Effect of the cathode gas diffusion layer on the water transport behavior and the performance of passive direct methanol fuel cells operating with neat methanol

Q.X. Wu, T.S. Zhao*, W.W. Yang

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

Abstract

The passive operation of a direct methanol fuel cell with neat methanol requires the water that is produced at the cathode to diffuse through the membrane to the anode to compensate the methanol oxidation reaction (MOR). Hence, the anode performance of this type of fuel cell can be limited by the water transport rate from the cathode to the anode. In this work, we theoretically show that the water transport from the cathode to the anode depends primarily on the design of the cathode gas diffusion layer (GDL). We investigate experimentally the effects of the design parameters of the cathode GDL, including the PTFE (polytetrafluoroethylene) content in the backing layer (BL), and the carbon loading and the PTFE content in the microporous layer (MPL) on the water transport and the performance of the passive DMFC with the help of a reference electrode. The results indicate that on one hand, these parameters can be adjusted to decrease the water concentration loss of the anode performance, but on the other hand, they can also cause an increase in the oxygen concentration loss of the cathode performance. Hence, an optimal balance in minimizing the both concentration losses is the key to maximize the cell performance.

1. Introduction

A passive direct methanol fuel cell (DMFC) is an electro-chemical device that directly converts the chemical energy stored in the methanol into electricity without using any liquid pumps and gas fans/blowers. Due to its attractive advantages such as ease in fuel storage and transportation, high specific energy, low temperature operation, compact structure and zero noise, the passive DMFC has been regarded as a promising candidate for powering mobile electronic devices including laptops, cellular phones, and personal digital assistants [1–10]. To achieve the feature of the high specific energy, the passive DMFC should be fed with concentrated methanol solution or neat methanol. However, since the sate-of-the-art membrane used in the passive DMFCs for conducting protons is permeable to methanol, DMFCs fed with concentrated fuel will cause severe methanol crossover through the membrane such that the cell performance and the fuel utilization efficiency will be reduced. For these reasons, fairly diluted methanol solution (i.e., 2.0–5.0 M) is usually fed to a passive DMFC, resulting in a tremendous reduction in the specific energy of the fuel cell system.

In order to limit the methanol-crossover rate with concentrated methanol, past efforts have mainly focused on modifying the anode structure of the passive DMFC to control the methanol delivery rate [11–18]. Nakagawa et al. [12–14] employed a hydrophobic porous carbon plate with a high transfer resistance between the fuel reservoir and the anode current collector to reduce the methanol delivery rate. With the optimized design of the porous plate, the methanol-crossover rate was significantly reduced and their passive DMFC can run with 22.0 M methanol solution without sacrificing cell performance. Rather than adding a new layer to the passive DMFC, Wu and Zhao et al. [15] recently proposed a novel micro-fluidic flow field to operate the passive DMFC with highly concentrated methanol solution. In their design, the evaporation from the small meniscus in each flow passage can lead to an extremely large interfacial mass-transfer resistance, creating a bottleneck of methanol delivery to the anode catalyst layer (CL). They showed that by utilizing this micro-fluidic flow field, as high as 18.0 M methanol solution can be fed to the passive DMFC and a good performance was maintained. In an attempt to use neat methanol, other investigators [16–18] proposed the use of a pervaporation (permeation and evaporation) membrane that allowed the methanol concentration from the neat in the fuel reservoir to be declined to an appropriate level in the anode CL. Using this technique, Xu et al. [18] demonstrated that the power density of 34 mW cm⁻² and a high fuel efficiency of 62% can be achieved in a passive DMFC operating with neat methanol.

The above literature review indicates that increasing the mass-transfer resistance of methanol through the anode can effectively reduce methanol crossover so that the neat-methanol operation can be achieved. Another issue with the neat-methanol operation
is the water problem. As no water is carried in the fuel reservoir with the neat-methanol operation, the water required for the anode methanol oxidation reaction (MOR) needs to be passively transported from the cathode through the membrane by diffusion. Under this circumstance, the anode performance of this type of fuel cell becomes dependent on not only the water transport rate from the cathode to the anode but also the water concentration level in the anode CL. Therefore, the water management in the neat-methanol operation is critically important. However, only relatively few works [19–22] have been reported about the water management in the passive DMFC fed with neat methanol. Masdar et al. [21] studied the effect of a hydrophobic air filter on the water transport and cell performance in a semi-passive DMFC operating with neat methanol. They found that both the water management and the cell performance were improved by fixing a hydrophobic air filter to the cathode. Wu and Zhao et al. [22] recently proposed adding a thin layer that consisted of nanosized SiO2 particles and Nafion ionomer onto each side of the membrane to enhance the water retention in the membrane electrode assembly (MEA). Their results showed that the MEA with the water retention layers yielded a much higher power density than the MEA without water retention layers did. This work focuses on the study of the design of the cathode gas diffusion layer (GDL) on the water transport from the cathode to the anode and the effects associated with the change in the design of the cathode GDL. The design parameters investigated include the PTFE (polytetrafluoroethylene) content in the cathode backing layer (BL) and in the MPL, as well as the carbon loading in the MPL. As a change in the cathode design can affect not only the water transport (associated with the anode performance) from the cathode to the anode but also the oxygen transport (associated with the cathode performance), the respective anode and cathode overpotentials are measured with the help of a reversible hydrogen electrode as the reference electrode.

2. Analysis of water transport in the passive DMFC operating with neat methanol

Fig. 1 illustrates the design of a passive DMFC operating with neat methanol, which consists of a fuel reservoir, a pervaporation membrane, an evaporation control layer, a vapor chamber, an anode current collector, a MEA and a cathode current collector. Typically, the MEA is composed of an anode GDL, an anode CL, a polymer electrolyte membrane, a cathode CL and a cathode GDL. In the cathode CL, water is produced by the oxygen reduction reaction (ORR) and the oxidation of the permeated methanol. Accordingly, the total generation of water, $J_G$, can be expressed as:

$$J_G = \frac{i}{2F} + \frac{i_c}{3F},$$

(1)

where $i$ and $i_c$ stand for the cell current density and the parasitic current density accounting for the methanol crossover, respectively; $F$ is the faraday constant. Under the neat-methanol operation, as no water is carried in the fuel reservoir, part of the generated water, driven by the concentration gradient, is required to diffuse from the cathode CL to the anode to compensate the anode MOR; the diffusion flux, $J_D$, is given by:

$$J_D = D_{M}^{eff} \frac{C_{CL} - C_{ACL}}{\delta_{M}},$$

(2)

where $C_{CL}$ and $C_{ACL}$ are the water concentration at the cathode CL and anode CL, respectively; $D_{M}^{eff}$ represents the effective diffusivity of water through the membrane; $\delta_{M}$ denotes the thickness of the membrane. Simultaneously, water in the anode CL can be dragged by the proton migration from the anode to the cathode, termed as electro-osmotic drag (EOD); the water flux due to EOD, $J_E$, can be expressed as:

$$J_E = D_{M}^{eff} \frac{C_{ACL}}{\delta_{M}}.$$

Where $C_{ACL}$ is the water concentration at the anode CL.

In the anode CL, the CL was fabricated in-house by the decal method [23]. The catalyst ink was prepared by the method reported elsewhere [24] and sprayed onto a Teflon blank. The cathode CL was then transferred onto the membrane by hot pressing the catalyst coated Teflon blank and the anode electrode on the two sides of the membrane at 135°C and 4.0 MPa for 3 min. Carbon supported Pt (80% Pt) from E-TEK was used as cathode catalyst to form a CL with a loading of about 2.3 mg cm⁻². The content of Nafion® in the cathode CL was maintained to be about 20 wt.%. The advantage of the decal method for preparing the cathode is that it can ensure the effect of the cathode GDL be investigated using different cathode GDLs for the same cathode CL, the same membrane and anode. To study the effect of the cathode CL, Toray-090 carbon papers treated with different PTFE content s were tested. Then the treated BLs coated with MPLs of various PTFE contents and carbon loadings were tested to study the effect of the cathode MPL on water transport and cell performance.

3.2. Single cell fixture with a reference electrode

As shown in Fig. 1, the MEA used in this work was sandwiched between an anode and a cathode current collector. Both the current collectors were made of perforated 316L stainless steel plates with an open ratio of 47.8% and a thickness of 1 mm. Unlike conventional passive DMFCs, the passive DMFC used in this work consisted of an additional 10 mm thick vapor chamber with a CO₂ venting hole of 0.01 mm², an evaporation control layer with an open ratio of 15% and a pervaporation membrane with a thickness of 28 mm. The entire cell setup was then held together between an anode fixture with a 5.0 mL fuel reservoir and a cathode fixture, both of which were made of transparent organic glass.

On the anode of the passive DMFC, neat methanol stored in the fuel reservoir is first absorbed by the pervaporation membrane, in which it evaporates into methanol vapor driven by the concentration difference between the saturated methanol vapor concentration and the methanol vapor concentration at the pervaporation membrane/evaporation control layer interface. The methanol vapor then diffuses through the evaporation control layer, the vapor chamber, the anode current collector and the anode GDL to the anode CL, where it will react with water coming from the cathode to produce CO₂, protons and electrons. While on the cathode, oxygen from the ambient is transferred by diffusion into the cathode CL to react with protons and electrons to form water.
In order to study the role of water in the neat-methanol operation, the anode overpotential and cathode overpotential were measured, respectively, with a reference electrode, which is a reversible hydrogen electrode, fed with humidified hydrogen. The reference electrode, with an active area of 1 cm², consisted of a PTFE treated carbon paper, carbon supported Pt (60% Pt) CL with a loading of 4.0 mg cm⁻², and a strip-shaped Nafion 212 membrane. For simplicity, the membrane of the reference electrode overlapped with that of the working electrode during clamping the fuel cell fixtures to ensure each experiment used the same reference electrode. This detachable reference electrode showed no obvious difference compared to the one which shared the same membrane with the working electrode [25]. In addition, to avoid the influence of lateral diffusing methanol on the reference electrode, the distance between the working electrode and the reference electrode was kept at 5 cm. With the help of the reference electrode, the anode overpotential \( \eta_a \) and the cathode overpotential \( \eta_c \) can be easily determined by [26]:

\[
\eta_a = V_{a-r} - \frac{1}{2} IR - 0.02, \\
\eta_c = 1.21 - V_{cell} - IR - \eta_a,
\]

where \( V_{cell} \) and \( V_{a-r} \) represent the cell output voltage and the voltage difference between the anode and the reference electrode, respectively; \( I \) denotes the output current; \( R \) stands for the internal resistance of the DMFC; the constants, 0.02 and 1.21, represents, respectively, the thermodynamically reversible potential of the

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**Fig. 2.** Effect of the PTFE content in the cathode BL on cell performance.

**Fig. 3.** Effect of the PTFE content in the cathode BL on transient cell voltage at 90 mA cm⁻².
MOR and the reversible open circuit voltage of the DMFC. It should be recognized that under the neat-methanol operation, as no water is supplied to the fuel reservoir, the performance of the MOR becomes dependent on water concentration in the anode CL. For a given catalyst material and structure and at the same methanol delivery rate, the anode overpotential will decrease with an increase in the water concentration in the anode CL. Hence, under such a circumstance, the anode overpotential is an indicator of the water concentration level in the anode CL.

3.3. Determination of the water loss rate to the ambient

In the above-described passive DMFC operating with neat methanol, part of the water that is produced at the cathode diffuses to the anode to compensate the MOR, while the remainder is lost to the ambient. Under a given operating condition, as the total water production rate is fixed, a higher water loss rate from the cathode means a lower rate of water transport from the cathode to the anode. In this work, in order to understand the water transport on the cell performance, the water loss rate to the ambient for a given design of the cathode GDL was measured with the procedures as follows: (i) fill up the fuel reservoir with pure DI water (no methanol), and (ii) determine the mass of the water that is lost from the cathode to the ambient by weighting the change in the mass of water in the fuel reservoir for a period of time (24 h). Although the water loss rate to the ambient determined in such a way may be different from the in-situ data, the effect of the cathode GDL design can still be reflected by the measured data.

![Diagram](image_url)

Fig. 4. Effect of the PTFE content in the cathode BL on transient anode overpotential (a) and cathode overpotential (b) at 90 mA cm$^{-2}$. 
3.4. 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 current-voltage (I-V) curves. For each discharging current point along the I-V curve, a 60 s waiting time was used to obtain the stable voltage. All the performance tests of the passive DMFC were performed at room temperatures of 23.8–24.6 °C and the relative humidity of 63–75%. Although the change in the relative humidity may influence the water transport, our experimental results showed that the water loss rate and the cell performance were insensitive to this small change in the relative humidity, but rather sensitive to the change in the cathode structure. This suggested the change in the cathode structure played a prominent role in influencing water transport. Hence, our results and conclusions presented in this work were not affected by this small difference of the ambient humidity. Prior to the performance test, the MEA was installed in an active cell fixture and activated for 24 h at 60 °C. During the activation period, 2.0 M methanol was fed at 1.0 mL min⁻¹, while dry air was supplied under atmospheric pressure at a flow rate of 100 mL min⁻¹. To ensure that the DMFC was running at neat methanol, the MEA was dried at ambient temperature for 24 h before each test to remove the water that initially existed inside the membrane.

![Graph showing the effect of PTFE content in the cathode BL on water loss rate to the ambient.](image1)

**Fig. 5.** Effect of the PTFE content in the cathode BL on water loss rate to the ambient.

![Graph showing the effect of PTFE content in the cathode MPL on cell performance.](image2)

**Fig. 6.** Effect of the PTFE content in the cathode MPL on cell performance.
4. Results and discussion

4.1. Effect of the PTFE content in the BL

The effect of the PTFE content in the BL was studied by changing the PTFE content in the BL from 0 wt.% to 30 wt.% but using the same MPL composition (2.0 mg cm\(^{-2}\) carbon loading, 30 wt.% PTFE content), the same anode and membrane. Fig. 2 shows this effect on cell performance of the passive DMFC under the neat-methanol operation. It can be seen that the cell performance increases slightly with an increase in the PTFE content in the BL and a peak power density of 16.1 mW cm\(^{-2}\) is achieved when the PTFE content in the cathode BL is 30 wt.%. In addition, the long-term discharging (at 90 mA cm\(^{-2}\)) tests of the passive DMFC with various PTFE contents shown in Fig. 3 also exhibit a trend similar to that of the I-V curves: a higher PTFE content leads to a higher cell voltage. To understand the effect of the PTFE content in the cathode BL on the cell voltage, let us look at the measured anode and cathode overpotentials shown in Fig. 4. It is seen from Fig. 4a that an increase in the PTFE content in the cathode BL leads to a decrease in the anode overpotential. This is because the increase in the PTFE content in the cathode BL increases the mass-transfer resistance of water through the cathode BL, thereby reducing the water loss rate to the ambient, as shown in Fig. 5. Under the given operating conditions, the water loss rate decreases with the PTFE content in the cathode MPL.

Fig. 7. Effect of the PTFE content in the cathode MPL on transient cell voltage at 90 mA cm\(^{-2}\).

Fig. 8. Effect of the PTFE content in the cathode MPL on water loss rate to the ambient.
condition, as the total water production rate is fixed, a lower water loss rate from the cathode means a higher rate of water transport from the cathode to the anode, which tends to reduce the water concentration loss for the anode MOR and hence reduces the anode overpotential. In addition to its effect on the anode overpotential, the PTFE content in the cathode BL can also affect the cathode overpotential as shown in Fig. 4b, which shows that the cathode overpotential increases with an increase in the PTFE content. However, as the increase in the cathode overpotential is smaller than the decrease in the anode overpotential as a result of the increased PTFE content, the resulting cell voltage increases accordingly. Since a further increase in the PTFE content in the cathode BL may result in an increase in both the internal electrical resistance and mass-transfer resistance of oxygen, a too high PTFE content (>30 wt.%) in the cathode BL may be inappropriate. In summary, in order to enhance the water transport from the cathode to the anode in the DMFC operating with neat methanol, the PTFE content in the cathode BL can be higher than the values (0–15 wt.%) in diluted methanol operating systems, but the PTFE content that is higher than 30 wt.% is not suggested.

4.2. Effect of the PTFE content in the MPL

The effect of the PTFE content in the MPL was studied by testing the MEAs with the same anode and cathode BL (with 30 wt.% PTFE) but different cathode MPLs. The PTFE content in the MPL was varied from 10 to 20, 30, and 40 wt.% while keeping the same carbon loading (2.0 mg cm\(^{-2}\)). Fig. 6 shows that the cell performance increases with an increase in the PTFE content in the cathode MPL from 10 wt.% to 30 wt.%, but it remains the same when further

![Graph showing the effect of PTFE content on anode and cathode overpotentials.]

**Fig. 9.** Effect of the PTFE content in the cathode MPL on transient anode overpotential (a) and cathode overpotential (b) at 90 mA cm\(^{-2}\).
increasing the PTFE content to 40 wt.%. The transient voltage at a constant current density (90 mA cm$^{-2}$) shown in Fig. 7 also shows the same trend with the change in the PTFE content. The causes of the above behaviors are a little complicated. First, increasing the PTFE content in the MPL not only increases the hydrophobicity level of the MPL but also reduces the porosity of the MPL; both the effects tend to increase the water transport rate from the cathode to the anode, resulting in a lower water loss rate to the ambient, as evidenced from Fig. 8. This increase in the water transport rate from the cathode to the anode reduces the water concentration loss for the MOR, thereby lowering the anode overpotential as seen from Fig. 9a. In addition, it is worth mentioning that during the fabrication process of the MPL, the formation of some macro-pores (between 2 and 20 $\mu$m), or the so-called mud cracks [27], is hard to be avoided. Further, the more the PTFE content in the MPL, the greater the tendency for the mud cracks to form. These relatively larger mud cracks will bring in short-cuts for escape of water from the cathode CL. As a consequence, increasing the PTFE content in the MPL to 40 wt.% may not further raise the water concentration at the anode CL. This is why the anode overpotentials shown in Fig. 9a are the same for the PTFE content in the MPL changing from 30 to 40 wt.%. Meanwhile, it is also noticed in Fig. 9b that the change in the cathode overpotential is relatively smaller than that of the anode overpotential, suggesting that a higher PTFE content in the cathode MPL does not severely decrease the performance of the ORR. In summary, increasing the PTFE content in the cathode MPL can improve the cell performance, but this favorable effect may be limited by the presence of the mud cracks. Accordingly,
reducing the pore size and the number of mud cracks is a key issue in enhancing the transport of water from the cathode to the anode.

4.3. Effect of the carbon loading in the MPL

In addition to the PTFE content in the MPL, the effect of the carbon loading in the MPL on the performance of the passive DMFC operating with neat methanol were investigated by changing the carbon loading from 0 to 6.0 mg cm\(^{-2}\) while keeping the same PTFE content in the MPL (30 wt.%). It is interesting to see in Fig. 10 that the cell performance improves with the introduction of a hydrophobic MPL. This behavior is also consistent with the long-term discharging tests with various carbon loadings shown in Fig. 11. The presence of a hydrophobic MPL on the BL surface can create an additional mass-transfer resistance of water such that the water loss rate to the ambient decreases, as proved by the data shown in Fig. 12. Since the total generation rate of water by ORR is fixed under a given operating condition, a decrease in the water loss rate to the ambient implies an increase in the diffusion rate of water from the cathode to the anode. As a result, the water concentration loss for the MOR at the anode is decreased, hence reducing the anode overpotential as shown in Fig. 13a. In the meantime, it can also be seen in Fig. 10 that increasing the carbon loading from 2.0 to 4.0 mg cm\(^{-2}\) leads to an improved cell performance; but a further increase in the carbon loading to 6.0 mg cm\(^{-2}\) lowers the cell performance. The intermediate loading of 4.0 mg cm\(^{-2}\) is found to be the optimal value for the cell performance with a peak power density of 17.1 mW cm\(^{-2}\). The reasons leading to these results are explained as follows. When the carbon loading is changed from 2.0 to 4.0 mg cm\(^{-2}\), the thickness of the MPL increases, which further reduces the water loss rate to the ambient as indicated in Fig. 12. As a consequence, a higher transport rate of water from the cathode to the anode can be achieved, decreasing the water concentration loss at the anode, as proved by the measured anode overpotentials shown in Fig. 13a. Therefore, the cell performance improves when increasing the carbon loading from 2.0 to 4.0 mg cm\(^{-2}\). Nevertheless, a further increase in the carbon loading in the MPL to 6.0 mg cm\(^{-2}\) results in a too thick MPL and thus a too large mass-transfer resistance of oxygen. Hence, the oxygen concentration loss for the ORR at the cathode is aggravated. This point is supported by the measured data shown in Fig. 13b, which shows that the cathode overpotential exhibited an obvious increase (about 20 mV) when the carbon loading in the MPL is increased from 4.0 to 6.0 mg cm\(^{-2}\). This increase in the cathode overpotential outweighs the reduction in the anode overpotential shown in Fig. 13a. Thus, the cell performance becomes poorer when using a 6.0 mg cm\(^{-2}\) MPL. It is worth mentioning that the change in the carbon loading in the MPL may also influence the ohmic resistance of the fuel cell, thereby affecting the cell performance. However, the change in the measured internal resistances of the DMFCs with various carbon loadings in the MPL is rather small; the internal resistances with the carbon loadings of 0 mg cm\(^{-2}\), 2 mg cm\(^{-2}\), 4 mg cm\(^{-2}\) and 6 mg cm\(^{-2}\) are, respectively, 69.7 m\(\Omega\), 63.3 m\(\Omega\), 65.1 m\(\Omega\) and 67.3 m\(\Omega\). These results suggest that the ohmic resistance has negligible effect on the change in the cell performance in the present work. In summary, in general increasing the carbon loading in the MPL can reduce the anode water concentration loss, but the carbon loading should not be too high to avoid severely increasing the cathode oxygen concentration loss.

5. Conclusions

The success in the neat-methanol operation of DMFCs requires the water that is produced at the cathode to diffuse to the anode through the membrane to compensate the MOR. Hence, the anode performance of this type of fuel cell can be limited by the water transport rate from the cathode to the anode and the water concentration level at the anode CL, which depends primarily on the design of the cathode GDL. This work presents an experimental investigation of the effect of the cathode GDL on cell performance and respective overpotential at the anode and the cathode for a passive DMFC operating with neat methanol. The salient findings for the optimal design of passive DMFCs operating with neat methanol are summarized as follows:

(1) The cell performance increases slightly with the PTFE content in the cathode BL due to a reduction in the anode overpotential. Therefore, in order to enhance the cell performance, it is necessary to optimize the PTFE content in the cathode BL.
performance, the cathode BL in the DMFC should be treated with a higher PTFE content.

(2) Increasing the PTFE content in the MPL can improve the cell performance by facilitating the buildup of water within the MEA so that the anode overpotential can be reduced. However, this effect is limited by the presence of the mud-cracks, which reduces the mass-transfer resistance of water and thus the water concentration level in the anode CL.

(3) The presence of a hydrophobic MPL can notably upgrade the cell performance as a result of the decreased water concentration loss at the anode. However, a too high carbon loading will result in a too thick MPL, rendering an unfavorably large mass-transfer resistance of the oxygen and thus lowering the cell performance. In addition, the 4.0 mg cm\(^{-2}\) carbon loading in the MPL is found to be the optimal value to achieve the best cell performance.

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References


