

Open circuit voltage and methanol crossover in DMFCs

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Abstract

It is difficult to definitely measure the open circuit voltage (OCV) of a direct methanol fuel cell (DMFC). For example, after a cell is changed from a loaded state to a no load, open circuit state, the voltage increases quickly and reaches a peak value in seconds. Some might use this peak voltage as the OCV. However, the voltage starts to decline quite rapidly following the peak, and it takes several minutes to become stabilized at a lower value. This stabilized, lower voltage should be used as the OCV. Another unique and interesting phenomenon is the rapid cell voltage increase following an initial instant decline when a load is applied to a DMFC. This increase is believed to be due to diminishing of excess methanol that accumulates at the cathode side during the open circuit period. The effects of air flow rate, methanol concentration and cell temperature on the OCV, methanol crossover and cell performance were also studied. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Open circuit voltage; Methanol crossover; Direct methanol fuel cell

1. Introduction

Methanol is an attractive fuel because its energy density is much higher than that of hydrogen, and it is an inexpensive liquid that is easy to handle, store and transport [1–3]. A thermodynamic reversible potential for a methanol–oxygen fuel cell is 1.21 V at 25 °C [4]. This value is comparable to that for a hydrogen–oxygen fuel cell, which is 1.23 V. However, in practice, a direct methanol fuel cell (DMFC) has a much lower open circuit voltage (OCV). One of the major reasons is that methanol can cross through the proton-exchange membrane (PEM), such as Nafion[®], to reach the cathode side via physical diffusion and electro-osmotic drag (by protons). Such crossover not only results in a waste of fuel, but also lowers the cell performance. Most of the methanol crossing over will be electrochemically oxidized at the cathode. Such an oxidation reaction lowers the cathode potential and also consumes some cathode reactant. If a reaction intermediate, such as carbon monoxide adsorbs onto the catalyst surface, the cathode will be poisoned too, which further lowers its performance.

The effect of methanol crossover has attracted attention worldwide. Many factors, such as membrane material and modification, membrane thickness, methanol concentration, cell temperature and the pressure of cathode reactant have

been investigated [5–16]. Generally speaking, methanol crossover can be reduced by increasing membrane thickness and equivalent weight, by increasing the cathode reactant pressure, and by decreasing cell temperature and methanol concentration.

Due to the effects of all these factors, various OCVs have been reported. We believe that another factor, which has not been discussed in previous publications, may also contribute to the variation: OCV tends to be transitory, and different researchers may have taken different values as the OCV during this process. This paper discusses this factor along with the effect of air flow rate on OCV. Methanol crossover and cell performance under various conditions are also presented.

2. Experimental

The experiments were performed using a 25 cm² single cell purchased from Fuel Cell Technologies Inc. (Albuquerque, NM). Pt/Ru and Pt blacks were used as the anode and cathode catalysts, respectively, and they were coated on plain and Teflon[®]-treated 9-mil Toray paper, respectively. Anode and cathode with Pt/Ru and Pt loadings of 4.8 mg/cm², respectively, were hot-pressed onto a Nafion[®] 112 membrane at 130 °C for 3 min. Methanol was mixed with water, and the solution was pumped into the cell by a micropump (Micropump Inc., Vancouver, WA). The solution was re-circulated back to the mixing tank. The flow rate

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of the solution was controlled at 40 ml/min using a GW laboratory dc power supply (model: GPS-1830D). A condenser was used to condense methanol in the vapor phase and to allow the release of any gaseous product such as CO_2 . The temperature of the mixing tank was controlled by a hot-plate. The tubing connecting the mixing tank and the cell was heated by a heating tape. The temperatures of the mixing tank, methanol solution inlet to the cell, and the cell itself were monitored by thermocouples. Air was supplied to the cell by a compressor at ambient pressure, and its flow rate was adjusted using a flowmeter. Air flow rates of 180, 397, 643 and 920 ml/min correspond to air stoichiometries of 2.1, 4.6, 7.4 and 10.6, respectively, at a current density of 200 mA/cm^2 . The load was controlled by another GW laboratory dc power supply (model: GPR-1820HD), and the cell voltage was monitored by a voltmeter.

3. Results and discussion

Fig. 1 shows the change of OCV with time after a cell was changed from a load of 280 and 312 mA/cm^2 to a no load, open circuit state at 40 and 60°C , respectively. After the load was removed, the OCV increased greatly and reached a peak in 10 s. Rather than stabilizing at this voltage, it declined quite rapidly, and approached a stabilized OCV after 3 min. There was a difference of more than 0.1 V between the peak voltage and the stabilized voltage. Some may take the peak voltage as the OCV, others may randomly take a number in the declining region as the OCV, and still others may take a number after 3 min as the OCV. We think that a more accurate OCV should be one after OCV approaches a stabilized value based on the following

reasoning. As shown in Fig. 2, when a cell is loaded, the methanol concentration in the anode catalyst layer, C1, is reduced ($<C_3$, bulk methanol concentration) because some of the methanol is being oxidized. This reduced methanol concentration leads to a lower concentration of methanol, C2, at the cathode side, resulting from methanol crossover through the membrane. In other words, this amount of methanol crossover is that when the cell is loaded, which may largely differ from that when the cell is at open circuit. When the cell is switched to a no load state, in the very beginning, the methanol concentrations in both the anode and cathode catalyst layers are not much higher than C1 and C2, respectively, and thus, a highest OCV value is observed. With time, the methanol concentration within the anode catalyst layer will increase, and therefore, more methanol will be able to diffuse to the cathode side, resulting in a declining OCV. When the methanol concentration within the anode catalyst layer finally reaches that of the bulk solution, C3, the methanol concentration at the cathode reaches the highest level, C4, and thus, a lowest and stable OCV is achieved. This value represents the true OCV.

The effects of membrane material and thickness, methanol concentration, cell temperature and the pressure of the cathode reactant were widely studied in the past [5–16]. Here, we found that the OCV was also affected by the air flow rate at the cathode. Fig. 3 shows the results with 0.5 and 1.0 M methanol at various temperatures. Firstly, at the same cell temperature (i.e. 60°C), the OCV increased with decrease in methanol concentration (i.e. 0.5 M versus 1.0 M). Secondly, the effect of air flow rate on OCV was much less when either the cell temperature was lower (i.e. 40°C) or the methanol concentration was lower (i.e. 0.5 M). Thirdly, at the same methanol concentration (i.e. 1.0 M),

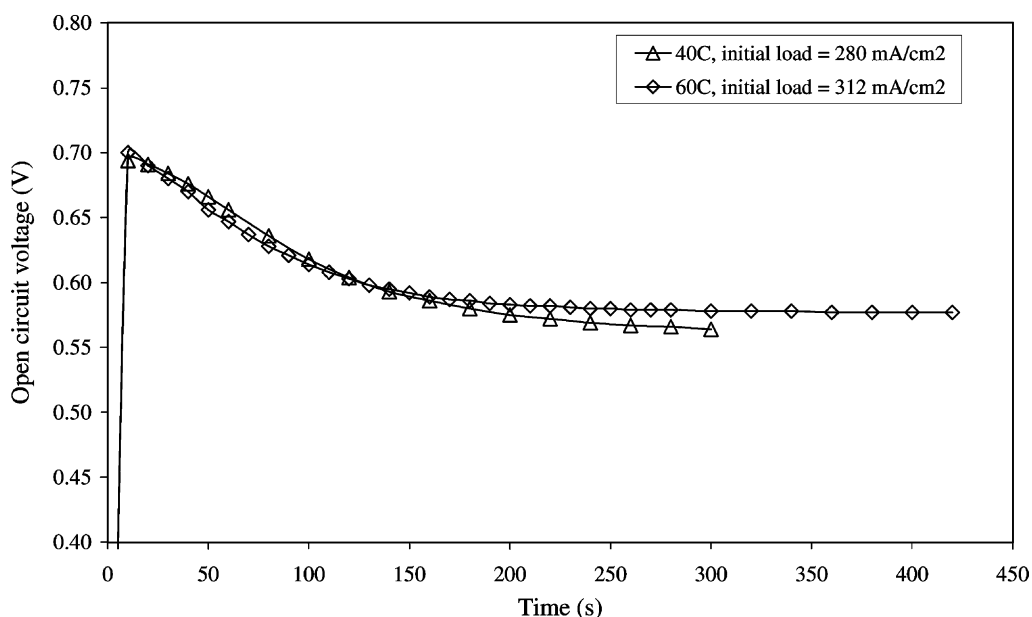
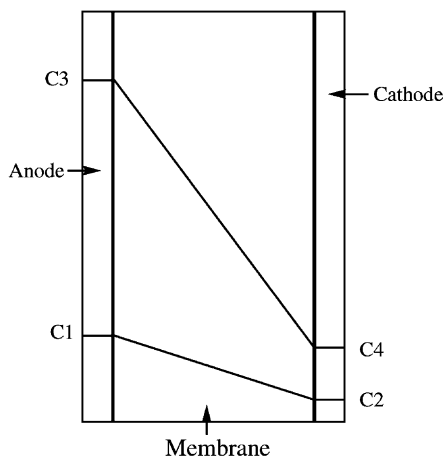


Fig. 1. Change of OCV with time after a cell is changed from a full load to no load condition; 1.0 M methanol, $T_{\text{cell}} = 60^\circ\text{C}$, air flow rate = 920 ml/min.



$$C1 > C2, C3 > C4, C3 > C1, C4 > C2.$$

Fig. 2. A schematic view of methanol concentrations within the anode and cathode catalyst layers when the cell is loaded (C1 and C2) and at open circuit (C3 and C4).

when the air flow rate was higher than approximately 600 ml/min, the OCV increased with cell temperature from 40 to 80 °C, and at each cell temperature, the OCV increased only slightly with air flow rate. However, the OCV started to decline quickly when the air flow rates were less than approximately 400 and 600 ml/min at 60 and 80 °C, respectively. The decrease in OCV as air flow rate is increased is probably because more methanol is taken away or blown out by air to lead to a higher methanol dissipation rate at the cathode. The detailed OCV values are summarized in Table 1.

Since the OCV is related to the concentration of methanol existing at the cathode, methanol crossover under various

Table 1
Effects of methanol concentration, cell temperature and air flow rate on OCV

Air flow rates (ml/min)	T (°C)			OCV (V)
	40	60		
	1.0 M	0.5 M	1.0 M	1.0 M
180	0.547	0.601	0.471	0.367
397	0.556	0.613	0.569	0.494
643	0.562	0.615	0.574	0.583
920	0.567	0.617	0.578	0.591
1120	0.567	0.618	0.581	0.597
1450	0.568	0.620	0.583	0.598

conditions was measured using an electrochemical technique [5,16]. During the measurement, nitrogen was introduced into the cathode side and a positive voltage was applied using a power supply. The reaction occurring at the cathode is the oxidation of methanol that crosses through the membrane. When the applied voltage is high enough to quickly oxidize all the methanol diffusing to the cathode side, a limiting current is achieved. This limiting current represents approximately the rate of methanol crossover at open circuit. Fig. 4 shows the crossover current density versus applied voltage at 60 °C with both 0.5 and 1.0 M methanol, respectively. Little crossover current was measured at voltages less than approximately 0.30 V because methanol oxidation needs a higher overpotential. The crossover current then increased quickly with the applied voltage, and approached a plateau at 0.9 V. Based on the limiting currents at 0.9 V, methanol crossover increased by approximately 50% when the methanol concentration was increased from 0.5 to 1.0 M (at 60 °C).

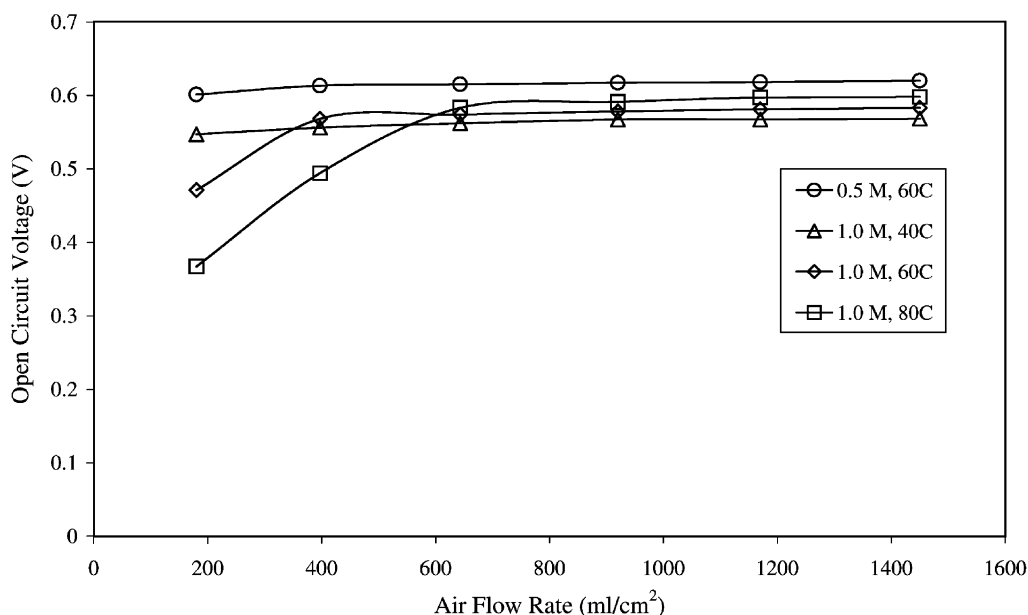


Fig. 3. OCV vs. air flow rate under various conditions.

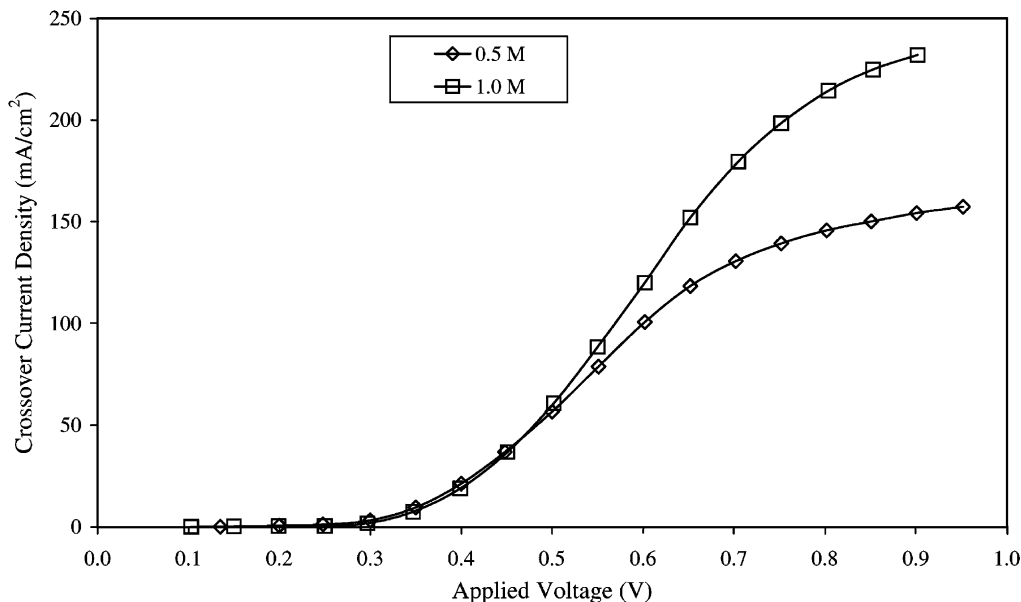


Fig. 4. Crossover current density vs. applied voltage. N_2 flow rate = 643 ml/min.

If a linear methanol concentration gradient through the thickness of the membrane is assumed, the diffusion coefficient of methanol can be estimated by using the limiting current at 0.90 V (232 mA/cm² for 1 M methanol) in Fig. 4, via the following equation:

$$I_{\text{crossover}} = \frac{nFAD_{\text{Meth}}C_{\text{Meth}}}{d_{\text{mem}}} \quad (1)$$

where $I_{\text{crossover}}$ is the limiting methanol crossover current (A), n the number of electrons involved in the oxidation of each methanol molecule, which is six if methanol is completely oxidized to CO_2 , F the Faraday constant, which is about 96,487 C/mol, A the geometrical active area of the electrode, D_{Meth} and C_{Meth} are the diffusion coefficient (cm²/s) and concentration (mol/cm³) of methanol within the membrane, respectively, and d_{mem} is the thickness of the membrane (cm). In order to solve this equation, C_{Meth} and d_{mem} need to be determined first. The equivalent weight of Nafion[®] membrane used is 1100 g/mol of sulfonate group, and the density of dry Nafion[®] membrane is approximately 2.1 g/cm³. Based on studies by Ren et al., the composition of a methanol/water fluid within the membrane is nearly identical with that of the equilibrating solution, and the numbers of methanol and water molecules held by each sulfonate group are 0.4 and 20.7, respectively (for 1 M methanol solution at 22 °C) [16]. The methanol concentration within a Nafion[®] membrane equilibrating with 1 M methanol is thus calculated to be:

$$C_{\text{Meth}} = \frac{0.4}{1100/2.1} = 7.6 \times 10^{-4} \text{ mol/cm}^3 \quad (2)$$

The thickness of dry Nafion[®] 112 membrane is 50 μm, but in the presence of methanol/water solution, it will swell

largely, although the stacking pressure of the cell will put some restriction on the swelling, especially in the thickness direction. If we assume a 50% swelling in the membrane volume and the thickness, then the thickness and C_{Meth} will be 75 μm and 5.1×10^{-4} mol/cm³, respectively. Therefore, the diffusion coefficient of 1 M methanol through a Nafion[®] 112 membrane at 60 °C would be:

$$\begin{aligned} D_{\text{MeTH}} &= \frac{I_{\text{crossover}}/A}{nFC_{\text{Meth}}/d_{\text{mem}}} \\ &= \frac{232 \times 10^{-3}}{(6 \times 96487 \times 5.1 \times 10^{-4})/(75 \times 10^{-4})} \\ &= 5.9 \times 10^{-6} \text{ cm}^2/\text{s} \end{aligned} \quad (3)$$

If we use the $C_{\text{Meth}} = 2.4 \times 10^{-4}$ mol/cm³ measured by Ren et al. [17] for 1 M methanol, and still assume a 50% increase in membrane thickness, D_{Meth} is calculated to be 12.5×10^{-6} cm²/s. These numbers are on the same order as those measured by others using a variety of methods [6,13,17].

One potential problem of measuring alcohol crossover using such an electrochemical oxidation technique is the potential poisoning of the positive electrode by intermediates formed during the alcohol oxidation [18]. Although Pt, used in the cathode, is an effective catalyst for methanol dehydrogenation, it could be seriously poisoned by CO in the absence of Ru, a noble metal that can dissociate water at lower potentials to create oxygen-containing surface groups that are needed to convert CO to CO_2 . In order to evaluate whether poisoning was a problem, the change of methanol crossover current with time was studied. Fig. 5 shows the result using 0.5 M methanol at 60 °C. With an applied voltage of 0.93 V, the crossover current density decreased quickly from 180 to 154 mA/cm² in the first 10 s, and then it

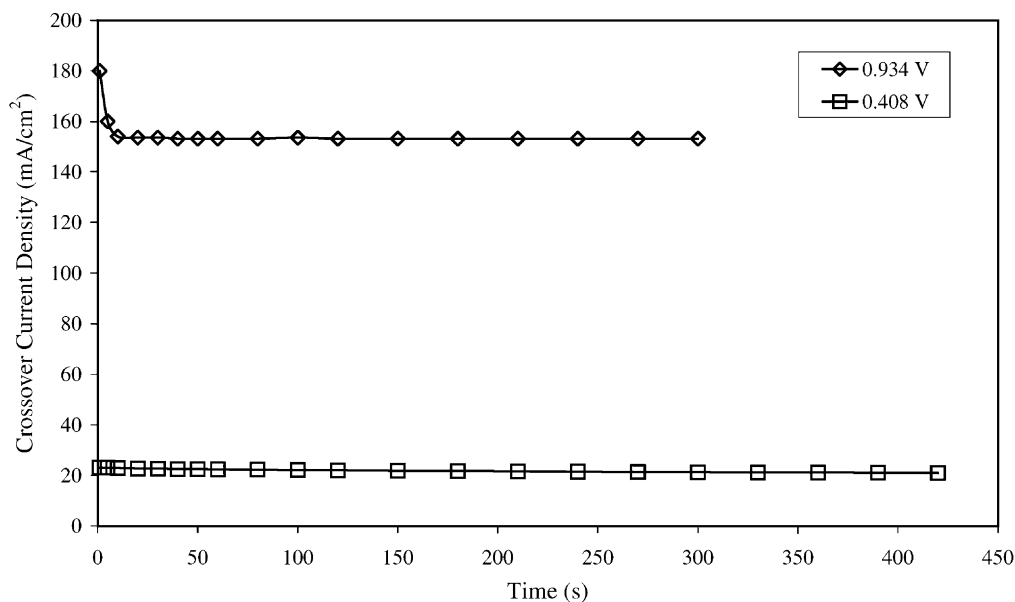


Fig. 5. Change of crossover current density with time; 0.5 M methanol, $T_{\text{cell}} = 60\text{ }^{\circ}\text{C}$, N_2 flow rate = 643 ml/min.

became very stable. The data within the first 10 s over-estimated the amount of methanol crossover due to contributions from both capacitance charging current and accumulation of excess methanol in the cathode compartment before the voltage was applied. Since the crossover current is so stable, it is concluded that no electrode poisoning occurs at such a high voltage, and thus, the crossover current measurement is not interfered. When a very low voltage was applied (i.e. 0.41 V), the oxidation current declined slightly with time, indicating that some minor

poisoning did occur, and it could interfere slightly with the measurement. However, any oxidation current measured at such low voltages does not represent the true methanol crossover current because the measurement is not carried out in the limiting current region.

Fig. 6 and Table 2 show the effects of cell temperature and nitrogen flow rate on the crossover oxidation current from 1.0 M methanol. The measurement was performed at an applied voltage of 0.60 V, which did not generate a limiting current, but the trend of oxidation current change should be

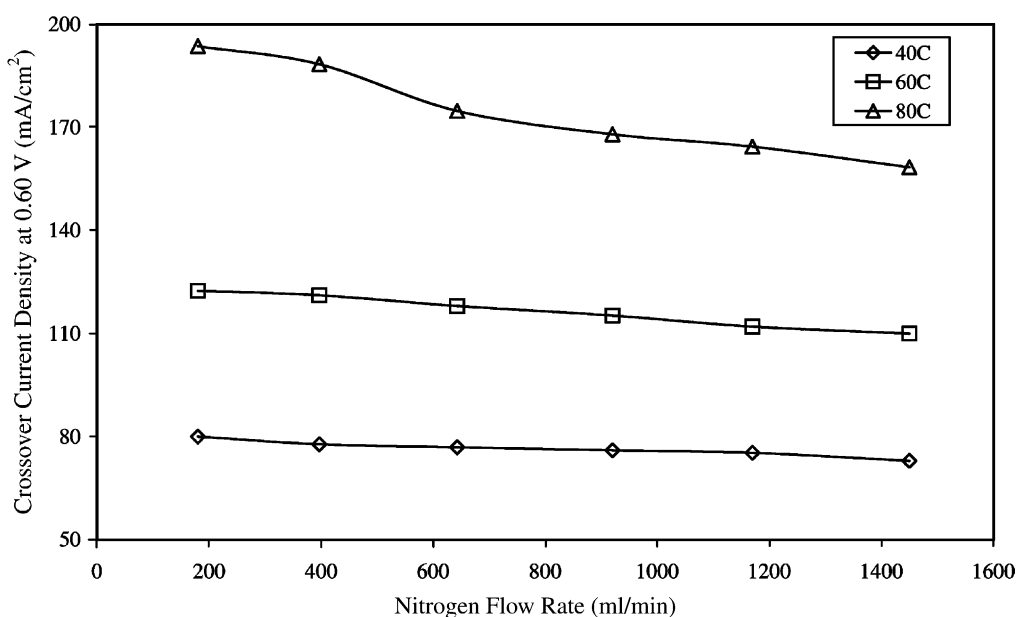


Fig. 6. Effects of cell temperature and N_2 flow rate on methanol crossover current measured at 0.60 V. Methanol concentration = 1.0 M.

Table 2
Effects of nitrogen flow rate and cell temperature on methanol crossover

Air flow rate (ml/min) measured at 0.60 V	Cell temperature (°C)		
	40	60	80
	Crossover current density (mA/cm ²)		
180	80.0	122.4	193.6
397	77.8	121.1	188.4
643	76.9	118.0	174.8
920	76.0	115.2	168.0
1170	75.3	112.0	164.4
1450	72.9	110.0	158.4

similar to that in the limiting current region. Clearly, the oxidation current increases largely with the cell temperature, but only slightly as the nitrogen flow rate is reduced. These observations are in good agreement with those regarding the OCV as shown in Fig. 3 and Table 1.

Another unique and interesting phenomenon was observed when a load, even as low as 24 mA/cm², was applied to a cell. Fig. 7 shows that the cell voltage declined immediately from the OCV of 0.567 to 0.400 V in the first 7 s, it then increased quickly to 0.428 V in the next 16 s, and finally stabilized at 0.433 V after 50 s. Such an increase

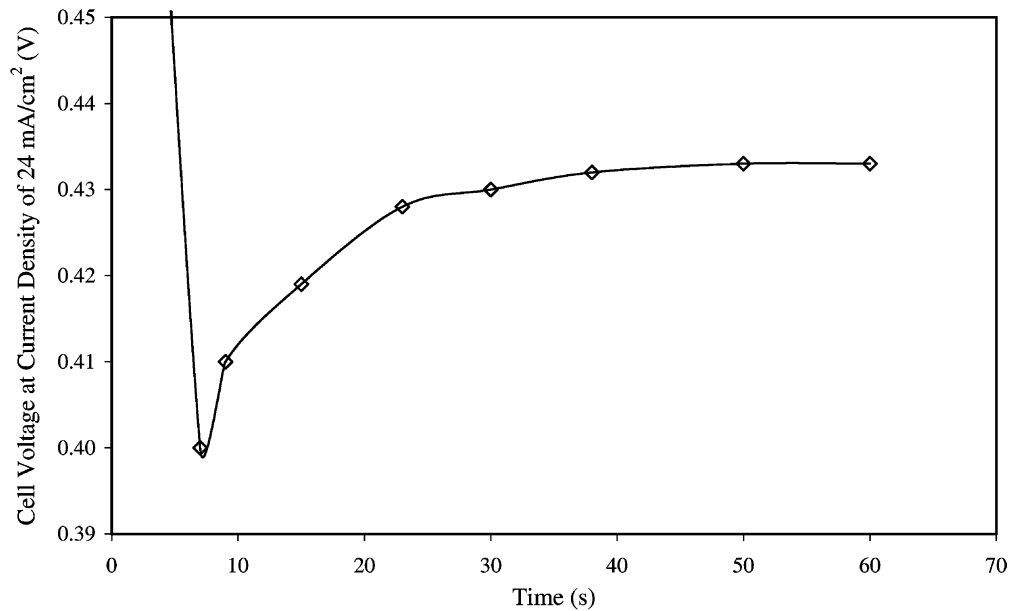


Fig. 7. Change of cell voltage after a load of 24 mA/cm² is applied. Methanol concentration = 1.0 M, T_{cell} = 40 °C, air flow rate = 920 ml/min.

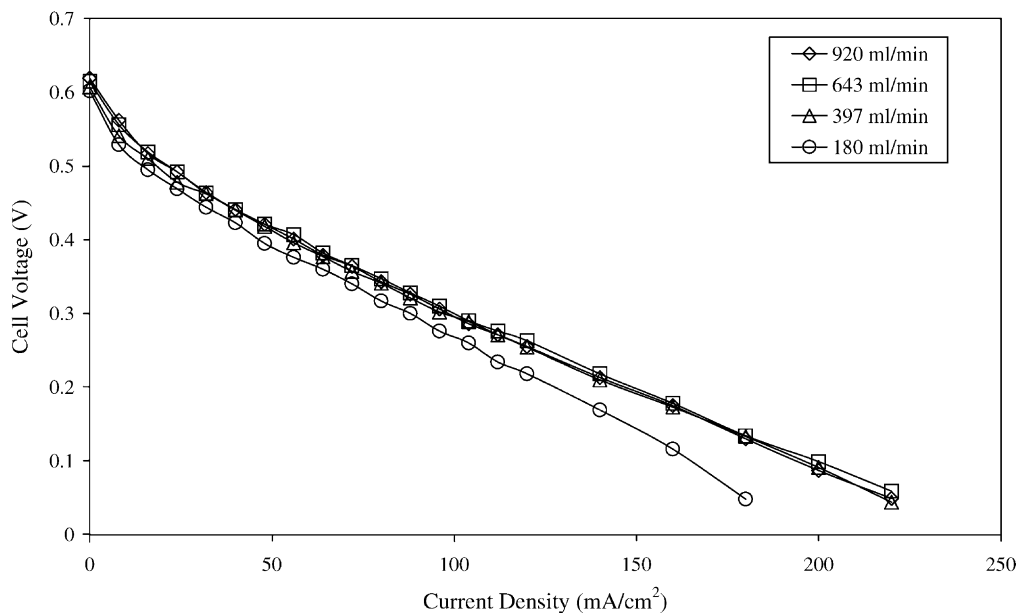


Fig. 8. Performance of 0.5 M methanol at 60 °C.

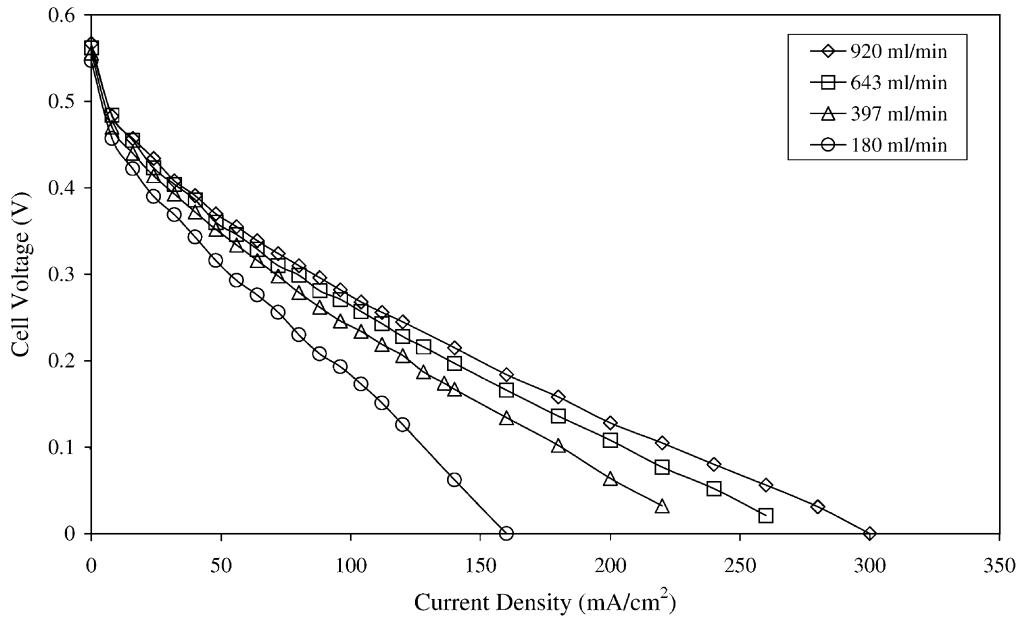


Fig. 9. Performance of 1.0 M methanol at 40 °C.

following the initial instant decline could be quite puzzling, and was rarely observed in hydrogen-air fuel cells. We conclude that it is also related to the methanol crossover. As shown in Fig. 2, when a cell is at an open circuit, the cathode compartment contains more methanol than when the cell is at a load because the load will consume some methanol to lower its concentration in the anode catalyst layer, which in turn results in less methanol crossing through the membrane. Just as a load is applied, the cathode is experiencing the highest methanol concentration corresponding to that at

open circuit, so the cell gives the lowest voltage. When the methanol concentration within the anode catalyst layer is decreased as it is reacted, the amount of methanol in the cathode also declines, resulting in an increase in cell voltage. When all the excess methanol in the anode is reacted and its concentration reaches C1, the amount of methanol in the cathode is decreased to C2, and thus, the cell voltage achieves the highest and stable value.

Figs. 8–11 show cell performance under various conditions. Using 0.5 M methanol at 60 °C, the cell performance

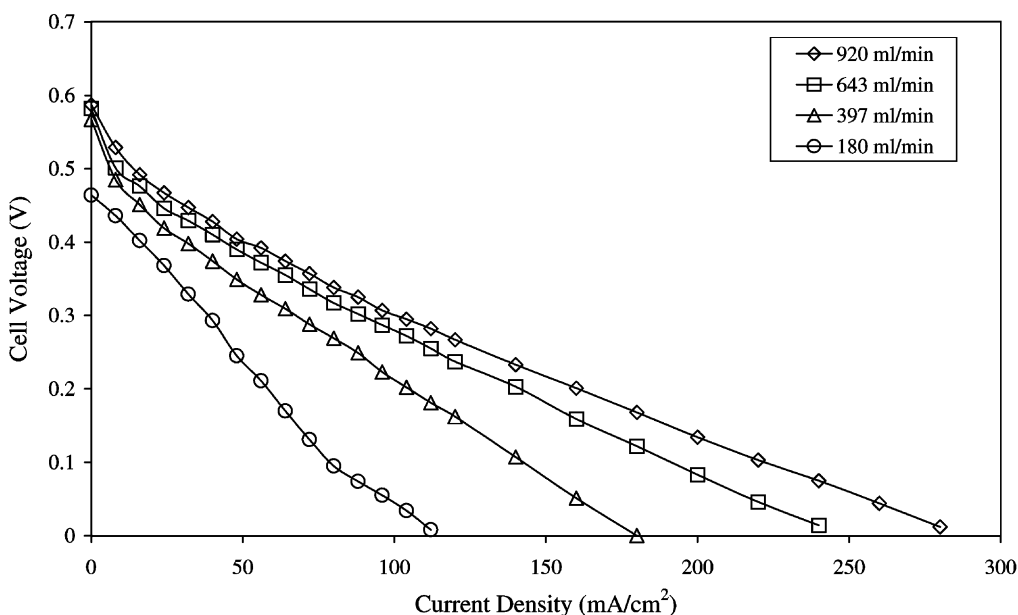


Fig. 10. Performance of 1.0 M methanol at 60 °C.

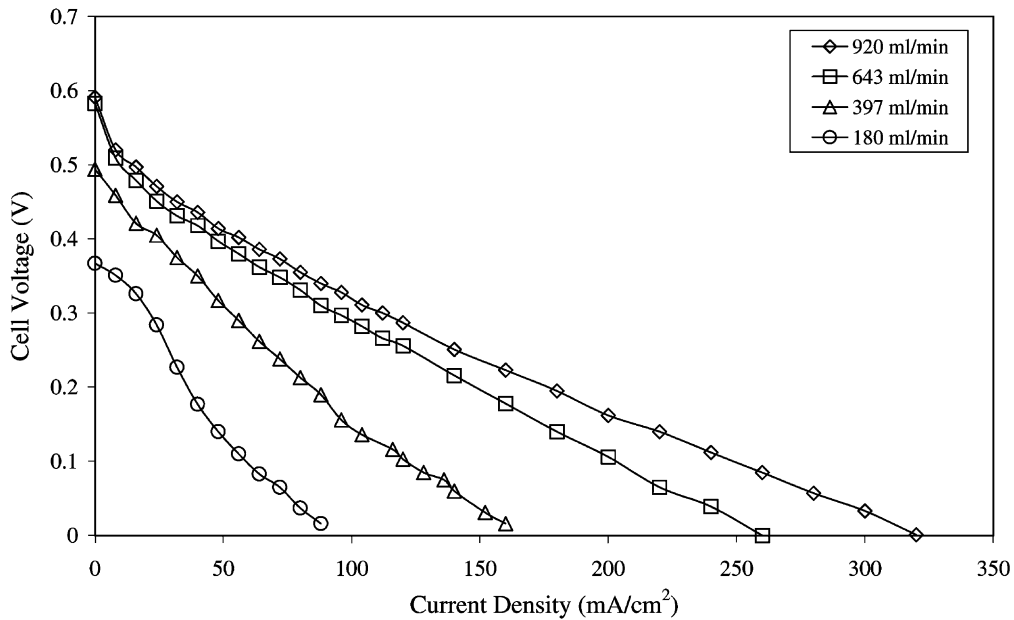


Fig. 11. Performance of 1.0 M methanol 80 °C.

was slightly lower at an air flow rate of 180 ml/min than at other air flow rates, as shown in Fig. 8. Using 1.0 M methanol, the performance increased continuously with air flow rate from 180 to 920 ml/min, and the difference enlarged as the cell temperature was increased from 40 to 60 °C and then to 80 °C, as shown in Figs. 9–11. Fig. 12 compares the relative performance under various conditions when the air flow rate is 180 ml/min. The cell showed the best performance when 0.5 M methanol was used (at 60 °C). At a methanol concentration of 1.0 M, the cell performance

declined when the cell temperature was increased from 40 to 60 °C and then to 80 °C. Higher temperature should favor both oxygen reduction and methanol oxidation reactions. However, the larger methanol crossover is apparently more dominating, resulting in lower performance at higher cell temperatures. At higher air flow rate of 920 ml/min, the cell performance increased slightly with temperature, and the cell showed the best performance at 80 °C, as shown in Fig. 13. This illustrates that higher air flow rates dissipate more methanol from the cathode compartment, and the

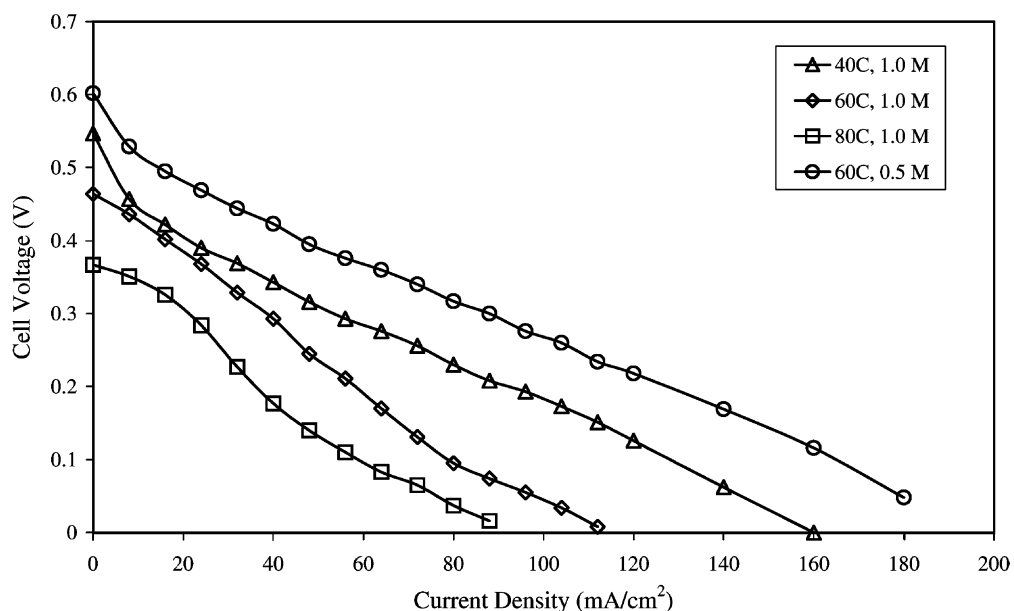


Fig. 12. Performance comparison under various conditions at an air flow rate of 180 ml/min.

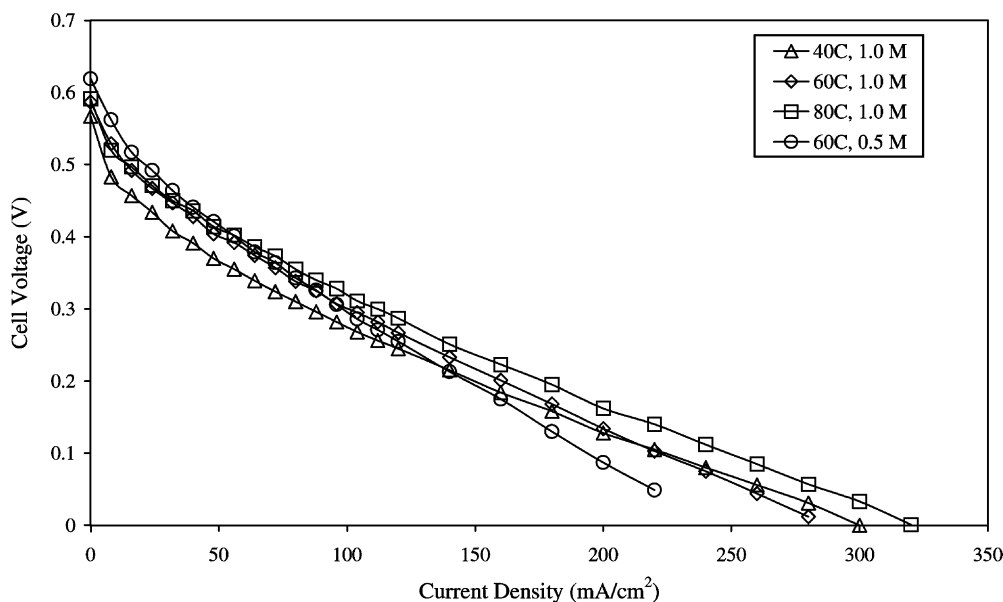


Fig. 13. Performance comparison under various conditions at an air flow rate of 920 ml/min.

temperature becomes a bit more dominating than methanol crossover.

4. Conclusions

Care should be taken when reporting an OCV of a DMFC. If the cell is on load before it is put to the open circuit condition, the OCV will jump up and reach a peak in seconds. The voltage at the peak is not the real OCV, and it is only a transitory value. Following the peak, the voltage will drop quickly and stabilize in several minutes. The stabilized voltage should be taken as the real OCV. OCV increases with air flow rate, and the effect is more pronounced when air flow rate is low, methanol concentration is high, and cell temperature is high. Since methanol crossover is highest at open circuit, the cell voltage experiences an immediate decline when a load is applied, followed by a quick increase before approaching stabilization. Such a phenomenon is very unique to DMFC, and is normally not observed in a hydrogen-air fuel cell. OCV is related to methanol crossover, and measuring methanol crossover using the electrochemical oxidation of methanol in the cathode compartment is a fast and reliable technique. Increasing either methanol concentration or cell temperature will lead to higher methanol crossover. Due to methanol crossover, the cell performance may be better at lower temperatures, especially when the air flow rate is low, even though lower temperatures do not favor oxygen reduction and methanol oxidation reactions.

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