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Journal of Power Sources 175 (2008) 458–463
JOURNAL OF POWER SOURCES
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Short communication

Influence of cathode oxygen transport on the discharging time of passive DMFC

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Received 30 July 2007; received in revised form 3 September 2007; accepted 3 September 2007
Available online 12 September 2007

Abstract

In this paper, the long-term discharge performances of passive DMFC at different currents with different cell orientations were investigated. Water produced in the cathode was observed from the photographs taken by a digital camera. The results revealed that the passive DMFC with anode facing upward showed the best long-term discharge performance at high current. A few independent water droplets accumulated in cathode when the anode faced upward. Instead, in the passive DMFC with vertical orientation, a large amount of produced water flowed down along the surface of current collector. The passive DMFC with vertical orientation showed relatively good performance at low current. It was concluded that the cathode produced less water in a certain period of time at smaller current. In addition, the rate of methanol crossover in the passive DMFC with anode facing upward was relatively high, which leaded to a more rapid decrease of the methanol concentration in anode. The passive DMFC with anode facing downward resulted in the worst performance because it was very difficult to remove CO_2 bubbles produced in the anode.

Keywords: Passive direct methanol fuel; Cell orientation; Discharging time; Oxygen transport

1. Introduction

The passive DMFC has been receiving increasing attention due to its advantages of the oxygen diffused into the cathode side from ambient air without any help of external devices, such as a pump or fan, and the methanol solution stored in the reservoir attaches to the anode plate and the methanol driven by concentration gradient between the reservoir and anode also diffuses into the anode. So passive DMFC can potentially result in higher reliability, lower cost, higher fuel utilization, and higher energy density, which are in favor of mobile equipments in future electronic devices [1–4]. A lot of work has been reported on passive DMFC, such as fuel concentration, membrane thickness, membrane electrode assembly (MEA), and fabrication [5–17]. Liu et al. and Kim et al. presented that the optimal concentration of methanol solution in passive DMFC was 4.0 mol L^{-1} [5,6]. Similar opinions about the effect of methanol concentration on the performance of passive DMFC can also be found in the literatures [7–9]. The utilizations of highly concentrated fuel of DMFCs with vapor fed have been reported [10,11]. To overcome methanol crossover that can lead to a mixed potential at the cathode, much work has been carried out on the modification of polymer membrane and development [12–14]. Chen and co-workers reported a suitable MEA for passive DMFC [15–17].

The passive DMFC for portable application should operate steadily with different cell orientations. However, the cell orientation has a significant effect on its performance when fuel and air supply to passive DMFC. Chen et al. [18] investigated the effect of orientation of the passive DMFC on its performance and the operation duration at a constant current density. Its performance with anode facing downward is the worst, and the passive DMFC with anode facing upwards showed the highest performance due to more effective removal of liquid water from the cathode than that with anode facing downward.

We believes that a lot of water produced in the cathode are various at the different discharge currents. Therefore, the long-term discharge performances of the passive DMFC with vertical orientation and anode facing upward are changed due to the changes of discharge currents. Above all, we investigated the long-term discharge performance of passive DMFCs with different cell orientations at different discharge currents, combining

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0378-7753/$ – see front matter
doi:10.1016/j.jpowsour.2007.09.007

with the observation of water accumulated in the cathodes using digital photographs.

2. Experimental

2.1. MEA fabrication

The metal loading in the anode was 2.0 mg cm^{-2} with 40 wt.% Pt-Ru (with an atomic ratio of 1:1)/C, while the metal loading in the cathode was 2.0 mg cm^{-2} using 40 wt.% Pt/C. The anode and the cathode inks were prepared with 20 wt.% Nafion (as binder) and 80 wt.% catalysts, respectively. Then the catalyst inks were scraped onto the GDLs, and then the electrodes were dried for 2 h in the vacuum oven at 80 °C. Furthermore, Nafion® ionomer solution of 0.5 mg cm^{-2} was coated onto the surface of each electrode. The Nafion 117 membranes were pretreated in four steps to remove the organic and inorganic contaminants before being applied to the electrodes. First, membranes were boiled in 3 wt.% H_2O_2 solution followed by washing in ultra-pure water. Then, the membranes were boiled in 0.5 mol L^{-1} H_2SO_4 solution. Finally, the membranes were boiled again in the ultra-pure water. Each step took about 1 h. The pretreated Nafion 117 membrane was sandwiched between the anode and the cathode, and then the assembly was hot pressed under a specific loading of 100 kg cm^{-2} for 90 s at 135 °C.

2.2. Single cell fixture

The prepared MEA was sandwiched between two graphite plates to make a passive DMFC. The cathode side of the graphite plates machined had many holes for air diffusion and the anode side machined through the graphite plates had channels and large open space for delivering and storing methanol solution, respectively. The oxygen diffused into the cathode side from ambient air without any help of external devices, such as a pump or fan, and the methanol solution stored in the reservoir attached to the anode side plate, and the methanol driven by concentration gradient between the reservoir and anode also diffused into the anode. The volume of the methanol reservoir was 10 cm^3. Aside the extension area of the bipolar plates served as a current collector, a heating tape was attached to the extension area to adjust the operating temperature of passive DMFC to a desired value during the experiments.

2.3. Electrochemical instrumentation and test conditions

The Fuel Cell Testing System (Arbin Instrument Corp.) connecting with a computer was employed to control the conditions of discharge and record the voltage–time curves. A solution of 2 mol L^{-1} aqueous methanol solution was fed to the anode side. The oxygen diffused into the cathode side from ambient air without any help of external devices. All the experiments of the passive DMFCs were performed at temperatures of 29–31 °C and the air relative humidity of 60–70%. Prior to the passive DMFC performance test, the MEA was installed in an active cell fixture and activated at 80 °C about 24 h. During the activation period, 2.0 mol L^{-1} methanol was fed at a flow rate of 3.0 mL min^{-1}, while oxygen was supplied under atmospheric pressure at a flow rate of 200 mL min^{-1}.

3. Results and discussion

Fig. 1 shows the performances of passive DMFCs with different cell orientations. The open-circuit voltage (OCV) of passive DMFC with anode facing downward is the highest. The OCV with anode facing upward is lower due to the serious methanol crossover from the anode to the cathode. The maximum power density of passive DMFC with vertical orientation is the highest. However, three orientations of passive DMFCs exhibit the similar performances.

Fig. 2 shows polarization curves and power density curves of passive DMFCs with vertical orientation operating at different methanol concentrations (0.5–2 mol L^{-1}). The highest OCV of 0.7 V is obtained at a methanol solution of 0.5 mol L^{-1}. The gradual decrease of OCVs with increase of methanol concentration results from the increase of methanol crossover through the Nafion 117 membrane. The similar results are also presented as the methanol concentrations from 1 to 2 mol L^{-1}. It can be seen that the performance of passive DMFC with methanol concentra-

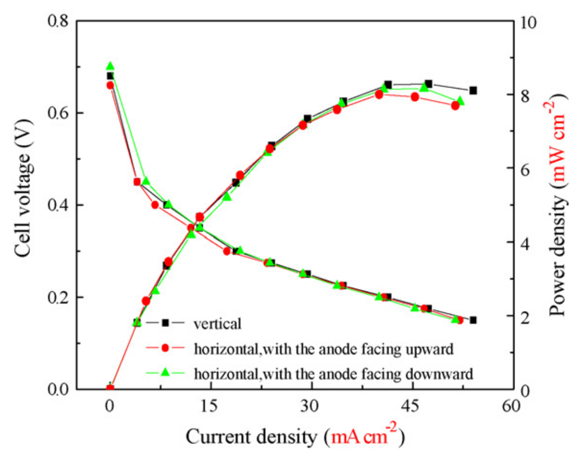

Fig. 1. Comparison in the passive DMFC performance among different passive DMFC orientations (2.0 mol L^{-1} methanol solutions).

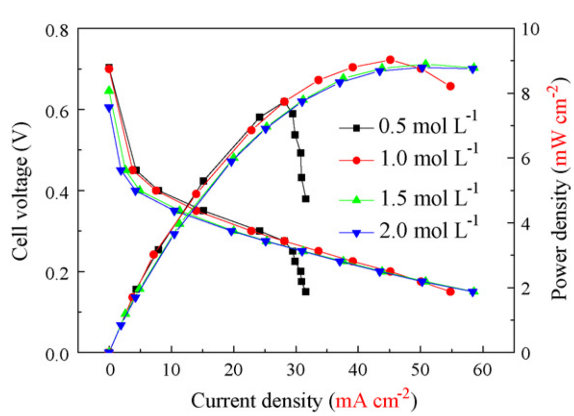

Fig. 2. Performance of a DMFC at various methanol concentrations under passive feed conditions. (Air temperature 20 °C, relative humidity: 60%, passive DMFC temperature 30 °C.)

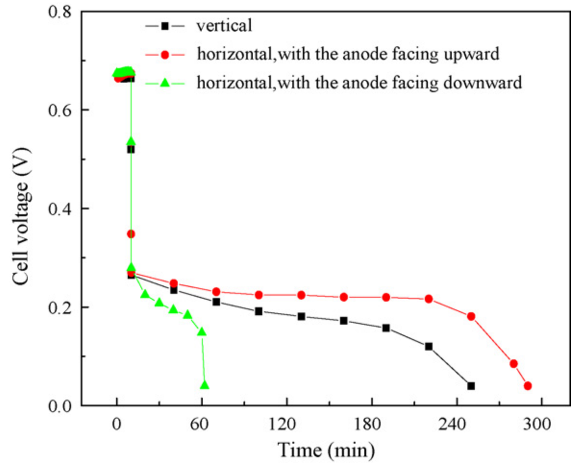

Fig. 3. Transient discharging voltage–time curves at a constant current (300 mA) with a start from the passive DMFC to be fueled with 2.0 mol L^{-1} methanol solutions (10 mL) at different passive DMFC orientations. (Air temperature 20 °C, relative humidity: 65%, passive DMFC temperature 30 °C.)

tion of 0.5 mol L^{-1} is the worst. Evidently, in the case of passive feed condition, methanol is only transported into the anode catalyst layer by a diffusion mechanism driven by the concentration gradient, and thus a lower methanol concentration leads to a worse performance of the passive DMFC.

Fig. 3 shows the transient discharging voltages curves of passive DMFCs with different cell orientations at a constant current of 300 mA. The data were taken when the discharging voltages were relatively stable. The discharging voltage is the highest at the beginning test in the voltage–time curves, and then drops slowly until reaching to about zero. The slow drop of the discharging voltage is attributed to a gradual decrease of methanol concentration gradient with time. The passive DMFC with anode facing upward shows the highest transient discharging voltage and longer discharging time. In the initial discharge process, the transient discharging voltage of passive DMFC with vertical orientation is similar to that of passive DMFC with anode facing upward. However, the transient discharging voltage of passive DMFC with vertical orientation degrades after about 50 min. Photographs of accumulated water recorded by a digital camera in the cathodes of passive DMFCs with different cell orientations are shown in Fig. 4. Fig. 4(a) shows that a few of independent water droplets accumulate in cathode as the anode of DMFC faces upward. It is believed that the anode facing upward can affect the removal of liquid water in the cathode due to the gravity so that the passive DMFC with anode facing upward presents a more stable discharging. Fig. 4(b) shows that a large amount of produced water flows downstairs along the surface of current collector, which blocks more air paths. The long-term discharge performance of the passive DMFC with vertical orientation is worse than that of the passive DMFC with anode upward orientation because of the more difficult removal of water in the cathode of the passive DMFC with vertical orientation. Fig. 3 also shows that the long-term discharge performance of the passive DMFC with anode facing downward is the worst. There are two possible reasons responsible for this unstable operation [9]. Firstly, in this particular orientation with the anode facing downward, the removal of CO_2 bubbles becomes very difficult, and a large amount of bubbles may be accumulated in the anode catalyst layer due to the buoyancy force and block the paths for methanol to be transferred to the reaction sites. Secondly, since the cathode faced upward, it would be also very difficult for the liquid water to be removed from the cathode.

In order to reduce the influence of the accumulated water in the cathode, we carried out long-term discharge performance of passive DMFCs with different cell orientation at an air temperature of 45 °C. It is believed that the water produced in cathode is vaporized rapidly due to the enhanced air cell temperature. Fig. 5 shows the performance of the DMFC with vertical orientation has certainly been improved. Fig. 6(a and b) shows that there is no water accumulated in both cathodes of the passive DMFCs with anode upward and vertical orientation. The results of comparison between Figs. 3 and 5 indicate that the accumulated water in the cathode is the major reason of performance degradation of the passive DMFC with vertical orientation. In addition, Fig. 5 shows that the transient discharging voltage of passive DMFC with vertical orientation is a little higher than that of passive DMFC with anode facing upward. It is believed that the passive DMFC with vertical orientation shows the highest transient discharging voltage because of less crossover of methanol compared with the passive DMFC with anode upward orientation. Fig. 5 also shows that the long-term discharge performance of passive DMFC with anode facing downward is not markedly improved. Therefore, the water in the cathode is not

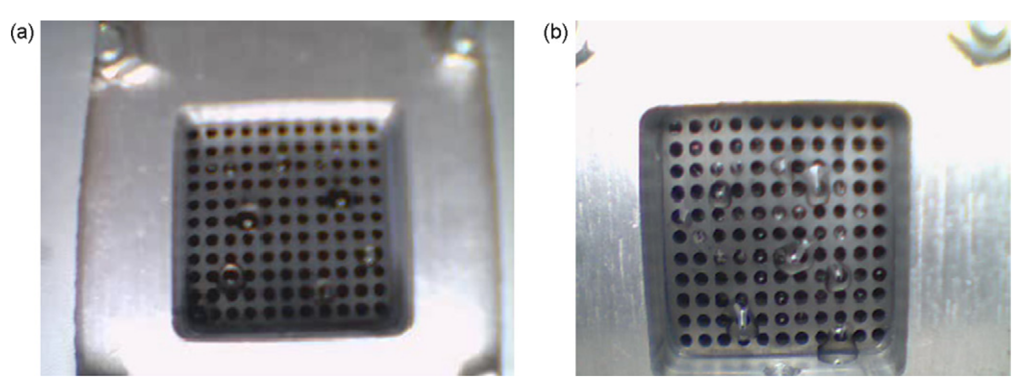

Fig. 4. Photographs of the water in the cathode of different passive DMFC orientations at a constant current 300 mA. (a) Anode facing upward and (b) passive DMFC with vertical orientation (discharging time: 200 min).

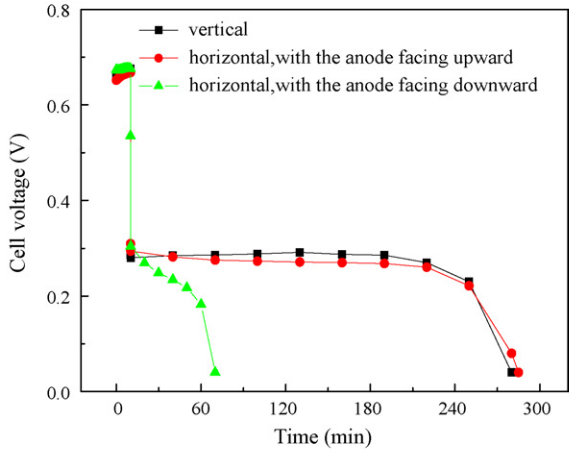

Fig. 5. Transient discharging voltage at a constant current (300 mA) with a start from the passive DMFC to be fueled with 2.0 mol L^{-1} methanol solutions (10 mL) at different passive DMFC orientations. (Air temperature 45 °C, relative humidity: 30%, cell temperature 30 °C.)

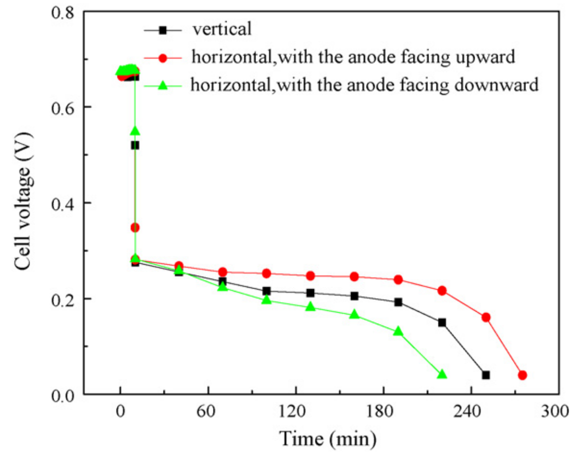

Fig. 7. Transient discharging voltage at a constant current (300 mA) with active 2.0 mol L^{-1} methanol solutions at different DMFC orientations. (Air temperature 20 °C, relative humidity: 63%, DMFC temperature 30 °C.)

the major reason of the performance degradation as the anode facing downward.

Furthermore, in Fig. 7, we compare the long-term discharge performance of DMFCs with active methanol at the anode in order to confirm the major factor that the performance of the DMFC with the anode facing downward decays. The long-term discharge performance of the DMFCs with vertical orientation and anode upward orientation are not markedly improved as shown in Fig. 7. But the long-term discharge performance of DMFC with active methanol at anode has a great enhancement compared with passive methanol at anode when the anode faces downward. It is believed that the produced CO_2 bubbles are easily removed through the flowing fuel in active DMFC. Therefore, it is confirmed that the accumulated CO_2 bubbles in the anode is the major reason for the performance degradation of the passive DMFC when the anode faces downward. It is believed that the difference between the performances of DMFCs with vertical and anode upward orientation is mainly caused by the accumulated water in the cathode.

We forecasted that the performances of the passive DMFCs with different orientations would be varied with discharging current due to various amount of water produced in a certain period of time. Fig. 8 shows the long-term discharge performance of passive DMFCs with different cell orientations at a current of 100 mA. The long-term discharge performance of passive DMFC with vertical orientation is better than that of the passive DMFC with anode facing upward. It is concluded that water produced in the cathode in a certain period of time at relative smaller discharging current is fewer than that at high discharging current (constant current 300 mA). Namely, the influence of accumulated water is relative small. In addition, compared with vertical orientation, a high rate of methanol crossover in the anode facing upward operation leads to a more rapid decrease of the methanol concentration in the fuel reservoir. Fig. 9 shows the long-term discharge performance of passive DMFCs with different cell orientations at a constant current of 200 mA. The discharging time of passive DMFC with vertical orientation is similar with the anode facing upward. At the beginning of discharging process, the passive DMFC with vertical orientation

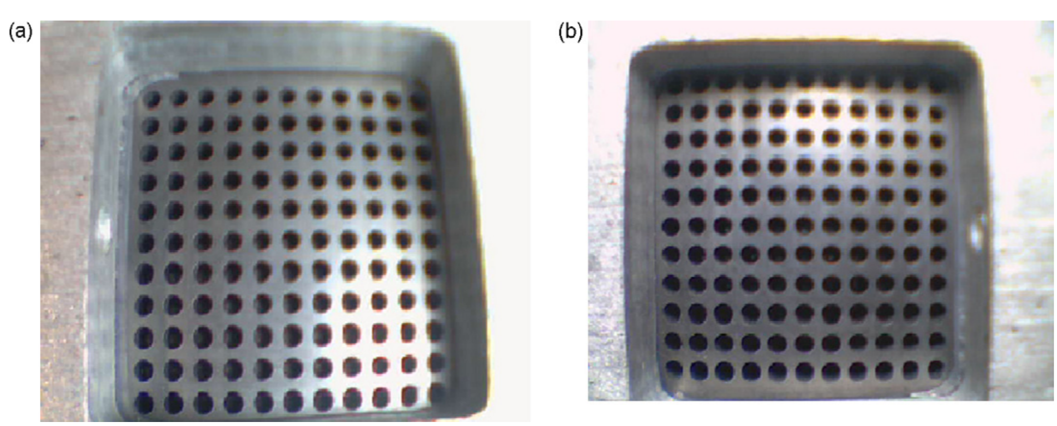

Fig. 6. Photographs of the water in the cathode of different passive DMFC orientations at air temperature 45 °C, relative humidity: 30%, passive DMFC temperature 30 °C, constant current 300 mA. (a) Anode facing upward and (b) passive DMFC with vertical orientation (discharging time: 200 min).

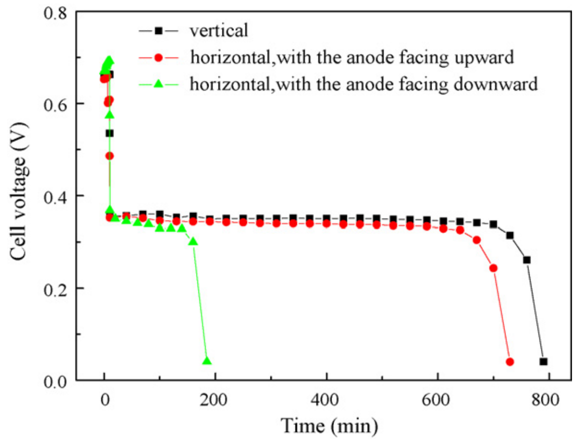

Fig. 8. Transient discharging voltage at a constant current (100 mA) with a start from the passive DMFC to be fueled with 2.0 mol L^{-1} methanol solutions (10 mL) at different passive DMFC orientations. (Air temperature 20 °C, relative humidity: 68%, passive DMFC temperature 30 °C.)

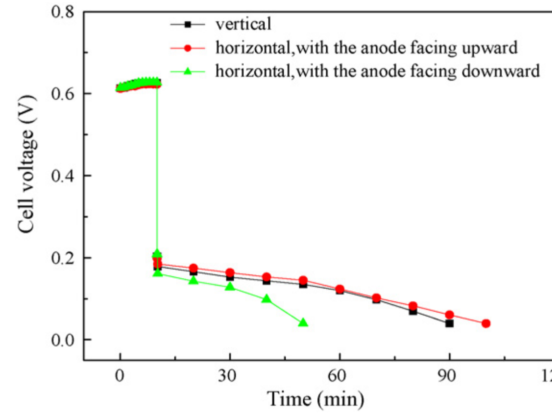

Fig. 10. Transient discharging voltage at a constant current (400 mA) with a start from the passive DMFC to be fueled with 2.0 mol L^{-1} methanol solutions (10 mL) at different passive DMFC orientations. (Air temperature 20 °C, relative humidity: 65%, passive DMFC temperature 30 °C.)

gives a higher discharging voltage. However, the passive DMFC with anode facing upwards shows a higher discharging voltage after about 250 min. Less water is produced in the cathode at the beginning of discharging process, so it can easily removed, and the passive DMFC with vertical orientation shows a higher discharging voltage. More water is produced with the discharging time, and the influence of accumulated water on the performance of passive DMFC becomes serious. The passive DMFC with anode facing upward shows a better performance due to the fact that the water could more easily remove from the cathode. Fig. 10 shows the long-term discharge performances of passive DMFCs with different cell orientations at a current of 400 mA. It is suggested that the performances of passive DMFCs with anode facing upward and vertical orientation greatly decrease, and their discharging times are very short. Although the cell with anode facing upwards leads to more effective removal of liquid water by the force of gravity at a current of 400 mA (44.4 mA cm^{-2}), the transfer rate of fuel and air in the electrode is the primary factor which affects the performance of cell as shown in Fig. 1.

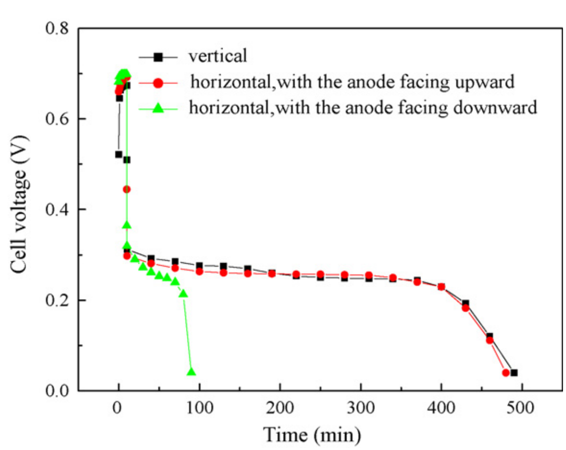

Fig. 9. Transient discharging voltage at a constant current (200 mA) with a start from the passive DMFC to be fueled with 2.0 mol L^{-1} methanol solutions (10 mL) at different passive DMFC orientations. (Air temperature 20 °C, relative humidity: 64%, passive DMFC temperature 30 °C.)

4. Conclusion

The performances of passive DMFCs were tested at different orientations. The experimental results revealed that the cell orientation had a significant effect on the long-term discharge performance. The long-term discharge performance of passive DMFC with anode facing downward was the worst because the removal of CO_2 bubbles became very difficult. The long-term discharge performance of passive DMFC with vertical orientation was better than that with anode facing upward under low current. With the increasing of the discharging current, a lot of water accumulated in cathode, which blocked paths of air transport. In this case, the long-term discharge performance of cell with anode facing upwards showed the best due to more effective removal of liquid water in the gravity. However, when current further increased to 400 mA, either its performance of passive DMFC with vertical orientation or with anode facing upward was poor because the cell with anode facing upwards leads to more effective removal of liquid water by the gravity, at a current of 400 mA (44.4 mA cm^{-2}). The slow transfer of fuel and air molecules into the electrode was primary factor which affected the performance of cell.

Acknowledgement

This work was supported by Natural Science Foundation of China (No. 20476020 and No. 20606007).

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