

# A direct 2-propanol polymer electrolyte fuel cell

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## Abstract

We report the performance of a polymer electrolyte membrane direct 2-propanol fuel cell (DPFC). The cell consisted of a Pt-Ru (atomic ratio of 1:1) black anode, a Pt black cathode, and a Nafion®-117 membrane electrolyte. The cell was operated at 90 °C with aqueous 2-propanol as fuel and with oxygen as oxidant. The performance of the cell operating on 2-propanol is substantially higher than when it was operating on methanol at current densities lower than ~200 mA/cm<sup>2</sup>. The electrical efficiency of the direct 2-propanol fuel cell is nearly 1.5 times that of the direct methanol fuel cell at power densities below 128 mW/cm<sup>2</sup>. Studies on the effects of electrocatalyst loading, of 2-propanol concentration, and of oxygen pressure on cell performance indicate that the cells operating on 2-propanol require lower anode and cathode loadings than cells operating on methanol. Cathode poisoning by 2-propanol is less severe than by methanol. Hydrogen gas evolution observed at the anode at low current densities indicated that catalytic dehydrogenation of 2-propanol occurred over the anode catalyst. A rapid voltage drop occurred at high current densities and after operating the cell for extended periods of time at constant current. The rapid voltage drop is an anode phenomenon.

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## 1. Introduction

We report the operation, performance, and investigation of a direct 2-propanol fuel cell (DPFC). Fuel cells that operate by direct combustion of methanol (DMFC) using Pt-Ru anode electrocatalysts are the most studied type of direct alcohol fuel cell [1–3]. The most imminent commercial application for such cells is likely as power sources for portable electronic devices [4,5]. The challenges associated with developing practical DMFC's include poisoning of anode electrocatalysts by CO or related species obtained from methanol, crossover of methanol from the anode to the cathode, and cathode poisoning by methanol [2,6]. One approach to address these issues is to use alcohols that are less prone to crossover and electrocatalyst poisoning than methanol. The electrooxidation of 2-propanol over platinum electrodes was studied by several groups during the 1990s [7–10]. The major oxidation product is acetone at low potentials (<0.4 V versus RHE), the mechanism of electrooxidation is proposed to occur via C–H activation at the alkoxy carbon, and the kinetics of the electrooxidation

are fast. Wang et al. reported the first fuel cell to operate directly on 2-propanol as fuel (DPFC) [9]. Their cell consisted of a Pt-Ru nanoparticle anode (4 mg/cm<sup>2</sup>), a Pt black cathode (4 mg/cm<sup>2</sup>), and an H<sub>3</sub>PO<sub>4</sub>-doped polybenzimidazole (PBI) membrane electrolyte. The cell was operated at 170 °C using methanol, ethanol, 1-propanol, and 2-propanol as fuel. 2-Propanol provided the worst cell performance as fuel of the alcohols tested. The cell voltage operating on 2-propanol at 200 mA/cm<sup>2</sup> was low, less than 0.2 V. During the course of our investigations Qi et al. [11,12] reported operation of a 2-propanol cell using Pt-Ru and Pt blacks as anode and cathode catalysts, respectively, Nafion® 112 as membrane electrolyte, and with air at the cathode. We now report and compare our results using 2-propanol and methanol as fuel in the same polymer electrolyte membrane direct alcohol fuel cell. The cell contained among the most active commercially available methanol anode catalyst (Johnson Matthey HiSPEC™-6000, specific surface area ~70 m<sup>2</sup>/gm), a relatively thick Nafion® 117 membrane, and high surface area unsupported Pt black cathode catalyst (specific surface area ~27 m<sup>2</sup>/gm). The cell was operated at relatively high temperatures (90 °C) using pure oxygen as oxidant to maximize the activity of the cathode in order to study the limitations of the anode.

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## 2. Experimental

The membrane electrolyte assemblies were made using the decal transfer method developed at Los Alamos National Laboratories [13]. Unsupported Pt-Ru black of nominal 1:1 atomic ratio (Johnson Matthey, HiSPEC™-6000, specific surface area  $\sim 70 \text{ m}^2/\text{g}$ ) and unsupported Pt black (Johnson Matthey, fuel cell grade, specific surface area  $\sim 27 \text{ m}^2/\text{g}$ ) were used as the anode and cathode catalysts, respectively. Catalyst/ionomer inks were prepared as follows: A suspension of catalyst in water was ultrasonicated for 30 min (to wet and disperse the catalyst), enough 5% Nafion® solution (ElectroChem. Inc) was then added to give a dry ink composition of 80 wt.% catalyst and 20 wt.% Nafion® ionomer, and the mixture was ultrasonicated for 2 h further to obtain an uniformly dispersed ink. A Nafion®-117 membrane was cleaned and converted into the acid form by boiling in 3%  $\text{H}_2\text{O}_2$  for 1 h, followed by boiling in 0.5 M  $\text{H}_2\text{SO}_4$  for 2 h, and finally boiling in ultra-pure water for 2 h with the water being changed every 30 min. The cleaned membrane was stored in ultra-pure water and dried on a heated vacuum table before use. The catalyst inks were painted onto  $5 \text{ cm}^2$  Teflon® decals to give a metal loading of approximately  $2 \text{ mg}/\text{cm}^2$  unless stated otherwise in the text. The catalyst inks were transferred from the Teflon® decals to the Nafion® membrane by hot-pressing ( $125\text{--}127^\circ\text{C}$ ,  $1450\text{--}1550 \text{ psi}$  for ca. 2.5 min). The membrane electrolyte assemblies were then mounted into commercial fuel cell hardware (ElectroChem. Inc.) using Teflon®-treated carbon papers (ElectroChem. Inc.) as backings/current collectors. Aqueous solutions of 2-propanol (Fisher scientific, certified ACS grade) or methanol (Sigma–Aldrich, ACS HPLC grade, 99.93%) were pumped through the anode flow field at  $4 \text{ ml}/\text{min}$ , zero back pressure, and circulated back to the fuel reservoir. Dry oxygen (Praxair, UHP) was supplied from a cylinder to the cathode at 600 standard cubic centimeter per minute (sccm) at 20 psi back pressure unless specified otherwise in the text. Pure oxygen was used to maximize the activity of the cathode. All experiments were carried out at  $90^\circ\text{C}$  cell temperature. The polarization curves were obtained using a 890 Series computer-controlled fuel cell test load (Scribner Associate Inc.). All reported cell potentials are not IR compensated. Each fuel cell was conditioned for 3 days before recording any polarization data as follows: The fuel cell was heated from ambient temperature to  $60^\circ\text{C}$  at open circuit with 1.0 M methanol solution circulating through the anode compartment and oxygen flowing through the cathode compartment. The cell was then operated under a constant, low load ( $20 \text{ mA}/\text{cm}^2$ ) for 4 h, the temperature was raised to  $90^\circ\text{C}$ , and the cell was operated at  $100 \text{ mA}/\text{cm}^2$  for another 4 h. The cell was then shut down by switching off the load, heating, methanol, and oxygen. The cell was then left overnight at room temperature. This procedure was repeated two more times each using fresh methanol solution. We find that the performance of DMFC's conditioned this way are both maximized and stable.

The cell was switched from operation on methanol to operation on 2-propanol as follows: After the methanol polarization data was recorded, pure water was pumped through the anode and cathode compartments of the cell for 4 h each to wash the methanol out of the cell and the Nafion® membrane. Oxygen was passed through the cathode compartment, and the cell was short-circuited for 10 s to burn off any traces of adsorbed methanol on the cathode and anode catalyst surfaces. A 2.0 M solution of 2-propanol was then fed to the anode compartment, the cell was heated to  $90^\circ\text{C}$  within 30 min at open circuit, and the electronic load was applied. The voltage–current polarization data were recorded from zero current (open circuit) to high currents in 0.05 A current increments. The current was held for 30 s after each increment before the cell voltage was recorded.

## 3. Results

We operated our cell at  $90^\circ\text{C}$ , a temperature typical for DMFC's. We found the performance of our cell to be substantially higher at this temperature than at  $60^\circ\text{C}$ . In contrast, Qi et al. found the performance of their cell at 60 and  $80^\circ\text{C}$  to be comparable. Fig. 1 shows typical voltage–current polarization curves of the same fuel cell operating on 2.0 M 2-propanol and 1.0 M methanol as fuel. The performance of the cell operating on 2-propanol is substantially higher than the cell operating on methanol at current densities lower than  $\sim 200 \text{ mA}/\text{cm}^2$ . For example, the cell voltage at  $120 \text{ mA}/\text{cm}^2$  is  $\sim 200 \text{ mV}$  higher operating on 2-propanol than on methanol. Similar observations were made by Qi et al. These performances are the highest we are aware of for a direct alcohol fuel cell. Unfortunately, the high performance of the cell operating on 2-propanol rapidly drops when the current density exceeds  $\sim 200 \text{ mA}/\text{cm}^2$ . The cell

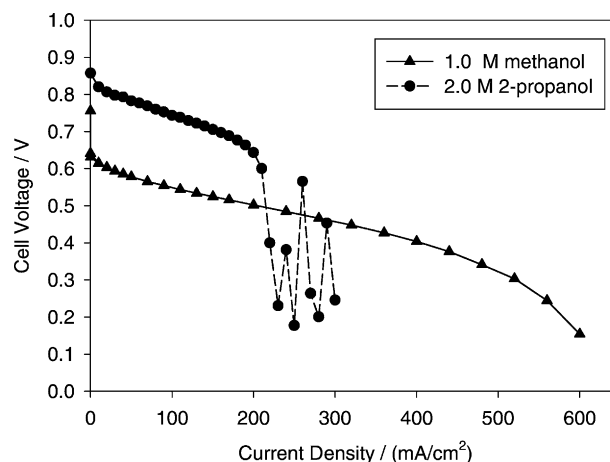


Fig. 1. Performance of a direct 2-propanol fuel cell vs. the same cell operating on methanol fuel. Cell operated at  $90^\circ\text{C}$ . Anode:  $2 \text{ mg}/\text{cm}^2$  Pt-Ru black (Johnson Matthey HiSPEC™-6000, real surface area  $\sim 70 \text{ m}^2/\text{gm}$ ), 2.0 M 2-PrOH or 1.0 M MeOH at  $4.0 \text{ ml}/\text{min}$ . Cathode:  $2 \text{ mg}/\text{cm}^2$  Pt-black catalyst (real surface area  $\sim 27 \text{ m}^2/\text{gm}$ ), 20 psi dry oxygen at 600 sccm.

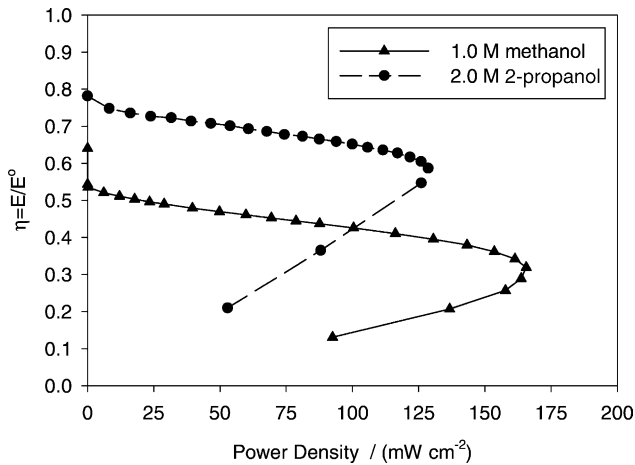


Fig. 2. Plots of electrical efficiency vs. power density for a direct 2-propanol fuel cell and the same cell operating on methanol fuel cell.

voltage oscillates around 0.2 V at current densities higher than 200 mA/cm<sup>2</sup>.

Fig. 2 compares the electrical efficiency (approximated here as  $\eta = E_{\text{cell}}/E^{\circ}$ , where  $E^{\circ} = 1.097\text{ V}$  [14] for 2-propanol, and 1.18 V for methanol [1–3]) and power density of the cell operating on 1.0 M methanol and 2.0 M 2-propanol. The high open circuit potential and rapid electrode kinetics of the 2-propanol cell result in an electrical efficiency nearly 1.5 times that of the cell operating on methanol at power densities below 128 mW/cm<sup>2</sup>. The maximum power density of the cell operating on 2-propanol approaches 75% of that operating on methanol. Further, the maximum power density of the cell operating on 2-propanol was achieved at 59% electrical efficiency, whereas the maximum power density with methanol was achieved at only 32% electrical efficiency.

The effects of electrocatalyst loading, of 2-propanol concentration, and of oxygen pressure on cell performance were

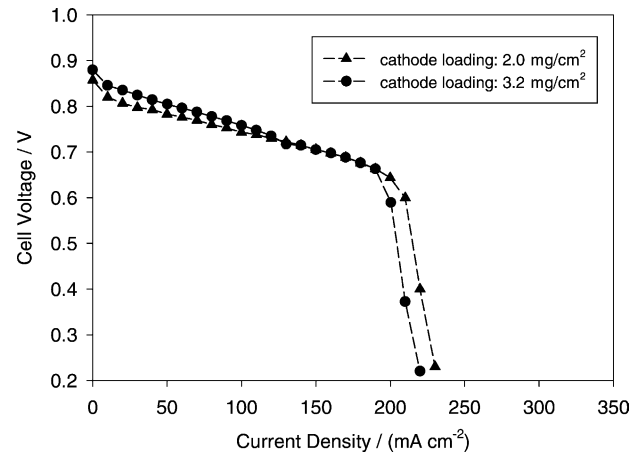


Fig. 3. Effect of cathode catalyst loading on the performance of a direct 2-propanol fuel cell.

investigated to gain insight into the origins of the performance drop at high current densities. Figs. 3 and 4 show the effects of cathode and anode electrocatalyst loading on cell performance, respectively. At constant anode loading, increasing the cathode loading from 2 to 3.2 mg/cm<sup>2</sup> Pt black did not significantly improve either the cell voltage at low current densities, nor did it decrease the voltage drop at high current densities (Fig. 3). This result shows that the cathode loading is not a major limiting factor in the performance of these cells operating on oxygen, and it suggests that cells operating on 2-propanol require lower cathode loadings than cells operating on methanol. At constant cathode loading, increasing the anode electrocatalyst loading from 2 to 4 mg/cm<sup>2</sup> results in an increase in the limiting current density, but it has no significant effect on the cell voltages at current densities lower than  $\sim 200\text{ mA/cm}^2$  (Fig. 4). This result strongly implies the voltage drop at high current densities is an anode phenomenon.

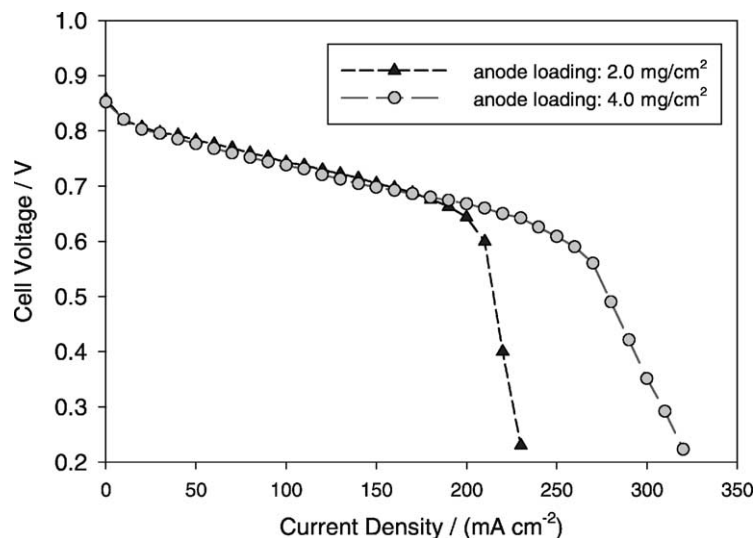


Fig. 4. Effect of anode catalyst loading on the performance of a direct 2-propanol fuel cell.

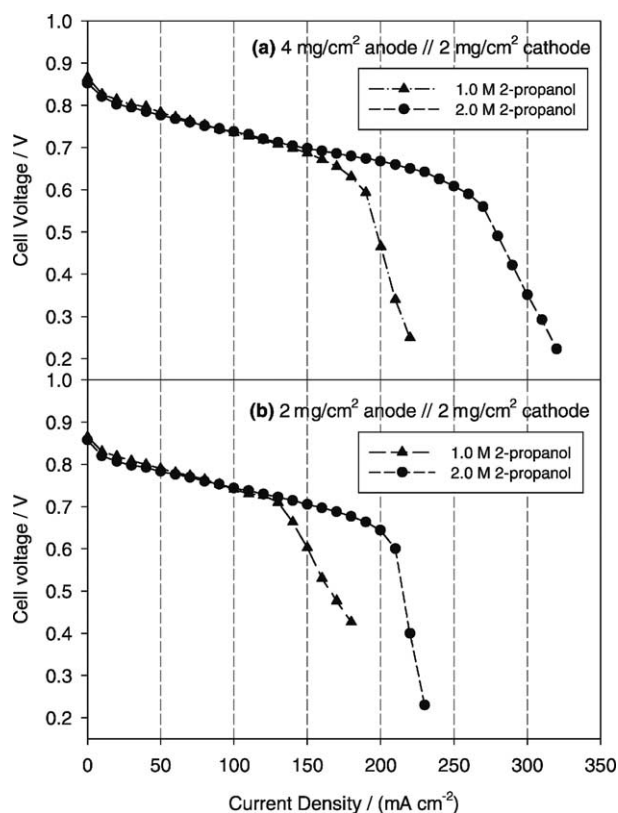


Fig. 5. Effect of 2-propanol concentration on the performance of a direct 2-propanol fuel cell.

Fig. 5 shows how the performance of two cells with different anode loadings changes upon increasing the concentration of 2-propanol in the fuel feed from 1.0 to 2.0 M. We found the cell voltage was largely independent of this change in concentration of 2-propanol when operating at current densities less than 200 mA/cm<sup>2</sup>. For both cells, however, the limiting current increased by ~80 mA/cm<sup>2</sup> upon the increase in 2-propanol concentration. This result is in contrast with those of Qi et al., who found the performance using 1 M was higher than when using 2 M 2-propanol. Qi et al. proposed the performance drop at higher concentrations of 2-propanol resulted from crossover and cathode poisoning. We propose the increase in performance of our cell with 2-propanol concentration results from use of a thicker Nafion<sup>®</sup> membrane (117 versus 112), from use of an oxygen cathode, and perhaps from use of a more active anode catalyst (Johnson Matthey HiSPEC<sup>™</sup>-6000). Use of higher concentrations (e.g. 3.0–4.0 M) of 2-propanol further increased the limiting current of the cells, but at the expense of weakening the membrane electrolyte assembly. Specifically, exposure to higher concentrations of 2-propanol under these operating apparently dissolved the recast Nafion<sup>®</sup> ionomer in the catalyst layer, resulting in delamination of the catalyst from the membrane. Further, we observed excessive swelling of the Nafion<sup>®</sup> membrane after disassembling cells that had operated on high concentrations of 2-propanol over a period of several hours. These results do imply, however,

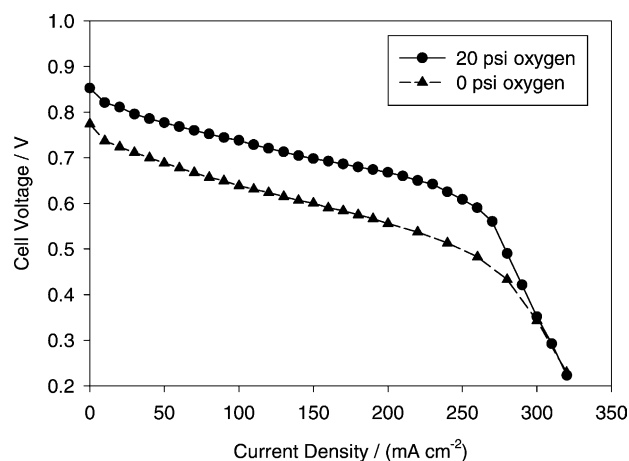


Fig. 6. Effect of oxygen pressure on the performance of a direct 2-propanol fuel cell.

that DPFC's can, in principle, operate at high concentrations of 2-propanol provided dissolution and swelling of the membrane can be avoided.

Fig. 6 shows the effect of reducing the oxygen pressure on cell performance. Reducing the oxygen pressure from 20 to 0 psi (gauge pressure) decreased the performance of the cell. For example, the open circuit voltage decreased by ~80 mV, and the voltage at 200 mA/cm<sup>2</sup> decreased by ~120 mV. We note that this decrease in cell voltage is substantially larger than the decrease in Nernst cathode potential (~5 mV)<sup>1</sup> calculated for this pressure change. This result implies that 2-propanol crossover occurs to some extent, that the presence of 2-propanol decreases the cathode potential, and that cathode poisoning by 2-propanol is less severe than by methanol [12]. The cathode appears less susceptible to poisoning by 2-propanol at higher oxygen pressures.

In accordance with the results of Qi et al., we also found that operation of the cell under constant load at current densities less than 200 mA/cm<sup>2</sup> results in rapid drops in cell voltage to nearly 0 V that abruptly occur after ~30 min of run time. We found that the performance is restored by either short circuiting the cell for brief periods of time, or by leaving the cell at open-circuit until the cell voltage is restored (~15 s). That short circuiting the cell restores performance may explain the oscillation observed at current densities higher than ~200 mA/cm<sup>2</sup> (Fig. 1).

2-Propanol dehydrogenates over Pt and other catalyst at moderately elevated temperatures to generate acetone and hydrogen. The reaction can be driven by removing hydrogen or acetone from the system, and it has been investigated as a method to upgrade heat [15–20]. This process apparently also occurs during operation of the 2-propanol fuel cell at 90 °C. Gas evolution at the anode is observed at low current

<sup>1</sup> For the cathode reaction:  $1/2O_2(g) + 2H^+ + 2e^- \rightarrow H_2O(l)$ , the change in equilibrium electrode potential with the change in oxygen pressure is estimated using Nernst equation  $\Delta E_{\text{cathode}} = RT/nF \ln(\Delta p_{O_2}/p^0)$ , where  $\Delta p_{O_2} = 20$  psi.



densities. This evolution slows to a stop as the current density is increased, and it resumes as the current density is then reduced. Thus it appears that some 2-propanol is internally reformed to acetone and hydrogen. The amount of hydrogen consumed by electrooxidation in the fuel cell increases with increasing current density. We note that hydrogen evolution was not reported by Qi et al.

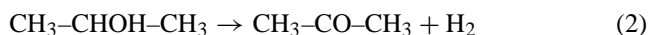
#### 4. Discussion

Our results, accompanied by those of Qi et al. indicate the following occurs during operation of the fuel cell on 2-propanol. The performance of the cell at different oxygen pressures indicates that 2-propanol crossover occurs, that the presence of 2-propanol reduces the cathode potential, but to a lesser extent than does methanol. It appears that cells can operate on 2-propanol with lower cathode loadings than cells can operate on methanol. Qi et al. reached a similar conclusion by reversing the connections of their cell and driving the current with an external power source.

The observation that increasing the cathode loading had little effect on the cell performance, combined with the observations that increasing either the anode loading or the 2-propanol concentration increased the maximum current density before the rapid voltage drop, indicates that the voltage drop is an anode phenomenon. We propose the following four reactions occur at the anode operating on 2-propanol fuel at 90 °C. First is the direct electrochemical oxidation of 2-propanol to acetone (Eq. (1)).



As per the kinetic and mechanistic studies of Pastor et al. [8] and Sun and Lin [10], this reaction is rapid, and it is the predominant direct electrochemical reaction of 2-propanol at low anode potentials. Second is the non-electrochemical catalytic dehydrogenation of 2-propanol to acetone (Eq. (2)).



Hydrogen evolution at the anode operating at current densities less than  $\sim 100 \text{ mA/cm}^2$  indicates the rate of this reaction is greater than the rate of electrooxidation in this current range. Third is electrooxidation of dihydrogen. Fourth is deep oxidation of 2-propanol or perhaps acetone. This deep oxidation appears to be the slowest of the four reactions at current densities less than  $\sim 200 \text{ mA/cm}^2$ , and it may lead to poisoning of the anode, as proposed by Qi et al. Another possibility is that a build up of acetone in the membrane/anode interface blocks mass transport to the anode. More investigation is required to determine the extent that these processes poison the anode. We note that increasing either the anode loading or the 2-propanol concentration had little effect on cell performance at current densities less than  $\sim 200 \text{ mA/cm}^2$ . This unusual result requires further investigation, but it does indicate that cells

can operate on 2-propanol fuel with lower anode and cathode loadings than cells operating on methanol. Increasing either the anode loading or the 2-propanol concentration did increase the maximum current that could be obtained before the rapid voltage drop. These results suggest that the rapid voltage drop occurs after a certain ratio of acetone to anode active sites of acetone to 2-propanol is reached in the anode-Nafion<sup>®</sup> assembly, and that acetone causes a rapid increase in the anode voltage, either by deep oxidation leading to poisoning, or by some sort of mass transport process. Again, further investigations are required to determine the origins of these observations.

#### 5. Conclusions

These results, with those of Qi et al. indicate that 2-propanol is a promising fuel candidate for a direct alcohol fuel cell. One of the more attractive features of such a system is the high operating efficiency at moderate current densities. The major challenges of this approach are anode poisoning by deep oxidation and by acetone buildup, and 2-propanol crossover. The development of anode catalysts and anode structures that are immune to these deficiencies is the more consequential of these challenges. The results presented here also suggest that internal reforming of *iso*-propanol to acetone and hydrogen in Nafion<sup>®</sup>-based fuel cells at temperatures greater than 80 °C is also a promising approach. These issues and further investigation of the proposals presented in this manuscript are under further investigation in these laboratories.

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#### References

- [1] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.M. Leger, J. Power Sources 105 (2002) 283.
- [2] A.S. Aricò, S. Srinivasan, V. Antonucci, Fuel Cells 1 (2001) 133.
- [3] J. Larminie, A. Dicks, Fuel Cell Systems Explained, Wiley, New York, 2000.
- [4] K. Kordesch, G. Simader, Fuel Cells and Their Applications, VCH, New York, 1996.
- [5] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (2000) 111.
- [6] S. Wasmus, A. Kuver, J. Electroanal. Chem. 461 (1999) 14.
- [7] P. Gao, S.C. Chang, Z.H. Zhou, M.J. Weaver, J. Electroanal. Chem. 272 (1989) 161.
- [8] E. Pastor, S. Gonzalez, A.J. Arvia, J. Electroanal. Chem. 395 (1995) 233.
- [9] J.T. Wang, S. Wasmus, R.F. Savinell, J. Electrochem. Soc. 142 (1995) 4218.

- [10] S.G. Sun, Y. Lin, *J. Electroanal. Chem.* 375 (1994) 401.
- [11] Z.G. Qi, M. Hollett, A. Attia, A. Kaufman, *Electrochem. Solid-State Lett.* 5 (2002) A129.
- [12] Z.G. Qi, A. Kaufman, *J. Power Sources* 112 (2002) 121.
- [13] X. Ren, M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 143 (1996) L12.
- [14] Calculated based the cell reaction:  $\text{CH}_3\text{-CHOH-CH}_3(\text{l}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{-CO-CH}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$  and the free energy of formation of these species obtained from the CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 2000.
- [15] W. Mooksuwan, S. Kumar, *Int. J. Energy Res.* 24 (2000) 1109.
- [16] N. Meng, Y. Ando, S. Shinoda, Y. Saito, *Bull. Chem. Soc. Jpn.* 72 (1999) 669.
- [17] Y. Saito, M. Yamashita, E. Ito, N. Meng, *Int. J. Hydrogen Energy* 19 (1994) 223.
- [18] M. Yamashita, T. Kawamura, M. Suzuki, Y. Saito, *Bull. Chem. Soc. Jpn.* 64 (1991) 272.
- [19] Y. Saito, H. Kaneyama, K. Yoshida, *Int. J. Energy Res.* 11 (1987) 549.
- [20] T.G. Kim, Y.K. Yeo, H.K. Song, *Int. J. Energy Res.* 16 (1992) 879.