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Effect of cell orientation on the performance of passive direct methanol fuel cells

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Abstract

A passive liquid feed direct methanol fuel cell (DMFC) with neither liquid pump nor a gas compressor was tested at different orientations. The experimental results showed that the vertical operation always yielded better performance than did the horizontal operation. It was further demonstrated that the improved performance in the vertical orientation was caused by the increased operating temperature as a result of a higher rate of methanol crossover, which resulted from the stronger natural convection in the vertical orientation. The constant current discharging tests showed that, although the vertical operation of the passive DMFC can yield better performance, the fuel utilization at this orientation is lower as a result of the increased rate of methanol crossover. It was also shown that the horizontal orientation with the anode facing upward rendered an effective removal of both CO_2 bubbles on the anode and liquid water on the cathode and thereby a relative stable operation. Finally, it was revealed that the horizontal orientation with the anode facing downward exhibited rather unstable and short discharging duration because of the difficulties in removing CO_2 bubbles from the anode and the liquid water from the cathode at this particular orientation.

Keywords: Passive direct methanol fuel cell; Cell orientation; Natural convection; Cell performance; Methanol crossover

1. Introduction

Direct methanol fuel cells (DMFCs) offer many advantages over the hydrogen-feed proton exchange membrane fuel cells (PEMFCs), such as high energy density (6100 Wh kg^{-1} at 25 °C), easy storage and transportation, simple system, as well as low cost. Therefore, the DMFC is one of the most promising candidates for powering portable devices and electric vehicles. Over the past decade, the DMFC with the fuel fed by a liquid pump and oxidant fed by a gas compressor have been extensively carried out [1–8]. Recently, a so-called passive DMFC, in which external pumps and other ancillary devices are completely removed, has been proposed and investigated [9–15]. In this work, we are concerned with a typical passive-feed DMFC shown in Fig. 1(a), which consists of a fuel reservoir, an anode current collector, a membrane electrode assembly (MEA), and a cathode current collector. On the anode, diluted methanol solution is introduced to the reaction zone primarily by diffusion without any external means of liquid transport. Similarly, on the cathode, oxygen is taken passively from the ambient air without any means of air movement. Apparently, this type of passive DMFC has a much simpler structure and more compact system than does the conventional active DMFC. Moreover, the parasitic power loss from ancillary devices in the active DMFC is also eliminated. Because of these advantages, the passive DMFC has received extensive attention.

Currently, one of the most challenging issues in DMFCs (both active and passive) is that methanol can permeate from the anode to the cathode through Nafion membranes. This methanol crossover problem results not only in the fuel loss but also a mixed potential on the cathode and thus a decrease in the overall cell performance. Methanol crossover is influenced by many factors such as the Nafion membrane permeability/thickness, the feed methanol concentration, the operating temperature, methanol transport in each component. Particularly, in the passive DMFC, the methanol transport from a built-in fuel reservoir to the anode catalyst layer relies on diffusion. To provide a sufficient flow rate of methanol at a given power density, methanol solution with a high concentration is usually needed. This high

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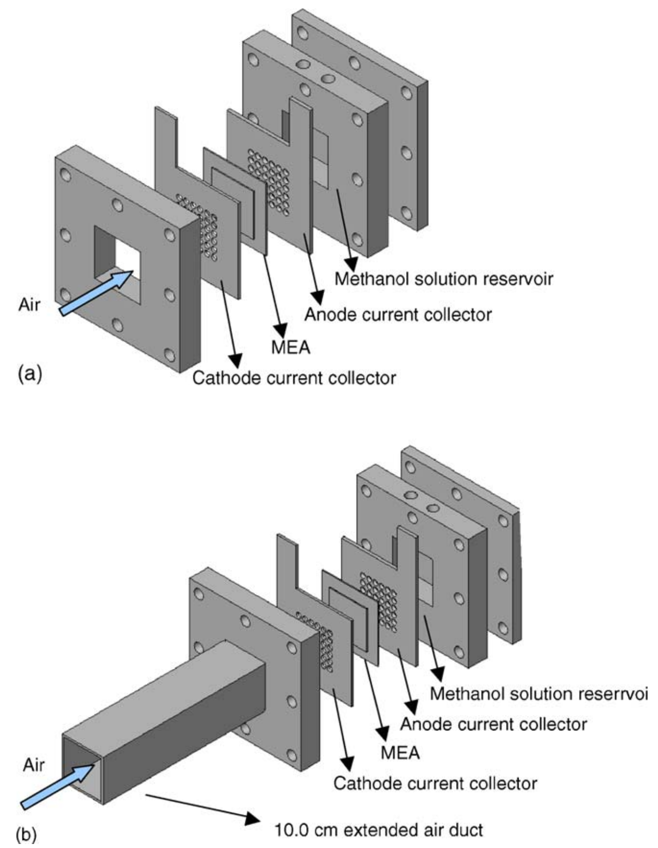

Fig. 1. Schematic of the passive DMFC: (a) without and (b) with an extended air duct.

methanol concentration, however, will also result in a high rate of methanol crossover. Chen and Yang [10] investigated the effect of operating conditions on the power density of an air-breathing DMFC. Liu et al. [11] studied sintered stainless steel fiber felt as the gas diffusion layer in an air-breathing DMFC. The concentration of methanol effect was also studied in this work. Kim et al. [12] fabricated and tested a single cell and monopolar DMFC stack operating under passive and air-breathing conditions. Shimizu et al. [13] reported their activities regarding the research and development of DMFCs that operated passively at room temperature. Park et al. [14,15] reported the optimal methanol solution appeared at 4.0 M in passive DMFCs. It was thought that better performance with a higher methanol concentration was because of the improved mass transfer of methanol from the reservoir to the anode catalyst layer. More recently, Liu et al. [16] found that when a passive DMFC is operated under a given ambient environment, a higher methanol concentration solution will lead to a higher operating temperature, which in turn causes faster electrokinetics of both methanol oxidation and oxygen reduction reactions and thereby a higher cell performance. The increased cell temperature was attributed to the exothermic reaction between the permeated methanol and oxygen. It should be recognized that the increased temperature difference between the cell and the ambient will lead to enhanced natural convection at the both anode and cathode. Therefore, the enhanced natural convection may enhance the diffusion of methanol from the fuel reservoir to the catalyst layer. The oxygen transport on the cathode may be also enhanced by the natural convection. In turn, the enhanced methanol transport as a result of the natural convection causes a higher rate of methanol crossover, and thereby a higher cell operating temperature. The strength of natural convection depends on the cell orientation. Therefore, methanol crossover and cell orientation are inherently linked in the passive DMFC, which affects the cell operating temperature and thus the performance. For this reason, it can be speculated that the effect of cell orientation on the performance of a passive DMFC is significant. In this work, we investigated the effect of orientation on the performance of the passive DMFC. We show how the cell orientation affects the rate of methanol crossover, which is related to the operating temperature and thus to the cell performance. It should be noted that when the cell is horizontally oriented with the anode facing downward, the generated CO_2 bubbles will accumulate on the surface of the anode current collector, blocking the methanol transport, and eventually ceasing the operation of the passive DMFC. For this reason, we focused on investigating the vertical orientation and the horizontal orientation with the anode facing upward. Hereafter, the horizontal orientation refers to the horizontal orientation with the anode facing upward, unless otherwise mentioned. Moreover, we also investigated the effect of cell orientation on the operation duration at a constant current density.

2. Experimental

2.1. Membrane electrode assembly (MEA)

The pretreated Nafion 115 membrane with a thickness of 125 μm was employed in this work. This pretreatment included boiling the membrane in 5 vol.% H_2O_2, washing in DI water, boiling in 0.5 M H_2SO_4 and washing in DI water for 1 h in turn. These pretreated membranes were kept in the DI water prior to the fabrication of MEAs. Single-side ELAT electrodes from ETEK were used in both anode and cathode, where carbon cloth (E-TEK, Type A) was used as the backing support layer with a 30 wt.% PTFE wet-proofing treatment. The catalyst loading on the anode side was 4.0 mg cm^{-2} with PtRu black (1:1 a/o), while the catalyst loading on the cathode side was 2.0 mg cm^{-2} using 40 wt.% Pt on Vulcan XC-72. Furthermore, 0.8 mg cm^{-2} dry Nafion® ionomer was coated onto the surface of each electrode. Finally, MEA with an active area of 4.0 cm^2 was fabricated by hot pressing at 135 °C and 4 MPa for 3.0 min. More detailed information about the MEA fabrication can be found elsewhere [17].

2.2. Single cell fixture

As shown in Fig. 1(a), the MEA mentioned above was sandwiched between two electrical current collectors, which were made of 316L stainless steel plates of 1.5 mm thickness on the anode and 1.0 mm on the cathode. A plurality of 2.6-mm circular holes were drilled in the both current collectors, serving as the passages of fuel and oxidant, which resulted in an open ratio of 47.8%. A 200-nm platinum layer was sputtered onto the surface of 316L stainless steel plates to reduce the contact resistance with the electrodes. The cell was held together between an anode and a cathode fixture, both of which were made of transparent organic glass. A 5.0 mL methanol solution reservoir was built in the anode fixture. Methanol was transferred into the catalyst layer from the built-in reservoir, while oxygen, from the surrounding air, was transferred into the cathode catalyst layer through the opening of the cathode fixture. The cell temperature was measured by a thermocouple (Type T), which was installed on the surface of the anode.

The passive DMFC was also tested by adding an extended air duct of 10.0 cm in length. The purpose of this experiment was to investigate how natural convection on the cathode affects the oxygen transport and the cell performance.

2.3. Electrochemical instrumentation and test conditions

An Arbin BT2000 electrical load interfaced to a computer was employed to control the condition of discharging and record the voltage–current curves. For each discharging current point along the *I–V* curve, a 60-s waiting time was used to obtain the stable voltage. The temperature of the cell was measured by the Arbin BT2000 built-in function.

All the experiments of the passive DMFCs were performed at room temperatures of 19–21 °C and a relative humidity of 35–50%. Prior to the passive DMFC performance test, the MEA was installed in an active cell fixture and activated at 70 °C about 24 h. During the activation period, 1.0 M methanol was fed at 1.0 mL min^{-1}, while oxygen was supplied under atmospheric pressure at a flow rate of 50 mL min^{-1}.

3. Results and discussion

Fig. 2 compares the performance of the passive DMFC oriented vertically and horizontally (with the anode facing upward). The experiments were performed with 2.0 and 4.0 M methanol solutions. It can be seen that the cell performance, including the limiting current density and the peak power density, increased as the methanol concentration was increased from 2.0 to 4.0 M. A maximum power density of 20 mW cm^{-2} was obtained with 4.0 M methanol solution at the vertical orientation. The increased performance as a result of a higher methanol concentration can be attributed mainly to the increased methanol permeation rate, which increases the operating temperature and thus improves the electrokinetics of both methanol oxidation and oxygen reduction reactions [16]. It is interesting to notice from Fig. 2 that for the same methanol concentration, the vertical orientation yielded a better performance than did that the horizontal one at moderate and high current densities. However, at low current densities, the performance of the horizontal cell is better than the vertical one. The variations in the open circuit voltage (OCV) with methanol concentration at the horizontal and vertical orientations are shown in Fig. 3. It is clear from this figure that the vertical orientation yielded significantly lower OCVs than did the horizontal one. The lower OCV and the lower performance at low current densities at the vertical orientation may be attributed to the fact that the rate of methanol crossover from the anode to the cathode is higher. To prove this point, we measured the cell operating temperature when the passive DMFC was oriented differently. The temperature was measured by installing a thermocouple at the outer surface of the anodic diffusion layer. Fig. 4 shows the transient cell operating

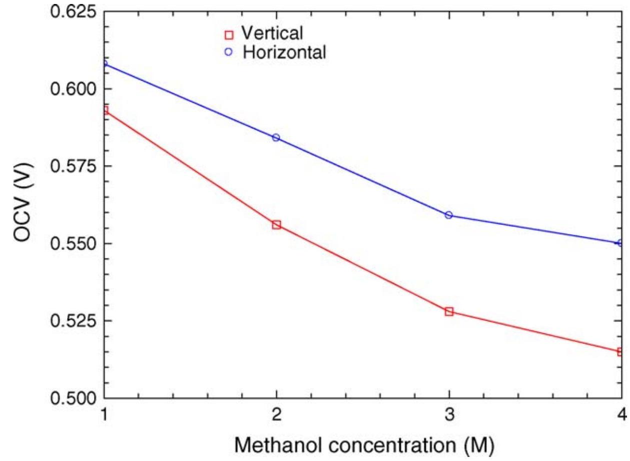

Fig. 3. The effect of cell orientation on the OCV with different methanol solutions.

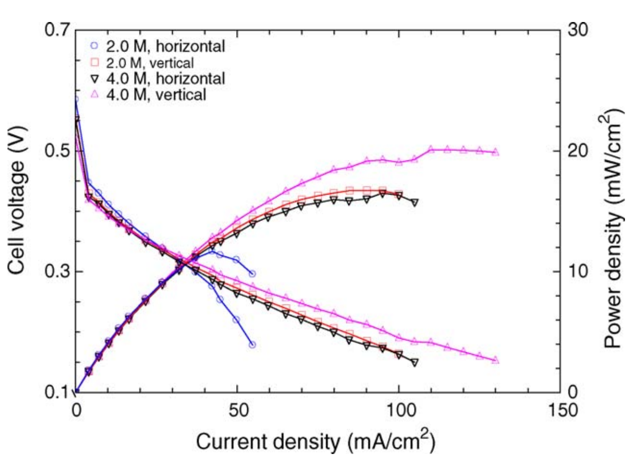

Fig. 2. The effect of cell orientation on the performance of the passive DMFC with different methanol solutions.

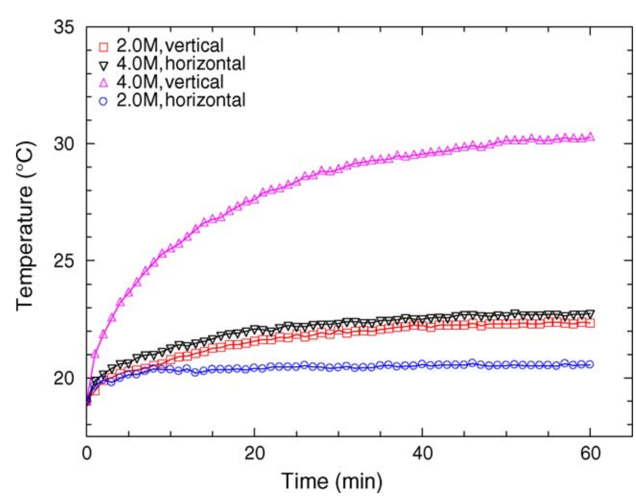

Fig. 4. Variation in the cell operating temperature.

temperature when the cell started operation with the 2.0 or 4.0 M methanol solution. Apparently, the vertical orientation exhibited a higher operating temperature than did the horizontal one. The higher operating temperature was mainly caused by the exothermic reaction between the permeated methanol and oxygen on the cathode. Thus, the rate of methanol crossover is higher in the vertical case than in the horizontal case. This explains why the vertical cell yielded a lower OCV and lower performance at low current densities. On the other hand, the higher temperature in the vertical case led to the improved electrochemical kinetics of methanol oxidation and oxygen reduction reaction, thereby a better performance at high current densities. In addition, a higher operating temperature results in a lower internal resistance of the cell, which may also contribute to the improved performance at high current densities. In summary, the increased operating temperature as a result of the increased methanol crossover is the major reason that yields a higher performance of the passive DMFC operated at the vertical orientation.

The mechanism that leads to a higher operating temperature in the vertical orientation than in the horizontal case is complicated. This depends not only on the rate of methanol crossover but also on the oxygen supply on the cathode. In the horizontal orientation, the oxygen transport from the surrounding air to the cathode is due primarily to diffusion, which may not provide a sufficient oxygen rate demanded by the both oxygen reduction reaction and the exothermic reaction between the permeated methanol and oxygen on the cathode, especially in the case with a higher methanol concentration. Because of the lack of oxygen in the case of the horizontal orientation, the permeated methanol cannot be oxidized completely on the cathode, producing less heat and thus a lower cell temperature. However, when the passive DMFC is vertically oriented, the oxygen transport from the air to cathode is enhanced by natural convection. The increased oxygen supply will lead to a faster exothermic reaction between the permeated methanol and oxygen, producing more heat, and thereby resulting in a higher cell operating temperature and better cell performance. In addition, in the vertical cell, natural convection in the anode fuel reservoir may also aid the methanol transport to the catalyst layer, whereas natural convection is too weak to affect the methanol transport in the horizontal cell. Therefore, the methanol permeation rate from the anode to the cathode in the vertical cell is higher than in the horizontal cell, leading to more heat generation on the cathode, and thereby resulting in a higher cell operating temperature and a better performance. The lower OCV and lower voltages at low current densities in the vertical cell shown in Figs. 2 and 3 also prove that the methanol crossover is more serious in the vertical cell. This fact reveals that natural convection enhanced the methanol transfer from the fuel reservoir to the anode in the vertical cell, which led to the increased methanol concentration at the anode catalyst layer and thus higher methanol permeation rate. As a result, a larger mixed potential is formed on the cathode at the vertical orientation to reduce the OCV and cell voltage at low current densities. However, the exothermic reaction between the permeated methanol and the oxygen from the ambient air produces more heat at the vertical orientation, leading to a higher cell operating temperature and cell performance at moderate and high current densities.

The above discussion indicates that the better performance of the passive DMFC in the vertical orientation is caused by the increased operating temperature as a result of a higher methanol permeation rate and a higher oxygen transfer rate, both of which are associated with the stronger natural convection in the vertical orientation. To investigate how natural convection affects the cell performance, we measured the performance of the vertical cell with an extended air duct (10.0 cm long), as shown in Fig. 1(b). The oxygen supply to the cathode in such a case relies mainly on the surrounding air which diffuses through the air duct and natural convection is rather weak. Thus, the experiments by adding the extended air duct allowed us to exclude the effect of natural convection on the oxygen supply. We tested the cell with 2.0 and 4.0 M methanol solutions for the cases with and without the extended air duct on the cathode. The experimental results are shown in Fig. 5. From Fig. 5(a), it can be seen that for 2.0 M methanol solution, the performance for the cases with and without the extended air duct are almost the same, implying that the oxygen supply with this lower methanol solution was sufficient even with the extended air duct. The lower limiting current density in the horizontal cases were primarily

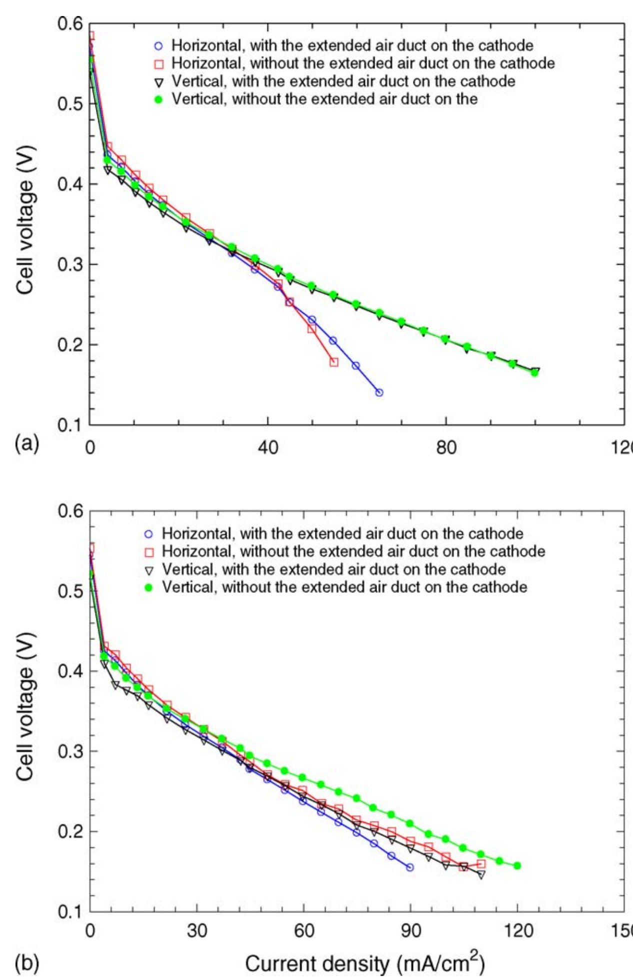

Fig. 5. Comparison in the cell performance among different cell orientations without/with the extended air duct on the cathode: (a) 2.0 M and (b) 4.0 M.

caused by the methanol transport on the anode. This indicates that methanol transport from the reservoir to the anode is crucial for low methanol concentration in passive DMFCs. For the 4.0 M methanol operation, as shown in Fig. 5(b), the performance without the extended air duct is better than that with the extended air duct at the both orientations. The addition of the extended air duct resulted in an extremely weak natural convection, if any, even at the vertical orientation. For high methanol concentration operation, the larger amount of oxygen on the cathode is needed due to serious methanol crossover. Therefore, the lower performance with the extended air duct was caused by the lower oxygen transfer rate. However, although the cell without the extended air duct yielded a better performance than did with the extended air duct, the cell performance in the vertical orientation was still better than that in the horizontal orientation. Based on these experimental results, it is understood that when the effect of natural convection is excluded by adding an extended air duct on the cathode, the cell in the vertical orientation always showed a better performance than in the horizontal orientation. This indicates that the lack of oxygen is not the main reason leading to lower performance of the passive DMFC at the horizontal orientation than that at the vertical orientation. Therefore, the better performance in the vertical orientation can be attributed to the fact that a higher cell operating temperature was caused by more serious methanol crossover because the natural convection in the fuel reservoir enhanced the methanol transfer rate to increase the methanol concentration at the anode catalyst layer. As such, more heat was produced on the cathode through the exothermic reaction between the permeated methanol and the oxygen, leading to a higher cell operating temperature and thus a better cell performance. To further demonstrate this point, we also tested the passive DMFC with oxygen supplied by a pump while keeping the methanol supplied passively. To this end, the cathode current collector for the air-breathing operation mode was replaced by a current collector made of a 316L stainless steel plate with a thickness of 1.0 mm, in which a single serpentine flow field, consisting of a flow channel with a cross sectional area of 1.0 mm × 1.0 mm, was formed. Similarly, to reduce the contact resistance between the cathode current collector and electrode, a 200-nm platinum layer was sputtered onto the surface of the cathode current collector. Pure oxygen was supplied with the flow rate controlled by a mass flow meter (Omega FMA-7105E). To make sure that all the experiments were performed with the same mass transfer rate of oxygen and with the same heat removal from the cell by the oxygen stream, oxygen was supplied at a sufficiently high oxygen flow rate of 50 mL min^{-1}. The performance between the vertical and horizontal cell under the condition of the passive methanol feed but the active oxygen feed is compared in Fig. 6(a) (2.0 M operation) and Fig. 6(b) (4.0 M operation). It can be seen from the both figures that, like in the air-breathing operation mode, the vertical cell with the active feed of oxygen also exhibited higher performance than did the horizontal cell. Fig. 7 compares the measured cell operating temperatures between the vertical and horizontal cell under the condition of the active feed oxygen. It is clear from Fig. 7 that the vertical cell exhibited a much higher operating temperature than did the horizontal cell. Since under

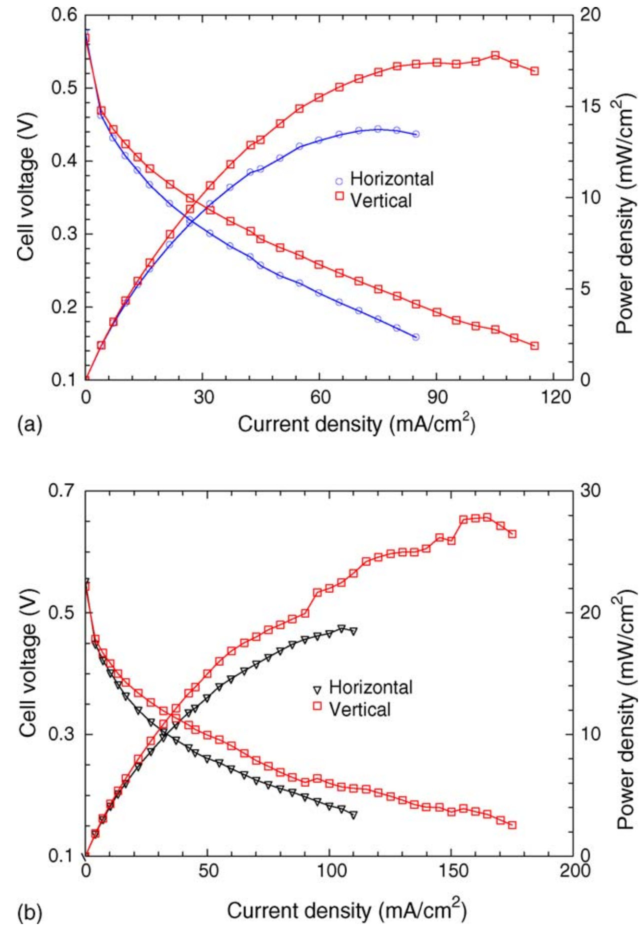

Fig. 6. Comparison in the cell performance with the active oxygen feed among different cell orientations: (a) 2.0 M and (b) 4.0 M.

the condition of the active oxygen feed, the oxygen supply was sufficient, the increased operating temperature in the vertical cell was due solely to the higher rate of methanol crossover in the vertical cell, which produced more heat on the cathode. Since the key difference between the vertical and horizontal cell operation is that natural convection is much stronger in the vertical case, the increased rate of methanol crossover in the vertical cell operation is attributed to the enhanced methanol feed by natural convection. In addition, the comparison between Figs. 2 and 6 indicates that the active oxygen feed operation yielded much better cell performance than did the air-breathing operation. This fact indicates that there is plenty of room for increasing the supply of oxygen in the air-breathing DMFC.

In this work, we also tested the long-term operation of the passive DMFC at different orientations. The transient discharging cell voltage of the passive DMFC at a constant current density (60 mA cm^{-2}) with a start from the cell to be fueled with 5.0 mL methanol solution at 4.0 M is shown in Fig. 8. It is seen that the vertical operation generally showed higher performance than did the horizontal operation, especially in the middle of the discharging period. The voltage of the vertical cell increased at the beginning because of the increase in the cell operating temperature with time as a result of methanol crossover. However, after 2 h, the vertical cell voltage began to decrease with time.

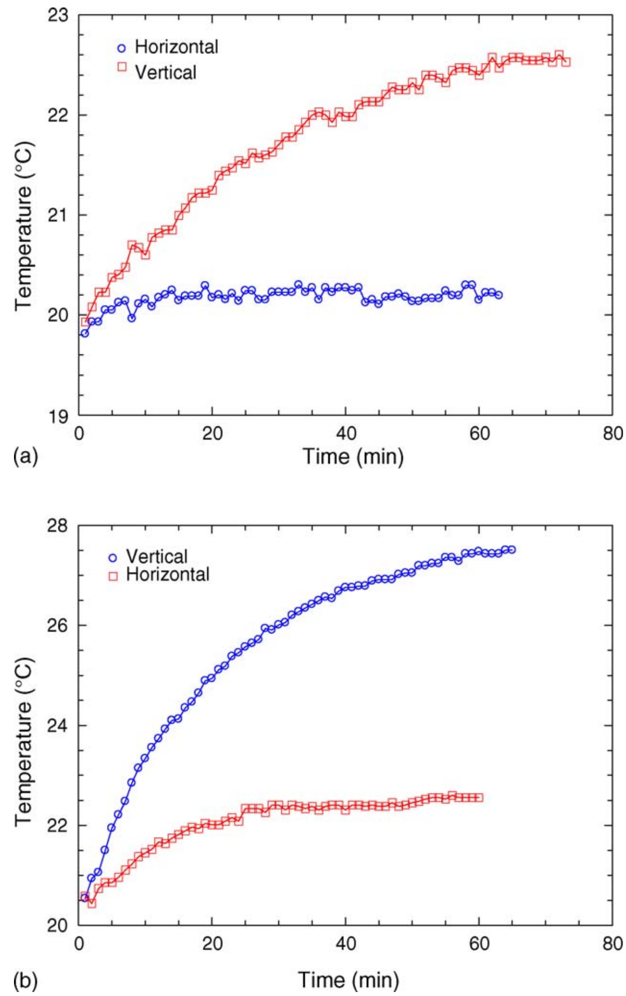

Fig. 7. Comparison in the cell operating temperatures with the active oxygen feed among different cell orientations: (a) 2.0 M and (b) 4.0 M.

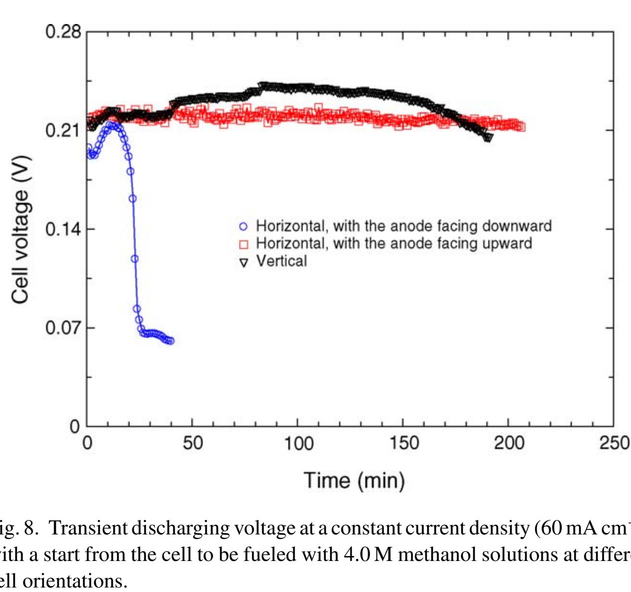

Fig. 8. Transient discharging voltage at a constant current density (60 mA cm^{-2}) with a start from the cell to be fueled with 4.0 M methanol solutions at different cell orientations.

This is mainly because the higher rate methanol crossover in the vertical operation led to a rapider decrease in the methanol concentration in the fuel reservoir, which in turn resulted in a lower rate of methanol crossover and thereby a lower operating temperature and lower voltage. In addition, it was also observed that a larger amount of liquid was accumulated on the cathode in the vertical operation because of a higher rate of water crossover and a lower rate of water removal in the vertical cell. On the other hand, the horizontal operation with the anode facing upward yielded relatively stable voltages. This is in part because the rate of methanol crossover in the horizontal cell is relatively lower, resulting in a small increase in the operating temperature, and in part because the downward-facing cathode renders an easier removal of liquid water on the cathode. We also tested the passive DMFC in the horizontal orientation with the anode facing downward. It is seen from Fig. 8 that this orientation resulted in an extremely unstable operation. Initially, the cell voltage increased due to an increase in the cell temperature, but it dropped rapidly after about 20-min operation. There are two major reasons responsible for this unstable operation. First, in this particular orientation with the anode facing downward, the removal of CO_2 bubbles becomes rather difficult and a large amount of bubbles may be accumulated at the anode catalyst layer due to the buoyancy force, blocking the paths for methanol to be transferred to the reaction sites. Secondly, since the cathode faced upward, it would be rather difficult for the liquid water to be removed from the cathode. As a result, both the CO_2 bubble accumulation on the anode and the liquid water accumulation on the cathode led to a very short and unstable operation when the cell was oriented horizontally with the anode facing downward.

It should be mentioned that although the vertical operation of the passive DMFC can yield better performance, the fuel utilization in this orientation is lower as a result of the increased rate of methanol crossover. On the other hand, although the passive DMFC in the horizontal orientation with the anode facing upward has lower performance, the more effective removal of liquid water due to the gravity in this particular orientation renders a more stable discharging. Therefore, all these effects need to be considered in practical applications.

4. Concluding remarks

A passive DMFC was tested at different orientations. The experimental results revealed that the cell orientation has a significant effect on the performance. The vertical operation always yielded better performance than did the horizontal operation. It was demonstrated that the improved performance in the vertical cell was caused by the increased operating temperature as a result of a higher rate of methanol crossover, which resulted from the stronger natural convection in the vertical orientation. The constant current discharging tests showed that, although the vertical operation of the passive DMFC can yield better performance, the fuel utilization in this orientation is lower as a result of the increased rate of methanol crossover. It was also shown that the horizontal orientation with the anode facing upward rendered an effective removal of both CO_2 bubbles on the anode and liquid water on the cathode and thereby a relative stable operation. Finally, it was revealed that the horizontal orientation with the anode facing downward exhibited rather unstable and short discharging duration because of the difficulties in removing CO_2 bubbles from the anode and liquid water from the cathode in this particular orientation.

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