

Liquid-feed direct oxidation fuel cells using neat 2-propanol as fuel

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Abstract

Neat 2-propanol was used as the fuel in liquid-feed direct oxidation fuel cells. The fuel that was intentionally not mixed with any amount of water was oxidized directly at the fuel cell anode. The fuel cell showed very good performance. For example, at a cell temperature of 60 °C and an air flow rate of 970 ml/min, the cell output voltage was as high as 0.485 V at a current density of 200 mA/cm². This performance was among the highest numbers ever reported for liquid-feed direct oxidation fuel cells. The energy density of a fuel cell using a neat fuel is expected to be much higher than that of one using dilute fuel solutions because the latter needs to carry between 10 and 30 parts by weight of water for each part of alcohol.

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1. Introduction

Direct oxidation fuel cells using liquid methanol as the fuel have attracted intensive research worldwide [1–4]. Compared to hydrogen, methanol has a much higher energy density per unit volume, and it is easy to be produced, transported and stored. However, a direct methanol fuel cell (DMFC) performs much worse than a H₂/air fuel cell because of a sluggish methanol oxidation reaction and the crossover of methanol through a Nafion-type membrane to reach the cathode side [5–10].

Other small organic molecules such as ethanol, 1-propanol and 2-propanol [11], dimethoxymethane, trimethoxymethane, and trioxane [12,13], and ethylene glycol and dimethyl oxalate [14] were also studied as fuels for direct oxidation fuel cells. It was very encouraging that Narayanan and co-workers found that dimethoxymethane, trimethoxymethane, and trioxane performed comparably to methanol [12,13], and that these three chemicals could be oxidized at lower potentials than methanol. Recently, Qi et al. reported that some secondary alcohols such as 2-propanol could perform much better than methanol in dilute aqueous solutions, especially at current densities less than ca. 200 mA/cm² [15–17]. The better performance of 2-propanol appears

to be the result of a faster oxidation reaction kinetics of 2-propanol, and its lower tendency for crossover.

All the direct oxidation fuel cells reported so far use dilute aqueous solutions as their fuels. The fuel concentration is normally less than 10 wt.%, and most frequently around 3 wt.%. The other 90–97 wt.% is water. The presence of 10–30 parts water per part alcohol not only results in a bulky fuel cell system, but also seriously limits its energy density. In addition, a large amount of water from the anode compartment transports through the membrane to the cathode side, and causes serious flooding of the cathode.

In order to minimize this flooding, a high air flow rate has to be used. Using a high air flow rate, however, not only consumes more parasitic power, but also makes it difficult to balance water within the fuel cell system. In the event that the water that is taken away by exhaust air should not be effectively recovered, a even larger water reservoir will be needed to compensate for the water lost.

This paper reports a direct oxidation fuel cell that uses neat 2-propanol as the fuel without adding any water. This eliminates the need of carrying a large amount of water with the fuel and thus reduces the bulkiness of the fuel cell system and increases its energy density.

2. Experimental

The tests were carried out using a 25 cm² single cell purchased from Fuel Cell Technologies Inc. (Albuquerque,

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NM). Unless otherwise specified, Pt/Ru and Pt blacks were used as the anode and cathode catalysts, and they were applied onto Teflon[®]-treated 6 and 9 mil (1 mil equals 25 μm) Toray paper, respectively, to achieve Pt/Ru and Pt loadings of 4.8 and 7.8 mg/cm^2 , respectively. These electrodes were hot-pressed onto a 50 μm thick sulfonated polyetheretherketone membrane (SPEEK) to form a membrane-electrode assembly. Neat 2-propanol was pumped into the cell by a micropump (Micropump Inc., Vancouver, WA), and then re-circulated back to the fuel tank. The alcohol flow rate was controlled at 6.5 ml/min by 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 products. The temperature of the alcohol tank was controlled by a hot plate. The stainless steel tubing used to connect the alcohol tank and the cell was heated by a heating tape. The temperatures of the fuel tank, inlet of alcohol to the cell, and the cell itself were monitored by thermocouples. Ambient air was supplied to the cell, and its flow rate was adjusted using a flowmeter. Unless otherwise specified, air was humidified at the cell temperature by passing it through a stainless steel water bottle before feeding it to the cell. The fuel cell load was controlled by another GW laboratory dc power supply (Model: GPR-1820HD).

3. Results and discussion

Fig. 1 shows the performance of neat 2-propanol at a cell temperature of 60 $^{\circ}\text{C}$ and air flow rates of 180, 397, 643, and 920 ml/min , respectively. The fuel cell performance

increased apparently from air flow rate of 180–397 and then to 643 ml/min , but a less increase was observed when it was further increased to 920 ml/min . At all the air flow rates, the fuel cell performance was very impressive. For example, at an air flow rate of 920 ml/min the cell voltage output was as high as 0.485 V at a current density of 200 mA/cm^2 , corresponding to a power density of 97 mW/cm^2 . Such a performance is among the highest for all the liquid-feed direct oxidation fuel cells reported to date.

It can also be seen from Fig. 1 that all the V - I curves have a linear region at lower current densities, and this region extends to higher current densities at higher air flow rates. But in the higher current density region, all the V - I curves showed a faster voltage decline. This quicker decline was due to mass transport limitation and poisoning of the fuel cell anode by the intermediates or products formed from 2-propanol oxidation [17].

Neat 2-propanol showed high performance even at temperatures close to room temperature. Fig. 2 illustrates the fuel cell performance at a cell temperature of 30 $^{\circ}\text{C}$ under different air flow rates. A large increase was observed when the air flow rate was increased from 180 to 397 ml/min , but further increase in air flow rates only increased the cell performance slightly. Compared to Fig. 1, the linear V - I region became shorter. Although the performance was lower than that at 60 $^{\circ}\text{C}$, it was still pretty high. For example, at an air flow rate of 920 ml/min , the cell output voltage was 0.598 V at a current density of 80 mA/cm^2 , which corresponds to a power density of 48 mW/cm^2 .

The formation of poisoning species from 2-propanol oxidation adversely affected the highest currents the cell

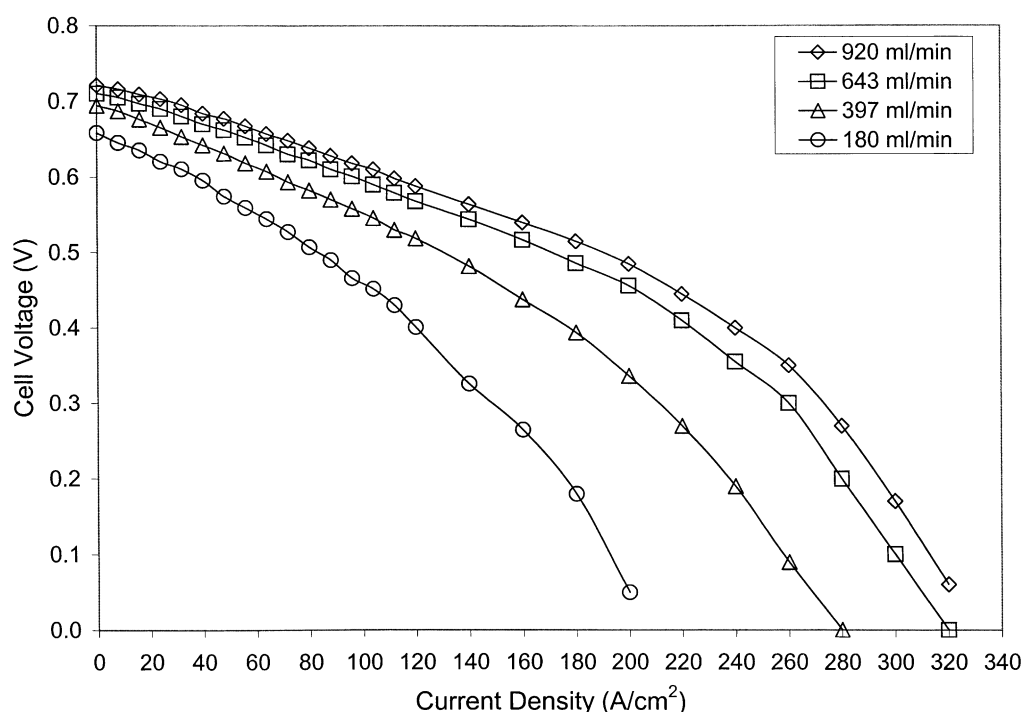


Fig. 1. Performance of a neat 2-propanol fuel cell under different air flow rates at a cell temperature of 60 $^{\circ}\text{C}$.

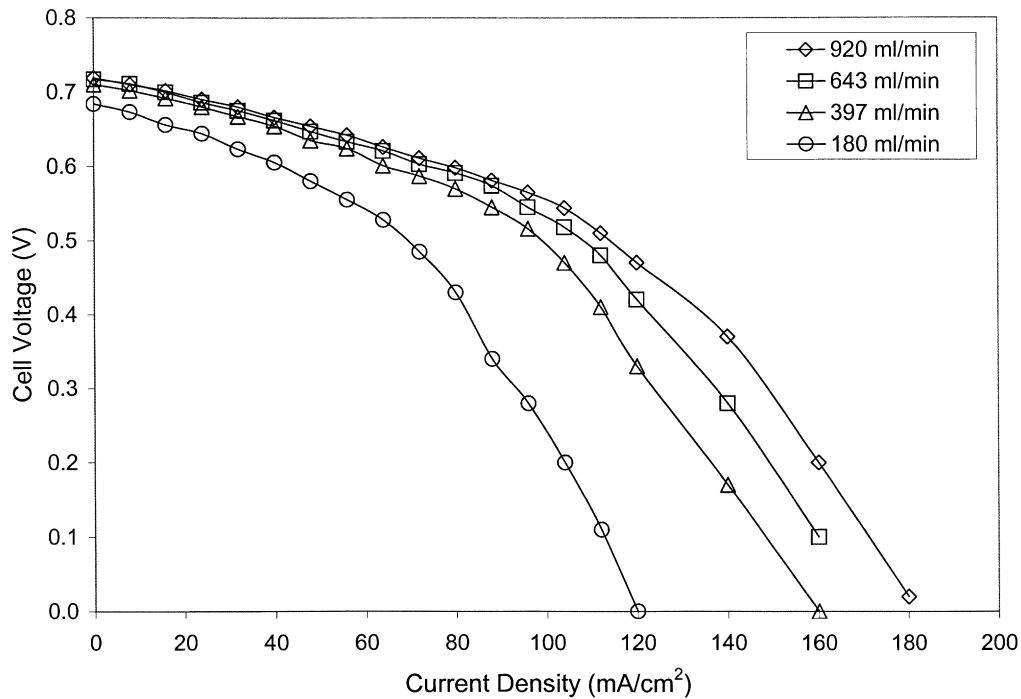


Fig. 2. Performance of a neat 2-propanol fuel cell under different air flow rates at a cell temperature of 30 °C.

can generate and sustain. Fig. 3 illustrates the fuel cell stability with time at three different current densities at a cell temperature of 30 °C with an air flow rate of 397 ml/min. At a current density of 100 mA/cm², the cell lost its performance in 5 min. Obviously, the fuel cell could not be operated effectively at such a current density under this condition.

When the current density was reduced to 52 mA/cm², the situation was improved largely. The cell only showed a gradual decline within the first 40 min. Then a quicker decline started, which was followed by another gradual decline. Such a declining pattern could be explained as follows: the poisoning species continuously accumulated

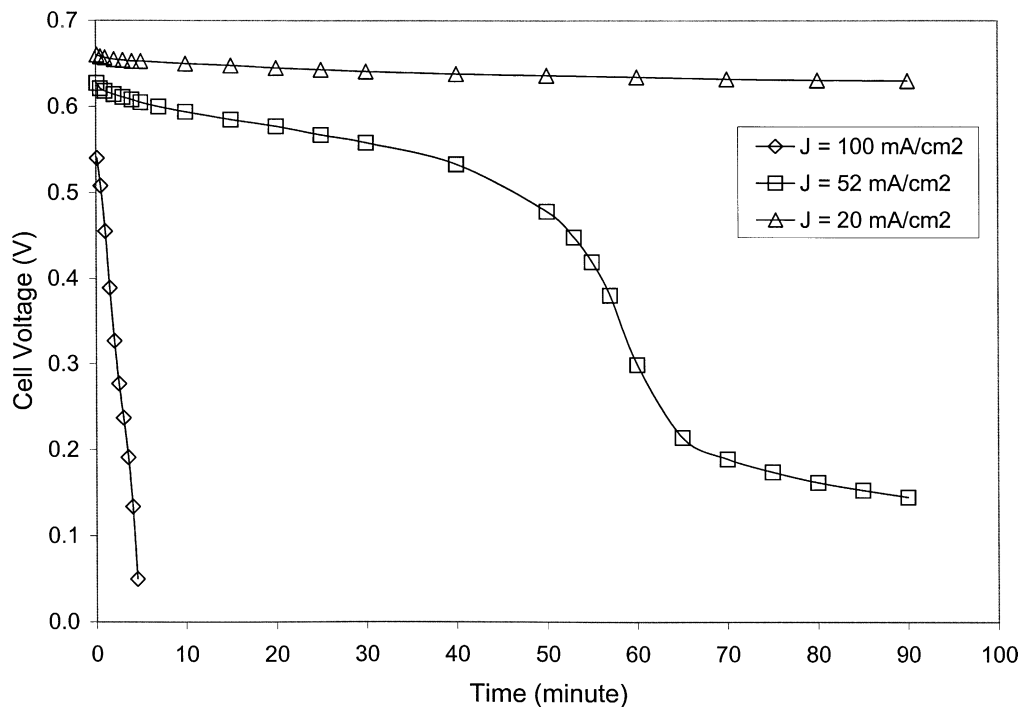


Fig. 3. Stability of a neat 2-propanol fuel cell at current densities of 20, 52 and 100 mA/cm², respectively. Cell temperature: 30 °C; air flow rate: 397 ml/min.

onto the catalyst surface when the fuel cell was working, and after ca. 40 min of operation, the amount of accumulated poisoning species reached such a level that a very limited catalyst surface remained, resulting in a quick decline in the cell voltage. Since poisoning species forms at the anode, it is expected that this quick cell voltage decline is due to an increase in the anode overpotential. The increase in anode overpotential, on the other hand, weakened the adsorption strength of the poisoning species, and thus a slower voltage decline was resulted after the quicker decline.

The situation was further improved when the cell was operated at a current density of 20 mA/cm^2 . The cell only showed a slight decline within the 90 min studied. Clearly, when an equilibrium between the adsorption and desorption of the poisoning species was established, the catalyst still had enough active surface to support the current.

Interestingly, it was observed that the cell could refresh itself to certain extent when it was shut down. During the shut-down period, the flows of both air and 2-propanol were stopped, and the cell was left at open circuit. Fig. 4 shows some of the results. The test was performed at a current density of 60 mA/cm^2 and a cell temperature of 30°C . Curve 1 was obtained after the cell was in a shut-down state for 20 min following an initial operation at 20 mA/cm^2 . The cell was then shut down for 2 min. Afterwards, curve 2 was obtained when the cell was re-started. It can be seen that curve 2 was not only lower than curve 1, but also declined faster. This indicates that the poisoning species formed during the operation of curve 1 was carried over to the operation of curve 2. But unexpectedly, curve 2's first 2 min performance was better than curve 1's last performance (i.e.

the first few points from curve 2 were higher than the last point from curve 1). This implies that during the 2 min shut-down period, the cell gained some extra active surface area. In other words, the cell refreshed itself to some extent during the shut-down period. Hence, when it was restarted, it possessed a better performance. However, the gain in active surface area seemed to be very limited, and most of the poisoning species formed during the operation of curve 1 still remained on the catalyst surface, so the cell performance declined faster when the test was continued during the operation of curve 2.

Curves 3–5 are the results after the cell was sequentially shut down for 5, 12, and 20 min, respectively. Although not much, but the cell performance became slightly better with a longer shut-down period, indicating that more catalyst refreshment occurred. Finally, the polarity of the cell was switched to about -0.4 V (cathode minus anode) for 30 s. Consequently, the cell was largely refreshed, leading to a much better performance, as shown by curve 6.

Self-refreshing by shutting down the cell was found to be more effective if the cell was operated at a smaller current density such as 20 mA/cm^2 between each shut-down period.

Application of direct oxidation fuel cells to handheld electronics such as cellular phones is currently an actively researched area. In such an application, the current density does not need to be high, but a high energy density is important. Customers prefer to have a power source that lasts a long time between each recharging. Due to the superior performance of neat 2-propanol, especially at smaller current densities, a direct 2-propanol fuel cell could become a major choice. In addition, since the cell can refresh

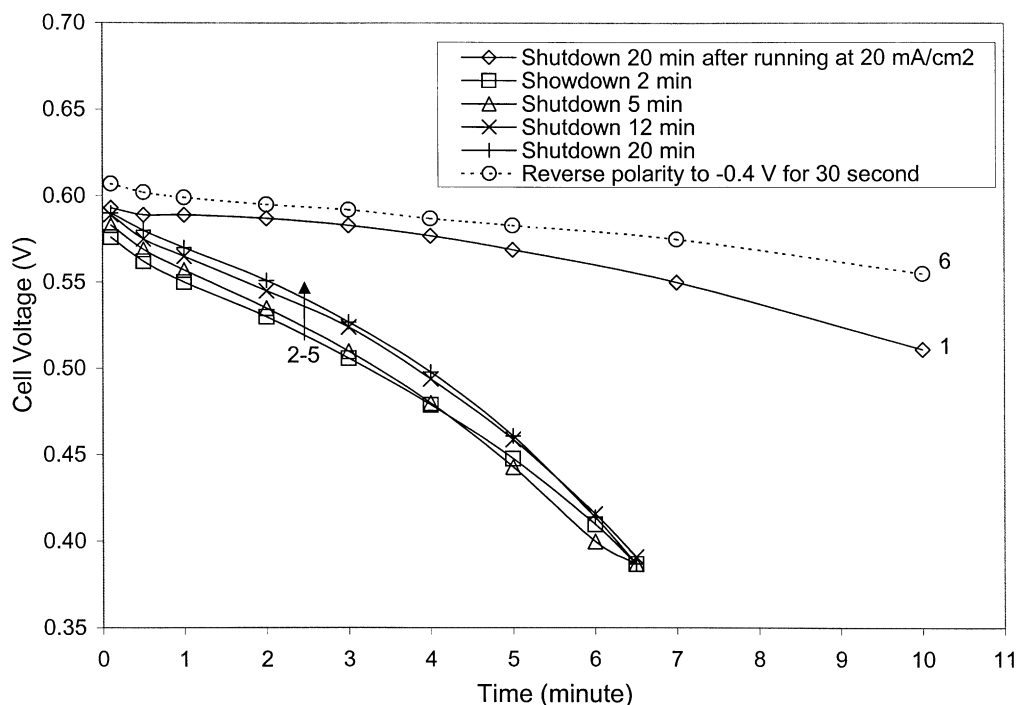


Fig. 4. Effect of cell idling and reversed potential on its refreshment. Cell temperature: 30°C ; air flow rate: 397 ml/min ; current density: 60 mA/cm^2 .

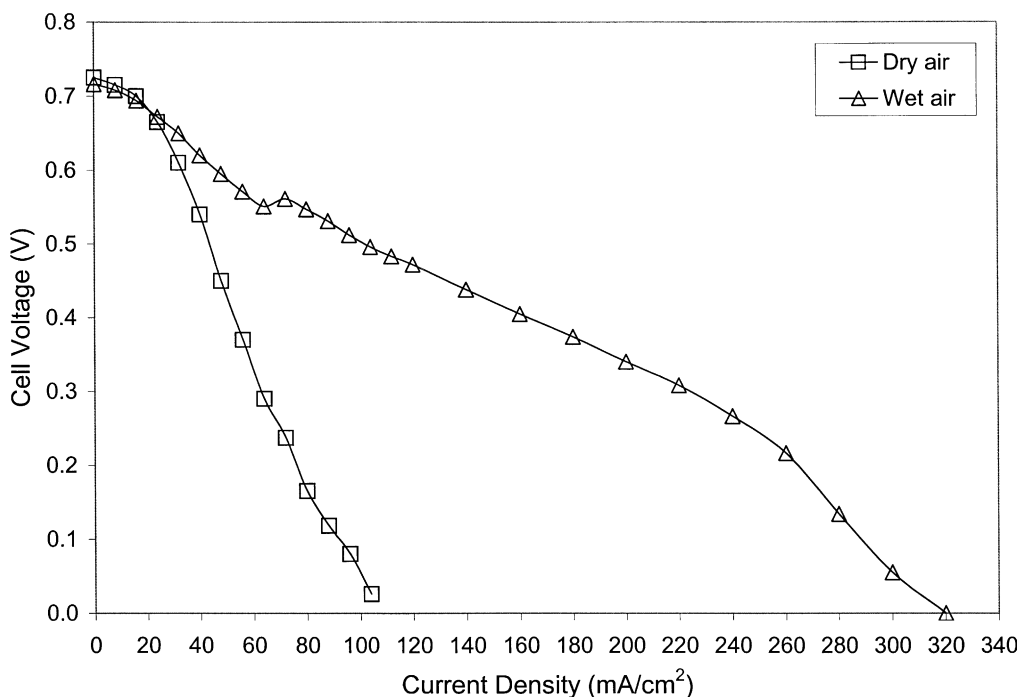


Fig. 5. Effect of air humidification on performance. Cell temperature: 60 °C; air flow rate: 920 ml/min.

itself when not in operation, and the refreshment is more effective if the cell is operated at smaller current densities, such a cell is particularly suitable for cellular phone-type electronics that is not continuously used.

Different from using a dilute aqueous fuel solution where the membrane is fully hydrated by the water present in the fuel mixture, a direct oxidation fuel cell using neat alcohol needs external humidification. Air humidification was found to be quite effective to hydrate the membrane as well as the catalyst layers, as shown in Fig. 5. The cell voltage dropped quickly when dry air was used. Obviously, the only water that was formed at the cathode via oxygen reduction reaction was not enough to humidify the cell. When air was humidified at the cell temperature, the cell performance increased dramatically. Its performance was still not as good as the one shown in Fig. 1, probably because the membrane was not adequately hydrated yet when the data were taken. More humidification could be achieved by using a humidification temperature higher than the cell temperature.

Since neat 2-propanol contains no water, flooding of cathode by water transporting from the anode to the cathode is prevented. This should lead to an increased fuel cell performance. This expectation is confirmed by the results shown in Fig. 6, where the performance of neat 2-propanol, neat methanol, and 1 M 2-propanol aqueous solution was compared. The tests were performed in the sequence of neat 2-propanol, neat methanol, 1 M 2-propanol aqueous solution, and neat 2-propanol again.

The performance of neat methanol was so low (curve 8) that it could not compare with 2-propanol at all. At current densities less than 40 mA/cm², 1 M 2-propanol solution had

the best performance, but it declined quickly as the current density was increased (curve 9). This test was performed after the cell was used to test neat methanol, and inexplicably, it took an abnormally long time for the cell open circuit voltage to increase to the number shown in Fig. 6. We suspected that the cell, especially the SPEEK membrane, was adversely affected by neat methanol during its test process. However, when neat 2-propanol was tested again, the cell still possessed a good performance (curve 10), although it was a little lower than the initial test (curve 7).

The slow open circuit voltage increase when using 1 M 2-propanol aqueous solution could be due to the fact that the anode substrate was teflonated. Teflonation made the substrate more hydrophobic, and then it could hinder the 2-propanol aqueous solution from passing through to reach the catalyst layer. Hence, an MEA whose anode substrate was not teflonated was prepared, and the result is shown in Fig. 6 as curve 11. During the test, air was not humidified to minimize cathode flooding. This substrate did perform much better, indicating that a teflonated substrate did seriously limit the transportation of aqueous alcohol solution. However, even with enhanced performance by using unteflonated substrate, it was still lower than that when neat 2-propanol was used at current densities higher than 90 mA/cm². So, under either substrate situation, neat 2-propanol performs better than a diluted solution.

Alcohol crossover was measured electrochemically and the results are shown in Fig. 7. All the curves have four distinct regions: initial quick increase in the low voltage region, a plateau in the low–middle voltage region, another quick increase in middle–high voltage region, and finally, a plateau

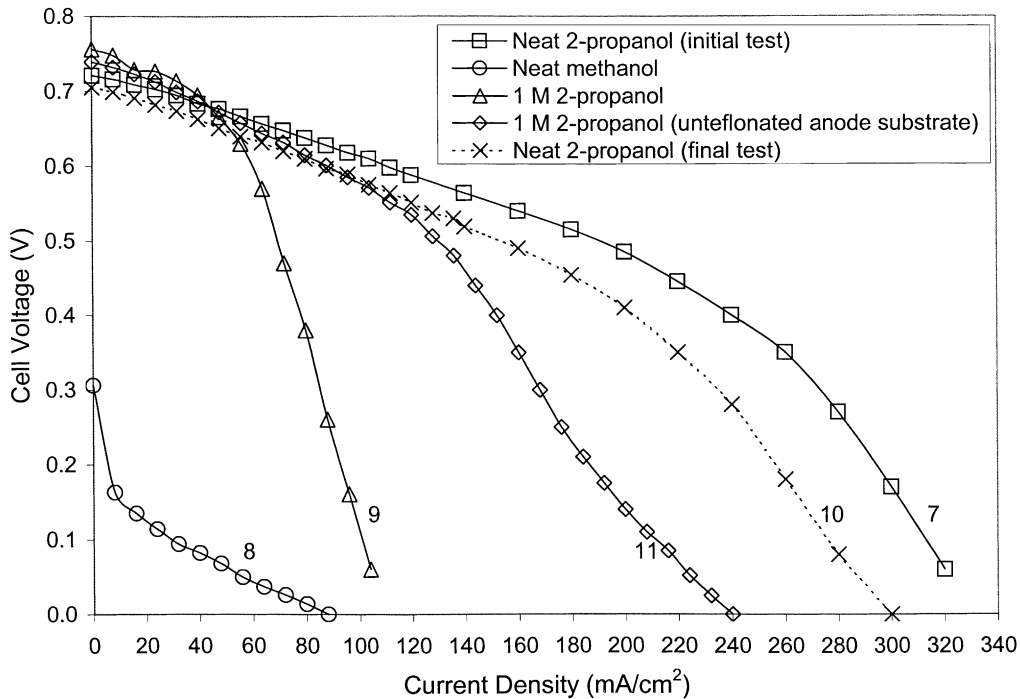


Fig. 6. Performance of neat 2-propanol, neat methanol, and 1 M 2-propanol at a cell temperature of 60 °C. Air flow rate: 920 ml/min.

in the high voltage region. The formation of the first plateau region was probably due to the formation of poisoning species from 2-propanol oxidation. When a higher voltage was applied, the adsorption of poisoning species became weaker, resulting in the release of more active surface area. Hence, a higher current was obtained. The limiting current in

the highest voltage region (i.e. higher than ca. 0.8 V) should be taken as the current representing the alcohol crossover.

Following conclusions can be drawn from the results shown in Fig. 7. First, when the cell temperature was increased from 30 to 60 °C, the alcohol crossover was doubled (curve 12 versus curve 13). Second, the crossover of 2-propanol from

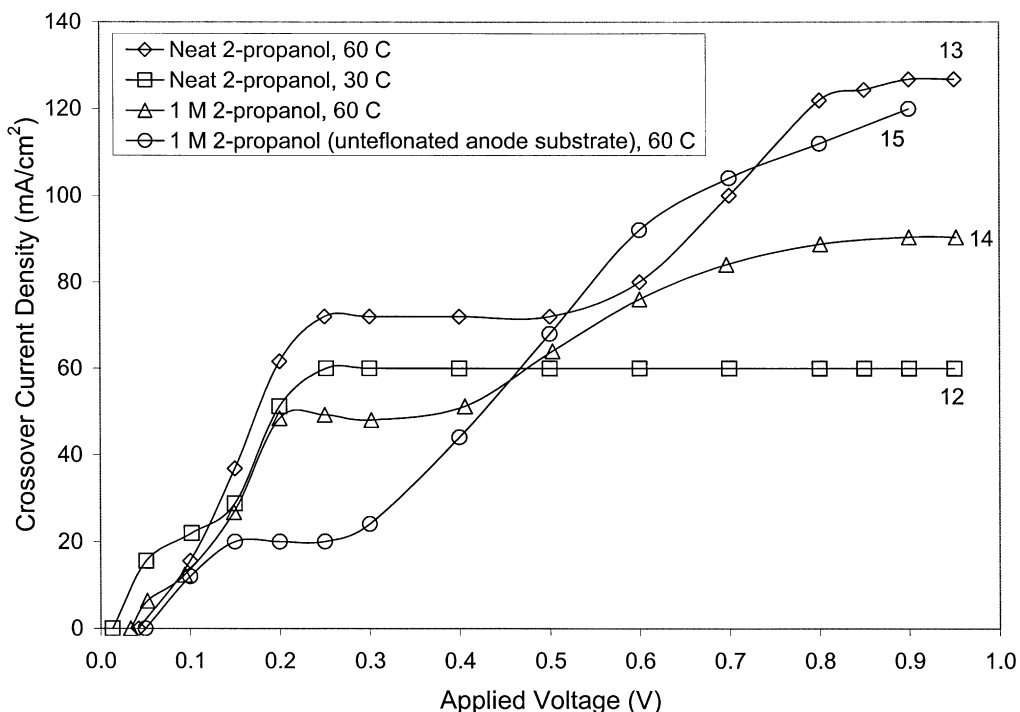


Fig. 7. Crossover current density of 2-propanol under various conditions.

1 M aqueous solution was about 2/3 of that from neat 2-propanol (curve 14 versus curve 13). For a comparison, the crossover current through an MEA whose anode substrate was not teflonated was also shown in Fig. 7 as curve 15. Its limiting crossover current was similar to that of neat 2-propanol (curve 15 versus curve 13). It was not surprising that comparable crossover currents resulted between neat 2-propanol and 1 M aqueous solution. This was because the SPEEK membrane swells much less in the absence of water, making it more effective in blocking alcohol crossover, even the neat alcohol concentration is much higher.

4. Conclusions

High performance was achieved when neat 2-propanol was used as the fuel for a liquid-feed direct oxidation fuel cell. The swelling of the SPEEK-type membrane was low in the absence of water, so the crossover of neat 2-propanol through the membrane was similar to that of 1 M 2-propanol aqueous solution. Cathode flooding by water transportation from anode to cathode was avoided because neat 2-propanol contained no water. But air was needed to be humidified in order to hydrate the membrane. The power density of a neat 2-propanol fuel cell would be dramatically higher than that of a traditional fuel cell that is fed with a dilute solution consisting of only ca. 3 wt.% fuel.

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