# Electrochemical oxidation of 1-methoxy-2-propanol in direct liquid fuel cells

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## Abstract

Some interesting features have been observed when 1-methoxy-2-propanol was studied in direct liquid fuel cells. Air flow rate ranging from 180 to 920 ml/min had no effect on performance, but the performance increased largely when the cell temperature was increased from 40, to 60, and then to 80 °C. The open circuit voltage of the cell was around 0.70 V, which was 0.08–0.33 V higher than that when methanol was used. At low air flow rates, 1-methoxy-2-propanol performed much better than methanol in the entire current density region at 60 and 80 °C. At high air flow rates, methanol performed better than 1-methoxy-2-propanol at current densities higher than 100 mA/cm$^2$, but the latter performed better than the former at current densities less than ca. 50 mA/cm$^2$. The crossover current density of 1.0 M 1-methoxy-2-propanol through a Nafion® 112 membrane was estimated electrochemically, and it was 25.6, 60.8 and 96.0 mA/cm$^2$ at cell temperatures of 40, 60, and 80 °C, respectively, measured at 0.90 V. These numbers were much smaller than those of methanol that, e.g. had a crossover current density of 232 mA/cm$^2$ at 0.9 V and 60 °C. One problem with using 1-methoxy-2-propanol as a fuel was that the cell anode seemed to be seriously poisoned by the oxidation intermediates at anode overpotentials lower than ca. 0.2 V. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* 1-Methoxy-2-propanol; Methanol; Direct liquid fuel cell; Crossover current

## 1. Introduction

Methanol, the simplest alcohol containing only one carbon atom, is the most popular and widely used fuel in direct liquid fuel cells [1,2]. Unfortunately, methanol can move through a proton-exchange membrane (PEM) such as Nafion® via physical diffusion and electro-osmotic drag (by protons). Such a crossover not only results in a waste of fuel, but also greatly lowers the entire cell performance [3–7]. Most of the methanol crossing over will be electrochemically oxidized at the cathode. Such oxidation reactions lower the cathode potential and also consume 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.

Reducing methanol crossover will translate to higher fuel efficiency, and several approaches have been reported to be effective. Ren et al. showed that the methanol crossover rate through a 1200 eq. weight (EW) membrane was only 52% of that through an 1100 EW membrane [8]. Banerjee et al. described that incorporation of a thin layer of polymer having a higher ratio of backbone carbon atoms to those of the cationic exchange side chain could reduce methanol crossover rate [9]. Hobson et al. used low dosage electron beam to treat the surface of a Nafion® 117 membrane to reduce methanol crossover to 7% of that of the parent membrane, and to improve the overall cell performance up to 51% [10]. A membrane composed of polystyrene sulfonic acid (PSSA) and poly(vinylidene fluoride) (PVDF) was claimed to exhibit lower methanol crossover [11]. Modifying a membrane by in situ polymerization of monomers such as pyrrole and *N*-methylpyrrole also reduced methanol permeability [12].

Another barrier to the commercialization of a direct methanol fuel cell (DMFC) is the sluggish methanol oxidation reaction. Moreover, some intermediates such as carbon monoxide from methanol oxidation can strongly adsorb onto the surface of catalysts to cause them to be seriously poisoned. Pt alloys such as Pt/Ru have a much higher CO-tolerance, so they are widely used as the anode catalyst.

Other short chain organic chemicals such as ethanol, 1- and 2-propanol [13], dimethoxymethane, trimethoxymethane, and trioxane [14,15], and ethylene glycol and dimethyl oxalate [16] were also tested as fuels for direct liquid fuel cells. Wang et al. showed that ethanol, 1- and 2-propanol performed much worse than methanol, especially

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2-propanol [13]. Poor performance of ethylene glycol and dimethyl oxalate were reported by Peled et al. [16]. However, dimethoxymethane, trimethoxymethane, and trioxane showed comparable performance to methanol as found by Narayanan and co-workers [14,15]. They reported that these three chemicals could be oxidized at lower potentials than methanol, and thus, they could be better fuels than methanol. For example, using Nafion[®] 117 as the membrane and oxygen as the oxidant with a pressure of 20 psig, cell voltages of 0.25, 0.50 and 0.33 V were achieved at a current density of 50 mA/cm$^2$ when dimethoxymethane, trimethoxymethane and trioxane were oxidized at cell temperatures of 37, 65 and 60 °C, respectively [15].

We observed some interesting features when a new fuel, 1-methoxy-2-propanol, was oxidized in direct liquid fuel cells. The initial motive of studying this fuel was based on the facts that 2-propanol could perform much better than methanol under certain conditions [17] and that di- or trimethoxymethane gave comparable performance to methanol [14,15]. The structure of 1-methoxy-2-propanol is very similar to 2-propanol, with a $CH_3O-$ group replacing a $CH_3-$ group. We thought that the $CH_3O-$ group would be easier to be oxidized than a $CH_3-$ group, then 1-methoxy-2-propanol could perform even better than 2-propanol. Although the experimental results were different from what we expected, they were quite encouraging and interesting.

## 2. Experimental

The experiments were performed using a 25 cm$^2$ 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. Unless otherwise specified, anode and cathode with Pt/Ru and Pt loadings of both 4.8 mg/cm$^2$, respectively, were hot-pressed onto a Nafion[®] 112 membrane at 130 °C for 3 min. Alcohols were diluted to 1.0 M with water before they were pumped into the cell by a micropump (Micropump Inc., Vancouver, WA). The mixture was then re-circulated back to the mixing tank. The alcohol flow rate was controlled at 40 ml/min using a GW Laboratory DC Power Supply (Model GPS-1830D). A condenser was used to condense the alcohol 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 connection between the mixing tank and the cell was heated by heating tapes when needed. The temperatures of the mixing tank, alcohol mixture inlet to the cell, and the cell itself were monitored by thermocouples. Air was supplied to the cell by a compressor and exited the cell without any back pressurization. The air flow rate was adjusted using a flowmeter. The load was controlled by a 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 performance of 1.0 M 1-methoxy-2-propanol at a cell temperature of 60 °C and at air flow rates of 180, 397, 643, and 920 ml/min, respectively. These flow rates correspond to air stoichiometries of 2.1, 4.6, 7.4 and
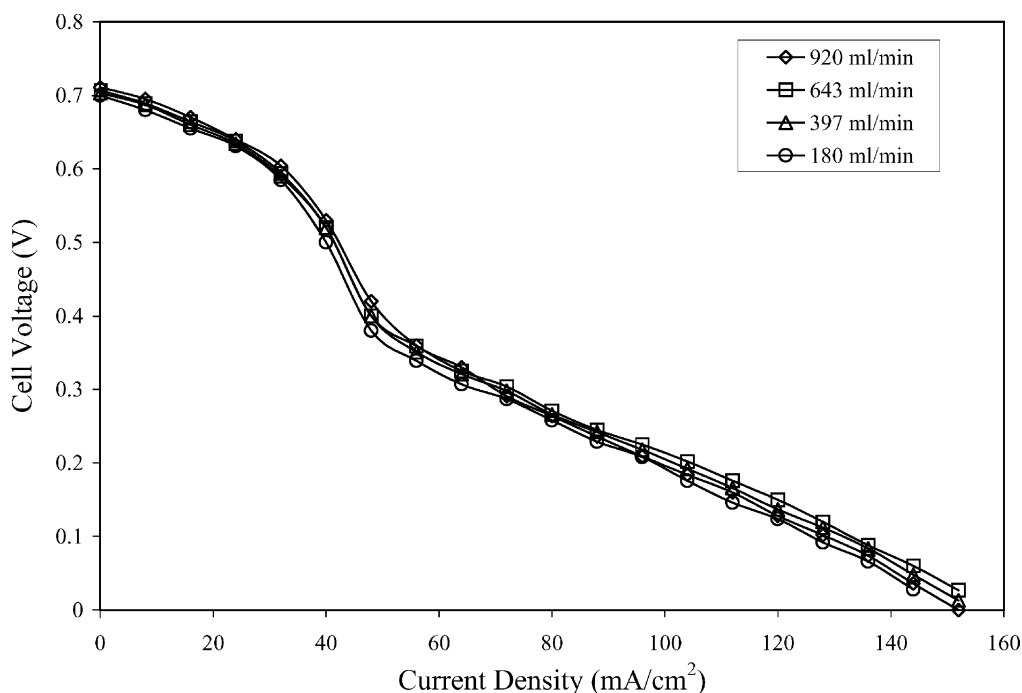


Fig. 1. Performances of 1-methoxy-2-propanol at air flow rates of 180, 397, 643, and 920 ml/min. $T_{cell}$, 60 °C; 1-methoxy-2-propanol, 1.0 M.
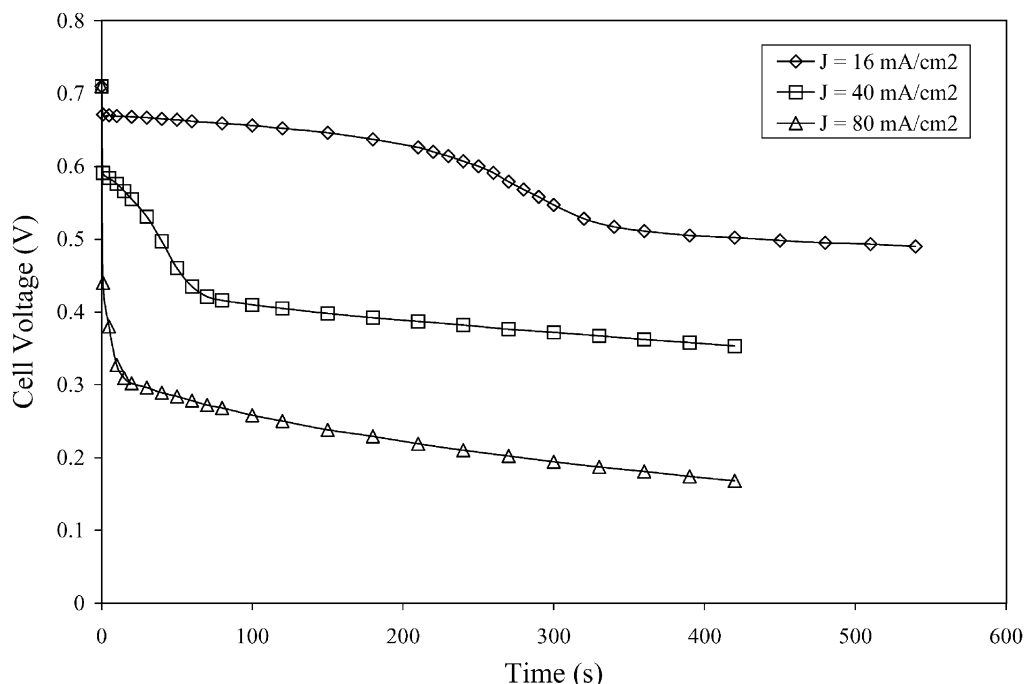
Fig. 2. Performance decline with time at current densities of 16, 40, and 80 mA/cm$^2$. $T_{cell}$, 60 °C; air flow rate, 920 ml/min; 1-methoxy-2-propanol, 1.0 M.

10.6, respectively, at a current density of 200 mA/cm$^2$. One conclusion drawn from the results was that changing air flow rates from 180 to 920 ml/min had no effect on the performance of the cell. This was an advantage of 1-methoxy-2-propanol over methanol. Methanol often requires higher air flow rate to achieve a respectable performance, but running air at a high flow rate makes water balancing difficult in a fuel cell system. One distinct and puzzling feature of 1-methoxy-2-propanol oxidation was the rapid cell voltage decline from ca. 0.63 to 0.40 V. This decline is normally observed in the high current density region due to mass transport limitation in both PEM fuel cells and direct methanol fuel cells (DMFCs). However, based on all the electrochemical measurements throughout this paper, we concluded that the decline here was due to poisoning of the cell anode by the intermediates from 1-methoxy-2-propanol oxidation, rather than because of mass transport limitation. After the quick decline, the decrease of voltage slowed down even when higher current densities were drawn from the cell.

This slow-down was presumably due to the increase in anode overpotential, which was high enough to oxidize some of the poisoning species.

It was found that the rate of anode poisoning was related to the current density as shown in Fig. 2. The open circuit voltage of the cell was about 0.710 V. When a small current of 16 mA/cm$^2$ was applied, the voltage dropped to 0.671 V immediately. It then declined gradually to 0.626 V in the first 210 s (decline rate = 0.22 mV/s). A quicker decline started and dropped the voltage to 0.528 V in another 110 s (decline rate = 0.89 mV/s). This fast decline was followed by a slower decline at a rate of 0.17 mV/s. When a current of 40 mA/cm$^2$ was applied, the cell voltage dropped from 0.710 to 0.591 V immediately. It then quickly declined to 0.416 V in 79 s at a rate of 2.2 mV/s, which was followed by a much slower decline of 0.19 mV/s. When a current of 80 mA/cm$^2$ was applied, following the immediate drop from 0.710 to 0.440 V, the voltage quickly dropped to 0.309 V in 14 s at a rate of 9.4 mV/s. It was then followed by a slower

Table 1
Cell voltage decline characteristics at three current densities

| | | | |
|---|---|---|---|
| Current density (mA/cm$^2$) | 16 | 40 | 80 |
| Open circuit voltage (V) | 0.710 | 0.710 | 0.710 |
| Initial voltage after load applied (V) | 0.671 | 0.591 | 0.440 |
| Quick decline time intervals (s) | 210–320 | 0–80 | 0–15 |
| Voltage decline rate before quick decline (mV/s) | 0.22 | N/A[a] | N/A |
| Voltage decline rate during quick decline (mV/s) | 0.89 | 2.2 | 9.4 |
| Voltage decline rate after quick decline (mV/s) | 0.17 | 0.19 | 0.35 |

[a] N/A: not applicable.

decline of 0.35 mV/s. These results, summarized in Table 1, clearly show that electrode poisoning proceeded very fast, especially at higher current densities.

Open circuit voltage was slightly affected by anode poisoning. For example, after a cell was operated at a current density of 24 mA/cm$^2$ (in the voltage quick decline region) for 5 min using 1.0 M 1-methoxy-2-propanol at 60 °C, the following open circuit voltage (measured after waiting for 30 s) decreased from 0.709 to 0.700 V.

Anode poisoning was reversible by simply reverse the polarity of the electrodes, i.e. by applying a positive voltage on the anode using a power supply. Such refreshment was performed before each V–I curve was collected so that the poisoning was not carried over to the next measurement.

Due to the lack of equipment available at the time, the products from the oxidation of 1-methoxy-2-propanol were not analyzed. Wang et al. reported that the electro-oxidation of 2-propanol yielded mainly acetone [13]. Inferred from his study, the major product from the oxidation of 1-methoxy-2-propanol could be $CH_3OCOCH_3$, i.e. two hydrogen atoms are extracted from each 1-methoxy-2-propanol molecule, $CH_3OCHOHCH_3$.

The cell was also tested at temperatures of 40 and 80 °C with the air flow rate ranging from 180 to 920 ml/min. Features similar to those shown in Fig. 1 were obtained. Fig. 3 compares the performances at 40, 60 and 80 °C when the air flow rate was 180 ml/min. Clearly, the cell performed better as the temperature was increased from 40, to 60, and then to 80 °C. The rapid decline started earlier at a cell temperature of 40 °C, presumably because the reaction intermediates adsorb more strongly and their oxidation proceeds slower at a lower temperature. The slightly higher

performance at 60 °C, than at 80 °C at current densities less than 50 mA/cm$^2$ is believed to be due to a lower alcohol crossover rate at 60 °C than at 80 °C as shown in Fig. 7.

Fuel mixtures containing 0.5 and 2.0 M 1-methoxy-2-propanol were also tested, and slight difference in performance was observed. The best performance was achieved when 1.0 M solution was used, and 0.5 M solution performed better than 2.0 M solution at current densities less than ca. 80 mA/cm$^2$.

The performance of 1-methoxy-2-propanol was compared with methanol under various conditions as shown in Figs. 4 and 5. At a high air flow rate of 920 ml/min, methanol performed better than 1-methoxy-2-propanol at current densities higher than 100 mA/cm$^2$; but, encouragingly, 1-methoxy-2-propanol performed better than methanol at current densities less than ca. 50 mA/cm$^2$. Also, the open circuit voltage of the 1-methoxy-2-propanol cell was at least 0.11 V higher than that of methanol cell. More encouragingly, at a low air flow rate of 180 ml/min, 1-methoxy-2-propanol performed better than methanol in the entire current density region at 60 and 80 °C. The open circuit voltage of the 1-methoxy-2-propanol cell only slightly declined when the air flow rate was decreased from 920 to 180 ml/min, but that of the methanol cell declined substantially from 0.567, 0.587 and 0.591 to 0.547, 0.464, and 0.367, respectively, at cell temperatures of 40, 60, and 80 °C, respectively. The performance of methanol cell at 80 °C was extremely poor. The poor performance and lower open circuit voltage at higher temperatures was due to higher methanol crossover. Table 2 summarizes the open circuit voltage for both 1-methoxy-2-propanol and methanol cells.
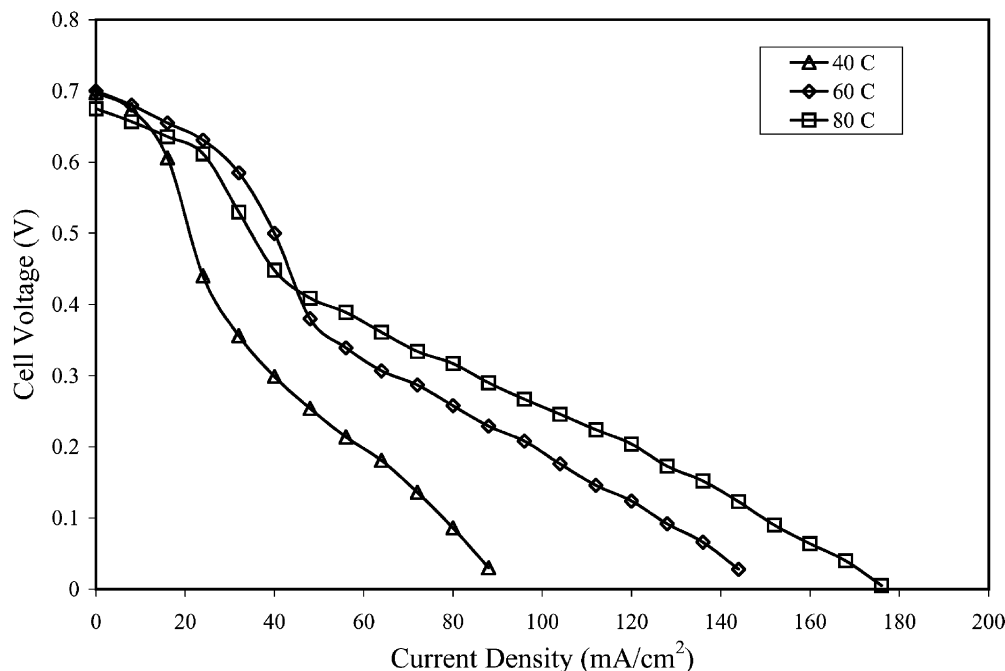


Fig. 3. Performances of 1-methoxy-2-propanol at cell temperatures of 40, 60, and 80 °C. Air flow rate, 180 ml/min; 1-methoxy-2-propanol, 1.0 M.
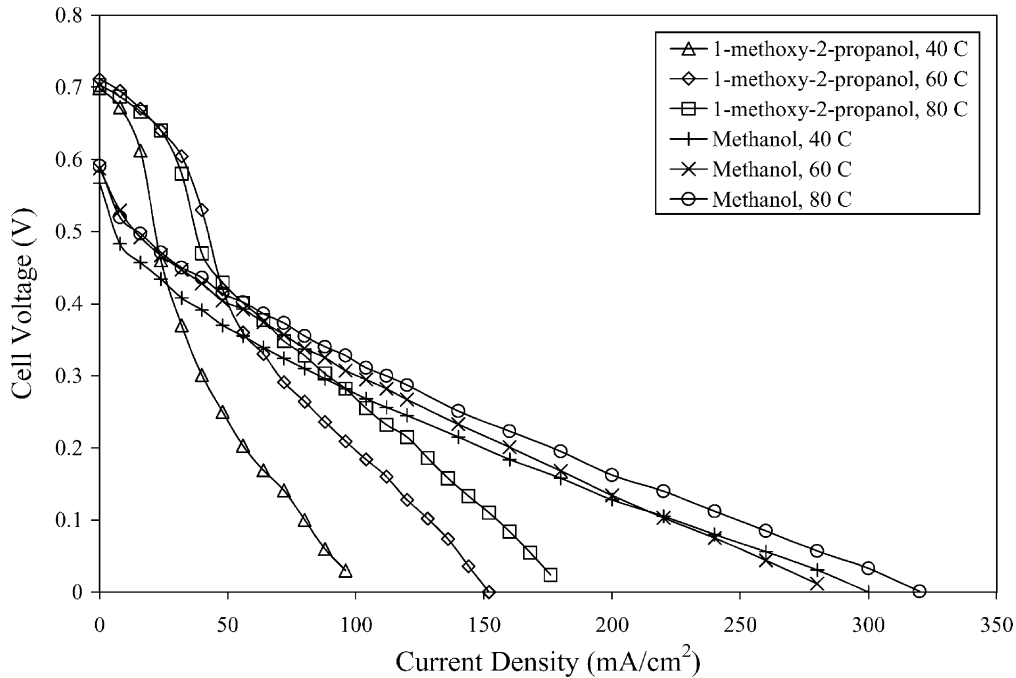
Fig. 4. Performances of 1-methoxy-2-propanol vs. methanol at air flow rate of 920 ml/min and at cell temperatures of 40, 60, and 80 °C. Alcohol, 1.0 M.
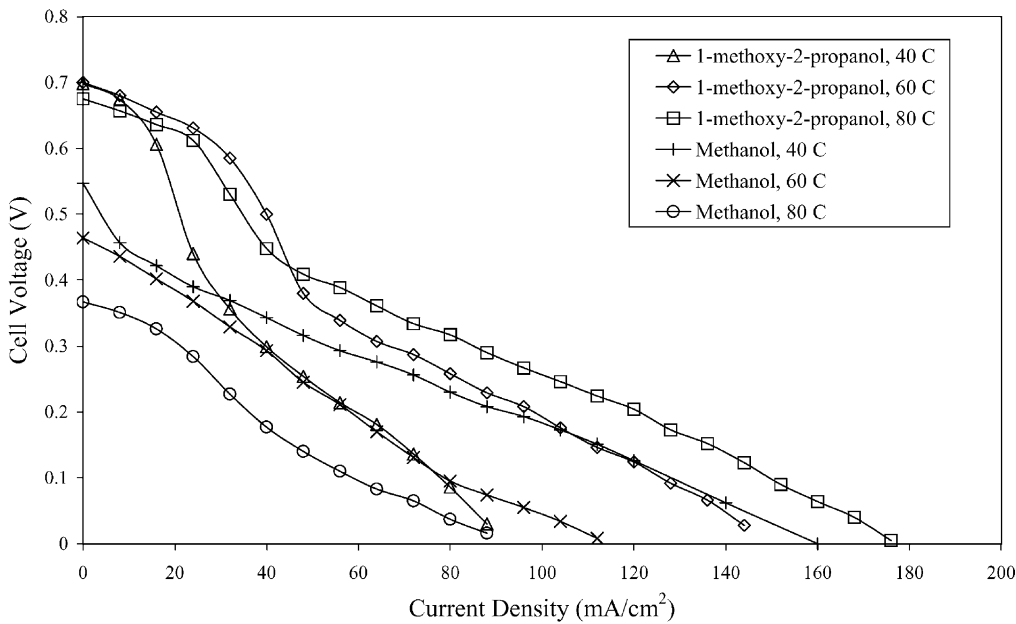


Fig. 5. Performances of 1-methoxy-2-propanol vs. methanol at air flow rate of 180 ml/min and at cell temperatures of 40, 60, and 80 °C. Alcohol, 1.0 M.

Table 2
Open circuit voltage

| $T_{cell}$ (°C) | OCV (V) | | | |
|---|---|---|---|---|
| | 1-Methoxy-2-propanol | | Methanol | |
| | Air (920 ml/min) | Air (180 ml/min) | Air (920 ml/min) | Air (180 ml/min) |
| 40 | 0.699 | 0.698 | 0.567 | 0.547 |
| 60 | 0.711 | 0.700 | 0.587 | 0.464 |
| 80 | 0.703 | 0.675 | 0.591 | 0.367 |

The crossover current density of 1-methoxy-2-propanol through a Nafion® 112 membrane was estimated using an electrochemical oxidation technique. Fig. 6 shows the experimental setup for measuring alcohol crossover current at open circuit voltage (with methanol as an example). During the measurement, nitrogen was introduced into the cathode side and a positive voltage was applied at this electrode using a power supply. The reaction occurring at the cathode was the oxidation of the alcohol that crosses through the membrane. When the applied voltage was high enough,
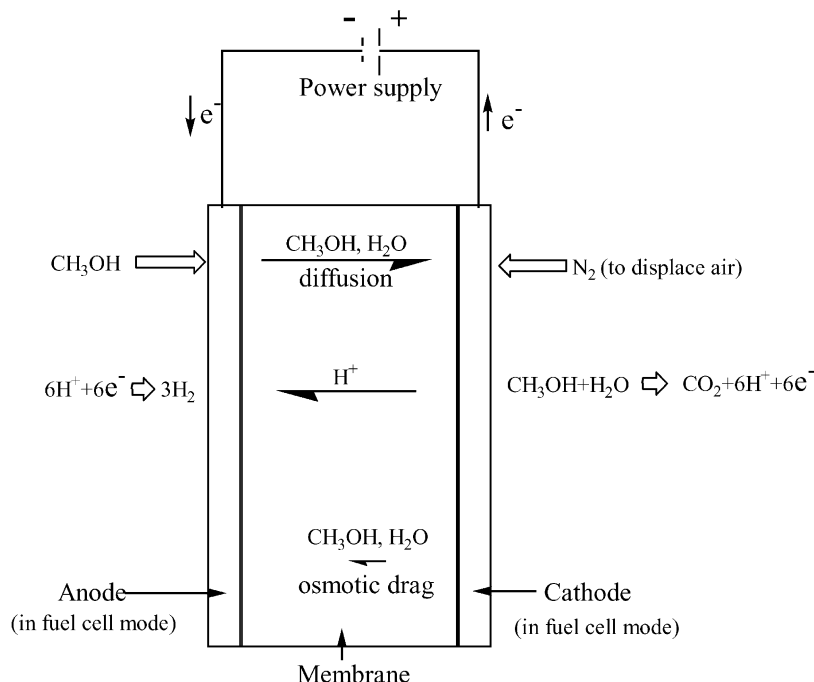
Fig. 6. Setup for the electrochemical measurement of alcohol crossover current at open circuit voltage.

the limiting current represented approximately the rate of alcohol crossover. The reaction occurring on the anode side was the reduction of protons to hydrogen. These protons came from the alcohol oxidation at the positive electrode and migration to the other side of the membrane. This technique may underestimate the amount of alcohol crossing through the membrane from the anode to the cathode, because when protons move to the other side of the membrane, they drag some alcohol back [8]. However, the number of alcohol molecules dragged by each proton is very low [18], so the error caused by this dragging is minimal. In addition, the measurement represents the amount of alcohol crossing through the membrane at open circuit. This amount is normally more than that when the fuel cell is under a load because the consumption of alcohol reduces its concentration in the catalyst layer, which in turn decreases the alcohol crossover.

Fig. 7 shows the crossover current densities of 1-methoxy-2-propanol at cell temperatures of 40, 60, and 80 °C, respectively. The crossover current was low when the applied voltage was lower than 0.2 V. We found that this was not because 1-methoxy-2-propanol could not be oxidized at such low voltage, but because the cathode catalyst was quickly poisoned. This was actually similar to what we observed in Figs. 1–3, except that the cathode catalyst, Pt, might be more easily poisoned than the anode catalyst, Pt/Ru. The crossover current then increased and finally reached a plateau when the applied voltage was higher than 0.65 V at 40 °C, and 0.85 V at 60 and 80 °C. Based on the current densities at around 0.9 V, the amounts of 1-methoxy-2-propanol crossing through the membrane increased almost

linearly with the cell temperature as it was increased from 40, to 60, and then to 80 °C. It was observed that electrode poisoning continued even in the high voltage plateau region, and this partly contributed to the formation of the plateaus. This poisoning was believed to cause an underestimation of the amount of 1-methoxy-2-propanol crossing through the membrane.

In order to determine how large an error this poisoning might cause when the crossover of 1-methoxy-2-propanol was estimated, the change of crossover current densities with time was studied, and the results are shown in Fig. 8. A voltage of 0.95 V was applied during these measurements. At all three temperatures, the crossover current declined with time, and the decline proceeded fastest in the beginning. The data within the first few seconds could overestimate the amount of alcohol crossing over due to contributions from capacitance charging current, and due to the initial accumulation of alcohol in the cathode compartment before the voltage was applied. At the same time, the current after 100 s might underestimate the amount of alcohol crossing over because the electrode was seriously poisoned by then. A number in-between should represent the true amount of alcohol crossing over. Based on this analysis and the curves shown in Fig. 8, an error of up to 50% could occur, especially at 40 °C. For the data presented in Fig. 7, each point was taken after waiting for about 15 s; and it was hoped that these would represent readings close to the actual amount of alcohol crossing over.

The crossover current of methanol was also measured similarly for comparison. Fig. 9 shows the results measured at 60 °C for 1 M methanol. Clearly, methanol had a much
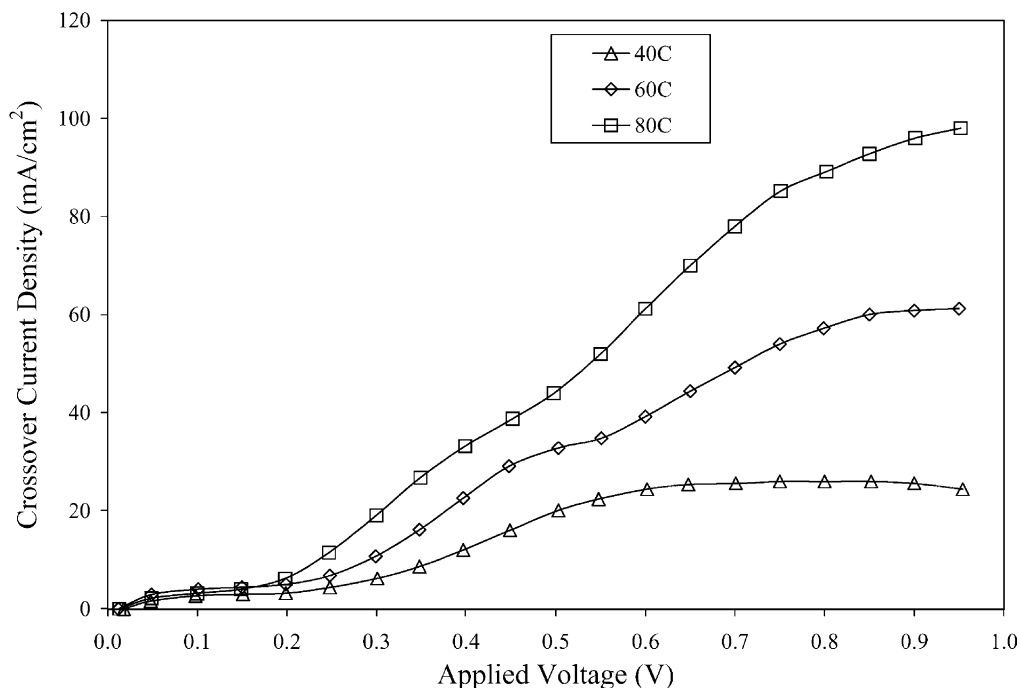
Fig. 7. Crossover current densities of 1-methoxy-2-propanol vs. applied voltage at temperatures of 40, 60, and 80 °C. Nitrogen flow rate, 643 ml/min; 1-methoxy-2-propanol, 1.0 M.

higher crossover current than 1-methoxy-2-propanol under the same conditions (i.e. 232 mA/cm$^2$ versus 60 mA/cm$^2$ at 0.9 V). Two different features were observed from the measurement of methanol crossover. Firstly, there was almost no current generated at potentials <0.30 V. This was not due to poisoning as in the 1-methoxy-2-propanol case, but because methanol oxidation needs an overpotential higher than at least ca. 0.30 V. In other words, methanol is more difficult to oxidize than 1-methoxy-2-propanol. Secondly, no serious poisoning was observed during methanol oxidation, therefore, underestimation of methanol crossover due to electrode poisoning was much less.
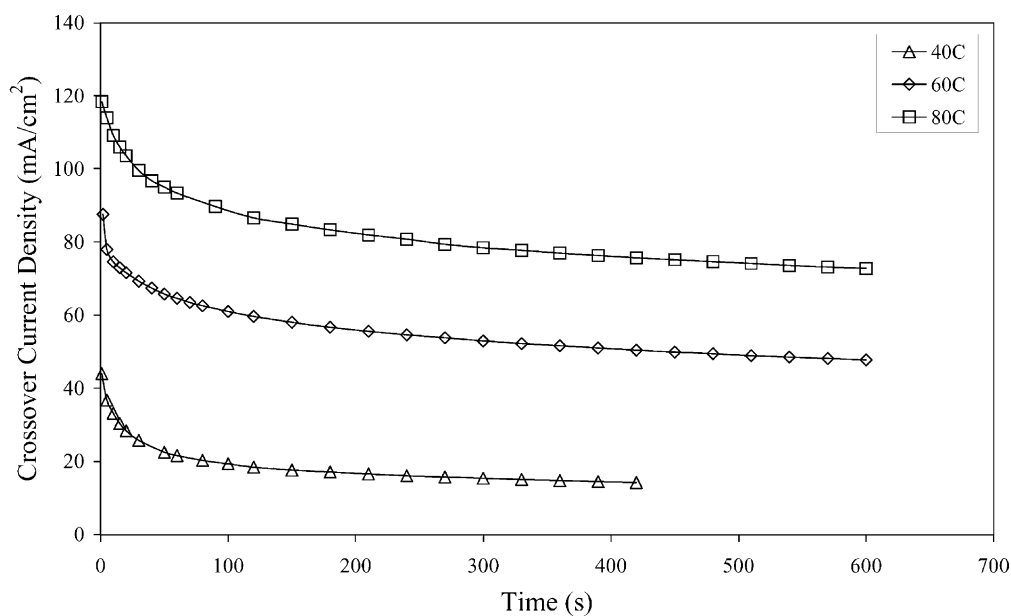


Fig. 8. Decline of the crossover current densities of 1-methoxy-2-propanol vs. time at temperatures of 40, 60, and 80 °C. Nitrogen flow rate, 643 ml/min; 1-methoxy-2-propanol, 1.0 M; applied voltage, 0.95 V.
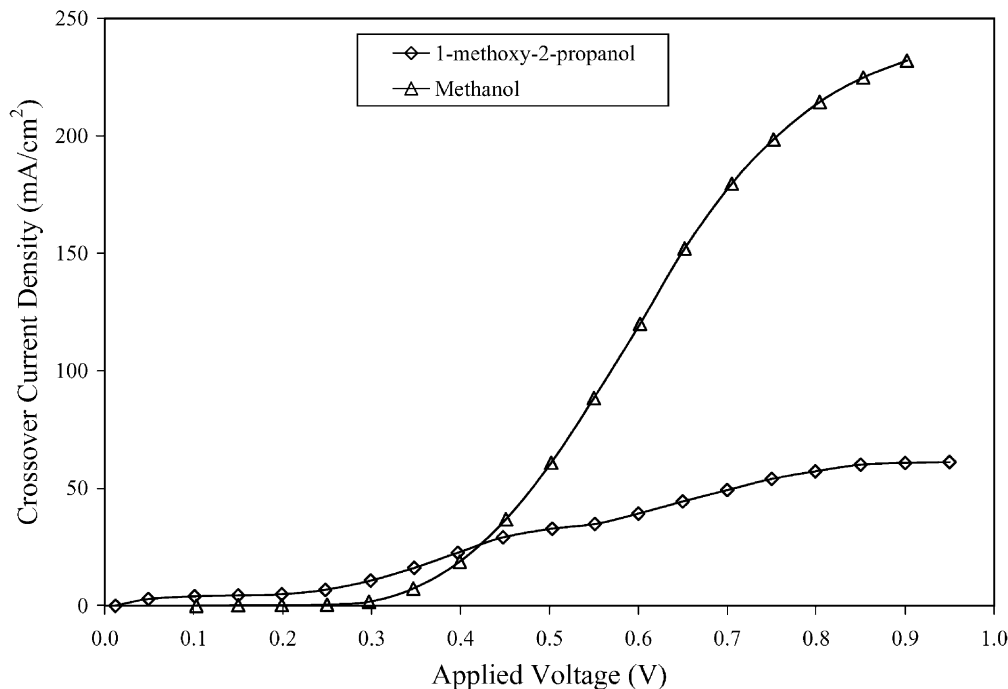
Fig. 9. Crossover current density of 1-methoxy-2-propanol vs. methanol. Nitrogen flow rate, 643 ml/min; alcohol, 1.0 M; cell temperature, 60 °C.

## 4. Conclusions

The electrochemical oxidation of 1-methoxy-2-propanol in a direct liquid fuel cell showed some interesting features. Firstly, it is easier to oxidize than methanol, but its oxidation intermediates or products poison the catalyst quickly. Such a poisoning resulted in an early decline in cell voltage, which could be mistaken as due to a mass transport limitation. When the anode overpotential was high enough (ca. 0.2 V) to oxidize some of these poisoning species, the decline of voltage slowed down. Secondly, 1-methoxy-2-propanol performed better than methanol over the entire current density region at low air flow rates at 60 and 80 °C. The reasons for this are that 1-methoxy-2-propanol is easier to oxidize than methanol and that methanol has a crossover current ca. four times that of 1-methoxy-2-propanol through the Nafion® 112 membrane. This better performance is one advantage of 1-methoxy-2-propanol over methanol. At high air flow rates, some of the methanol crossing through the membrane was carried away or blown out by air, and the performance of the methanol fuel cell increased markedly. It showed better performance than 1-methoxy-2-propanol at current densities higher than 100 mA/cm$^2$; but at current densities less than 50 mA/cm$^2$, 1-methoxy-2-propanol still performed better. In contrast, air flow rate had little effect on the performance of 1-methoxy-2-propanol fuel cells. This is another advantage of 1-methoxy-2-propanol over methanol because water will be easily balanced for a direct liquid fuel cell using 1-methoxy-2-propanol as the fuel. Thirdly, it was a challenge to measure the crossover of 1-methoxy-2-propanol electrochemically, because the electrode was continuously poisoned during the measuring process. This poisoning might underestimate the amount of 1-methoxy-2-propanol crossing through the membrane, and the error could be as high as 50%.

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