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ORIGINAL PAPER

Effect of wettability of anode microporous layer on performance and operation duration of passive air-breathing direct methanol fuel cells

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Abstract The influence of the wettability of the anode microporous layer (MPL) on both cell performance and operation duration of air-breathing direct methanol fuel cells (DMFCs) was investigated. The experimental results demonstrated that a passive DMFC with a hydrophilic MPL (DMFC-L) in the anode gas diffusion layer (GDL) showed performance superior to that with a hydrophobic MPL (DMFC-B), when the performance evaluation was conducted by applying a holding time of 45 s at each current density. DMFC-B showed good performance at medium and high current densities when a holding time of 150 s was used. The observation of water accumulation on the cathode of DMFC-L indicated that the decreased performance resulted mainly from blockage of the oxygen supply path. The constant-current discharging test showed that DMFC-B exhibited a lower performance at the beginning of discharge. However, it showed a lower rate of water accumulation on the cathode and thereby relatively stable operation. Operating the passive DMFCs at high water evaporation rate confirmed the important role of the wettability of anode GDLs for cathode oxygen transport.

Keywords Passive direct methanol fuel cells · Oxygen transport · Cathode flooding · Anode gas diffusion layer

1 Introduction

Direct methanol fuel cells (DMFCs) employing methanol as fuel are very attractive candidates for powering portable and mobile devices. In the conventional active fuel cell system, both fuel and oxidant are fed by forced convection. Such systems need ancillary components such as pumps and valves for fuel and oxidant delivery, which add significant complexity and parasitic power loss. Consequently, passive DMFCs that require no pump and fan have recently received much attention [1–12]. However, this simple design usually has lower system performance due to the difficulties of preventing flooding at the cathode and the high transport resistance of reactants [4, 13, 14].

Cathode flooding causes a decrease in performance and fuel efficiency due to blockage of the oxygen supply to the cathode. For this reason, it is essential to investigate the mechanism of water accumulation at the cathode to achieve more stable operation [15], especially for passive DMFCs. It is clear from the insightful studies presented by Wang et al. [16–18] that the water at the cathode of a DMFC includes water produced by oxygen reduction and the oxidation of the crossed-over methanol, as well as water crossover from anode to cathode through the membrane. Lu et al. [17] stated that, for a thick membrane such as Nafion® 117, 15 water molecules are dragged from the anode and 3 water molecules are created by the reaction when one methanol molecule is consumed. Xu et al. [19] experimentally determined the water crossover through the membrane for a DMFC. They found that the amount of water transported to the cathode is far greater than that produced by the oxygen reduction reaction and the oxidation of the crossover methanol. Song and co-workers [20] investigated the influence of the existence of a microporous layer (MPL) in the cathode gas diffusion layer (GDL) on

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the water crossover behavior in an air-breathing DMFC. They found that the introduction of a hydrophobic MPL in cathode gave a significant decrease in water crossover from anode to cathode, and improved stability under continuous operation. Most recently, Liu et al. [18] observed that a hydrophobic MPL is more suitable than a hydrophilic MPL as the anode diffusion layer for DMFCs, because a membrane electrode assembly (MEA) with a hydrophilic anode MPL induces large voltage fluctuations during constant-current discharge.

On the other hand, many papers have emphasized [8, 21–23] the importance of the hydrophilic anode MPL in the case of low-temperature DMFCs, due to its lower methanol transfer resistance. Thus, to better understand the role of the anode GDL in the operation of air-breathing DMFCs, systematic studies focusing on the effect of wettability of the anode MPL on both cell performance and operation duration were carried out in the present study.

2 Experimental

2.1 MEA fabrication

The anode and cathode consist of a backing layer, a microporous layer, and a catalyst layer. A teflonized (15% Teflon) carbon paper (Toray TGH-H-120) of a 0.38 mm thick was employed as the backing layer in these electrodes. The carbon paper was sintered at 340 °C for 30 min. To prepare the microporous layer for the anode, Vulcan XC-72 carbon was suspended in a mixture of water and isopropanol and agitated in an ultrasonic water bath. Teflon suspension (15 wt.%, hydrophobic) or Nafion (15 wt.%, hydrophilic) solution was added as desired. The resultant slurry was sprayed onto the carbon paper using an air brush, followed by drying at 100 °C. The hydrophobic microporous layer was further sintered at 340 °C for 30 min. The microporous layer for the cathode was prepared in the same manner as the hydrophobic microporous layer for the anode. The loading of carbon in the microporous layer for both anode and cathode was 1.0 mg cm^{-2}.

Commercial Nafion 117 membranes (Dupont) were used as the electrolyte for all MEAs. Pretreated Nafion 117 membranes were cleaned by boiling the membranes successively in 10% H_2O_2 solution, deionized (DI) water, 0.5 mol l^{-1} H_2SO_4 solution, then DI water again. In each step the solution was boiled for 1 h. A commercially available platinum black (HiSPEC^{TM} 1000, Johnson Matthey) and a platinum ruthenium black (HiSPEC^{TM} 6000, Johnson Matthey) were used as the cathode and anode catalyst, respectively. The mixture of DI water, catalyst powder, and Nafion ionomer was sonicated for 1 h, then the catalyst ink was deposited on the microporous-layer-coated carbon paper also by air brush. The loading of the anode and the cathode catalysts on the paper was 2.5 and 2.0 mg Pt cm^{-2}, respectively. The ratio of catalyst to Nafion ionomer was fixed at 4:1 (dry weight) for both anode and cathode catalyst layers. Finally, 0.5 mg cm^{-2} Nafion was uniformly coated on the anode and cathode catalyst layers and dried at 80 °C for 2 h. The MEA was formed by sandwiching the Nafion 117 membrane between the anode and cathode and hot pressing it at 130 °C under 10 MPa pressure for 3 min. The active area of the MEA was 4.41 cm^2. The passive DMFCs using MEAs with hydrophobic and hydrophilic anode microporous layers are abbreviated as DMFC-B and DMFC-L, respectively.

2.2 Experimental setup and test conditions

All the experiments were performed in an environmental chamber at 24 ± 1 °C. A methanol solution (4 M aqueous methanol) was stored in a methanol reservoir attached to the anode side, and the methanol was allowed to diffuse into the anode catalyst layer driven by the concentration gradient between the reservoir and the anode. Oxygen was supplied to the cathode from the open air. The volume of the methanol reservoir in the anode compartment was 8 ml, and the cathode plate had 27 holes with a diameter of 3.6 mm. To achieve reproducible results, all curves were recorded after a 120 min waiting time [24]. The voltage–current curves were recorded using an electronic load (BT 2000, Arbin, USA). To investigate the effect of scan rate of the electronic load on the cell performance, holding times of 45 s (fast scan model) and 150 s (slow scan model) at each current density were applied, and the voltage values were obtained at the last second. Images of droplets on the surface of the cathode GDL were recorded with a digital camera (S800, Samsung, Korea). The cell temperature was measured with a thermocouple (type T) installed on the outer surface of the anode GDL.

2.3 Environmental chamber setup

An environmental chamber was utilized to control ambient temperature and relative humidity (RH). Acrylic plates were used to produce a 600 × 500 × 500 mm rectangular box. The air passed into the preheating room, in which there was a ceramic electric heater and a humidifying window. Then the heated and humidified air was sent to the fuel cell testing room, in which a type T thermocouple and humidity measuring instruments were used to monitor the temperature and humidity. At the two ends of the chamber two electric fans were installed to produce a positive flow, inhibiting the surrounding vapor from spreading to the reaction chamber and ensuring sufficient air supply. To reduce the impact of forced convection on the cathode, two metal meshes were fixed on the both sides of the testing room. The chamber was surrounded with 15-mm-thick polyethylene foam to act as thermal insulation.

3 Results and discussion

Figure 1 shows the transient open-circuit voltage (OCV) and operating temperature of the passive DMFCs with different anode GDLs. The passive DMFC with hydrophilic anode GDL (DMFC-L) exhibited lower stable OCV and higher cell temperature than that of the hydrophobic GDL (DMFC-B). It is generally accepted that methanol crossover to the cathode not only lowers the OCV of passive DMFCs, but also causes heat generation due to the exothermic oxidation of permeated methanol at the cathode catalyst layer [13, 24, 25]. Consequently, this result demonstrates that use of hydrophobic anode GDL leads to a lower rate of methanol crossover than does the hydrophilic GDL, in the case of air-breathing DMFCs. The methanol permeability difference for the passive DMFC with hydrophilic and hydrophobic anode GDLs can be attributed to the structural difference between Nafion and Teflon. It is well known that Nafion has a dual structure with hydrophobic regions interspersed with hydrophilic domains [11], whereas Teflon is a highly hydrophobic material. The hydrophilic domain in the GDL of DMFC-L becomes water-rich after 2 h operation in the open-circuit condition. This facilitates methanol diffusion from anode to cathode and hence leads to higher methanol crossover rate.

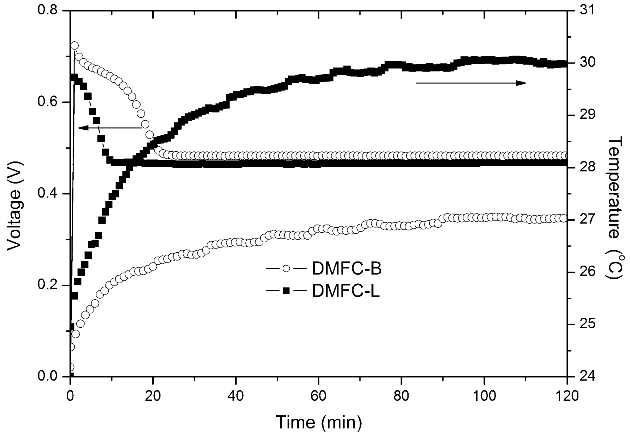

Fig. 1 Comparison of the transient open-circuit voltage and temperature of DMFCs with different anode GDLs

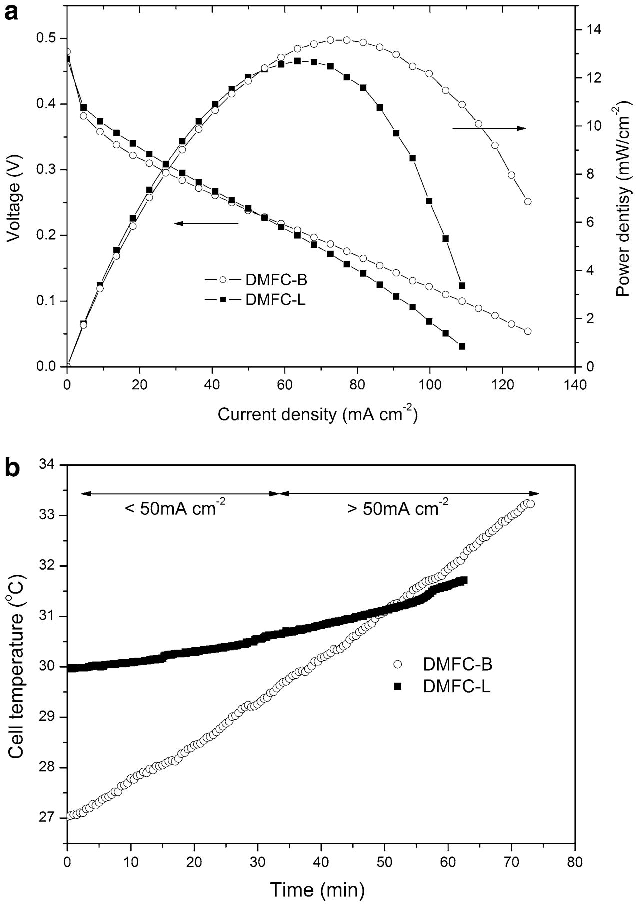

Fig. 2 **a** Cell performance of DMFC-L and DMFC-B evaluated with a holding time of 150 s at each current density. **b** Variation of the cell operating temperature during the performance evaluation

Figure 2 shows cell performance of DMFC-L and DMFC-B evaluated in the slow scan mode, and the corresponding cell temperature changes. It is apparent from Fig. 2a that, at low current densities (<50 mA cm^{-2}), the cell performance of DMFC-L is superior to that of DMFC-B. The reason is that the cell operating temperature of DMFC-L is higher than that of DMFC-B during the initial period of performance evaluation, as indicated by the measured temperature shown in Fig. 2b. The higher cell temperature of DMFC-L improves the electrochemical kinetics of both methanol oxidation and oxygen reduction reactions, and thereby the cell performance. However, that is not the case at medium to high current densities. Figure 2a shows that the cell performance of DMFC-B at medium to high current densities (>50 mA cm^{-2}) is considerably better than that of DMFC-L. It is interesting to note that Zhang et al. [21] studied the wettabilities of the anode GDLs on the performance of active DMFCs at room temperature, and found that MEAs with hydrophilic anode MPLs exhibit performance superior to that of MEAs with hydrophobic anode MPLs at high current densities, due to improved methanol accessibility to the anode catalyst layer. The inconsistency between the literature and our results is attributed mainly to the different ways to remove the water from the cathode GDL. Because of the difficulty of water removal in the case of air-breathing DMFC, the cell voltage is very sensitive to water accumulated during cell performance evaluation, because it usually has detrimental consequences: (1) the accumulated water at the cathode limits access of oxygen to the catalytic sites, and drastically reduces the cathode voltage, (2) blockage of the oxygen supply suppresses the temperature rise in the cell due to the oxidation of crossed-over methanol at the cathode, and (3) evaporation of the accumulated water causes enhanced heat loss from the cell to the ambient environment. Figure 3 shows photographs of accumulated water on the cathode of passive DMFCs immediately after the cell performance evaluation in slow scan mode. The cathode surface of DMFC-L appears to have been partially flooded by a large amount of water puddles, whereas a few isolated water droplets formed on the cathode surface in the case of DMFC-B. This result reveals that the higher performance of DMFC-B at higher current densities may be due primarily to more efficient oxygen transport from the atmosphere to the cathode catalyst layer and less heat loss, as a result of reduced water coverage on the cathode surface.

To reduce the influence of water flooding on the cell performance of DMFC-L and DMFC-B, the polarization curves were obtained in the fast scan mode, because the amount of water accumulation on the cathode at a given current density was proportional to the operating time. Figure 4 shows the cell performance of DMFC-L and DMFC-B evaluated in the fast scan mode and the corresponding cell temperature changes. It is apparent that the cell performance of DMFC-L at medium and high current densities was greatly improved. Figure 5 shows photographs of water accumulated on the cathode of passive DMFCs immediately after cell performance evaluation in

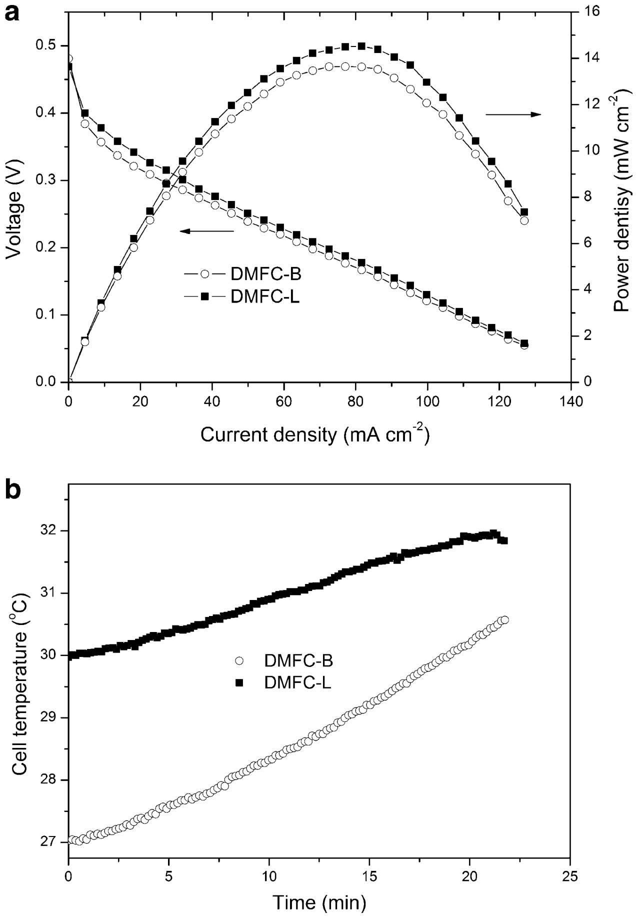

Fig. 4 **a** Cell performance of DMFC-L and DMFC-B evaluated with a holding time of 45 s at each current density. **b** Variation of the cell operating temperature during the performance evaluation

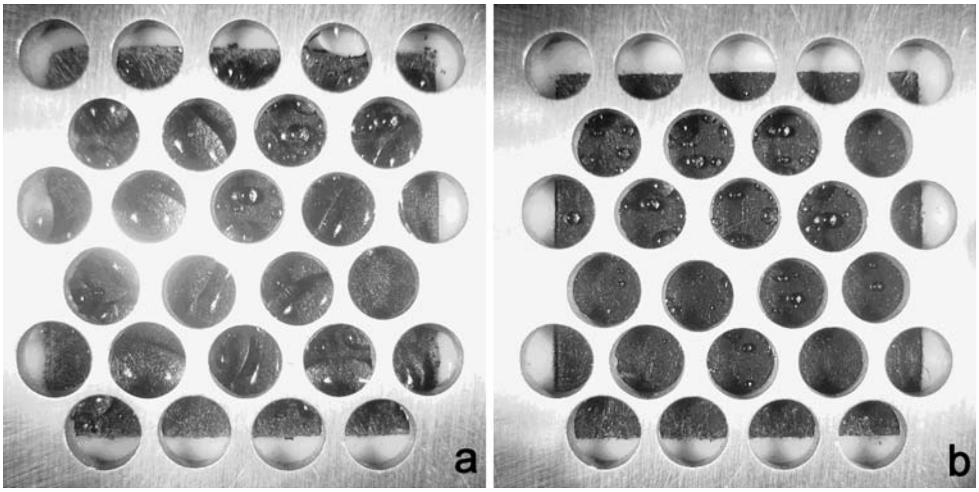

Fig. 3 Photographs of accumulated water on the cathodes of **a** DMFC-L and **b** DMFC-B immediately after cell performance evaluation in the slow scan mode

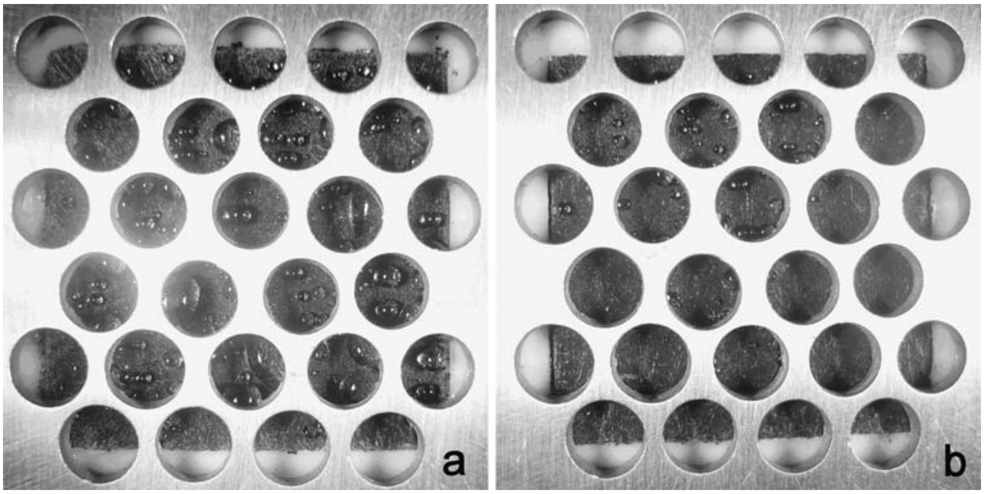

Fig. 5 Photographs of accumulated water on the cathode of **a** DMFC-L and **b** DMFC-B immediately after the cell performance evaluation in the fast scan mode

the fast scan mode. It is clear from this figure that the water coverage on the cathode surface of DMFC-L was substantially reduced compared with that in the slow scan mode. The enhanced cell performance of DMFC-L evaluated in the fast scan mode can thus be attributed mainly to improvement of oxygen transport from the surrounding air to the cathode and its higher cell operating temperature (Fig. 4b). It is interesting to note that no performance enhancement was observed when DMFC-B was tested in the fast scan mode. This implies that DMFC-B does not suffer serious water flooding problem in the slow scan mode.

Figure 6a shows the transient discharging cell voltage of the passive DMFCs at constant current density 15 mA cm^{-2} at 24.3 °C, 90% RH. It is apparent that the performance of DMFC-L was superior to that of DMFC-B at the beginning of the discharging period. Similar behavior was observed for current densities of 60 and 80 mA cm^{-2} (Fig. 6b and c). The higher performance of DMFC-L at the beginning of the discharging process can be attributed to the combined effects of lower methanol transfer resistance [21], higher cell operating temperature, and less water accumulation during this period. However, after a particular operation time, the voltage of DMFC-L begins to decline rapidly to zero, whereas the voltage decay of DMFC-B is considerably slower (Fig. 6).

The rapid decrease in the performance of DMFC-L could be attributed to both methanol consumption and flooding of the electrode. To reduce the influence of methanol consumption on the discharge time of passive DMFC-L, the transient discharging cell voltage of DMFC-L with active 4 M methanol solution was recorded at constant current densities 60 and 80 mA cm^{-2} at 24.7 °C and 90% RH. The data, shown in Fig. 7, reveal that the discharge time of active DMFC-L was similar to that of passive DMFC-L. Thus it was confirmed that consumption of methanol was not the cause of the performance degradation of the passive DMFC-L.

Figure 8 compares images of the accumulated water formed on the cathode surface of DMFC-L and DMFC-B at various times at current density 60 mA/cm^2. It is apparent that the rate of water accumulation on the cathode of DMFC-L was much higher than for DMFC-B, and most areas of the cathode GDL of DMFC-L were filled by liquid water after about 40 min operation (Fig. 8b). The continuing accumulation of water resulted in complete occupation of the breathing hole and blockage of the air supply (Fig. 8c). Therefore, the worse long-term discharging performance of DMFC-L is caused mainly by the higher rate of water accumulation on the cathode than in the case of DMFC-B. The reason for the lower rate of water accumulation on the cathode of DMFC-B is in part because the hydrophobic MPL is capable of depressing the anode liquid water saturation and inducing hydraulic water permeation from the cathode to anode [18], resulting in a smaller net amount of water transported from the anode through the membrane to the cathode, It is also due, in part, to the lower methanol crossover rate of DMFC-B, which leads to a lower rate of water production by oxidation of the permeated methanol.

Furthermore, by operating the passive DMFCs under conditions of high water evaporation rate the same considerations may apply. It is well known that the water accumulated on the cathode of passive DMFCs is

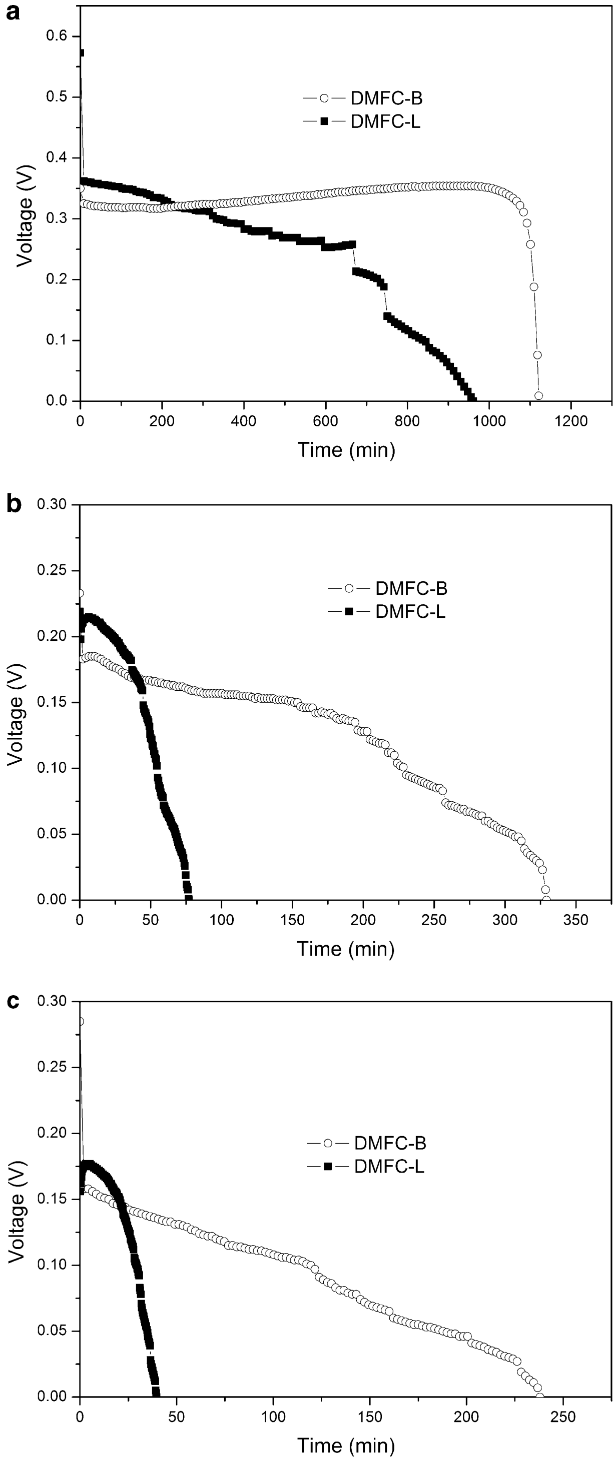

Fig. 6 The transient discharging cell voltage of passive DMFCs at constant current densities **a** 15, **b** 60, and **c** 80 mA cm^{-2}, at 24.3 °C and 90% RH

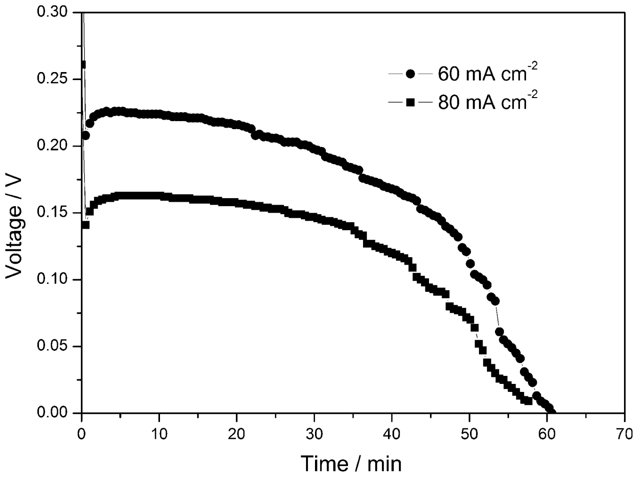

Fig. 7 The transient discharging cell voltage of DMFC-L with active 4 M methanol solution at constant current densities 60 and 80 mA cm^{-2}, at 24.7 °C and 90% RH (methanol solution feed flow rate of 1.0 ml min^{-1})

vaporized more rapidly at lower RH. Testing of the long-term discharge performance of DMFC-L and DMFC-B was carried out at 63% RH. Figure 9 shows the transient discharging cell voltages of DMFC-L and DMFC-B at constant current densities of 15 and 80 mA cm^{-2} at 24.5 °C and 63% RH. Comparison of Figs. 6 and 9 indicates that the discharging time of DMFC-L is greatly improved at lower RH. These results further confirm that blockage of the oxygen supply resulting from the accumulated water on the cathode is mainly responsible for the rapid performance degradation of DMFC-L. In addition (Fig. 9a) no significant further improvement of the discharging time was observed when DMFC-B was operated at current density of 15 mA cm^{-2} in the drier air condition. This result suggests that the influence of accumulated water on the long-term performance of DMFC-B is relative small in this particular condition.

4 Conclusions

Comparative studies of a passive DMFC with different anode GDLs were carried out in this work. The experimental results reveal that the wettability of anode GDLs is essential to cathode oxygen transport. It is demonstrated that the fast scan performance of DMFC-L is consistently superior to that of DMFC-B over the whole spectrum of current density. However, in the slow scan mode, a significant decrease in the cell performance of DMFC-L at medium and high current densities is observed, which results principally from blockage of the oxygen supply due to water droplets accumulated during the cell performance evaluation. Constant-current discharging tests show that, although DMFC-L can yield better performance at the beginning of operation, it

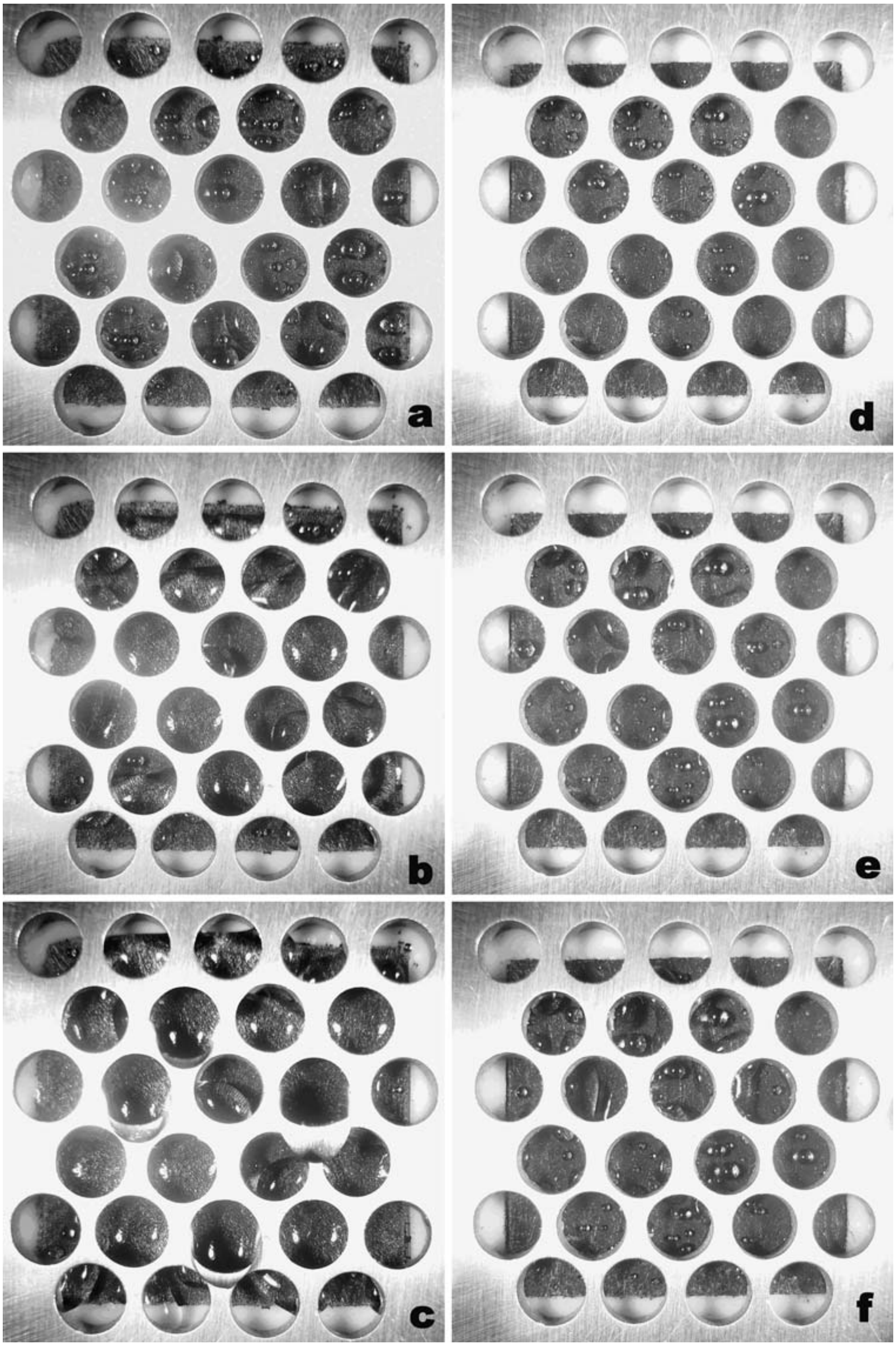

Fig. 8 Comparison images of accumulated water formed on the cathode surface of DMFC-L (**a**, **b**, **c**) and DMFC-B (**d**, **e**, **f**) at various times, at current density of 60 mA cm^{-2}

exhibits rather unstable long-term performance because of the higher rate of water accumulation on the cathode. Operating the passive DMFCs at high water evaporation rate confirms the important role of the wettability of anode GDLs on the operation duration of the passive DMFC.

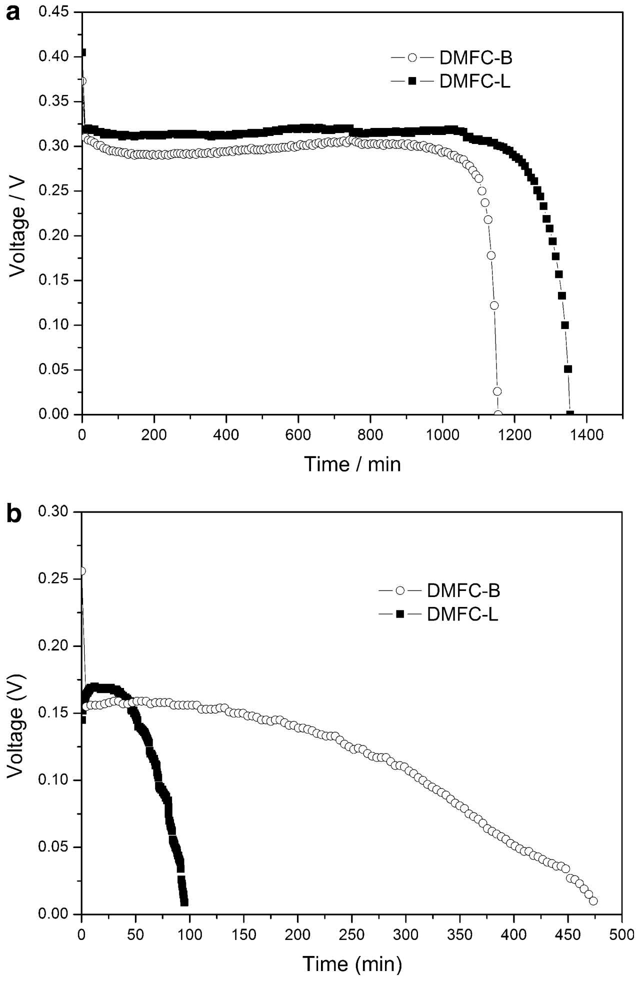

Fig. 9 The transient discharging cell voltage of the passive DMFCs at constant current densities **a** 15, **b** 80 mA cm^{-2}, at 24.5 °C and 63% RH

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