

# Performance of 2-propanol in direct-oxidation fuel cells

Zhigang Qi\*, Arthur Kaufman

*H Power Corporation, 60 Montgomery Street, Belleville, NJ 07109, USA*

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## Abstract

A direct-oxidation fuel cell using 2-propanol as fuel has been evaluated. The cell performance, open circuit voltage (OCV), and alcohol crossover were measured at various alcohol concentration, cell temperature, and air/nitrogen flow rate. The cell shows much higher performance than a direct methanol fuel cell, especially at current densities less than ca. 200 mA/cm<sup>2</sup>. This performance is the highest among any direct-liquid-oxidation fuel cells. The cell open circuit voltage can be as much as 0.27 V higher than that of a methanol cell, while the amount of 2-propanol crossing through the membrane can be as low as 1/7 of that of methanol. Therefore, a direct 2-propanol fuel cell can have much higher fuel and fuel cell efficiencies. One problem associated with using 2-propanol as fuel is the anode poisoning by reaction intermediates and a frequent cleaning of the electrode surface is needed.

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*Keywords:* 2-Propanol; Methanol; Fuel cell; Crossover current; Open circuit voltage

## 1. Introduction

Hydrogen is the cleanest and most efficient fuel used in a fuel cell. Since its oxidation rate at a fuel cell anode is high enough even at room temperature, it is widely used in low temperature fuel cells such as proton-exchange membrane (PEM) fuel cells, alkaline fuel cells and phosphoric acid fuel cells. However, the production, transportation and storage of pure hydrogen are very challenging tasks, which require a lot of further development and improvement. Hydrogen can also be produced on-board through reforming hydrocarbon fuels such as methane, propane and methanol; but this not only makes the entire fuel cell system more complicated, but also dramatically increases its cost. Moreover, any carbon monoxide (CO) remaining in the reformed gas, even at ppm levels, will poison the electrodes of a PEM fuel cell to lower its performance.

The problems associated with hydrogen have encouraged worldwide search for other fuels that can be directly oxidized without through a reforming step. Methanol, the simplest alcohol containing only one carbon atom, is the most popular and widely used fuel. A direct-oxidation fuel cell using methanol as fuel (called a direct methanol fuel cell, DMFC) has a long history. Early DMFCs used liquid electrolyte such

as a dilute sulfuric acid for proton transportation [1,2]. Major problems of using liquid electrolyte are corrosion of cell materials caused by the strong acid, poisoning of electrodes by the adsorption of sulfate anions, and leakage of electrolyte through the surrounding materials. For example, the electrolyte could gradually leak out through the pores of the air cathode, which also causes fuel loss and cathode poisoning. In order to alleviate such a leaking problem, an additional solid proton-exchange membrane was interposed between the anode and cathode [3–5]. In recent years, liquid electrolyte is seldom used in a DMFC, and only a proton-exchange membrane such as Nafion<sup>®</sup> is used as the electrolyte [6,7]. Nafion<sup>®</sup> membranes have excellent chemical, mechanical, thermal and electrochemical stabilities, and their ionic conductivity can reach as high as 0.1 S/cm. The kinetics of methanol oxidation and oxygen reduction at the electrode/membrane/electrode interfaces were found to be more facile than at the electrode/sulfuric acid/electrode interfaces. Since the fuel and water solution is free from sulfuric acid, corrosion of cell materials becomes less severe. The cell could be operated at temperatures as high as 120 °C, while sulfuric acid tends to degrade at temperatures higher than 80 °C. Also, the absence of conducting ions in the fuel and water solution substantially eliminates the parasitic shunt currents in a multi-cell stack. Recently, Davis [8] claimed that adding formic acid into the methanol and water solution would increase the conduction of protons within the anode structure, without poisoning the catalysts because formic acid is a clean-burning fuel.

\* Corresponding author. Tel.: +1-973-450-4400x478;

fax: +1-973-450-9850.

E-mail address: zqi@hpower.com (Z. Qi).

Unfortunately, methanol can still seriously permeate Nafion<sup>®</sup> and other types of proton-exchange membranes via physical diffusion and electro-osmotic drag by protons [9–13]. Such crossover not only results in a large waste of fuel, but also greatly lowers cathode performance. Most of the methanol crossing over will be electrochemically oxidized at the cathode. Such oxidation reactions not only lower the cathode potential but also consume some oxygen. If the reaction intermediate such as carbon monoxide adsorbs onto the catalyst surface, the cathode will be poisoned, which further lowers its performance.

A variety of methods have been studied to reduce methanol crossover. Banerjee et al. [14] 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 the methanol crossover rate, although the membrane resistance would increase. It was suggested that the polymer with a higher carbon atom ratio be preferably orientated on the anode side. Prakash et al. [15] described a polymer membrane composed of polystyrene sulfonic acid (PSSA) and poly(vinylidene fluoride) (PVDF). It was claimed that such a PSSA–PVDF membrane exhibited lower methanol crossover, which translates to higher fuel and fuel cell efficiencies. Pickup et al. [16] described a modified ion exchange membrane that possessed lower methanol crossover. They modified existing membranes such as Nafion<sup>®</sup> by in situ polymerization of monomers, such as aryls, heteroaryls, substituted aryls, substituted heteroaryls or a combination thereof. The modified membrane could exhibit reduced permeability to methanol crossover often without a significant increase in ionic resistance.

Another barrier to the commercialization of DMFCs is the sluggish methanol oxidation reaction. Moreover, some intermediates from methanol oxidation such as carbon monoxide can strongly adsorb on 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-propanol and 2-propanol [17], dimethoxymethane, trimethoxymethane, and trioxane [6,18], and ethylene glycol and dimethyl oxalate [19] were also tested as fuels for direct-liquid-oxidation fuel cells. Wang et al. [17] showed that ethanol, 1-propanol, and especially 2-propanol, performed much worse than methanol. Low performances of ethylene glycol and dimethyl oxalate were presented by Peled et al. [19]. However, dimethoxymethane, trimethoxymethane, and trioxane showed comparable performance to methanol as per Narayanan et al. [18] and Surampudi et al. [6]. 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<sup>®</sup> 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<sup>2</sup> when dimethoxymethane, trimethoxymethane and trioxane were oxidized at cell temperatures of 37, 65 and 60 °C,

respectively [6]. However, these performances were still very low.

In a preliminary study, we reported that 2-propanol could actually be a better fuel than methanol in the lower current density region [20]. This paper presents a detailed study on the performance of a direct 2-propanol fuel cell (D2PFC). Its open circuit voltage (OCV) and alcohol crossover under various conditions were also studied.

## 2. Experimental

The experiments were performed using a 25 cm<sup>2</sup> 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<sup>®</sup>-treated 9-mil Toray paper, respectively. Anode and cathode with Pt/Ru and Pt loadings of both 4.8 mg/cm<sup>2</sup>, respectively, were hot-pressed onto a Nafion<sup>®</sup> 112 membrane at 130 °C for 3 min to form a membrane-electrode assembly (MEA). Alcohols were diluted 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 by 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<sub>2</sub>. The temperature of the mixing tank was controlled by a hot plate. The connection between the mixing tank and the cell was heated by a heating tape. 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. Air flow rate was adjusted by using a flowmeter. The load was controlled by another GW laboratory dc power supply (Model: GPR-1820HD), and the cell voltage was monitored by using a voltmeter.

## 3. Results and discussion

Fig. 1 shows that the flow rate of a 0.5 M 2-propanol solution has only a slight effect on the fuel cell performance at a cell temperature of 60 °C. The cell was operated at a current density of 32 mA/cm<sup>2</sup> when this experiment was performed. The largest performance increase of ca. 4 mV occurred when the flow rate was increased from 2.4 to 6.6 ml/min; afterwards, the performance increase slowed down. A total of 14 mV was observed when the flow rate was increased from 12 to 73 ml/min. At flow rates lower than ca. 7 ml/min, the flow of solution was not continuous, and thus, caused a quicker decrease in the fuel cell performance. In all the following experiments, the flow rate of 2-propanol solution was set at 38 ml/min, which corresponds to a reaction stoichiometry of ca. 220 and 75 for a 1.0 M 2-propanol

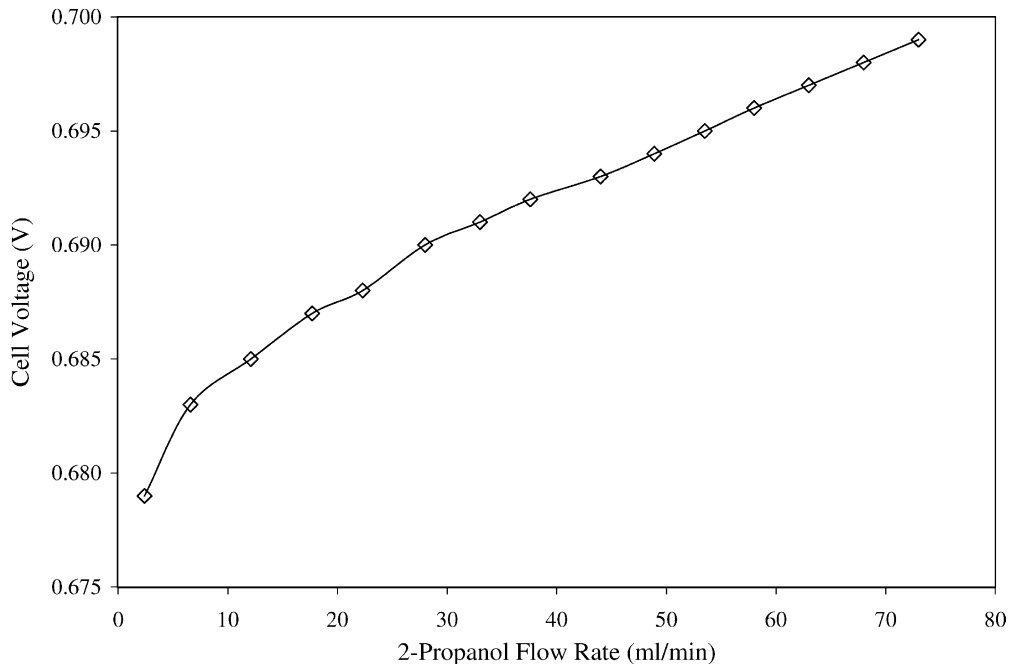


Fig. 1. Effect of 2-propanol flow rate on fuel cell performance.  $T_{\text{cell}} = 60\text{ }^{\circ}\text{C}$ , 2-propanol = 0.5 M, air flow rate = 180 ml/min, and cell current density = 32 mA/cm<sup>2</sup>.

solution and a 1.0 M methanol solution, respectively, at a current density of 200 mA/cm<sup>2</sup>.

Fig. 2 shows the performance of a 1.0 M 2-propanol solution at a cell temperature of 60 °C with air flow rates at 180, 397, 643, and 920 ml/min, respectively. These air flow rates correspond to reaction stoichiometries of 2.0, 4.4, 7.1, and 10.2, respectively, at a current density of 200 mA/cm<sup>2</sup>.

Air flow rate should be as slow as possible in order to balance water in the entire fuel cell system, and to reduce the parasitic power loss from the air pump or compressor. As shown by Fig. 2, the cell performance increased gradually and moderately when air flow rate was increased. In addition, the voltage decline accompanying the current density increase accelerated suddenly at current densities higher

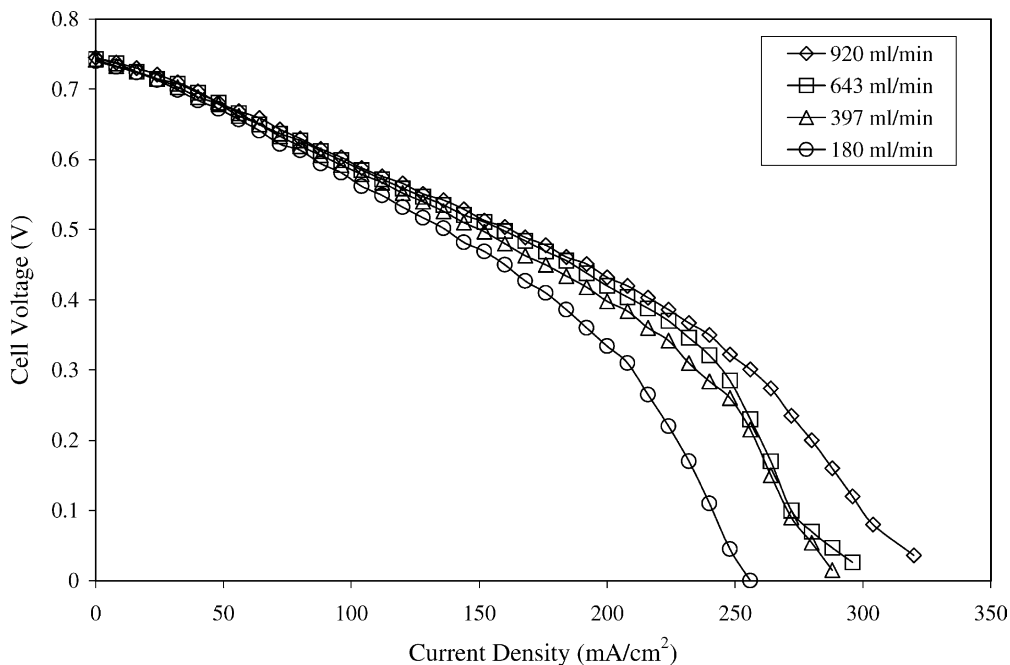


Fig. 2. Performance of a 2-propanol fuel cell at various air flow rates.  $T_{\text{cell}} = 60\text{ }^{\circ}\text{C}$ , and 2-propanol = 1.0 M.

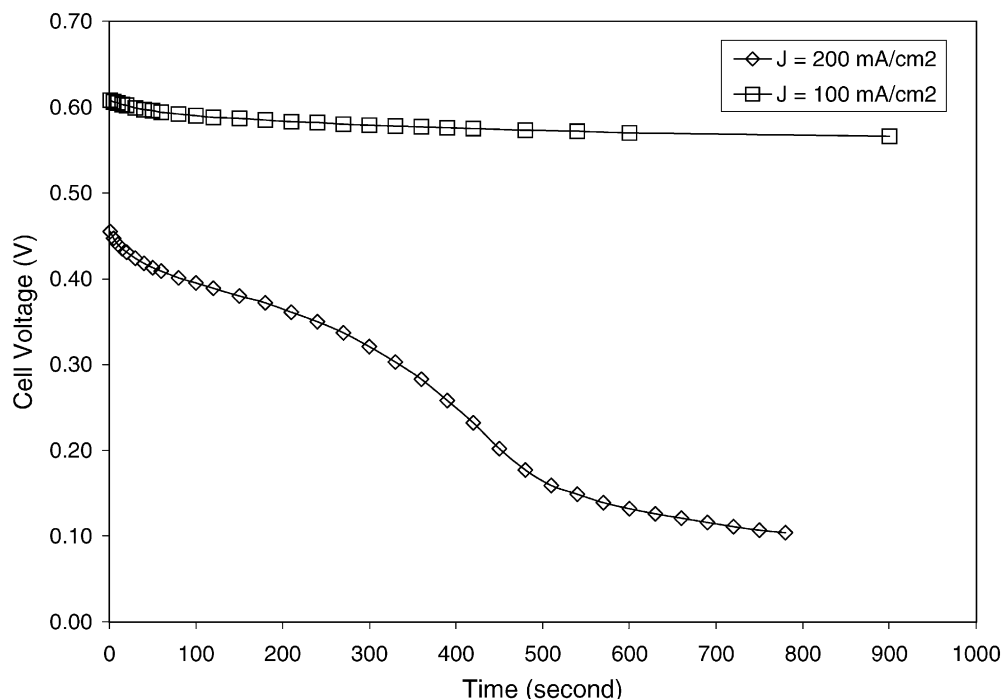


Fig. 3. Change of fuel cell performance with time at current densities of 100 and 200 mA/cm<sup>2</sup>, respectively.  $T_{\text{cell}} = 60 \text{ }^\circ\text{C}$ , 2-propanol = 1.0 M, air flow rate = 643 ml/min.

than ca. 200 mA/cm<sup>2</sup>. This quicker decline at higher current densities is normally due to increased mass transport limitation. However, we found that another factor also contributed to this decline in a direct 2-propanol fuel cell (D2PFC).

Fig. 3 shows the cell voltage change with time when constant current densities of 100 and 200 mA/cm<sup>2</sup> were generated, respectively. At 100 mA/cm<sup>2</sup>, the cell voltage declined from 0.606 to 0.566 V in 900 s; while at 200 mA/cm<sup>2</sup>, the cell voltage declined from 0.455 to 0.104 V in 780 s. Such a speedy decline is normally not observed in a hydrogen/air or a direct methanol fuel cell (DMFC). When the polarity of the cell was reversed briefly at the end of the voltage decline, the cell voltage resumed to its initial value when the same current density was generated; and then, it declined as before. Based on this observation, it was concluded that the cell anode was continuously poisoned by reaction intermediates or products, and that a higher current led to a faster poisoning due to a quicker formation and accumulation of the poisoning species. When the polarity of the cell was reversed, the anode was cleaned by the applied voltage, and thus its performance resumed to its original value. Please also note that the  $V-I$  curves were obtained from lower currents to higher currents. During this process, anode poisoning continued with time, but in the lower current density region, the accumulation was slower, and its effect on the cell performance would also be minor. As the current was increased, the poisoning not only accumulated, but also proceeded faster; and finally, there was not enough active surface for the reaction to proceed, resulting in a quicker decline at current densities higher than ca.

200 mA/cm<sup>2</sup>. Therefore, in addition to an increased mass transport limitation, accumulated anode poisoning was another factor to cause the cell voltage to decline quickly in the higher current density region.

Due to the formation of poisoning species, each data point, especially those in the higher current density region, might have continued to decline if there was a longer time before the data were taken. Therefore, the  $V-I$  curves should be treated as transitory. For all the  $V-I$  curves reported here, the cell polarity was reversed at the end of each testing to ensure that the poisoning was not transferred to the next test.

$V-I$  curves similar to those shown in Fig. 2 were obtained under a variety of 2-propanol concentrations and cell temperatures. Fig. 4 illustrates the  $V-I$  curves obtained at an air flow rate of 920 ml/min. At current densities higher than 60 mA/cm<sup>2</sup>, 0.5 M 2-propanol gave the worst performance. This was most likely due to a higher mass transport limitation. At current densities less than ca. 20 mA/cm<sup>2</sup>, 0.5 M 2-propanol was actually among the best performers. Without considering the most transitory and quickest voltage decline region where current density larger than 200 mA/cm<sup>2</sup>, the cell performance increased as the cell temperature was increased from 40 to 60 °C and then to 80 °C for 1.0 M 2-propanol. At the same cell temperature of 60 °C, 1.0 M 2-propanol gave the best performance, followed by 2.0 M 2-propanol, and then by 0.5 M 2-propanol. The inferior performance of 2.0 to 1.0 M 2-propanol was believed to be due to a higher 2-propanol crossover, as discussed later.

Some variation was observed when a lower air flow rate of 180 ml/min was used, as shown in Fig. 5. Similarly, at

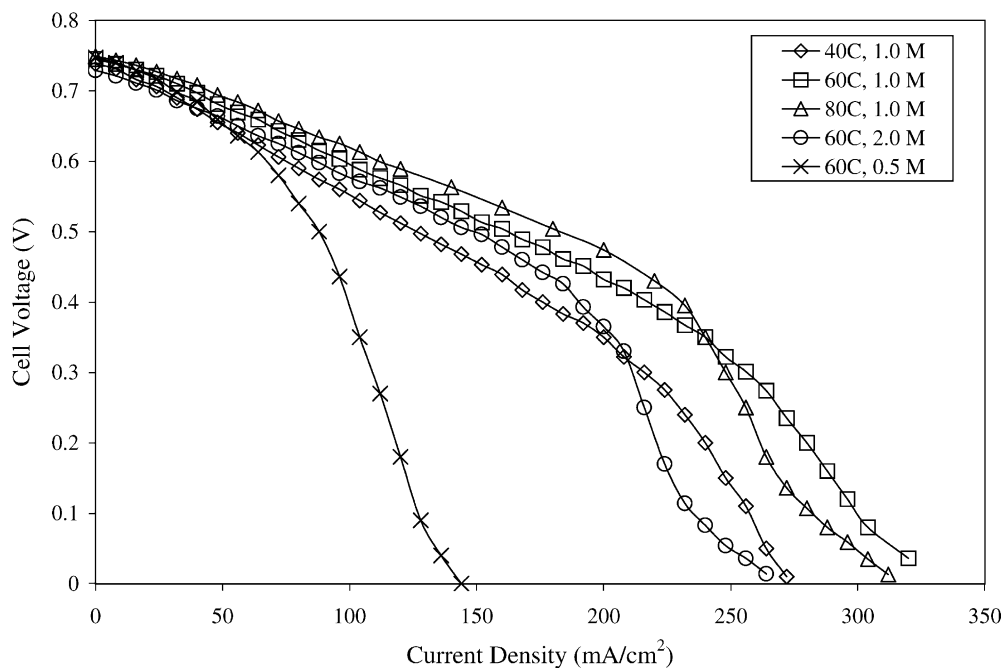


Fig. 4. Effects of cell temperature and 2-propanol concentration on performance at an air flow rate of 920 ml/min.

current densities higher than  $70 \text{ mA/cm}^2$ , 0.5 M 2-propanol gave the worst performance, although it was one of the best performers at current densities less than ca.  $50 \text{ mA/cm}^2$ . At current densities lower than  $70 \text{ mA/cm}^2$ , 2.0 M 2-propanol was the worst performer, due to higher alcohol crossover. With 1.0 M 2-propanol, the cell performance increased as the cell temperature was increased from 40 to  $60 \text{ }^\circ\text{C}$ , but there was little change from 60 to  $80 \text{ }^\circ\text{C}$ . At a cell temperature of

$60 \text{ }^\circ\text{C}$ , 1.0 M 2-propanol gave the best performance, followed by 2.0 M 2-propanol at current densities higher than  $70 \text{ mA/cm}^2$ , or by 0.5 M 2-propanol at current densities lower than  $70 \text{ mA/cm}^2$ .

For comparison, the performance of a methanol cell was measured under similar conditions. As an example, Fig. 6 shows the performance of 1.0 M 2-propanol versus 1.0 M methanol at a cell temperature of  $60 \text{ }^\circ\text{C}$ . Firstly, the OCV of

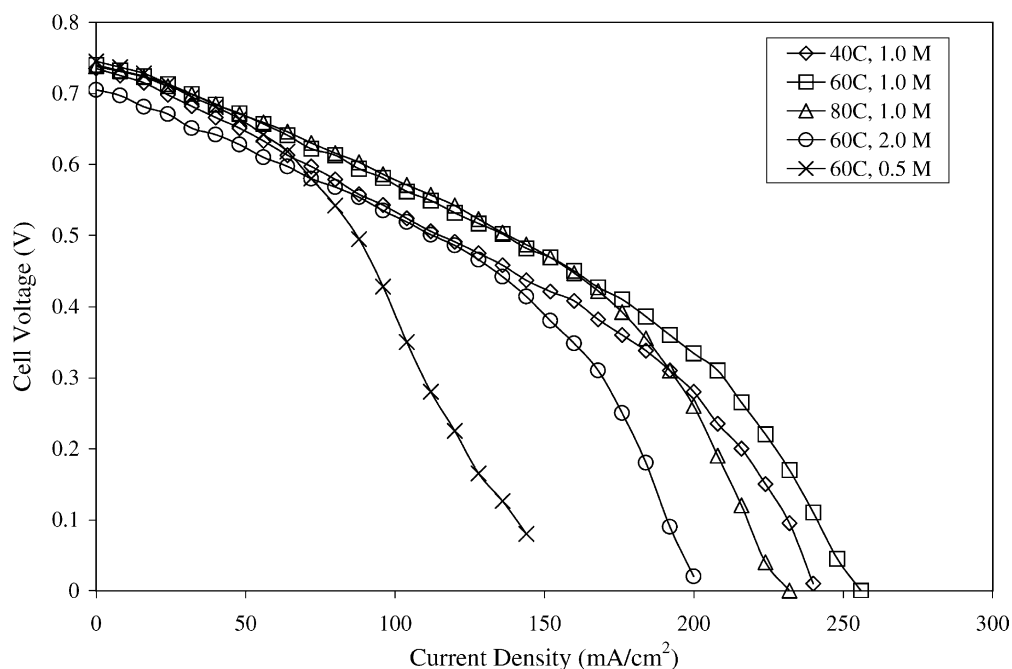


Fig. 5. Effects of cell temperature and 2-propanol concentration on performance at an air flow rate of 180 ml/min.

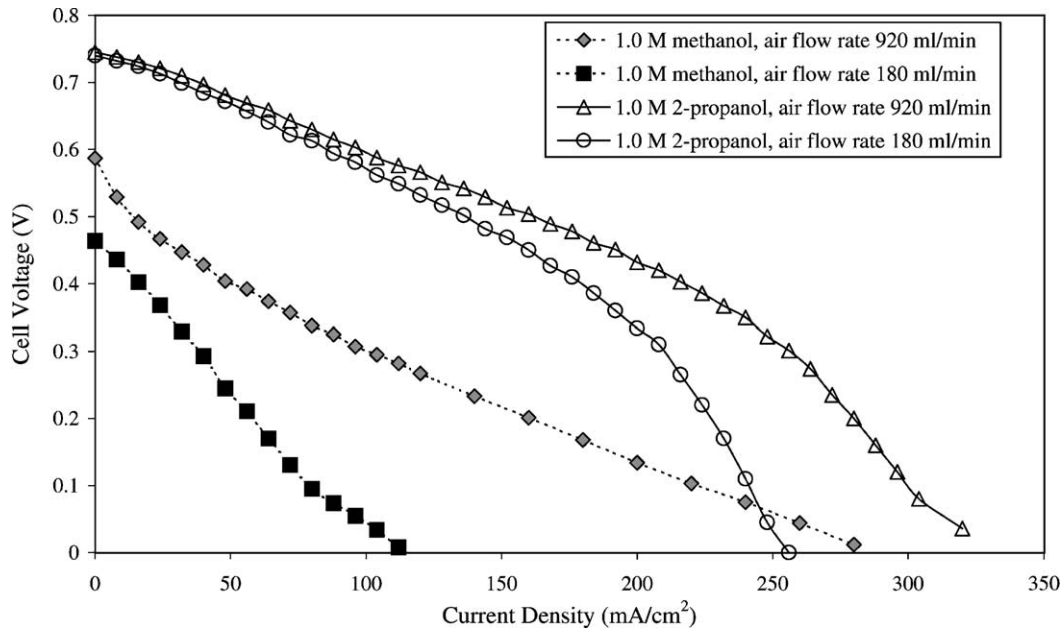


Fig. 6. Performance of a direct 2-propanol fuel cell vs. a direct methanol fuel cell.  $T_{\text{cell}} = 60\text{ }^{\circ}\text{C}$ , alcohol concentration = 1.0 M.

the 2-propanol cell was ca. 0.16 and 0.27 V higher than that of the methanol cell at air flow rates of 920 and 180 ml/min, respectively. Secondly, 1.0 M 2-propanol performed much better than 1.0 M methanol over the entire current density region. Thirdly, the 2-propanol cell only showed moderately worse performance at an air flow rate of 180 than at an air flow rate of 920 ml/min, while for the methanol cell, an air flow rate of 180 ml/min gave much worse performance than an air flow rate of 920 ml/min. Being able to use a low air flow rate is critical in balancing water in a liquid fuel cell system, and thus, it is a great advantage. Some of the experimental results presented above are summarized in Table 1.

The OCV of a 2-propanol cell obtained under a variety of conditions is presented in Fig. 7. The general trend was that the OCV declined slightly with a decrease of the air flow rate. However, due to an increased alcohol crossover, as discussed later, air flow rate had a larger effect when either the cell temperature was higher or 2-propanol concentration

was higher. At a 2-propanol concentration of 1.0 M, the OCV increased for 10 mV as the cell temperature increased from 40 to 60  $^{\circ}\text{C}$ , but the increase was less than 4 mV when the cell temperature was further increased from 60 to 80  $^{\circ}\text{C}$ . At an air flow rate of 180 ml/min, the cell actually had a slightly lower OCV at 80  $^{\circ}\text{C}$  than at 60  $^{\circ}\text{C}$ . At a cell temperature of 60  $^{\circ}\text{C}$ , the OCV decreased slightly as the 2-propanol concentration was increased from 0.5 to 1.0 M, but a much larger decrease was observed when the concentration was further increased from 1.0 to 2.0 M.

As a comparison, Fig. 7 also illustrates the OCV of a methanol cell at 60  $^{\circ}\text{C}$ . Firstly, it is striking to see that a 2-propanol cell had an OCV as much as 0.27 V higher than a methanol cell. Secondly, for the DMFC using 1.0 M methanol solution, its OCV dropped significantly from 0.57 to 0.47 V when the air flow rate was declined from 397 to 180 ml/min. Thirdly, when the methanol concentration was increased from 0.5 to 1.0 M, the OCV of the DMFC decreased for as much as 50 mV. In contrast, when 2-propanol

Table 1  
Performance of a D2PFC vs. a DMFC<sup>a</sup>

Cell temperature ( $^{\circ}\text{C}$ )	Alcohol concentration (M)	Cell voltage (V) at indicated current densities ( $\text{mA}/\text{cm}^2$ )							
		48		104		144		200	
		2-Propanaol	Methanol	2-Propanaol	Methanol	2-Propanaol	Methanol	2-Propanaol	Methanol
40	1.0	0.653	0.352	0.533	0.234	0.457	0.160	0.335	0.064
60	0.5	0.653	0.418	0.340	0.289	0.020	0.200	CNR	0.091
	1.0	0.679	0.349	0.579	0.202	0.510	0.097	0.398	CNR
	2.0	0.643	NM	0.548	NM	0.476	NM	0.300	NM
80	1.0	0.686	0.317	0.595	0.136	0.530	0.052	0.407	CNR

NM: not measured; CNR: can not reach such a current density even at a cell voltage of 0 V.

<sup>a</sup> The data were taken at an air flow rate of 397 ml/min.

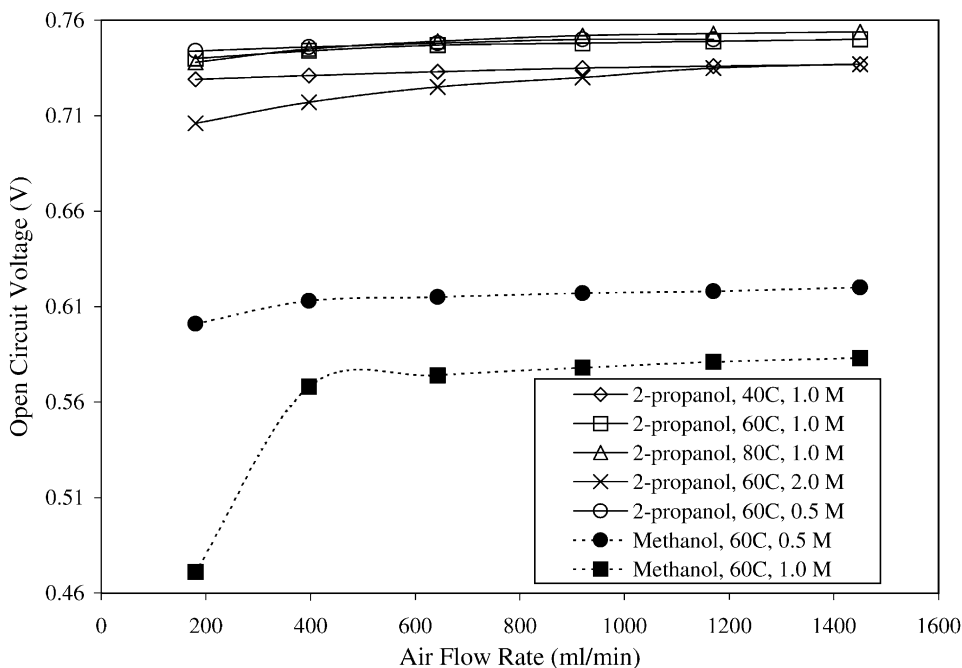


Fig. 7. Open circuit voltage of a direct 2-propanol fuel cell and a direct methanol fuel cell under various conditions.

concentration was increased from 0.5 to 1.0 M, the OCV of the 2-propanol cell only declined slightly.

Since the cell performance and OCV are largely related to the fuel crossover, the crossover current of 2-propanol was measured electrochemically, and the results are shown in Fig. 8. When these experiments were performed, nitrogen rather than air was passed through the cathode compartment

of the fuel cell, and a positive voltage was applied. As 2-propanol crosses through the membrane to reach the cathode, it is oxidized by the applied voltage. The value of the measured limiting current density represents how fast 2-propanol crosses through the membrane. Firstly, all the curves showed four distinct regions: from 0.0 to 0.2 V, the crossover current increased quickly with the applied

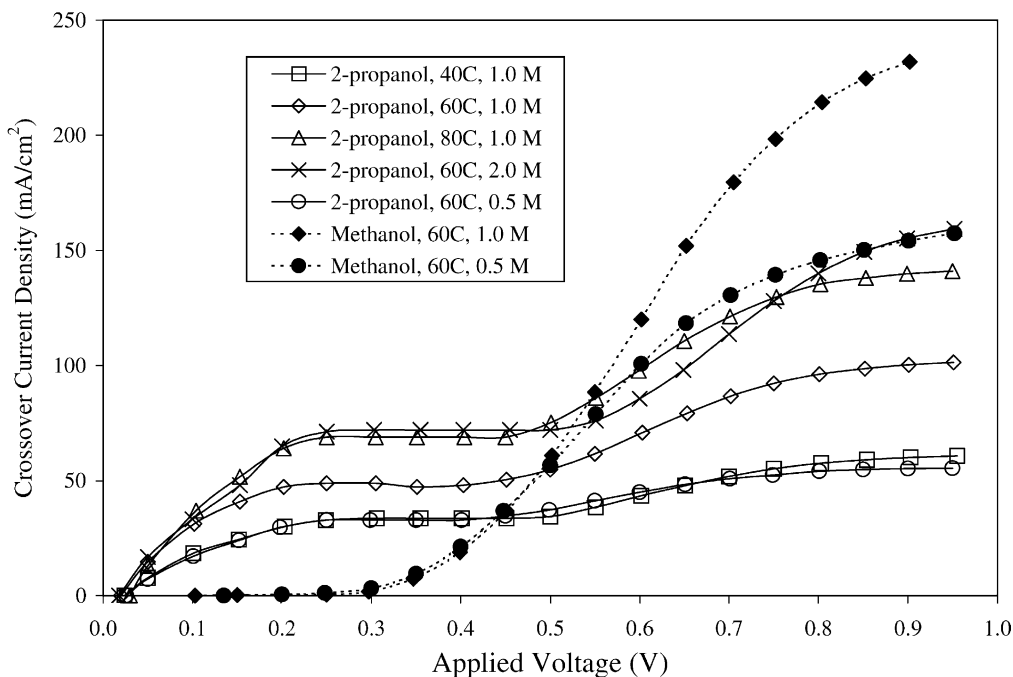


Fig. 8. Alcohol crossover current density vs. applied voltage in a direct 2-propanol fuel cell and a direct methanol fuel cell under various conditions. Nitrogen flow rate = 643 ml/min.

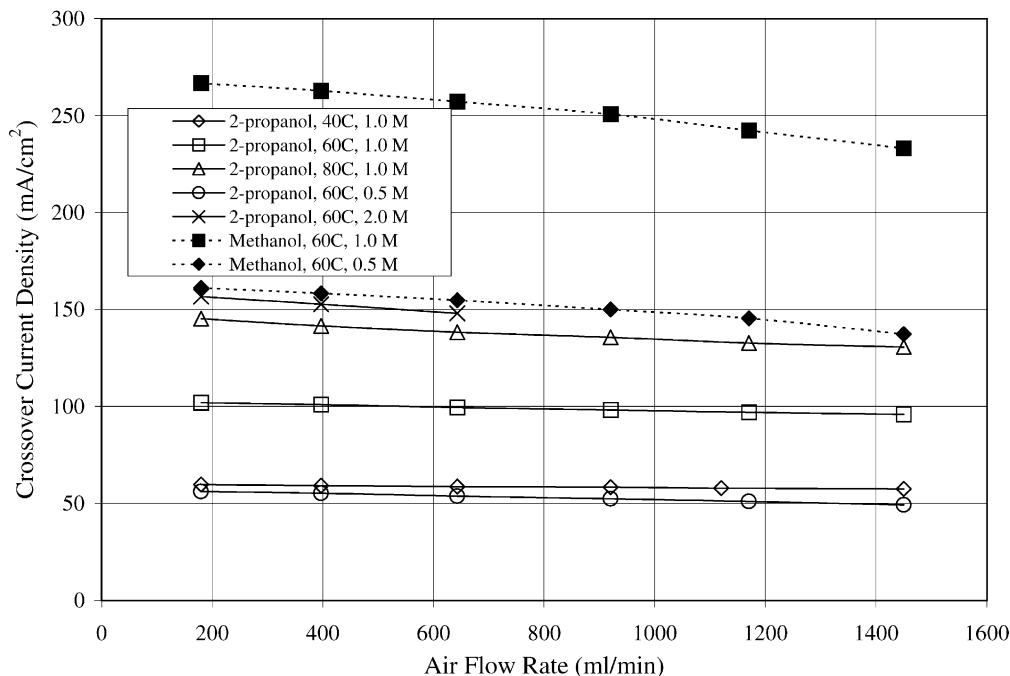
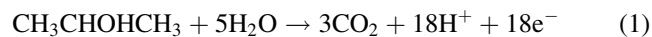


Fig. 9. Alcohol crossover current density vs. nitrogen flow rate in a direct 2-propanol fuel cell and a direct methanol fuel cell under various conditions (applied voltage = 0.93 V).

voltage; from 0.2 to 0.5 V, the crossover current stayed flat; from 0.5 to 0.8 V, the crossover current increased quickly again; from 0.8 to 0.95 V, the crossover current approached a plateau. It should be careful not to take the current in the flat region from 0.2 to 0.5 V as the limiting crossover current. The formation of this flat region was found to be due to quick poisoning of the cathode, where Pt was used as the catalyst, by the intermediates from 2-propanol oxidation. Each data point could have gone even lower if longer time were waited before the data were taken. As the applied voltage went higher than 0.5 V, the catalyst surface seemed to be cleaned by the positive voltage, and the currents increased again until a mass transport limitation of 2-propanol through the membrane was approached at voltages higher than ca. 0.8 V. A more accurate crossover current should be measured at voltages higher than 0.8 V. Secondly, at a 2-propanol concentration of 1.0 M, the crossover current increased almost linearly as the cell temperature was increased from 40 to 60 °C and then to 80 °C. Meanwhile, at a cell temperature of 60 °C, the crossover current increased significantly from 0.5 M 2-propanol to 1.0 M, and then to 2.0 M. Thirdly, under the same conditions, 2-propanol showed a much smaller crossover current than methanol. Finally, in contrast to 2-propanol, methanol showed little crossover current at applied voltages less than 0.3 V. This did not mean that there was no methanol crossing through the membrane, but rather that methanol could not be oxidized at voltages less than 0.3 V. Methanol crossover current then increased quickly at voltages higher than 0.3 V, and it approached a plateau after over 0.8 V.

Fig. 9 shows the effect of air flow rate on the 2-propanol crossover current under a variety of conditions at an applied voltage of 0.93 V. The general trend was that the crossover current declined slightly as the air flow rate was increased. A similar trend was observed with methanol, but the crossover current of methanol was more than double that of 2-propanol under the same conditions. Table 2 summarizes the OCV and crossover current in a 2-propanol cell and a methanol cell.

Eqs. (1) and (2) show the oxidation reactions of methanol and 2-propanol, assuming complete reactions to form CO<sub>2</sub> as the final product:



For each methanol molecule, six electrons are produced, while for each 2-propanol molecule, 18 electrons are produced. In other words, for a complete oxidation of each 2-propanol molecule, three times as large current should be observed compared to a complete oxidation of each methanol molecule. Therefore, the amount of 2-propanol crossing through the membrane is less than 1/7 of that of methanol based on the crossover currents shown in Fig. 9 and Table 2. This reduced 2-propanol crossover should greatly increase both fuel and fuel cell efficiencies.

Another advantage of 2-propanol over methanol is its higher electrochemical energy density. Since 2-propanol has a similar density as methanol (0.785 g/cm<sup>3</sup> versus 0.791 g/cm<sup>3</sup>), and the molecular mass of 2-propanol (60.10 g/mol) is



Table 2  
OCV and alcohol crossover current density in a D2PFC and a DMFC<sup>a</sup>

Cell temperature (°C)	Alcohol concentration (M)	$J_{\text{crossover}}$ (mA/cm <sup>2</sup> ) <sup>b</sup>		OCV (V)	
		2-Propanol	Methanol	2-Propanol	Methanol
40	1.0	58.7	NM	0.733	0.562
60	0.5	53.8	153.2	0.748	0.615
	1.0	99.5	254.4	0.747	0.574
	2.0	148.0	NM	0.725	NM
80	1.0	138.3	NM	0.749	0.583

NM: not measured.

<sup>a</sup> The data were taken at an air flow rate of 643 ml/min.

<sup>b</sup> Crossover current was measured at 0.93 V.

less than double that of methanol (32.04 g/mol), and the complete oxidation of one 2-propanol molecule produces three times as much electrons as one methanol molecule, the electrochemical energy density of 2-propanol is ca. 1.5 times that of methanol at per unit volume or mass.

Still another advantage of 2-propanol over methanol is its lower toxicity. Handling 2-propanol is much safer than handling methanol. Besides, 2-propanol gives off a noticeable smell, so, any leakage of 2-propanol can be detected immediately.

A further advantage of 2-propanol over methanol is its lower activation voltage. Based on the data shown in Fig. 8, the activation overpotential of 2-propanol is less than 0.04 V, but that of methanol is around 0.30 V. This will also translate to higher fuel cell efficiency.

#### 4. Conclusions

2-Propanol performs much better than methanol in direct-oxidation fuel cells. It has not only a much higher open circuit voltage but also a much lower crossover current. If a complete alcohol oxidation to carbon dioxide is assumed, the crossover current of 2-propanol is only about 1/7 of that of methanol. A fuel cell using 2-propanol as fuel could have an electrochemical energy density 1.5 times that of a methanol cell. However, intermediates from the oxidation of 2-propanol poison the anode more severely, and a periodical cleaning of the electrode surface by methods such as an electrical pulse is needed to refresh the electrode.

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