

Real time measurements of methanol crossover in a DMFC

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Abstract

Methanol crossover is a serious problem in a direct methanol fuel cell (DMFC), which causes significant voltage loss and waste of fuel. Due to methanol crossover, most DMFCs must operate on a fuel with a very low methanol concentration; yet very low methanol concentration also causes a poor cell performance. Thus, it is very important to find the optimal operating conditions of methanol concentration and other operating parameters. In this research, methanol crossover rate in a DMFC is determined by measuring the carbon dioxide concentration at the cathode exit in real time. By measuring methanol crossover and cell performances at different inlet methanol concentrations and various operating conditions three types of characteristics are identified in the relationships between methanol crossover and cell current density. Further analysis of these relationships between methanol crossover and cell performances reveals the optimal methanol concentration and other operating parameters, at which the cell reaches optimal performance without incurring excessive methanol crossover. Furthermore, transient peaks of methanol crossover have been identified when the cell voltage suddenly changes. Analyses of these peaks show that they are caused by the hysteresis of methanol concentration at the interface between the anode catalyst layer and the membrane.

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1. Introduction

Direct methanol fuel cell (DMFC) is a promising energy conversion device for the future. However, methanol crossover from the anode to the cathode is a very serious problem that severely reduces the cell voltage, current density, fuel utilization and hence the cell performance. Since methanol can be dissolved into water to any degree and the commonly used solid polymer electrolyte, Nafion[®], readily absorbs water as well as methanol, methanol crossover is thus unavoidable with the current DMFC technology. Several methods have been invented or proposed to reduce methanol crossover in DMFCs, such as adding ZrO₂ to the membrane [1], using a PTFE improved Nafion[®] as the electrolyte membrane [2], adding a thin layer of palladium [3,4], etc. All these methods are capable of reducing methanol crossover to a certain extent, but none can prevent methanol crossover and all of these methods also increase the impedance for proton transport through the membrane. The transfer of proton inside the Nafion[®] electrolyte membrane depends on the water content

inside the membrane [5–7]. Understanding on the relationship between methanol crossover and cell operation conditions is very important in identifying optimal cell operating conditions.

Several methods have been used to measure methanol crossover in DMFCs and some of them are: (1) mass spectroscopy method [8,9]; (2) gas chromatography method [10,11]; (3) gas analyzer method [12]; (4) CO₂ detection method by using a carbon dioxide sensor [13,14]. All these methods detect the amounts of methanol crossover to the cathode by measuring all or part of CH₃OH, CO₂, CO contents in the cathode exhaust. Most of the methanol crossing over to the cathode reacts with oxygen and turns into carbon dioxide. The methods based on mass spectroscopy and gas chromatographies can measure precisely the amount of CH₃OH, CO₂, CO, etc. at the cathode exit, but generally they are expensive, time consuming and not in real time.

Many operating conditions affect the process of methanol crossover, such as cell temperature, anode methanol concentration, air humidification temperature, methanol feeding flow rates, and so on. Experimental studies on the cell performance and methanol crossover under different operating conditions can help to find the optimum operating conditions for a DMFC without excessive methanol crossover. Wang et al. [9] found

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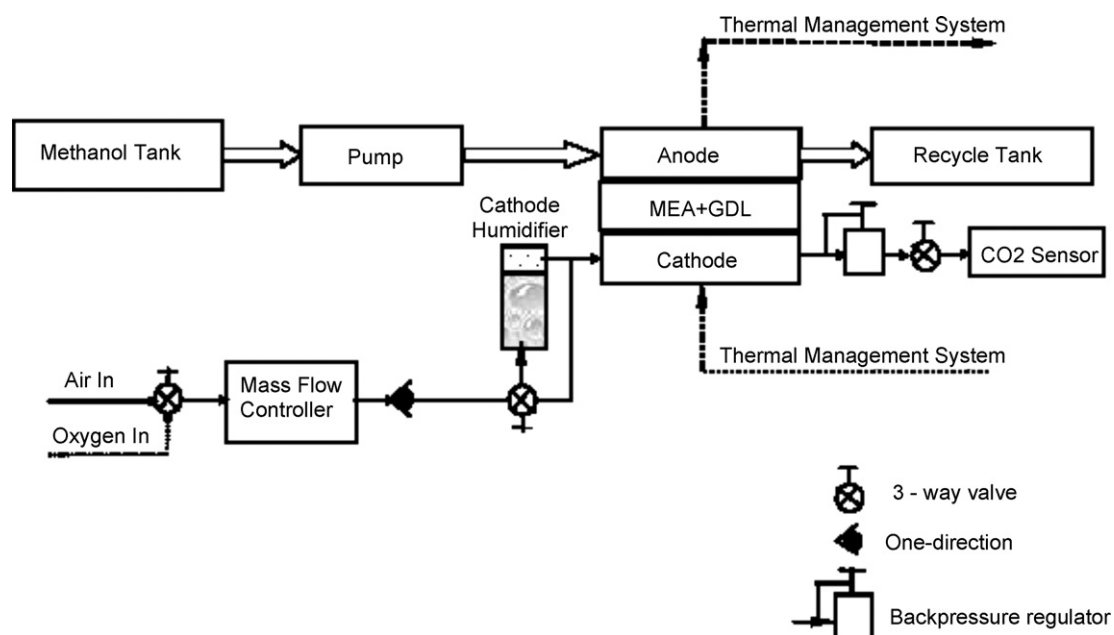


Fig. 1. Schematic of the experimental system.

that most of the methanol crossing over reacts to form CO_2 at the cathode with the platinum of the cathode acting as a heterogeneous catalyst. They also found that cathode open-circuit potential is inversely proportional to the amount of CO_2 formed and the poison effects on cathode catalyst. Schaffer et al. [10] developed an improved gas chromatographic method to study methanol crossover in a DMFC and this method was used to study methanol diffusion and drag coefficient in a DMFC and show good correspondence with literature values. Hikita et al. [12] studied the methanol crossover and DMFC performance with different thickness of electrolyte membranes and different concentration of methanol solution. Thimas [14] reported cell performance, fuel utilization, and overall conversion efficiency of a DMFC using a carbon dioxide sensor to measure the amount of methanol crossover.

Systematic and real-time studies of the relationship between the cell operating conditions and methanol crossover are very limited, but yet they are very important in understanding the effects of methanol crossover and in searching for the optimal operating conditions. In this research, a series of experiments on the performance of a DMFC and corresponding methanol crossover have been conducted under different operating conditions. The carbon dioxide detection method is used to measure methanol crossover in a DMFC. Because the carbon dioxide penetration from the anode to the cathode is normally neglected [14], and the amount of the methanol un-reacted into carbon dioxide only consists of a few percent of the total amount of methanol crossover to the cathode side [15], the method of using a carbon dioxide sensor to detect the amount of methanol crossover is accurate enough. Besides, it is very convenient and is capable of monitoring the amount of methanol crossover continuously and in real time. Furthermore, transient characteristics of methanol crossover when the cell voltage suddenly changes have also been studied.

2. Experiments

The experimental system is schematically shown in Fig. 1. The fuel cell test station was manufactured by Fuel Cell Technology Inc. A major component of the test station is the HP[®] 6050A system DC electronic load controller, which is capable of controlling the electrical load on the fuel cell as well as measuring its voltage versus current responses. This experimental system also provides control over anode and cathode flow rates, cell operating temperature, operating pressure, and humidification temperature for the cathode. The cathode mass flow rate is controlled and measured by a MKS[®] mass flow controller, and the anode flow rate is controlled and measured by a peristaltic pump by Gilson Inc.

The experimental fuel cell consists of two 316 stainless steel end plates, two graphite collector plates with machined serpentine flow fields, two carbon cloth diffusion layers, two catalyst layers, and an electrolyte polymer membrane. The cell was kept at a constant temperature through the thermal management system during each experiment. The membrane used was Nafion[®] 117, the gas diffusion layers were carbon cloth, the catalysts were Pt-Ru on the anode side with a loading of 4 mg cm^{-2} and Pt on the cathode side with a loading of 4 mg cm^{-2} . The total active area of the cell was 50 cm^2 . The carbon dioxide sensor used in this test was GMP221 Carbon dioxide probe from Vaisala Oyj, Finland.

The overall anode reaction in a DMFC is,



The main reaction occurs on the cathode side is,



Methanol crossover from the anode to the cathode is caused by the driving forces of concentration gradient, pressure gradient and electro-osmosis [14],

$$Q = \frac{D\Delta c}{t} + \frac{c_2 K \Delta P}{t} + \frac{\lambda_m}{nF} I \quad (3)$$

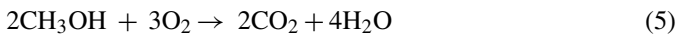
where the first term is due to concentration gradient, second term pressure gradient, and the third term electro-osmosis.

In Eq. (3), D , the effective diffusivity of methanol in the membrane; t , the thickness of the membrane; Δc , the difference in methanol concentration across the membrane; c_2 , methanol concentration at the interface between the anode catalyst layer and the Nafion[®] polymer membrane; K , a constant related to the effective hydraulic permeability; λ_m , methanol electro-osmotic drag coefficient, $\lambda_m = X_{c|ac/m} \lambda_w$; λ_w , number of water molecules dragged by each proton; $X_{c|ac/m}$, the methanol mole fraction at the interface between the anode catalyst layer and the membrane.

When the methanol concentration is low, the following formulation can be used to calculate the methanol mole fraction at the above-mentioned interface, where the methanol density is taken to be $794.44921 \text{ kg m}^{-3}$.

$$X_{c|ac/m} = \frac{c_2}{18\{1000 - (c_2 \times 32 \times 1000)794.44921\}} \quad (4)$$

When methanol reaches the cathode side, most reacts with oxygen and turns into CO_2 , and only a very small amount becomes the intermediate products CH_xO_y and CO [15].



The exhaust of the cathode may include O_2 , $\text{CH}_3\text{OH}(v)$ - vapor methanol, $\text{CH}_3\text{OH}(l)$ - liquid methanol, $\text{H}_2\text{O}(l)$ - liquid water, $\text{H}_2\text{O}(v)$ - water vapor, CO_2 , CO , and CH_xO_y . The amount of methanol that turns into CH_xO_y and CO is negligible [12]. The concentration of water vapor is a constant for each experiment since the temperature is held constant and the cathode exhaust is saturated.

3. Results and discussions

3.1. Steady state results

In the steady state experiments, in order to eliminate possible transient effects, a series of test with different delay time have been conducted and the results are shown in Fig. 2. The delay time is the time period between the point when the cell operating conditions are changed to the point when data are collected. The cathode flow rate was 600 sccm and the same flow rate was used in all the following steady-state experiments. From Fig. 2, it is clear that 120 s delay time is more than enough to obtain accurate results, and 120 s delay time was used in all the following steady state experiments.

The methanol crossover flux per active area is determined from,

$$N_m = \frac{Q X_{\text{CO}_2}}{6 \times 10^{-4} v A} \quad (6)$$

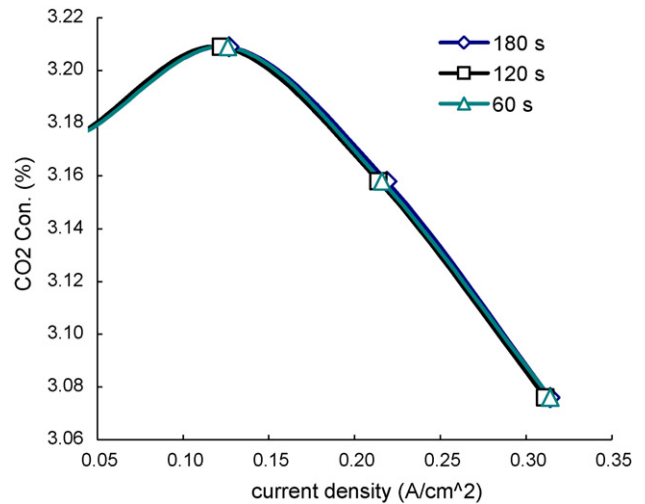


Fig. 2. Experimental results with different delay time. Cell temperature, 70°C ; no cathode humidification; methanol concentration 1 M; methanol flow rate, 6 ml min^{-1} ; oxygen flow rate, 600 sccm; cell active area, 50 cm^2 ; cathode loading, Pt-Ru 4 mg cm^{-2} ; anode loading Pt, 4 mg cm^{-2} .

where N_m , methanol mole flux ($\text{mmol cm}^{-2} \text{ min}^{-1}$), A , cell active area (cm^2), Q , cathode flow rate $Q = Q_{\text{O}_2} + Q_{\text{CO}_2} + Q_{\text{H}_2\text{O}}$ (sccm), X_{CO_2} , carbon dioxide mole fraction at the cathode exit, Q_{O_2} , oxygen flow rate (sccm), Q_{CO_2} , carbon dioxide flow rate (sccm), $Q_{\text{H}_2\text{O}}$, water vapor flow rate (sccm), v , gas molar specific volume. $v = RT/P$, where P is pressure and R is gas constant, T is the temperature in K at the sensor position.

3.1.1. The temperature effects

A group of experiments have been carried out to study the effects of operating temperature on the cell performance and methanol crossover. The cell operating conditions are listed as follows: the methanol concentration is 1 M and the feeding flow rate is 6 ml min^{-1} ; the cathode reactant is oxygen and feeding flow rate is 600 sccm. The experimental results for cell temperature ranges from 30 to 80°C are shown in Figs. 3 and 4.

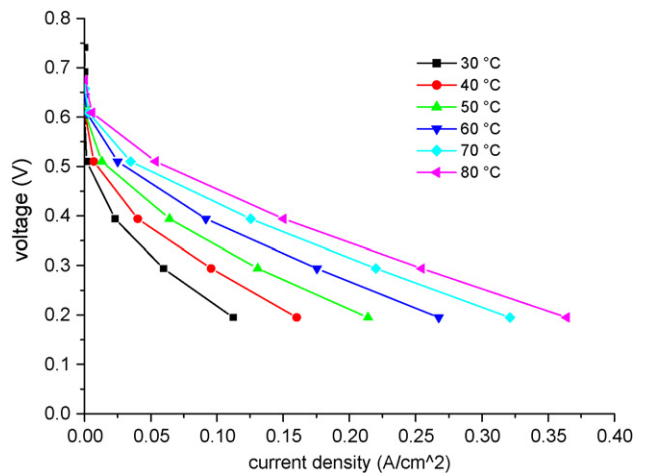


Fig. 3. Polarization curves at different cell temperature. No cathode humidification; methanol concentration 1 M; methanol flow rate, 6 ml min^{-1} ; oxygen flow rate, 600 sccm.

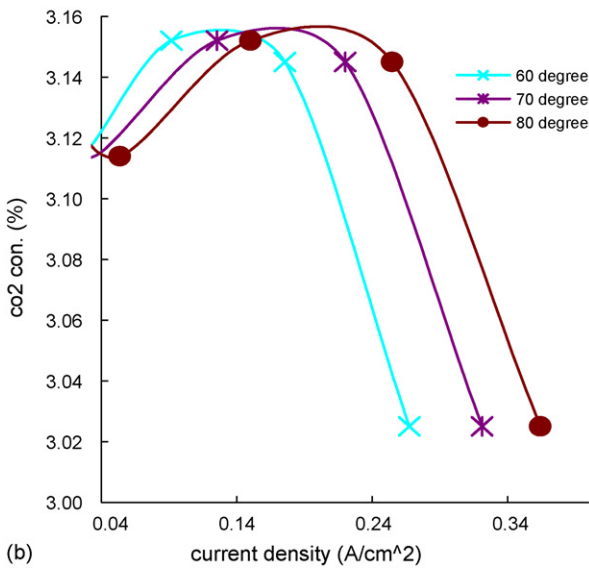
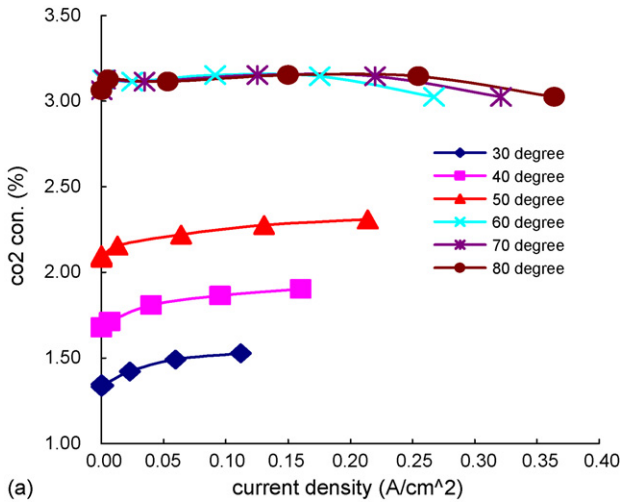


Fig. 4. (a) Methanol crossover rate at different cell temperatures. No cathode humidification; methanol concentration 1 M; methanol flow rate, 6 ml min⁻¹; oxygen flow rate, 600 sccm. (b) Methanol crossover rate at different cell temperatures. Same as “a” with a different scale. No cathode humidification; methanol concentration 1 M; methanol flow rate, 6 ml min⁻¹; oxygen flow rate, 600 sccm.

Figs. 3 and 4 show that the performance of the fuel cell increases with the increase in the cell temperature. The methanol crossover rate to the cathode also increases with the increase of the cell temperature. If the cell temperature is below 60 °C, the methanol crossover rate increases with the increase in the cell current density. For cell temperature over 60 °C, methanol crossover rate versus current density curve is convex: it increases with the increase in the cell current density at the low current density region, reaches a maximum point at certain cell current density, and then decreases as the cell current density further increases. This parabolic characteristic of methanol crossover curve agrees well with the modeling predications by Ge and Liu [16]. It is due to the fact that methanol crossover is a combination of diffusion part $-D\Delta c/t$ and proton drag part $(\lambda_m/nF)I$ (the permeation caused by the pressure difference is negligible

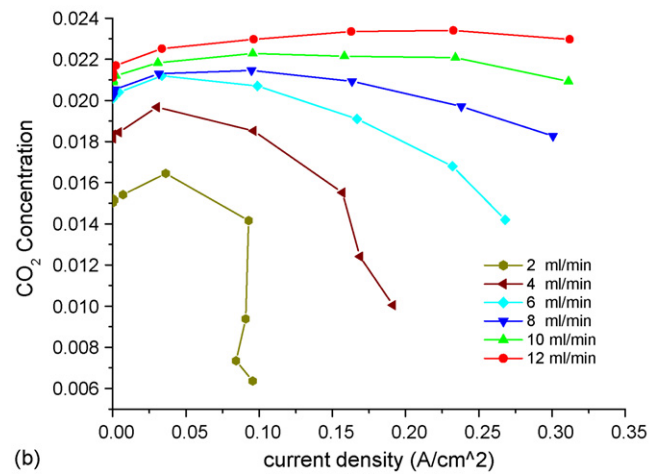
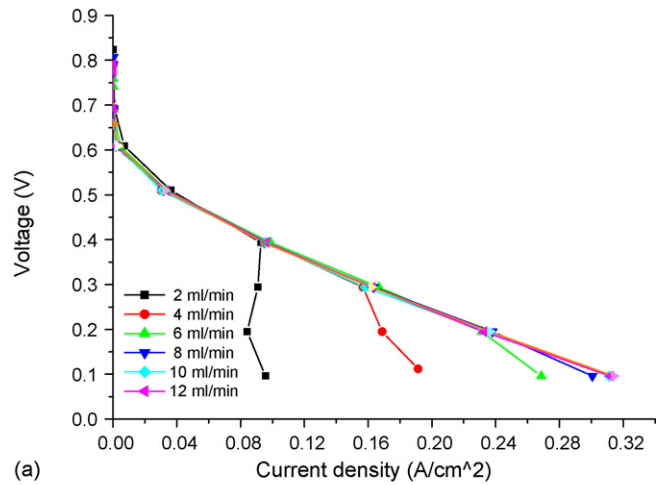
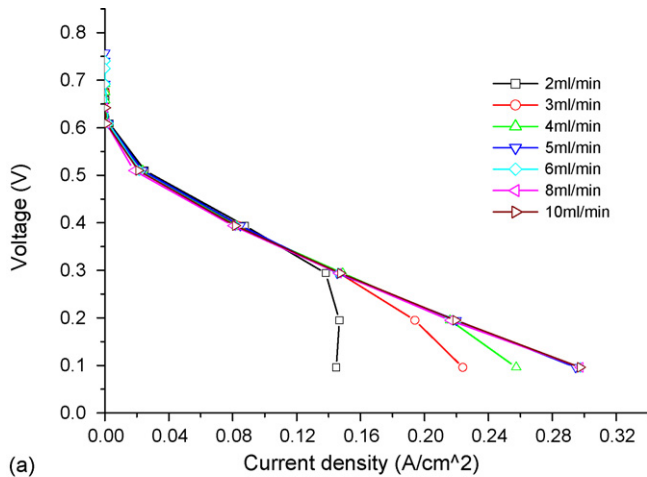
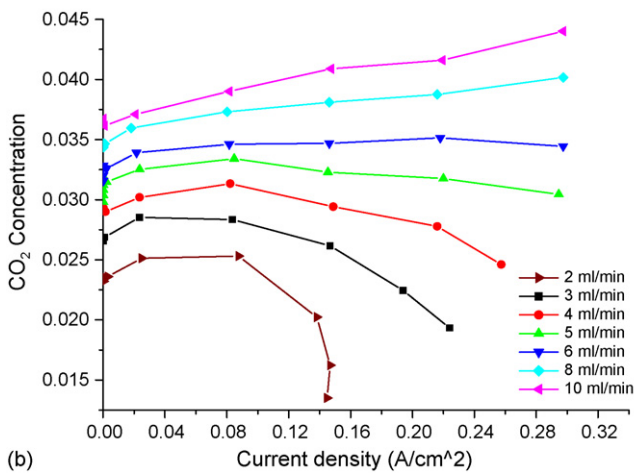


Fig. 5. (a) Polarization curves at different anode flow rates. Cell temperature, 70 °C; no cathode humidification; methanol concentration 0.5 M; oxygen flow rate, 600 sccm. (b) Methanol crossover rate at different anode flow rates. Cell temperature, 70 °C; no cathode humidification; methanol concentration 0.5 M; oxygen flow rate, 600 sccm.

because the operating pressure on both sides are equal). The diffusion part $-D\Delta c/t$ decreases with the increase of the current density since the methanol concentration in the anode catalyst layer decreases with increasing current density; while the proton drag part $(\lambda_m/nF)I$ increases with the increase of the current density if the methanol concentration at the interface between the anode catalyst layer and the electrolyte membrane is constant. However, at high current densities the methanol concentration at the interface between the electrolyte membrane and the anode catalyst layer is lower, which leads to a decrease in λ_m , and thus a decrease in the crossover due to the proton drag part. When the cell temperature is low, for example at 30 °C, the reaction rate is low. The methanol concentration at the interface does not change significantly, so the methanol crossover due to the diffusion does not change much regardless of current density values, while the proton drag part increase almost linearly with the increase of the current density. When the cell temperature is high, for example at 60 °C, the reaction rate is high and the methanol crossover induced by the diffusion and the proton drags are at the same



(a)



(b)

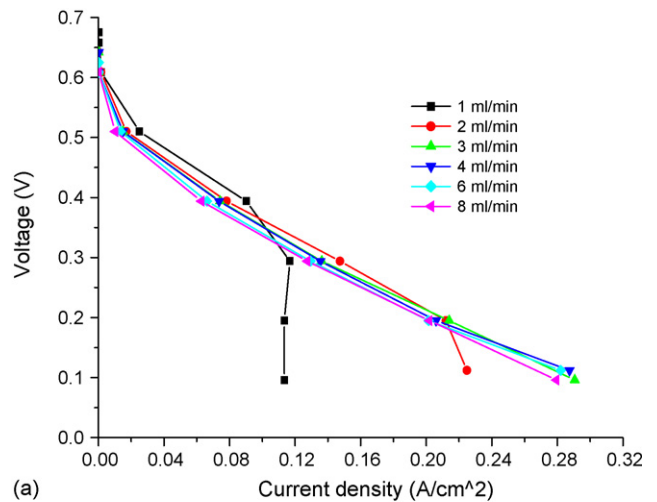
Fig. 6. (a) Polarization curves at different anode flow rates. Cell temperature, 70 °C; no cathode humidification; methanol concentration 1 M; oxygen flow rate, 600 sccm. (b) Methanol crossover rate at different anode flow rates. Cell temperature, 70 °C; no cathode humidification; methanol concentration 1 M; oxygen flow rate, 600 sccm.

order, the sum of these two parts is of parabolic shape as shown in Fig. 4b.

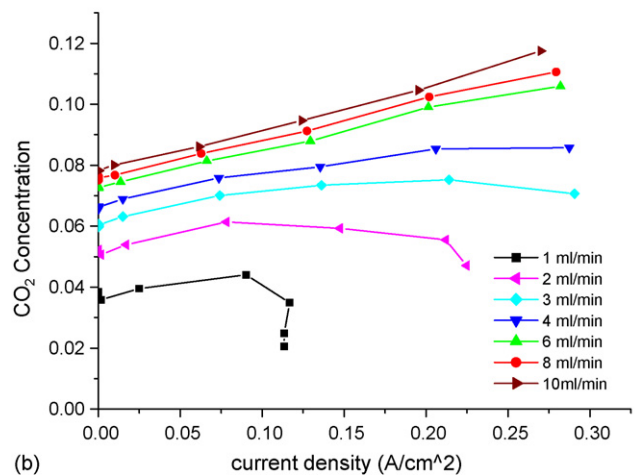
3.1.2. Effect of methanol flow rate

Three groups of experiments with different anode methanol flow rates have been carried out to study their effects on the cell performance and methanol crossover. Other cell operating conditions are cell temperature at 70 °C; no cathode humidification; cathode oxygen feeding flow rate is 600 sccm. The results for methanol concentrations of 0.5 M, 1 M and 2 M are shown in Figs. 5–7, respectively.

From Figs. 5b, 6b and 7b three types of characteristics can be identified in the curves of methanol crossover rate versus current density: the parabolic type, the horizontal type, and the monotonously increasing type. (1) In the parabolic type, the methanol crossover rate increases with the increase in cell current density initially and reaches the maximum at certain value and then decreases with further increase in cell current; (2) In the monotonously increasing type, methanol crossover rate increases monotonously with the increase in cell current



(a)



(b)

Fig. 7. (a) Polarization curves at different anode flow rates. Cell temperature, 70 °C; no cathode humidification; methanol concentration 2 M; oxygen flow rate, 600 sccm. (b) Methanol crossover rate at different anode flow rates. Cell temperature, 70 °C; no cathode humidification; methanol concentration 2 M; oxygen flow rate, 600 sccm.

density; (3) In the horizontal type, the methanol crossover rate almost remains constant. It does not change significantly with cell current density and can be regarded as a transition state between the parabolic type and the monotonously increasing type.

Comparing the methanol crossover curves with the corresponding polarization curves in Figs. 5–7, it can be found that generally when the methanol crossover curve is close to the transition state, i.e. the horizontal type, the fuel cell reach its optimal performance. Any increase in flow rate will generally not increase the cell performance, yet the methanol crossover rate will increase. When the curves are below the horizontal type, they are the parabolic type and it shows that the methanol supply at high current density is not enough; while for the monotonously increasing type, it shows that the methanol supply is too high. The excessive methanol does not improve cell performance and it may even cause the cell performance to decrease. These results indicate that the horizontal type corresponds to the optimal anode flow rate.

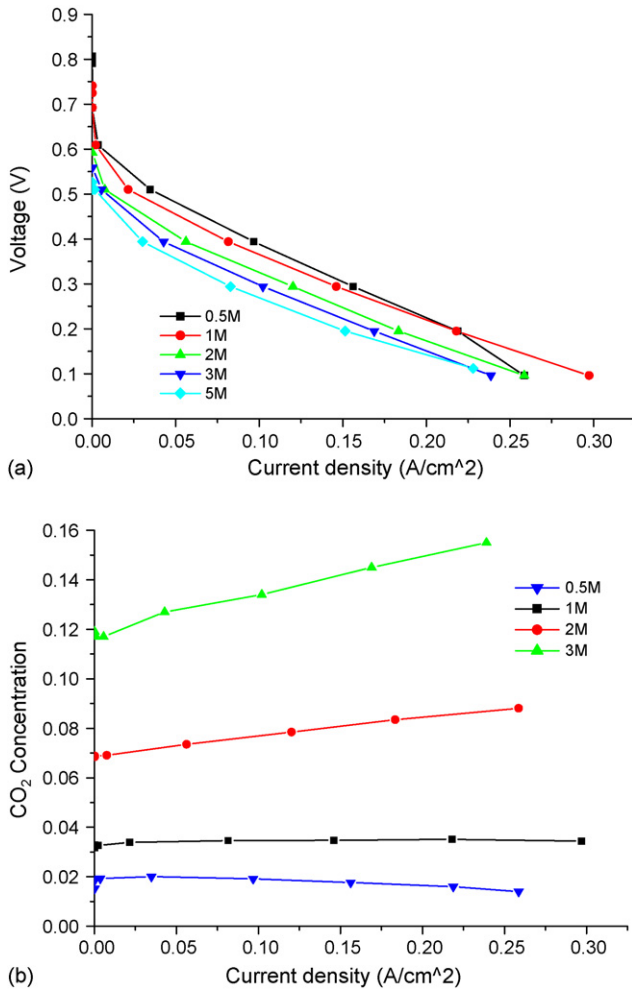


Fig. 8. (a) Polarization curves at different methanol concentrations. Cell temperature, 70 °C; no cathode humidification; methanol flow rate 6 ml min⁻¹; oxygen flow rate, 600 sccm. (b) Methanol crossover rate at different methanol concentrations. Cell temperature, 70 °C; no cathode humidification; methanol concentration flow rate, 6 ml min⁻¹; oxygen flow rate, 600 sccm.

3.1.3. Different methanol concentration

One group of experiments with different methanol concentrations has been carried out to study the effect of methanol concentration on the cell performance and methanol crossover. Cell operating conditions are cell temperature at 70 °C; no cathode humidification; cathode supply is oxygen and the flow rate is 600 sccm. The experimental results are shown in Fig. 8a and b. It can be seen that the optimal performance occurs when the methanol concentration are 1 M or 0.5 M depending on the current density. Here again, the optimal cell performance corresponds to the cases when methanol crossover versus current density curves are horizontal. When the cell is supplied with methanol concentration higher than 1 M, the cell performances are worse and the methanol crossover curves are of the monotonously increasing type.

3.1.4. Effects of cathode humidification temperature

Two groups of experiments have been designed to study the effect of cathode humidification temperature on the cell performance and corresponding methanol crossover. The cell

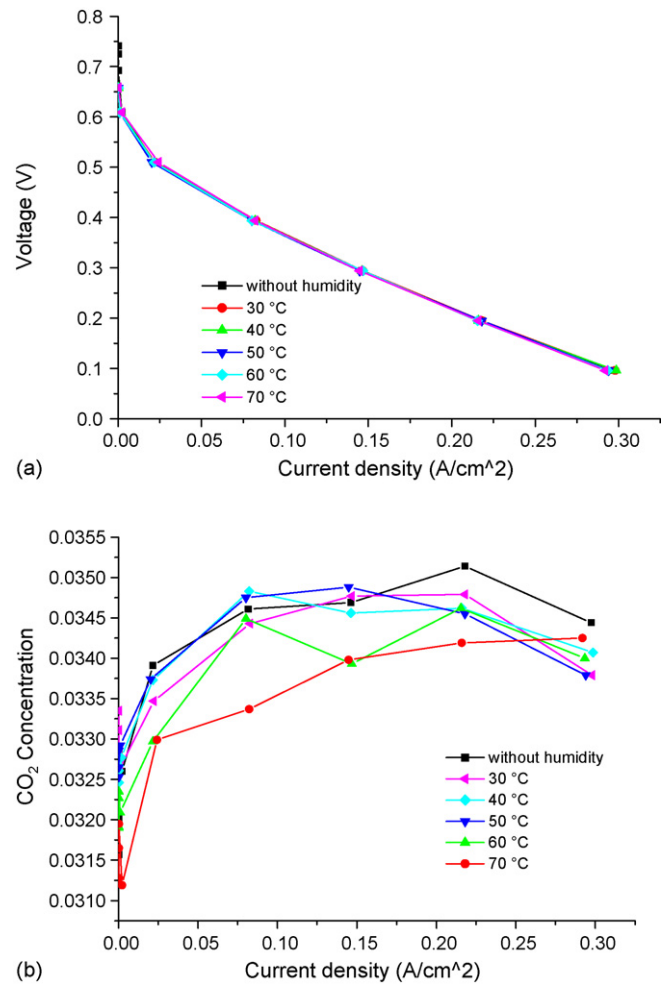


Fig. 9. (a) Polarization curves at different cathode humidification temperatures. Cell temperature, 70 °C; methanol concentration, 1 M; methanol flow rate, 6 ml min⁻¹; oxygen flow rate, 600 sccm. (b) Methanol crossover rates at different cathode humidification temperatures. Cell temperature, 70 °C; methanol concentration, 1 M; methanol concentration flow rate, 6 ml min⁻¹; oxygen flow rate, 600 sccm.

operating temperature was 70 °C and the cathode oxygen feeding flow rate is 600 sccm. The results for methanol of 1 M and 2 M are shown in Figs. 9 and 10 correspondingly, which show that cathode humidification has no effect on the cell performance. However, when the cathode humidification temperature is higher, the corresponding methanol crossover rate is a little lower. This can be contributed to the less water diffusion to the cathode when the content of water at the cathode is high and water transfer is accompanied with methanol transfer.

3.2. Transient state

To study the methanol crossover characteristic during transient states when the cell voltages suddenly changes a series experiments have been carried out. Cell temperature is 60 °C; methanol concentration is 1 M and methanol flow rate is 6 ml min⁻¹; oxygen flow rate is 600 sccm. The results are shown in Figs. 11 and 12. From Fig. 11a and b, it can be seen that, when the cell operating voltage suddenly changes, there is a peak in the CO₂ concentration. If the change in cell voltage is posi-

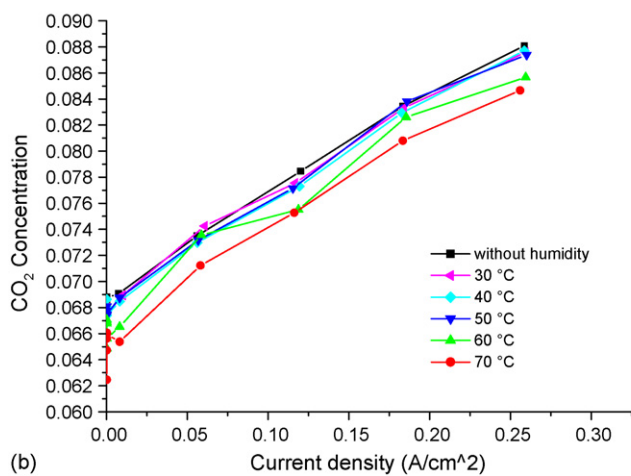
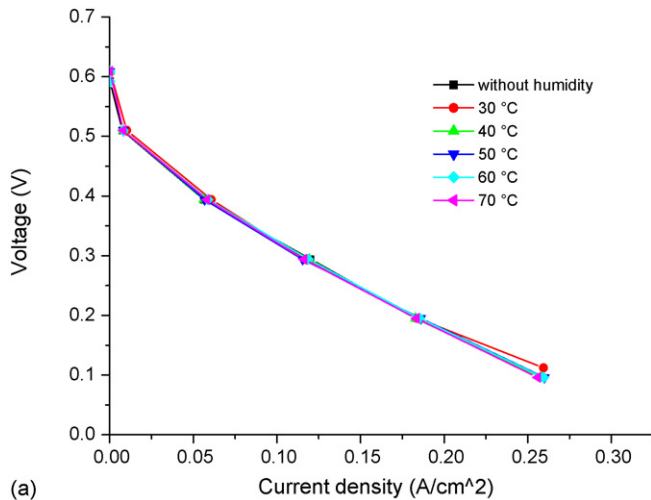


Fig. 10. (a) Polarization curves at different cathode humidification temperatures. Cell temperature, 70 °C; methanol concentration, 2 M; methanol flow rate 6 ml min⁻¹; oxygen flow rate, 600 sccm. (b) Methanol crossover rates at different cathode humidification temperature: cell temperature, 70 °C; methanol concentration, 2 M; methanol concentration flow rate, 6 ml min⁻¹; oxygen flow rate, 600 sccm.

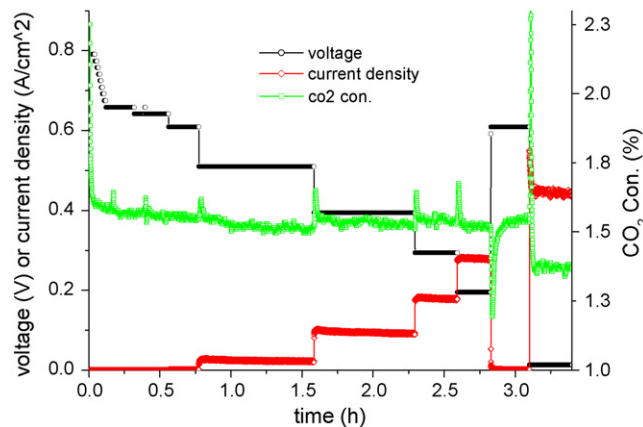


Fig. 11. Transient characteristics of methanol crossover when cell voltage suddenly changes. Cell temperature, 60 °C; no cathode humidification; methanol concentration 1 M and methanol flow rate, 6 ml min⁻¹; oxygen flow rate, 600 sccm.

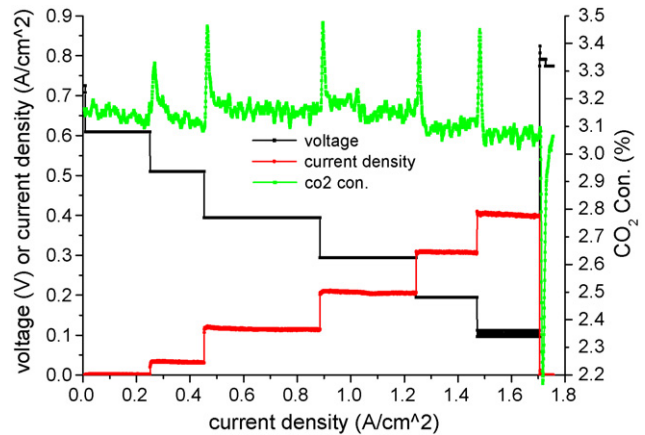


Fig. 12. Transient characteristics of methanol crossover when cell voltage suddenly changes. Cell temperature, 70 °C; no cathode humidification; methanol concentration 1 M and methanol flow rate, 6 ml min⁻¹; oxygen flow rate, 600 sccm.

tive, the peak is negative; otherwise the peak is positive. The greater the change in voltage is, the greater is the amplitude of the peak in CO₂ concentration. This can be explained by the fact that when the cell voltage changes, the cell current density change almost immediately, but the methanol concentration at the interface between the membrane and anode catalyst layer cannot change immediately due to the limitation of mass diffusion. It takes some time for the methanol concentration at this interface to reach its new equilibrium value. For instance, when the cell voltage suddenly decreases, it can be seen that the cell current increases immediately to its new value and a peak is formed in the methanol crossover curve. At the beginning of the change, the methanol crossover is caused by the new higher cell current and the old higher methanol concentration (Eq. (3)), thus a very high methanol crossover rate. As time progresses, the cell current remains the same, but the methanol concentration at the anode side decreases due to the new higher consumption rate (higher current), thus the methanol crossover decreases. When the interface methanol concentration reaches its new equilibrium, the methanol crossover rate also reaches its new equilibrium value, which is caused by the new current and new methanol concentration. The same results can be seen in Fig. 12, where the cell operating temperature is higher at 70 °C and thus the cell current is also higher. Due to the higher current, the peaks of the CO₂ concentration are also higher than those shown in Fig. 11, where the cell temperature is lower at 60 °C.

4. Conclusions

A series of experiments have been conducted to determine the methanol crossover rate in a DMFC by measuring the carbon dioxide concentration at the cathode exit in real time. In addition to the steady-state experiments, transient behaviors of methanol crossover when the cell voltage suddenly changes have also been studied. Based on the experimental studies and analyses, the following conclusions can be made.

- The cell performance increases with cell temperature; methanol crossover increases with temperature when the cell

temperature is below 60 °C and remains almost constant from 60 to 80 °C; at low temperature, the methanol crossover rate versus current density curve is monotonously increasing type, while at high temperature, the curves are of parabolic type.

- By measuring the methanol crossover and cell performances at different anode flow rates and different inlet methanol concentrations three types of characteristics are identified in the relationships between methanol crossover and cell current density: (a) the monotonously increasing type, (b) The parabolic type, (c) the horizontal type. It is found that the horizontal type corresponds to the optimal operating conditions.
- Cathode humidification has no effect on the cell performance.
- Due to methanol diffusion hysteresis, when the cell operating voltage suddenly changes, a peak in methanol crossover is observed. When cell voltage change is positive the peak in methanol crossover is negative, and when the cell voltage change is negative the peak in methanol crossover is positive. The greater the change in cell voltage is, the greater is the peak in methanol crossover.

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