ABSTRACT

Methanol and water absorption in 1100 and 1200 e.w. Nafion \textsuperscript{\textregistered} membranes was determined by weighing P\textsubscript{2}O\textsubscript{5} dried and methanol solution equilibrated membranes. Both methanol and water absorption in the 1200 e.w. membrane is about 70-74 \% of that in the 1100 e.w. membrane. The methanol cross-over rate corresponding to that in a direct methanol fuel cell (DMFC) at open circuit was measured using a voltammetric method in the DMFC configuration and under the same cell operating conditions (temperature, humidification and concentration of feed methanol solution). Accounting for the thickness difference between the membrane samples, the methanol cross-over rate through a 1200 e.w. membrane is 52 \% of that through a 1100 e.w. membrane. To resolve the cathode and anode performances in an operating DMFC, a dynamic hydrogen electrode (DHE) was used as a reference electrode. Results show that in DMFC operation the cathode could be flooded due to the high water and methanol cross-over rates, especially through the 1100 e.w. membrane at a cell temperature below 80 °C. An increase in methanol cross-over rate as incurred by increasing the concentration of the feed methanol solution, increasing the cell operating temperature or using a membrane more permeable to methanol decreases the cathode potential of the DMFC at open circuit. As the cell current density is increased, the cathode potential of the DMFC can approach the cathode potential of a H\textsubscript{2}/air cell, thanks to the consumption of methanol at the anode and consequent decrease in methanol cross-over rate.
INTRODUCTION

Recently, direct methanol fuel cells (DMFCs) using polymer electrolyte membrane have demonstrated improved performance (1-5). Compared to fuel cell systems using H₂ from methanol reforming, DMFCs have the advantage of simpler system, and with further development may even achieve higher overall energy efficiency(6). Two major obstacles that currently delay application of DMFCs are the low activity of methanol electro-oxidation catalysts and the cross-over of methanol through the polymer electrolyte membrane. It has been realized that methanol cross-over to the cathode not only lowers fuel utilization but also adversely affects the oxygen cathode (7), resulting in a relatively low cell performance. Two methods of measuring methanol cross-over rate in the fuel cell configuration are currently in use; an optical, infrared (IR) method measuring CO₂ emission flux in the cathode effluent (8,9), and a voltammetric method developed in this laboratory (10,11). The IR method can be used to study effects of the DMFC operating conditions, particularly cell current, on methanol cross-over rate. The voltammetric method gives the methanol cross-over current relevant to the cross-over rate in the DMFC at open circuit, and is especially useful for membrane characterization. In this paper, the methanol cross-over currents through 1100 e.w. and 1200 e.w. membranes were measured using the voltammetric method. IR measurements for the DMFC at O.C. conditions were also used to confirm the methanol cross-over rate. The effects of methanol cross-over on DMFC performance were evaluated using a dynamic hydrogen reference electrode (DHE).

EXPERIMENTAL

The thin-film catalyst layers on the Nafion® membranes were formed using the decal method developed in this laboratory previously for H₂/air fuel cell (12). The anode catalyst for methanol oxidation was unsupported Pt-RuOₓ (RV 30-30 from E-Tek, Inc) and the cathode catalyst for oxygen reduction was 60% Pt on carbon support (from E-Tek, Inc). To prepare the catalyst ink mixtures, 5% Nafion® solution (1100 E.W., Solution Technology, Inc) was added to the water-wetted catalysts. Suitable anode ink composition was 85 weight percent (w/o) Pt-RuOₓ and 15 w/o Nafion®, and the cathode ink composition was 88.5 w/o 60% Pt on carbon support and 11.5 w/o Nafion®. To prepare the membrane/electrode assembly (MEA), anode and cathode inks were uniformly painted onto two Teflon blanks (5 cm²) to give a 2 mgcm⁻² Pt-RuOₓ on the anode and 1.2 mgcm⁻² Pt on the cathode. After drying at 145 °C for 10 minutes, the catalyst layers were transferred and bound to a pre-dried Nafion® membrane (60 °C on a vacuum table for 45 min.) by hot pressing at 125 °C and 105 atm for 120 s. After the Teflon blanks were peeled off, the cells employing the catalyst/membrane assembly were assembled as shown in Fig.1. It should be noted that in our more recent DMFC studies, we have reached MeOH/air cell current densities of 0.3 A cm⁻² at 0.5 V using higher catalyst loading, more active anode catalyst and further optimized MEA preparation (5). While the MEA's
prepared here were somewhat less active, they were prepared identically for the two membranes.

RESULTS AND DISCUSSION

Water And Methanol Absorption

Samples of Nafion® 117 and Nafion® 1210 (10 mil, 1200 e.w.) membranes were pretreated as previously described (4), i.e., by boiling for over 1 hour in each step in 3% H₂O₂, deionized (D.I.) water, 0.5 M H₂SO₄, and again in D.I. water. Wet membrane porosity (ε) and water/methanol fluid uptake were determined at 22 °C by weighing P₂O₅ dried and solution equilibrated membranes. Eq. 1 was used to calculate the membrane porosity (13):

\[
ε = \frac{\text{fluid uptake volume}}{\text{total volume}} = \frac{(W_{\text{wet}} - W_{\text{dry}}) \cdot ρ_{\text{dry}}}{(W_{\text{wet}} - W_{\text{dry}}) \cdot ρ_{\text{dry}} + W_{\text{dry}} \cdot ρ_{\text{sol}}}
\]  

[1]

where \(ρ_{\text{dry}}\) is the dry membrane density (2.0 g/cm³ for non-porous PTFE assumed for the dry Nafion® membrane) and \(ρ_{\text{sol}}\) the solution density. The overall uptake of solution molecules per sulphonic acid group in the membranes was calculated using Eq.2, and the results are listed in Table 1 and 2 for N117 and N 1210 membranes, respectively.

\[
λ_{\text{total}} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \cdot \frac{E.W.\text{memb.}}{18x_{\text{H₂O}} + 34(1-x_{\text{H₂O}})}
\]

[2]

where \(x_{\text{H₂O}}\) is the molar fraction of water in the solution. Our previous NMR and voltammetric experiments have shown that the water and methanol reside almost completely in the ion-cluster pores and the connecting channels of the membranes (10), confirming that water and methanol are excluded from the hydrophobic PTFE region due to their very low solubility in that region. Furthermore, the NMR studies showed that the composition of the fluid within the membrane is nearly identical with that of the equilibrating solution (10). The uptake of water molecules per sulphonic acid group (\(λ_{\text{H₂O}}\)) and uptake of methanol molecules per sulphonic acid group (\(λ_{\text{MeOH}}\)) were then calculated from the \(λ_{\text{total}}\) using Eq. 3;
From the results listed for both membranes in Tables 1 and 2, it shows that for a membrane in contact with a methanol solution the water molecule uptake remains nearly constant while the methanol molecule uptake increases with the concentration of methanol solution. The methanol molecule uptake is in addition to the water molecules uptake by the membrane in contact with pure water, only with the most concentrated (>10 M) methanol solutions, some drop in water uptake is observed. This result indicates that the degree of membrane swelling increases as the concentration of contacting methanol solution is increased. For the methanol concentration region studied, the water uptake by a N1210 membrane is about 73 % of that by a N117 membrane. The methanol uptake by a N1210 membrane is also 70-74 % of that by a N117 membrane.

Methanol Permeation Rate

The limiting currents (J$_{lim}$) of methanol permeating through our MEA’s in fuel cell configuration were measured using the voltammetric method as previously described(10). Figure 1 (bottom) shows the transport processes and electrode reactions involved during the measurement. A methanol solution was fed to the left-side electrode as in a DMFC. Methanol would permeate through the left carbon cloth backing, the thin (~ 3 μm) Pt-RuO$_x$ catalyst layer, and the Nafion® membrane. Permeated methanol flux was determined by measuring the limiting current density (J$_{lim}$) resulting from the mass transport controlled methanol electro-oxidation at the Nafion® membrane/Pt catalyst interface on the right side of the cell. The right side compartment was kept in inert atmosphere of humidified N$_2$ or pure water. The cell used for permeation measurement (thereafter referred as “permeation cell”) is operated by imposing an external voltage, with hydrogen evolution as the counter process on the left side of the cell in Figure 1. The equivalent methanol cross-over currents in the DMFC (J$_{cross-over}$) at open circuit are actually higher than the measured J$_{lim}$. This is because in the “permeation cell” there is a backward methanol transport associated with the electro-osmotic drag of fluid by the reverse protonic current of J$_{lim}$. The difference between J$_{lim}$ and J$_{cross-over}$ increases with more concentrated methanol feeds. We have recently developed a mathematical model to derive a correction which shows that Eq. 4 can be used to calculate J$_{cross-over}$ from J$_{lim}$ (11). The correction factor K$_{dl}$ is a function of the overall electro-osmotic drag coefficient of the proton transport in the membrane and the concentration of feed methanol solution. Table 3 lists the methanol cross-over rate through N117 and N1210 membranes at 80 °C.

\[
J_{cross-over} = \frac{J_{lim}}{K_{dl}}
\]  

[4]
In Fig. 2, \( J_{\text{lim}} \) and \( J_{\text{cross-over}} \) from Table 3 are plotted against the concentration of feed methanol solution. If the cross-over current is limited by methanol diffusion through the membrane, then
\[
J_{\text{cross-over}} = 6FD_mCp/d \quad \text{(where } D_m \text{ is the methanol diffusion coefficient in membrane; } C \text{ - concentration of feed methanol solution; } p \text{ - partition coefficient and } d \text{ - membrane thickness).}
\]

\( J_{\text{cross-over}} \) exhibits the expected linear dependence on methanol concentration. The dependence of measured \( J_{\text{lim}} \) on \( C \) had noticeable curvature explained by the effect of electro-osmotic drag (11).

**DMFC Performance**

Figs. 3 and 4 show the performance of DMFC’s using N117 and N1210 membranes at 80 °C, using liquid methanol solution/air (20psig, humidified at 85 °C) feeds. Higher methanol cross-over rate through the N117 membrane than that through the N1210 membrane results in lower OCV of the cell using N117 membrane. For each membrane, increase in the concentration of methanol feed solution lowers the cell potential at open circuit. Even though the cell resistance with membrane N1210 is higher than that of the cell with N117 (0.36 \( \Omega \text{ cm}^2 \) vs. 0.16 \( \Omega \text{ cm}^2 \)), the DMFC using N1210 shows better performance at 80 °C than the DMFC using N117. To resolve the anode and cathode performance, our cells also contained a dynamic hydrogen electrode (DHE) as reference. Our DHE exhibited good stability with no serious potential drifting even at a cell current up to 1000 mACm\(^{-2}\) (a potential drift amounting to ±50 mV at a cell current up to 500 mACm\(^{-2}\) was reported by Küver et al for their DHE (14)).

**Validity of DHE as Reference Electrode in an Operating DMFC.**

Fig. 5 shows the schematic diagram of DHE in DMFC structure. The DHE electrodes are a pair of carbon cloth discs (1.5 mg cm\(^{-2}\) Pt on carbon support and 0.5 mg cm\(^{-2}\) 1100 e.w. Nafion® loadings) of 3 mm in diameter. The center of DHE electrode was separated from the edge of fuel cell electrodes by 5.5 mm. A galvanostatic circuit provided a current density of 6 mA cm\(^{-2}\), which is 140 times higher than that used by Küver et al (14). Our DHE electrode exhibited stable potential, and also eliminated the pre-charge step used by Küver et al (14). Following are descriptions of a set of experiments we performed to verify the validity of DHE in an operating fuel cell.

**DHE in H\(_2\)/H\(_2\) Cell.**

By feeding both cell anode and cathode with H\(_2\) (20 psig, 0.6 L min\(^{-1}\) and 115 °C humidified), the fuel cell electrodes act at zero cell current as reversible hydrogen electrode (RHE). The measured potential of the DHE vs. the RHE was -3 mV for the current density used in the reference electrode loop. By applying an external voltage across the H\(_2\)/H\(_2\) cell, the cell acts like a H\(_2\) pump. Fig. 6 shows the electrode polarization curves of H\(_2\) oxidation on Pt-RuO\(_x\) and H\(_2\) evolution on Pt obtained by using the DHE. The polarizations are small and of similar magnitude, reflecting the fast and reversible electrode processes of H\(_2\) oxidation and H\(_2\) evolution.
One of the problems of the previously reported DHE in fuel cell structure was the serious potential drift when the cell was under high current (14). This was explained as due to changes in the water (and therefore, the protonic) activity in the vicinity of the reference electrode caused by the electro-osmotic drag of water along the protonic cell current. This problem was solved in our DHE by separating the DHE and the fuel cell electrodes sufficiently apart (4 mm) so that the membrane potential at DHE is fixed at mid potential drop across the membrane. This was verified by measuring the membrane resistances across ref-anode, and across ref-cathode. As shown in Fig. 7, the potential drops across ref-anode and across ref-cathode were identical, at half of the potential drop between anode and cathode, even at a cell current density up to 1200 mA cm\(^{-2}\). The potential drop between the two reference electrodes at zero current in the reference electrode loop (both electrodes act as RHE) was also measured and found to be essentially zero with the H\(_2\) pump cell under current.

DHE in DMFC. Fig. 8 compares three methanol anode polarization curves, two were measured against DHE and one against H\(_2\) evolution counter electrode in a well humidified N\(_2\) atmosphere in the driven two electrode cell configuration. The polarization curves of methanol oxidation in DMFC measured with DHE reference and with the driven two electrode cell (H\(_2\) evolution on the counter cell electrode in a well humidified N\(_2\) atmosphere) are nearly identical. This verified that a stable DHE potential in the operating DMFC. In comparison, the H\(_2\) evolution counter cell electrode serves as a poor reference electrode in the driven two electrode cell. At a too low cell current, the counter electrode had a higher potential than the DHE reference electrode; and at a too high cell current, the counter electrode had a lower potential than the DHE reference. In the former case, trace amount of O\(_2\) in the N\(_2\) stream may affect the counter electrode potential, and in the latter case, the over-potential of H\(_2\) evolution at the counter cell electrode (as shown in Fig. 6) becomes noticeable.

Resolved Anode and Cathode Performance in DMFC. By using DHE as reference electrode, the DMFC performance shown in Figs. 3 and 4 could be further resolved to show anode and cathode polarizations. Figs. 9 and 10 show anode polarization with various concentrations of feed methanol solutions. The sharp cell potential drops at a cell current density above 50 mAm\(^{-2}\) seen in Figs. 3 and 4 with 0.2 M methanol feed were now clearly due to the anode concentration polarization of methanol transport through the anode carbon cloth backing. With 1 M methanol feed, some concentration polarization still exists at a cell current density above 200 mA cm\(^{-2}\). The anode of the DMFC using a N1210 membrane showed slightly better activity than that of the DMFC using a N117 membrane.

Figs. 11 and 12 show the air cathode polarization curves in DMFC's and H\(_2\)/Air cells constructed from anode and cell polarization curves. The air cathode of the H\(_2\)/air cell using a N117 membrane had better performance than that of the H\(_2\)/air cell using a N1210 membrane (at 0.8 V, cell current is 350 mAm\(^{-2}\) for N117, and below 200 mA cm\(^{-2}\) for N1210). The air cathode with a N1210 membrane showed significant histeresis in the downward and upward cell voltage scans, exhibiting higher potential in the upward cell voltage scan (after passing high current). This phenomenon indicates a poorly hydrated N1210 membrane. Uribe et al reported that in a less well humidified Naftion \(^\text{\textregistered}\) membrane, the O\(_2\) reduction electrode process at Pt becomes sluggish (15). In the upward potential scan of the H\(_2\)/Air cell, arrival of water by electro-osmotic drag and water formed through
O₂ reduction at a higher current density earlier applied hydrates the membrane near the vicinity of cathode, and thus cathode potential increases. In contrast, the air cathode polarization curves in the DMFC using a N1210 membrane did not show such histeresis. This indicates that the air cathode in the DMFC is well hydrated due to the fact that the anode is in contact with a liquid methanol solution feed.

Fig. 11 shows that the cathode potential of DMFC at open circuit decreases with increase in methanol cross-over rate, caused by increasing the concentration of feed methanol solution. There is also a rapid decrease in the cathode potential at a cell current density > 200 mA cm⁻², which we believe is due to cathode flooding. More evidence for cathode flooding is indicated in Fig.13, which shows that there is a quite different changes in the cathode potential at a cell current > 200 mA cm⁻² below and above 80 °C. With the cell operated at a temperature above 80 °C, cathode water removal becomes more efficient, and the cathode is less likely to be flooded. The methanol cross-over rate in an operating fuel cell measured using an optical IR method, showed that as the cell current is increased the methanol cross-over rate decreases (8,10). This is because more methanol is consumed at the anode catalyst layer before it reaches the membrane. Consequently, the cathode potential in DMFC approaches that in the H₂/air cell as shown in Fig. 12 and 13 for the non-flooded cathodes. The increase in methanol cross-over rate caused at a higher cell temperature is also shown in Fig.13 to decrease the cathode potential of the DMFC at open circuit.

Although the air cathode with a N1210 membrane has poorer performance than that with a N117 membrane in H₂/air cell, the air cathode with a N1210 membrane performed considerably better in DMFC than that with a N117 membrane (Figs. 11 and 12). There is a relatively small potential loss at open circuit, and the polarization curves at higher current density matches more closely to the air cathode polarization curve in the H₂/air cell. The lower methanol cross-over rate as well as the lower water cross-over rate through a N1210 membrane are responsible to the better cathode performance in DMFC.

CONCLUSIONS

The following conclusions summarize the results presented here:

A Nafion® 1200 e.w. membrane exhibits lower water and methanol absorption than an 1100 e.w. membrane. Adjusted for the thickness difference, the methanol cross-over rate through a 1200 e.w. membrane is only half of that through a 1100 e.w. membrane. A product of the methanol cross-over current density (mA cm⁻²) and membrane resistance (Ω cm⁻²) can be used to select membranes for DMFC application, since this number eliminates thickness dependence of membrane protonic conductance and methanol flux. The smaller the product the better. The values of this product for 1200 e.w. and 1100 e.w. Nafion® membranes (for 1 M methanol feed) are 38.5 and 44.3 (mA Ω), respectively at 80 °C.

We verified that a DHE can serve as a stable reference electrode in a DMFC. Using a DHE, we found that, with our DMFC configuration, there is a noticeable methanol
concentration polarization with 1 M methanol feed in the anode carbon cloth backing when cell current density is >200 mA cm$^{-2}$. The anode of a DMFC using a N1210 membrane exhibits slightly better polarization curves than those of DMFC using a N117 membrane.

An increase in methanol cross-over rate decreases the air cathode potential at open circuit. Such methanol cross-over increase can be caused by using a feed methanol solution of higher concentration, a more methanol permeable membrane or a higher cell temperature.

Although the air cathode of H$_2$/air cell using a N1210 membrane is considerably poorer than that of H$_2$/air cell using a N117 membrane, the air cathode of a DMFC using a N1210 membrane has much better performance than that of DMFC using a N117 membrane, thanks to lower permeability of the MeOH solution at a given temperature. The higher water and methanol permeation through a N117 membrane causes cathode flooding in DMFC operation. Such cathode flooding can be relieved by operating the DMFC at a temperature above 80 °C, or using non-humidified air feed at a cell temperature below 80 °C. We have also optimized the cell structure recently to relieve the cathode flooding at a cell temperature below 80 °C to achieve better DMFC performance with a N117 membrane.

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### Table 1. Nafion® 117 membrane porosity and λ (uptake of solution molecules per sulphonic group) at 22 °C.

| MeOH conc. mol. dm⁻³ | Membrane Porosity | λtotal | λH₂O b | λMeOH |
|----------------------|-------------------|--------|--------|-------|
| 0.0 (D.I.Water)      | 0.4048 ± 0.0112 a | 20.76 ± 0.96 | 20.76 ± 0.96 | 0.0   |
| 1.0                  | 0.4131            | 21.07   | 20.69   | 0.38  |
| 2.0                  | 0.4233            | 21.52   | 20.71   | 0.81  |
| 4.0                  | 0.4396            | 22.13   | 20.40   | 1.73  |
| 6.5                  | 0.4571            | 22.47   | 19.46   | 3.01  |
| 8.0                  | 0.4953            | 25.31   | 20.99   | 4.32  |
| 10.0                 | 0.5052            | 25.11   | 19.48   | 5.62  |

a-- Average and standard deviation from ten samples;
b-- Average value of λH₂O for membrane in contact with all methanol solutions is 20.29 ± 1.21.

### Table 2. Nafion® 1200 ew 10 mil membrane porosity and λ at 22 °C.

| MeOH conc. mol. dm⁻³ | Membrane Porosity | λtotal | λH₂O b | λMeOH |
|----------------------|-------------------|--------|--------|-------|
| 0.0 (D.I.Water)      | 0.3142 ± 0.003 a  | 15.29 ± 0.22 | 15.29 ± 0.22 | 0.0   |
| 1.0                  | 0.3236            | 15.60   | 15.32   | 0.28  |
| 2.0                  | 0.3303            | 15.77   | 15.17   | 0.59  |
| 4.0                  | 0.3376            | 15.64   | 14.42   | 1.22  |
| 6.5                  | 0.3671            | 16.88   | 14.61   | 2.26  |
| 8.0                  | 0.3788            | 17.16   | 14.23   | 2.93  |
| 10.0                 | 0.3950            | 17.52   | 13.60   | 3.93  |
| 13.0                 | 0.4249            | 18.34   | 12.56   | 5.78  |

a-- Average and standard deviation from 7 samples;
b-- Average value of λH₂O for membrane in contact with all methanol solutions is 14.56 ± 0.64.
Table 3. Measured limiting current (\(J_{\text{lim}}\)) and calculated DMFC open-circuit cross-over current (\(J_{\text{cross-over}}\)) for N117 and N1210 membranes at 80 °C.

| MeOH conc. \(\text{mol dm}^{-3}\) | \(k_{\text{dl}}\) | N117 \(J_{\text{lim}}\) mA cm\(^{-2}\) | N117 \(J_{\text{cross-over}}\) mA cm\(^{-2}\) | N1210 \(J_{\text{lim}}\) mA cm\(^{-2}\) | N1210 \(J_{\text{cross-over}}\) mA cm\(^{-2}\) |
|-------------------------------|-----------------|------------------|------------------|------------------|------------------|
| 0.10                          | 0.9869          | 7.8              | 7.9              | -                | -                |
| 0.20                          | 0.9745          | -                | -                | 7.5              | 7.7              |
| 0.25                          | 0.9767          | 22.8             | 23.6             | 10.3             | 10.6             |
| 0.50                          | 0.9373          | 58.0             | 61.9             | 22.2             | 23.7             |
| 1.00                          | 0.8829          | 116              | 131              | 42               | 47.6             |
| 2.00                          | 0.7930          | 220              | 277              | 85               | 107              |

Figure 1. Schematic diagrams showing methanol permeation measurement in DMFC configuration; (a) and (g) graphite blocks with cross-patterned flow field; (b) and (f) carbon cloth backings; (c) Pt-RuO\(_x\) thin film catalyst layer; (d) Nafion\(^\circledR\) membrane; (e) Pt black thin film catalyst layer. For the permeation measurement, the humidified air feed in DMFC is replaced by a humidified nitrogen feed. The electro-oxidation of methanol permeated through membrane/electrode assembly takes place at e.

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Figure 2. Plots of $J_{\text{lim}}$, measured in the permeation cell, and $J_{\text{cross}}$ for the DMFC at open-circuit calculated from $J_{\text{lim}}$ using Eq. 4 vs. the concentration of feed methanol solution at 80 °C.

Figure 3. DMFC (MeOH/air) polarization curves using a N117 membrane with different MeOH feed concentration. Air at 20 psig at 0.6 L min$^{-1}$, 85 °C humidified, cell at 80 °C.
Figure 4. DMFC (MeOH/air) polarization curves using a N1210 membrane with different MeOH feed concentration. Air at 20 psig at 0.6 L min⁻¹, 85 °C humidified, cell at 80 °C.

Figure 5. Schematic diagram showing DHE circuit in DMFC structure. (a) and (g) graphite blocks with cross-patterned flow field; (b) and (f) carbon cloth backing; (c) Pt-RuOₓ thin film anode catalyst layer; (d) Nafion® membrane; (e) Pt thin film cathode catalyst layer. The flow channels were designed to pass over the pair of electrodes in the DHE circuit.
Figure 6. Polarization curves of $\text{H}_2$ oxidation on Pt-RuO$_x$ and $\text{H}_2$ evolution on Pt electrodes at 80 °C (with IR correction) measured with a DHE reference electrode. $\text{H}_2$ feed is at 20 psig, 0.6 L min$^{-1}$ and 115 °C humidified.

Figure 7. Membrane high frequency (8 k Hz) resistances measured between anode-cathode, anode- DHE ref and cathode- DHE ref at 80 °C, for a hydrogen pump cell with $\text{H}_2$ (20 psig, 0.6 L min$^{-1}$, 115 °C humidified) feed.
Figure 8. Methanol anode polarization curves at 80 °C measured in DMFC using DHE and in two electrode driven cell using H₂ evolution counter electrode. The DMFC was fed with 1 M methanol/air (20 psig, 0.6 L min⁻¹, 85 °C humidified) and the 2-electrode cell was fed with 1 M methanol/N₂ (20 psig, 0.6 L min⁻¹, 115 °C humidified).

Figure 9. DMFC anode polarization curves using a N117 membrane at 80 °C (iR corrected). See Figure 3 for cell operating conditions.
**Figure 10.** DMFC anode polarization curves using a N1210 membrane at 80 °C (iR corrected). See Figure 4 for cell operating conditions.

**Figure 11.** DMFC cathode polarization curves using a N117 membrane at 80 °C (iR corrected). See Figure 3 for cell operating conditions.
Figure 12. DMFC cathode polarization curves using a N1210 membrane at 80 °C (iR corrected). See Figure 4 for cell operating conditions.
Figure 13. Cathode polarization curves of DMFC and H$_2$/air cell using a N117 membrane at various cell temperatures (iR corrected). DMFC was fed with 1 M MeOH/air (20 psig, 0.6 L min$^{-1}$, humidified at 5 °C higher than the cell temperature). H$_2$/air cell was fed with H$_2$(20 psig, 0.6 L min$^{-1}$, humidified at 105 °C) and air (20 psig, 0.6 L min$^{-1}$, humidified at 115 °C for the flooded cathode, and 5 °C higher than the cell temperature for the normal cathode).