Int. J. Electrochem. Sci., 10 **(2015)** 2939 - 2949

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Investigation of Methanol Crossover and Water Flux in an Air-Breathing Direct Methanol Fuel Cell

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Received: 29 December 2014 / *Accepted:* 31 January 2015 / *Published:* 24 February 2015

An air-breathing direct methanol fuel cell (DMFC) is constructed to investigate methanol crossover and water flux by altering flow rate and concentration of methanol solution. The limiting methanol permeation current density through the anode and membrane is measured voltammetrically, which is sensitive to the flow rate and concentration of methanol solution. The performance variation trends are explained by quantitative analysis of water sources at the cathode. Water diffusion from anode along with methanol crossover plays major contribution to water flooding at the cathode, which decreases the air-breathing DMFC performance. The permeated methanol at the cathode places an extra demand for oxygen, and the optimum methanol solution concentration is largely dependent on the required current density and air flow rate.

Keywords: air-breathing direct methanol fuel cell, cathode, methanol crossover, water flux, water flooding

1. INTRODUCTION

Direct methanol fuel cell (DMFC) has been attracting much attention as a promising portable power sources due to the advantages of high theoretical energy density of methanol and simplicity of system architecture[1-4]. Some air-breathing DMFC devices for powering mobile phone, toy car, etc. have been successfully demonstrated, which eliminates the need of some auxiliary components such as gas compressors or fans and reduces the weight and size of fuel cell system[3,5-9]. In air-breathing mode, methanol crossover and water flux at the cathode is serious because air diffuses slowly into the electrode, resulting in a great challenge for obtaining a high DMFC performance.

In order to decrease the amount of methanol crossover, especially in high methanol concentrations, many approaches, such as increasing the thickness of electrolyte membrane and optimizing the structure of gas diffusion electrode, have been investigated[2,8,10-14]. Liu et al. and Kho et al. found that the exothermic reaction between permeated methanol and oxygen at the cathode increased the cell temperature and decreased open circuit voltage (OCV) in an air-breathing DMFC[11,12]. Yuan et al. used a porous metal fiber sintered felt as the anodic methanol barrier to decrease the amount of methanol crossover[15]. In addition, water management at the cathode is also critical to the performance of air-breathing DMFC[13,14,16-20]. Wang et al. designed a capillary-based cathode for air breathing DMFC using micro fabrication techniques. The surface of capillary treated by low temperature oxygen plasma improved the hydrophilic properties, which is better for removing water at the cathode[17]. Cathode catalyst layer with stepwise hydrophobicity distribution was investigated by Chen et al. This treatment was beneficial to water removal from the catalyst layer and oxygen diffusion toward the catalyst surface, increasing cell performance and stability[18].

Most of the studies are focused on improving the air-breathing DMFC performance by optimizing the membrane electrode assembly structure and investigating the effect of methanol crossover or water at the cathode on the performance separately. However, it is essential to comprehensively understand the correlation of methanol crossover and water at the cathode along with the effect of them on the air-breathing DMFC performance, which would minimize the adverse effect brought by methanol permeability and flooding problems. In this work, an air-breathing DMFC was constructed to comprehensively investigate methanol crossover and water flux by altering flow rate and concentration of methanol solution. Water diffusion from the anode along with methanol crossover played major contribution to water flooding at the cathode. The optimum methanol solution concentration was largely dependent on the required current density and air flow rate.

2. EXPERIMENTAL

2.1 Preparation of membrane & electrode assembly

10 wt.% and 30 wt.% PTFE wet-proofed SGL carbon papers (0.19 mm thick, SGL Carbon Group, Short Hills, NJ) were employed as the anode and cathode backing layers. To prepare the anode microporous layer, Vulcan XC-72 carbon black was dispersed into a water/alcohol solution along with 5 wt.% Nafion® solution and the mixture was then spread onto the anode backing layer. To prepare the cathode microporous layer, 10 wt.% PTFE solution was mixed with Vulcan XC-72 carbon black in a water/alcohol solution and the mixture was spread onto the cathode backing layer. The dry weight percent of Nafion® ionomer in the anode diffusion layer and PTFE in the cathode diffusion layer was about 10 wt.% and 20 wt.%, respectively.

Catalyst-coated membrane (CCM) was fabricated by using the modified decal method[21] originally developed by Wilson and Gottesfeld[22]. The catalyst was mixed into a water/alcohol solution along with a 5 wt.% Nafion® solution (Dupont) and the resulting mixture was ultrasonically agitated with vigorous mechanical stirring to form a homogeneous ink. The ink was then uniformly sprayed onto a piece of PTFE decal blank and then drying at room temperature. The resulting Pt-Ru (Johnson Matthey Corp.) loading was 3.3±0.1 mg cm^{-2} and the Nafion® content was 15 wt.% in the anode catalyst layer, while the Pt loading was 3.3±0.1 mg cm^{-2} and the Nafion® content was 10 wt.% in the cathode catalyst layer. The decal blanks containing anode and cathode catalyst layers were placed to two sides of the pretreated Nafion® 115 membrane in the Na$^+$ form and hot-pressed at 190 ^{o}C and 30 atm for 1.5 min. Then the decal blank was removed, the prepared CCM was re-protonated to the H$^+$ form in 0.5 mol L^{-1} sulfuric acid at 80 ^{o}C for at least one hour, followed by rinsing in deionized water. Finally, anode and cathode diffusion layers (2 cm×2 cm) were placed onto the corresponding sides of the CCM to form the MEA by hot-pressing at 140 ^{o}C and 30 atm for 1 min.

2.2 Single cell test and methanol crossover measurements

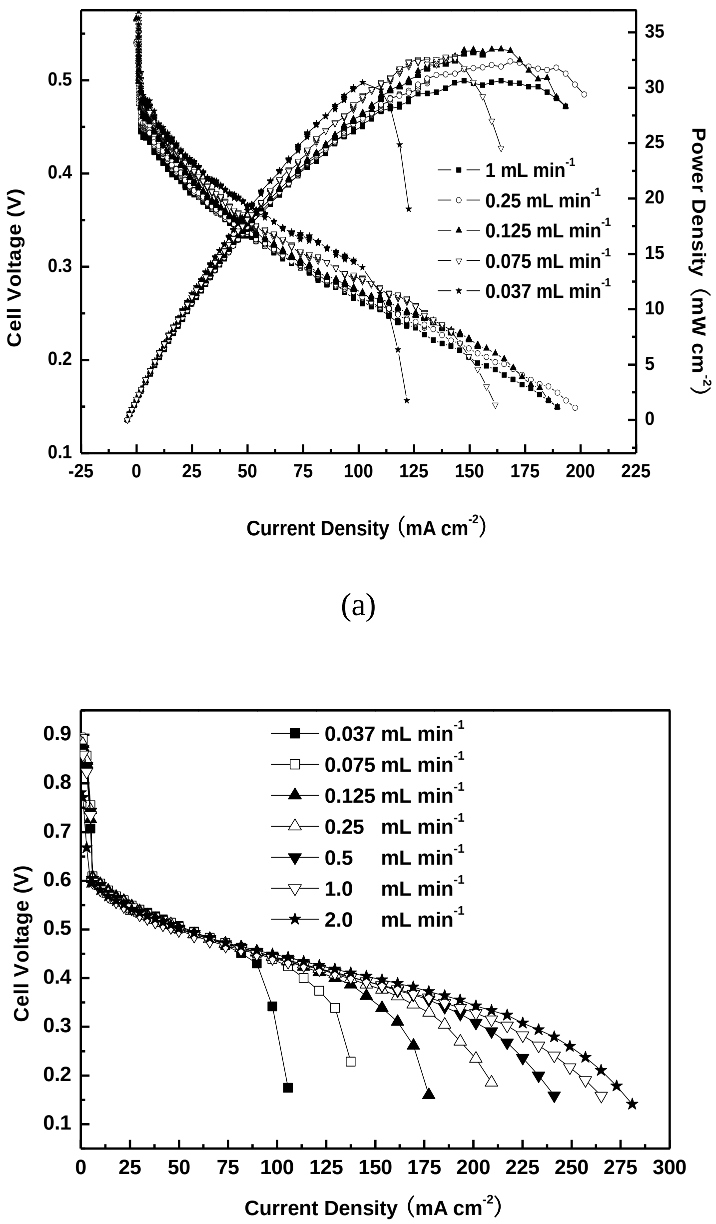
In the air-breathing DMFC mode, the MEA was fitted between anode and cathode stainless steel plates as shown in Fig. 1. The anode plate had a punctual flow bed to distribute methanol solution uniformly and to disperse the reaction products. The cathode plate had a series of 3 mm diameter holes to offer the passage of ambient air. In addition, there was a heating unit and a thermal couple at the anode. Based on this design, the cell temperature can be controlled precisely and conveniently, avoiding it varying due to the exothermic reaction between permeated methanol and oxygen at the cathode. In all the experiments, the cell temperature was controlled at 40 ^{o}C. Methanol solution was pumped through the DMFC anode at precisely controlled rate using a high pressure constant flow pump (Dalian Elite Analytical Instruments Co., Ltd.). The polarization curves were obtained using a Fuel Cell Test System (Arbin Instrument Corp.) under different operation conditions. For comparison, the performance of an active air-forced DMFC was also measured and the flow rate of atmosphere air was regulated by a mass flow controller in the Fuel Cell Test System with an error of 0.2 % between 10 mL min^{-1} and 500 mL min^{-1}. In the active air-forced DMFC mode and electrochemical measurements, the MEA was sandwiched between two stainless steel plates with the same structure as shown Fig. 1a. The methanol crossover rate at open circuit was determined electrochemically at a scan rate of 2 mV s^{-1} by measuring limiting oxidation current of methanol at the cathode in the presence of humidified nitrogen.

(a) (b)

Figure 1. The configurations of anode (a) and cathode (b) plates of the air-breathing DMFC.

3. RESULTS AND DISCUSSION

3.1 Effect of methanol solution flow rate



(a)

(b)

Figure 2. Comparison of DMFC performances in air-breathing mode (a) and active mode (b) with different flow rates of 1 mol L^{-1} methanol solution.

Fig. 2 (a) shows that the polarization curves at different flow rates of 1.0 mol L^{-1} methanol solution. It can be seen that the mass transfer limitation was obvious only at 0.037 and 0.075 mL min^{-1}. It is probably caused by a short supply of methanol and block of CO_2 ejection. At the flow rate of 0.125 mL min^{-1}, air-breathing DMFC shows the highest performance. When the flow rate increases further, DMFC performance begins to decrease because the amount of methanol crossover increases with the flow rate of methanol solution. When the cathode was fed with 240 mL min^{-1} of oxygen in the active mode, DMFC performance increases with the flow rate of methanol solution due to sufficient supply of oxygen for oxygen reduction reaction and methanol oxidation reaction at the cathode as shown in Fig. 2 (b). Thus the optimum flow rate of methanol solution on DMFC performance is dependent on the flow rate of oxygen at the cathode.

The measurement of limiting methanol crossover current density ($J_{crossover}$) at open circuit was performed as described by Ren and Gottefeld[23], methanol electro-oxidation process occurred at the Pt catalyst layer and hydrogen evolution at the PtRu catalyst layer as the counter electrode. The electrochemical reactions are as follows:

The Pt catalyst layer: $CH_3OH + H_2O - 6e^- \rightarrow CO_2 + 6H^+$

The PtRu catalyst layer: $6H^+ + 6e^- \rightarrow 3H_2$

As shown in Fig. 3, the limiting current density of permeated methanol at different flow rates of methanol solution is compared. It can be observed that the permeated methanol increases with the flow rate of methanol solution (< 1.0 mL min^{-1}), while the amount of methanol crossover does not change when the flow rate is larger than 1.0 mL min^{-1}. It was interesting to observe that the open circuit voltage (OCV) increased quickly from about 0.2 V to 0.6 V by drying the severely flooded cathode during the activation process. In addition, during the activation process and I-V curve test, liquid water was found to flow out of the cathode, which is similar to the reported phenomena[13,24]. The liquid water hindered the air diffusion into the cathode and affected the fuel cell performance[18,24]. As shown in Fig. 4, water at the cathode is contributed from four ways[13]: (1) water flux across the membrane from anode by diffusion, (2) water flux by electro-osmosis, (3) water produced by oxygen reduction reaction, (4) water produced by methanol oxidation reaction with oxygen. Water diffuses through the membrane along with methanol from the anode. The composition of the fluid within the membrane is nearly identical with that of the equilibrating solution[23]. So the amount of water diffusing from the anode to the cathode is also nearly proportional to the amount of methanol crossover in the methanol solution at the anode. Assuming that methanol solution concentration in the membrane remains 1.0 mol L^{-1}, the amount of water flux at the cathode by diffusion can be calculated as follows:

$$D_{H_2O} = \frac{\frac{x_{H_2O}}{x_{CH_3OH}} \times J_{crossover}}{6F} \qquad (1);$$

where x_{H_2O} is the molar fraction of water and x_{CH_3OH} is the molar fraction of methanol in the methanol solution, respectively, The ratio between x_{H_2O} and x_{CH_3OH} in 1 mol L^{-1} methanol solution is 53.31; *F* is Faraday's constant, 96485 C mol^{-1}.

On the other hand, assuming that the methanol permeating from the anode is completely oxidized to CO_2 at the cathode, water flux produced by the reaction of methanol and oxygen is calculated by:

$$R_{H_2O} = \frac{J_{crossover}}{3F} \qquad (2);$$

Thus, the water flux by diffusion of water and produced by oxidation of methanol from the anode at open circuit can be calculated by:

$$N_{cross} = D_{H_2O} + R_{H_2O} = \frac{55.31 \times J_{crossover}}{6F} \qquad (3)\ ;$$

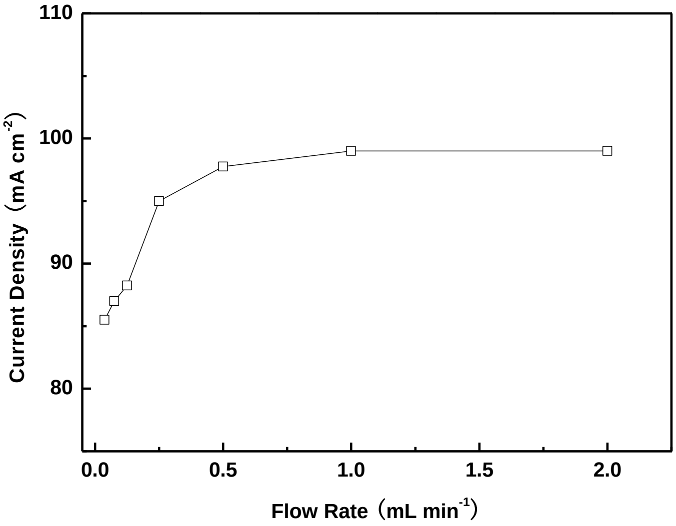


Figure 3. Comparison of the limiting current density for methanol crossover with different flow rates of 1 mol L^{-1} methanol solution.

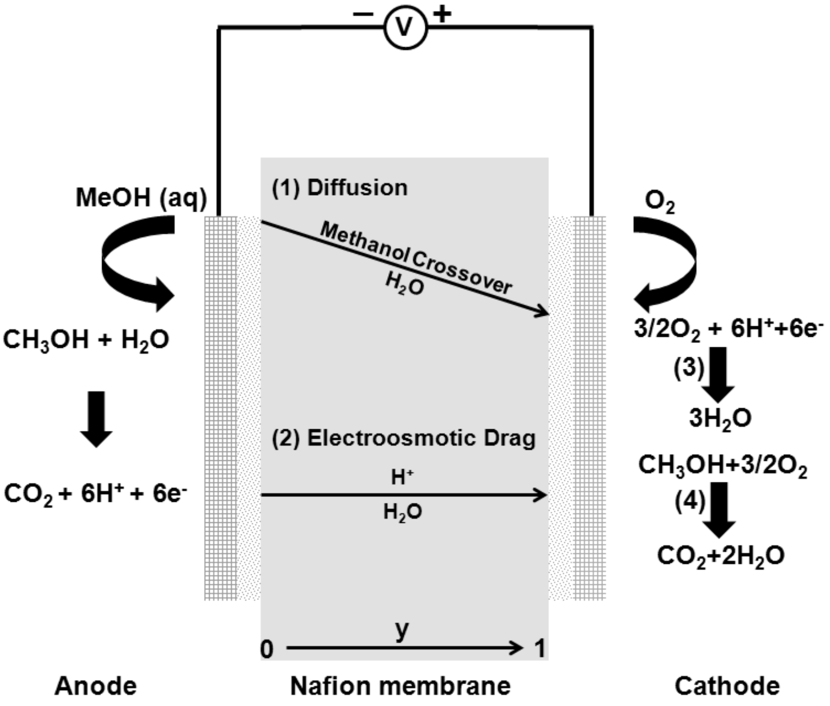


Figure 4. Diagram of water sources at the DMFC cathode.

In addition, the water flux produced by oxygen reduction reaction at the cathode can be calculated by the formula:

$$R'_{H_2O} = \frac{i_{cell}}{2F} \qquad (4)\ ;$$

where i_{cell} is the DMFC current density，mA cm^{-2}.

And the water flux through the membrane by electro-osmotic drag is calculated by the following formula:

$$D'_{water} = n_{H_2O/H^+} \frac{i_{cell}}{F} \qquad (5);$$

In Eq. 5, n_{H_2O/H^+} is the electro-osmotic drag coefficient. According to the reference[25], n_{H_2O/H^+} is 2.5 at 40 ^{o}C.

It can be seen that water produced by electro-osmotic drag is much more than that by oxygen reduction reaction, which is 4 times over the latter. Then the water flux produced by oxygen reduction reaction and electro-osmotic drag can be calculated by:

$$N_j = R'_{H_2O} + D'_{H_2O} = \frac{3 \times i_{cell}}{F} \qquad (6);$$

Fig. 5 shows that the calculated value of N_{cross} at different flow rates of methanol solution. In addition, the value of N_j was calculated and also shown in Fig. 5 according to the cell current density of 25, 50, 100 and 150 mA cm^{-2}, respectively. It can be observed that N_{cross} is much larger than N_j at different flow rates of methanol solution, suggesting that water and methanol diffusion played major contribution to cathode flooding. This result agrees with the numerical calculations based on a two-dimensional two-phase mass transport model[26]. N_{cross} at open circuit increases with the flow rate of methanol solution, especially smaller than 0.5 mL min^{-1}. While there is no obvious change for N_j at different flow rates of methanol solution. It can be concluded that water flux at the cathode mainly comes from water transport caused by methanol crossover at low flow rates (<0.5 mL min^{-1}) and becomes more serious with increasing the flow rate of methanol solution. It is different from the result by Ren et al. on the active DMFC[25]. In our experiments, the DMFC was operated at 40 ^{o}C in the air-breathing mode, the electro-osmotic drag coefficient and current density were relatively low, so N_{cross} is relatively larger than N_j at atmosphere pressure.

It can also been observed that N_j increases with the cell current density, indicating that water produced by oxygen reduction reaction and electro-osmotic drag increases with current density, resulting in water flooding and oxygen insufficiency in the cathode. Therefore, the combined effects of excessive methanol crossover and water transport through the membrane and oxygen insufficiency at high current density account for the difference of polarization curves in Fig. 2 (a). When the flow rate of methanol solution is lower than 0.125 mL min^{-1}, the cell performance is higher in active and ohmic polarization region. When the flow rate increases further, the effect of water and methanol crossover inhibits the improvement of cell performance[11,13]. The maximum cell performance was reached at the flow rate of 0.125 mL min^{-1}.

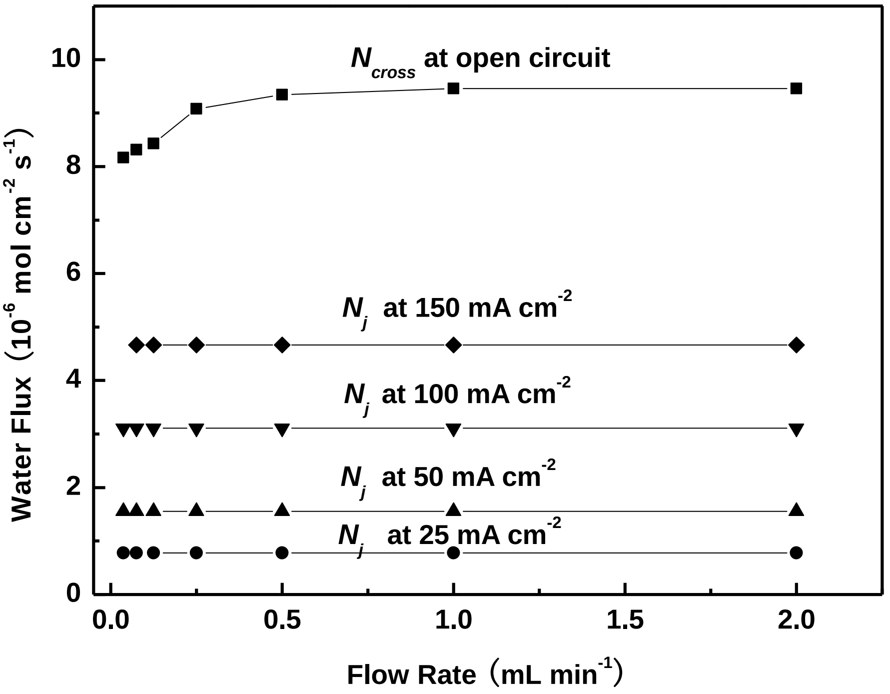
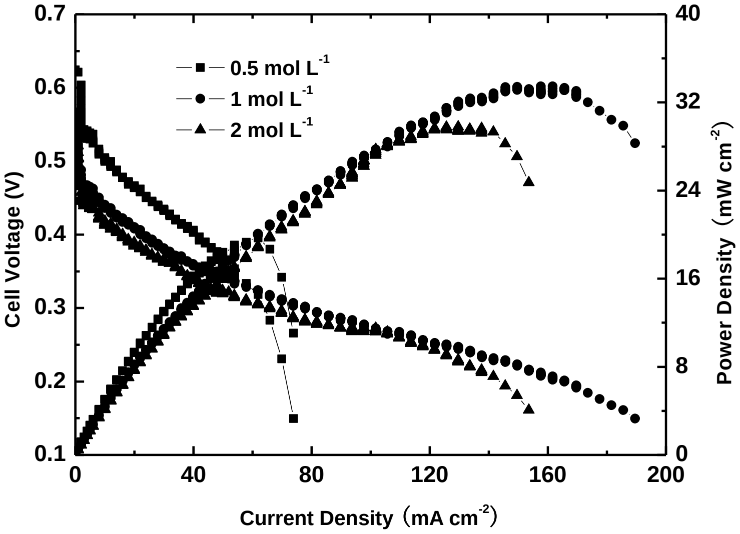


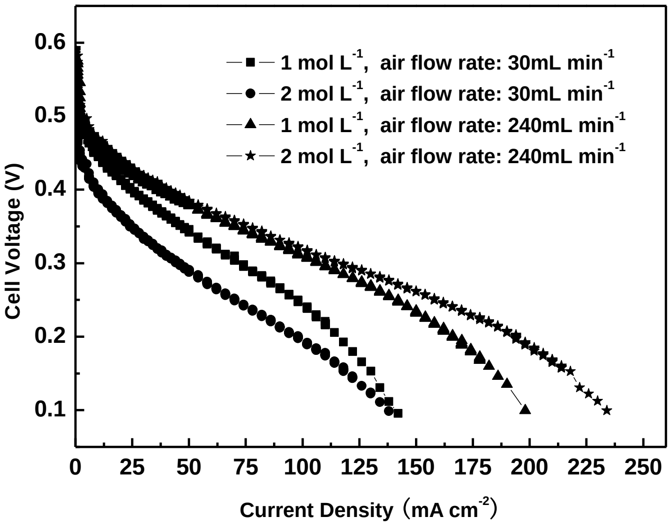
Figure 5. Comparison of water flux (N_{cross} and N_j) at different flow rates of 1 mol L^{-1} methanol solution .

3.2 Effect of methanol concentration

The performances of air-breathing DMFC fed with 0.5, 1.0 and 2.0 mol L^{-1} methanol solution are shown in Fig. 6 (a). At current density smaller than 58 mA cm^{-2}, the cell voltage sequence is 0.5 >1.0 >2.0 mol L^{-1}. However, at current density greater than 70 mA cm^{-2}, the cell voltage sequence is 1.0 >2.0 >0.5 mol L^{-1}. So the optimum methanol concentration should be correlated with the required current density[11]. In addition, the performance of air-breathing DMFC fed with 1.0 mol L^{-1} methanol solution is always higher than that of DMFC fed with 2.0 mol L^{-1} methanol solution. The mass transfer limitation occurs at 0.5 mol L^{-1} methanol. While for 2.0 mol L^{-1} methanol, the performance decreases mainly due to water flooding at the cathode, inhibiting air diffusion to the catalyst surface[11,13,24]. As shown in Fig. 7 (a), the limiting current density of methanol at the cathode increases with methanol solution concentration. N_{cross} increases with the same trend, indicating that water flooding is more serious than that at 1.0 and 0.5 mol L^{-1}. It can be seen from Fig. 7 that water diffusion from the anode along with methanol crossover (N_{cross}) is much more than water produced by cathodic oxygen reduction reaction and electro-osmotic drag (N_j).



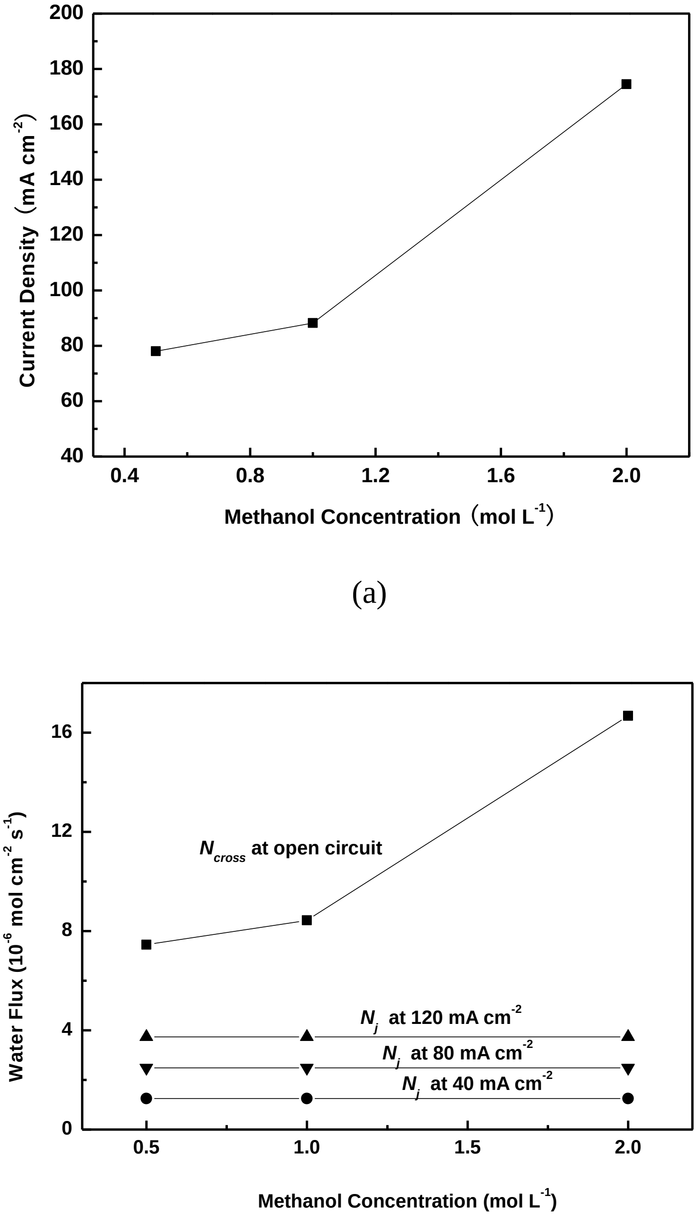
(a)



(b)

Figure 6. The performances of air-breathing DMFC (a) and active DMFC (b) fed with different concentrations of methanol solution at 0.125 mL min^{-1}.

By testing the performances of the same MEA in active air-forced DMFC mode with different methanol concentrations and air flow rates, the polarization curves were obtained and shown in Fig. 6 (b). At the air flow rate of 30 mL min^{-1}, the performance of DMFC fed with 1.0 mol L^{-1} methanol solution was greater than that of DMFC fed with 2.0 mol L^{-1} methanol solution. However, when the air flow rate increases from 30 to 240 mL min^{-1}, the performance of DMFC fed with 2.0 mol L^{-1} methanol solution is higher than that of DMFC fed with 1.0 mol L^{-1} methanol solution at current density greater than 125 mA cm^{-2}. Therefore, in the air-breathing mode, the air flow rate through the cathode is limited [11,13], and the performance is poor when fed with 2.0 mol L^{-1} of methanol concentration.



(a)

(b)

Figure 7. Comparison of cathodic methanol crossover current density (a) and water flux (N_{cross} and N_j) (b) with different concentrations of methanol solution.

4. CONCLUSIONS

An air-breathing DMFC was constructed to investigate methanol crossover and water flux by altering flow rate and concentration of methanol solution. The amount of methanol crossover and water flux is quantitatively measured and calculated by linear sweeping voltammetry. The amount of water flux through Nafion membrane is much higher than that produced by oxygen reduction reaction. The amount of methanol crossover increases with concentration of methanol solution, consuming more oxygen at the cathode. The optimum flow rate and concentration of methanol solution was largely dependent on the required current density and air flow rate.

ACKNOWLEDGEMENTS
This study was financially supported by the project of National Scientific Fund of China (Grant No. 21403023) and Specialized Research Fund for the Doctoral Program of Higher Education of China (Grant No. 20122124120004).

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