPa, which is sufficient to resist the variation in the pressure drop along the PCP, 0.216 kPa, in the vertical orientation. The convective flux was then restricted in the vertical orientation as in the horizontal orientation.

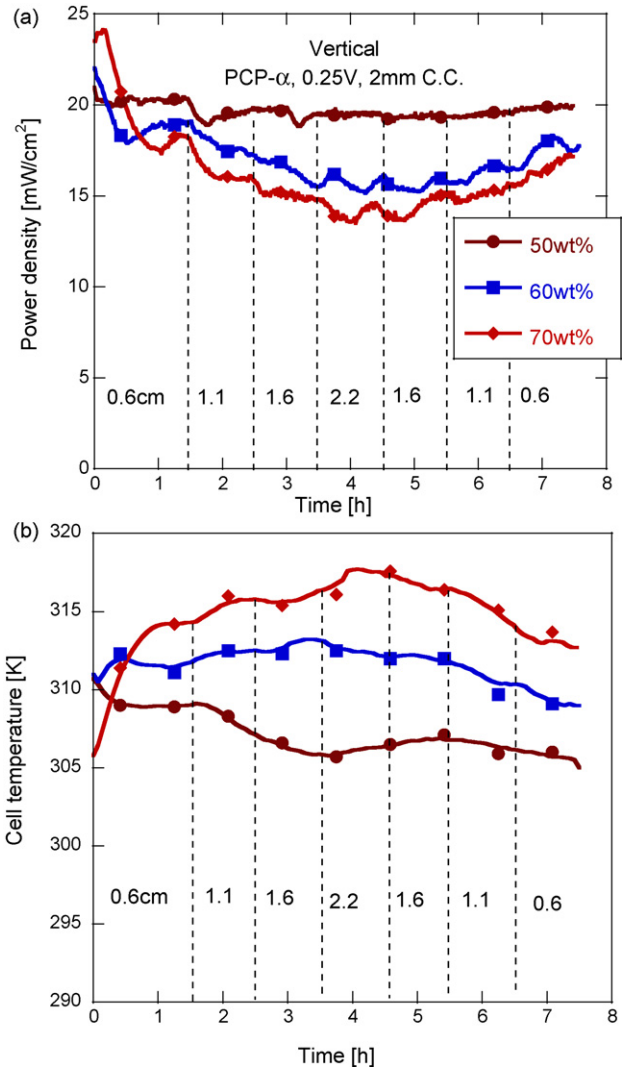

Fig. 8. Effect of methanol solution head in the reservoir in the vertical orientation, increasing from 0.6cm to 2.2 cm then decreasing to 0.6 cm, on (a) power density and (b) cell temperature in the case of using PCP-α using different methanol concentrations, 50, 60 and 70 wt% at 0.25 V.

4.2. Effect of solution head pressure in the vertical orientation

Fig. 8 shows the effect of the methanol solution head in the reservoir in the vertical orientation, increasing from 0.6 cm to 2.2 cm then decreasing to 0.6 cm, on (a) power density and (b) cell temperature in the case of using PCP-α with different methanol concentrations, 50 wt%, 60 wt% and 70 wt%; at 0.25 V. As shown in the figure at 50 wt%, the power density was about 20 mW cm^{-2}, and this performance was not affected by the solution head, whether increasing or decreasing. At 60 wt% and 70 wt%, the power densities were 18.5 mW cm^{-2} and 17.5 mW cm^{-2} at 1 h, respectively, and these values gradually decreased with the increase in the methanol level, 15 mW cm^{-2} and 13.5 mW cm^{-2} at 2.2 cm, respectively. Again, the power densities were gradually increased to their original values, i.e., 18.5 mW cm^{-2} and 17.5 mW cm^{-2}, respectively, with the gradual decrease in the solution head to 0.6 cm. The changes in the cell temperature coincide with that of the power density at 60 wt% and 70 wt%, i.e., lower performance reflects a higher MCO thereby a higher temperature, as shown in Fig. 8b, where, the cell temperature gradually increased with the gradual increase in solution head to 2.2 cm, then gradually decreased with the gradual decrease in solution head to 0.6 cm. On the other hand, at 50 wt%, the cell temperature was 309 K, and it gradually decreased to 306 K with the gradual increase in the solution head from 0.6 cm to 2.2 cm; then, it became nearly constant. This behavior of performance and temperature would be related to the low bubble point of the PCP, 1.1 kPa, that is conducive to a low pressure of the CO_2 gas. Therefore, this PCP could not resist the variations in the solution head pressure along the PCP, as discussed in the previous section. The increase in the solution head causes an increase in the solution head pressure at the bottom of the PCP, and this enhances the convective flux of the solution and vice versa. At 60 wt% and 70 wt%, the cell was not operated under limiting current as shown in Fig. 6. In this condition, the MCO increased with the solution head increasing, and therefore, performance decreased and cell temperature increased and vice versa.

Fig. 9 shows the effect of the methanol solution head in the reservoir in the vertical orientation, increasing from 0.6 cm to 2.2 cm then decreasing to 0.6 cm, on (a) power density and (b) cell temperature in the case of using PCP-β with a relatively high bubble point pressure, 12.2 kPa, and having the highest resistance in these experiments. As shown in the figure, initially the power density was

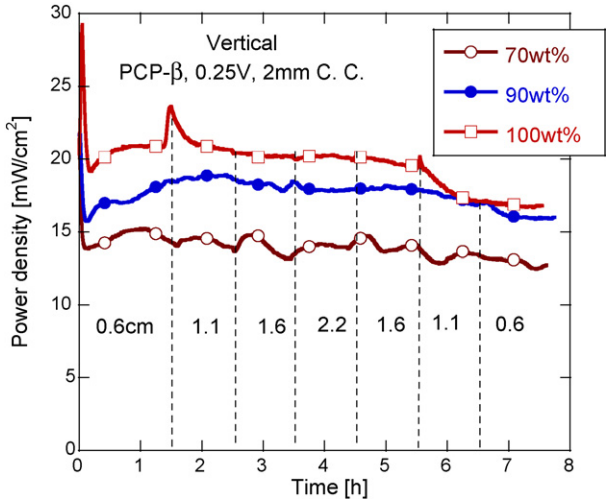

Fig. 9. Effect of methanol solution head in the reservoir in the vertical orientation, increasing from 0.6 cm to 2.2 cm then decreasing to 0.6 cm, on power density in the case of using PCP-β using different methanol concentrations, 70, 90 and 100 wt% at 0.25 V.

28 mW cm^{-2}; it rapidly decreased to 15 mW cm^{-2}, 18 mW cm^{-2}, and 20 mW cm^{-2} in the different methanol concentrations, 70%, 90% and 100%, respectively, and it was not affected on changing the solution heads either increasing or decreasing. The rapid reduction of the performance during the first few minutes would be related to the consumption of the methanol from the PCP, which was saturated with methanol under OCV conditions [14]. The stability of the performance under the different solution heads would be due to the high bubble point pressure of the PCP, 12.2 kPa, the high pressure of the CO_2 gas layer, which could resist the small variation in the solution head pressure, 0.054 kPa at 0.6 cm to 0.216 kPa at 2.2 cm. Therefore, the convective flux was restricted and performance was not affected even in 100% methanol. It was also clear from the figure that, this PCP has sufficient high sucking ability to fill all the pores to the top of the PCP with the solution, because the power density was not affected by the solution head up to the top, 2.2 cm.

From the viewpoints of increasing the energy density of the DMFC system and also providing a compact size for it, thinner electrode structures with a thinner PCP and/or a thinner gas layer are favored for actual applications. Hence, a thinner electrode structure combined with a PCP of 0.50 mm thickness and a thinner gas layer of 1.0 mm thickness, i.e., 1.0 mm current corrector, was tested

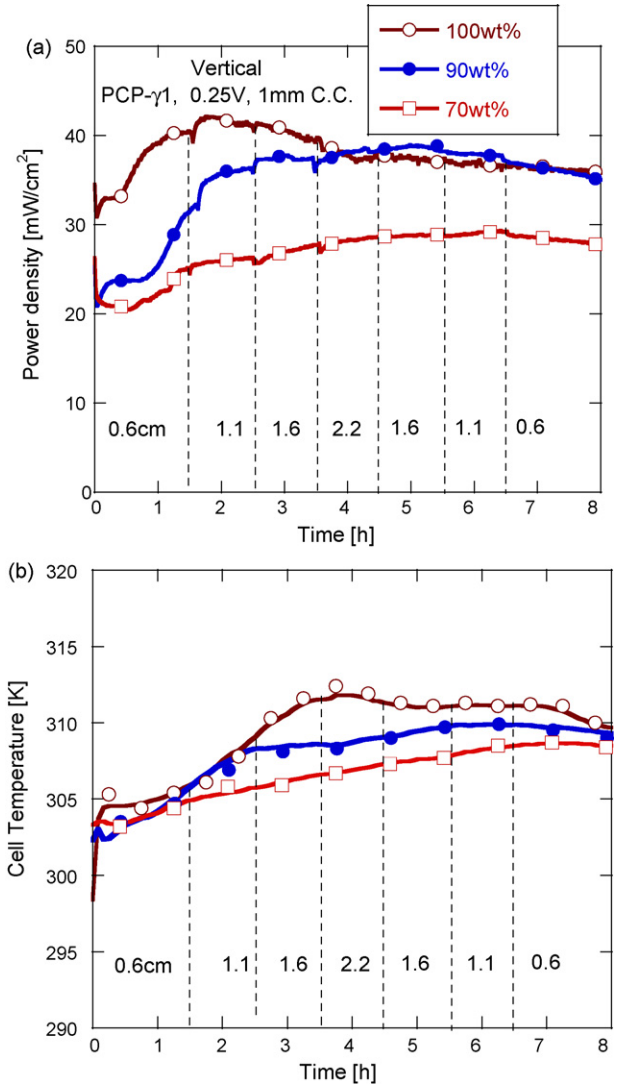

Fig. 10. Effect of methanol solution head in the reservoir in the vertical orientation, increasing from 0.6 cm to 2.2 cm then decreasing to 0.6 cm, on (a) power density and (b) cell temperature in the case of using PCP-γ1 using different methanol concentrations, 70, 90 and 100 wt% at 0.25 V.

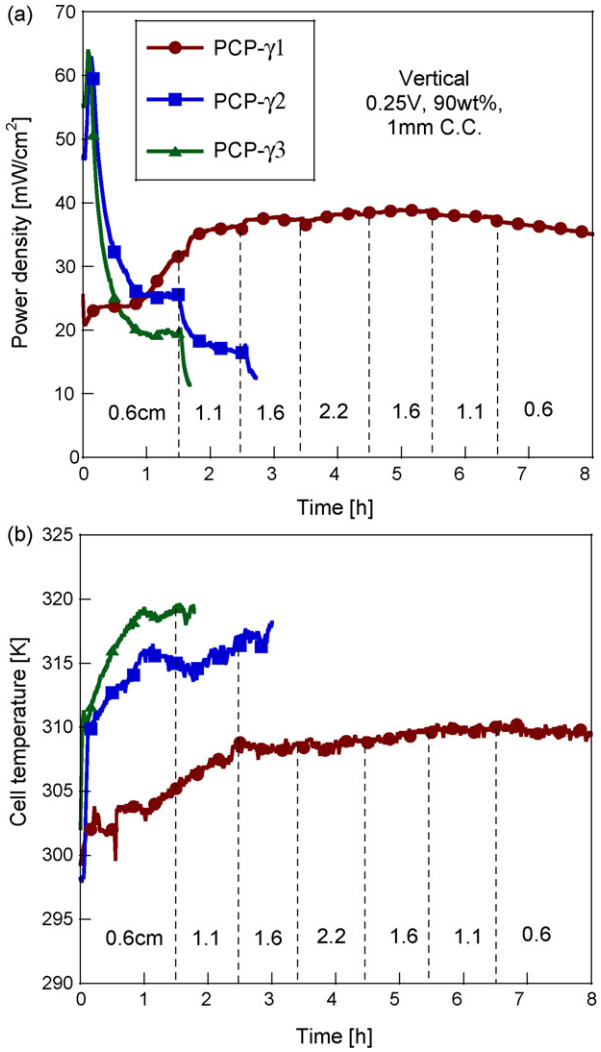

Fig. 11. Effect of methanol solution head in the reservoir in the vertical orientation, increasing from 0.6 cm to 2.2 cm then decreasing to 0.6 cm, on (a) power density and (b) cell temperature in the case of using PCP-γs with different resistances and bubble point pressures using 90 wt% methanol concentration at 0.25 V.

using a PCP-γ1 which has the highest bubble point pressure, 92 kPa, and a high resistance *R*, 8.3E9 m^{-1}. The cell performance, (a) the power density and (b) cell temperature, in the vertical orientation at different methanol concentrations, 70 wt%, 90 wt% and 100 wt%, is shown in Fig. 10. As is clear from the figure, the power density at the steady state that was attained after 1–3 h was not affected by the solution level, and the power density was over 35 mW cm^{-2} at 90% and 100%. It was successfully demonstrated that the vertical operation with the very thin electrode structure using 100% methanol could be achieved using a PCP with the proper properties. The gradual increase in the power density and the cell temperature at the initial 1–3 h suggested that the slow sucking rate of the methanol solution into the PCP is related to its very small pore diameter.

4.3. Effect of PCP resistance and bubble point pressure on cell performance in the vertical orientation

Fig. 11 shows the effect of the methanol solution head in the reservoir in the vertical orientation, increasing from 0.6 cm to 2.2 cm then decreasing to 0.6 cm, on (a) power density and (b) cell temperature in the case of using PCPs with different resistances and bubble point pressures using 90% methanol concentration at 0.25 V. As shown in the figure, in the case of PCP-γ2 and PCPγ3, power densities were initially high, about 60 mW cm^{-2}, but they rapidly decreased within 1 h to about 27 and 20 mW cm^{-2}, respectively. The variation in the performance must be due to the large MCO that is shown by the large increase in cell temperature as shown in Fig. 11(b). The high flux through these two PCPs was due to their lower resistances, 2.1×10^9 m^{-1} and 1.8×10^9 m^{-1}, respectively, as shown in Table 1. Their performance affected by the solution head was due to their low bubble point pressures, 5.4 kPa and 3.2 kPa, respectively; these low pressures could not resist the variation in the pressure drop along the PCP.

Although of the small dimensions of the current cell design, 2.2 cm wide, 2.2 cm long, the variations in the pressure along the PCP in vertical operation enhanced the convective flux through the PCP and affected cell performance. By controlling the PCP properties, vertical operation has been confirmed using a very high methanol concentration, 90% or above. In the actual operation of the passive DMFC, the cell dimensions will be scaled-up; therefore, the effect of cell orientation on performance may be critical. The performance of the scaled-version of this cell will be shown later in any elsewhere.

5. Conclusions

Vertical operation of a passive DMFC with PCP has been investigated using different methanol concentrations in order to clarify the proper PCP for vertical operation. The effect of solution head pressure at the anode side on cell performance has been tested using different methanol concentrations. Moreover, vertical operation of passive DMFCs using PCPs with different resistances and bubble point pressures has been investigated. The following conclusions were obtained:

(1) Control of methanol transport in the vertical operation of the DMFC with PCP was more sensitive to the properties of the PCP, i.e., bubble point pressure and resistance to methanol transport, than those in horizontal orientation.
(2) The non uniform distribution of the solution head pressure in the vertical orientation causes a convective flux through the PCP; therefore, cell performance was affected by cell orientation, when the bubble point pressure and the resistance of the PCP were not high enough.
(3) PCP that introduces a high pressure CO_2 gas layer, i.e., a high bubble point pressure, could resist the variations in the solution head pressure; thereby, the convective flux was controlled and stable performance was attained under the different cell orientations.
(4) By controlling PCP resistance and bubble point pressure, the DMFC could be operated efficiently in the vertical orientation under different solution levels within 2.2 cm using high methanol concentrations even up to 100% methanol.

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