Kinetcs and Stoichiometry of Methanol and Ethanol Oxidation in Multi-Anode Proton Exchange Membrane Cells

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The anode catalyst of a direct alcohol fuel cell (DAFC) influences its energy efficiency through both its effect on the cell potential and the reaction stoichiometry (average number of electrons released per fuel molecule; \( n_{\text{av}} \)). A method for determining these parameters simultaneously from a polarization curve (current vs. cell potential) is reported and various catalysts have been evaluated in a multi-anode cell. The cell was operated in crossover mode, in which fuel flows through the cathode chamber and diffuses though the membrane to be oxidized at the anode, to provide controlled mass transport conditions. Tafel analysis at low potentials provides kinetic information, while currents at high potentials provide \( n_{\text{av}} \) values and their potential dependence. The method allows a number of catalysts to be compared under the same conditions, and provides characteristic parameters that could be compared across research groups. It is shown that while PtRu alloy catalysts provide faster kinetics than Pt for both methanol of ethanol oxidation, Pt can provide similar stoichiometries for ethanol oxidation. The value of this methodology for catalyst screening is demonstrated with mixed Pt/C + PtRu/C anodes which show a pronounced synergistic effect relative to the individual Pt/C and PtRu/C catalysts.

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Direct alcohol fuel cells are emerging technologies for power production from renewable fuels. 1-5 Direct methanol fuel cells (DMFC) with polymer electrolyte membranes (PEM) are already well developed and have achieved small scale commercialization.3,6-8 Direct ethanol fuel cells (DEFC) are more attractive for sustainable energy production.9,10 However, although there have been a number of demonstration projects,6,8,10 performances are not yet sufficient for commercialization.10 Ethylene glycol11,12 and glycerol13 are also being studied as fuel options in fuel cells, but present more complex problems.

There are many challenges that are impeding the development of DAFC technology.1,7,10,14 Relative to hydrogen PEMFCs, which already have relatively large markets, DAFCs suffer from much larger anode overpotentials, efficiency and power losses due to fuel crossover, and incomplete oxidation of the fuel. The primary requirement for commercialization of ethanol, ethylene glycol and glycerol fuel cells is the development of anode catalysts that oxidize these fuels completely to carbon dioxide at low overpotentials.12,15-17 Better anode catalysts are also required for widespread implementation of DMFC technology.18

The importance of DAFC technology for a sustainable energy future based on clean and efficient use of renewable fuels has resulted in intensive studies of the electrochemical oxidation of alcohols and the development of thousands of different anode catalysts. Generally, these have been evaluated at ambient temperatures in liquid electrolytes by cyclic voltammetry and in many cases by chronoamperometry. Products have been analyzed in some cases by techniques such as FTIR spectroscopy,16,19-21 and differential electrochemical mass spectroscopy (DEMS).22-25 However, the complexity and cost of testing in fuel cells has limited the implementation of new catalysts, and it is difficult to predict which will be most suitable for further development. A number of recent publications have highlighted the need for new experimental protocols and methods for comparing the activities of different catalysts in order to account for poisoning26 and mass-transport27-29 effects, and differences in the average number of electrons transferred (\( n_{\text{av}} \)) due to differences in product distributions.27,28 Accounting for differences in \( n_{\text{av}} \) is crucial for the oxidation of ethanol and higher alcohols because it plays a central role in determining the cell efficiency30,31 and by-product emissions.9,32

The purpose of the work described here was to explore the use of multi-anode PEM electrolysis cells for the evaluation and comparison of different catalysts for methanol and ethanol oxidation. The method employed is based on the crossover mode of operation of a PEM methanol electrolysis cell described by Ren et al.33 In this configuration (Fig. 1), the fuel is delivered to the cathode and diffuses across the membrane to the anode, while the anode is flushed with \( N_2 \) to avoid interference from oxygen. Electrochemical reduction of hydronium ions at the cathode provides a stable reference potential (dynamic hydrogen electrode). The attraction of running the cell in crossover mode is the well-defined mass-transport limitation provided by diffusion of the fuel through the membrane, which simplifies analysis of the electrochemical kinetics and can provide the stoichiometry (\( n_{\text{av}} \)) of the reaction. The goals of this work were to develop procedures for comparing the kinetics and stoichiometries of methanol and ethanol oxidation at different catalysts. This would be valuable for catalyst screening, developing steady state kinetic models for these reactions in fuel cells, and providing characteristic parameters that can be compared across research groups. Commercially available catalysts have been used to develop, validate, and benchmark the methodology.

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Figure 1. Schematic diagram of the nine anode cell (top) and crossover mode of operation (bottom). R = H or CH₃.
Experimental

Materials.—The experiments were carried out with 99.8% methanol from ACP Chemical Inc., anhydrous ethanol (99.9%) from Commercial Alcohols Inc., and distilled and filtered deionized water. Nafion 115 and 117 membranes (Du Pont) were cleaned at 80 °C in 3% H2O2 (aq) (EMD Millipore) and 1 M H2SO4 (aq) (Fisher Scientific), rinsed with deionized water, and stored in deionized water. Anodes contained 15 mass% Nafion and the anodes prepared with polytetrafluoroethylene as a binder, while the PtRu black (HiSPEC 12100, 50% Pt and 25% Ru on a high surface area advanced carbon support; Alfa Aesar; Lot# M22A026); carbon supported PtRu (PtRu/C; 4.0 mg PtRu cm$^{-2}$); carbon supported Pt (Pt/C; various loadings; HiSPEC 13100, 70% Pt on a high surface area advanced carbon support; Alfa Aesar; Pt black (7E); carbon supported Pt (Pt/C; 4.0 mg Pt/C cm$^{-2}$; HiSPEC 12100, 50% Pt and 25% Ru on a high surface area advanced carbon support; Alfa Aesar; Lot# P17B047). The Pt black electrodes contained polytetrafluoroethylene as a binder, while the PtRu black anodes contained 15 mass% Nafion and the anodes prepared with supported catalysts contained 20% Nafion.

PEM cells.—Cells with four (4E) or nine (9E) separate anodes, a single 5 cm$^2$ Pt black cathode and a Nafion proton conducting membrane electrolyte were used (Fig. 1). Each cell was based on a commercial (ElectroChem Inc.) PEM fuel cell graphite plate flow field and hardware for the cathode side and a Lexan or Bakelite plate with a similar flow field for the anodes. The anode current collectors were graphite rods embedded in the Lexan or Bakelite plate. The anode catalyst area was 0.236 cm$^2$ (9E) or 0.385 cm$^2$ (4E) per anode. A cell with a single 5 cm$^2$ anode was used in one experiment to determine $n_\text{avg}$, as previously described. The applied potential was controlled with a MSTAT potentiostat from Arbin Instruments. The fuel was supplied by a NE-300 New Era Pump Systems syringe pump. A 60 W Watlow heat plate and a Digi Sense temperature controller were used to heat the cathode plate. The cell was preconditioned at 0.7 V for one hour at the operating temperature. Polarization curves were then obtained from 0.9 V to 0.0 V in 25 mV steps. Each potential was held for three minutes, with the current recorded every second. The reported currents are averages over the final two minutes.

Operating mode.—The cells were operated in crossover mode (Fig. 1) with the liquid fuel solution pumped through the cathode flow field while the anode flow field was purged with 10 mL min$^{-1}$ nitrogen (N$_2$) gas to prevent interference from oxygen. In this mode, the cathode approximates a dynamic hydrogen electrode, since the cathode reaction is $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2$. Furthermore, the steady fuel flux through the membrane to the anode side simplifies modeling of the kinetic and mass transport processes. The cell was operated with 0.1 M and 1 M aqueous solutions of ethanol and methanol (in water with no electrolyte or buffer) at a flow rate of 0.5 mL min$^{-1}$ and at temperatures of 50 and 80 °C.

Polarization curves for 1 M methanol and ethanol were corrected for the uncompensated resistance measured by impedance spectroscopy with a EG&G Model 273A potentiostat/galvanostat and EG&G Model 5210 Lock-in Amplifier operated with Power-Suite software. Since resistances did not vary significantly between electrodes, the same average values were applied to all electrodes in each cell. They were 0.44 $\Omega$ for the 9E cell and 0.61 $\Omega$ for the 4E cell at 50 °C.

Figure 2. Polarization curves for the oxidation of 1.0 M methanol at 50 °C at nine equivalent Pt black anodes. The solid line is the best fit of the average current at each potential to Eq. 3. The inset shows a Tafel plot (log(current) vs. E) for the average current and the best fit.

Results and Discussion

Methanol oxidation.—Initially, a cell was operated with nine Pt black anodes in order to determine the reproducibility between electrodes and develop a suitable kinetic analysis. Steady-state polarization curves for oxidation of 1.0 M methanol in crossover mode at nine equivalent electrodes are shown in Fig. 2. The current rose to the same limiting current density ($j_{\text{lim}}$) at each electrode, within a standard deviation of ±6.6%, illustrating the well-defined diffusion of methanol through the cathode and membrane to the anode. If the small effects of electro-osmotic drag are neglected, $j_{\text{lim}}$ is given by Eq. 1,

$$\ j_{\text{lim}} = n_\text{avg} F m C $$  

[1]

where $m$ is the mass transport coefficient, and $C$ is the concentration of methanol. Since $m$ depends on the thicknesses of both the cathode and the membrane, and diffusion characteristics of methanol within both of these layers, an accurate value is not available. However, it has been shown previously that methanol is completely oxidized to CO$_2$ ($n_\text{avg} = 6$) under these conditions, and so Eq. 1 can be used to determine $m$ from $j_{\text{lim}}$. Average values of $j_{\text{lim}}$ and $m$ are listed in Table 1. The $j_{\text{lim}}$ of 128 mA cm$^{-2}$ is similar to the value of 91 mA cm$^{-2}$ reported by Ren et al. for similar conditions.

Although detailed models are available for analysis of the polarization curves in Fig. 2, a simpler, more generic model based on first order kinetics is used here. Since the equilibrium potential was not controlled or known, the kinetic current ($i_k$) is written in terms of the standard rate constant ($k^0$) according to Eq. 2,

$$\ i_k = n_\text{avg} F A k^0 C \cdot \exp \left[ \alpha \left( E - E^0 \right) / RT \right] $$  

[2]

where $A$ is the electrode area, $\alpha$ is the electron transfer coefficient, and $E^0$ is the standard potential of 0.016 V for methanol oxidation. Assuming that the rate of the reverse reaction is negligible, the steady-state current density ($j$) as a function of potential is given by Eq. 3,

$$\ j = n_\text{avg} F k^0 C \left( 1 - j / j_{\text{lim}} \right) \cdot \exp \left[ \alpha \left( E - E^0 \right) / RT \right] $$  

[3]

![Table 1](image)

| Catalyst (cell) | Loading (mg cm$^{-2}$) | $j_{\text{lim}}$ (mA cm$^{-2}$) | $m \times 10^3$ (cm s$^{-1}$) | Tafel slope (mV) | $\alpha$ | $k^0 \times 10^{10}$ (cm s$^{-1}$) |
|-----------------|------------------------|-------------------------------|-----------------------------|-----------------|--------|----------------------------------|
| Pt black (9E)   | 4.0                    | 128 ± 6                       | 0.22 ± 0.01                  | 98 ± 6          | 0.66 ± 0.04 | 1.4 ± 0.8                      |
| Pt black (4E)   | 4.0                    | 158 ± 8                       | 0.27 ± 0.01                  | 81 ± 5          | 0.79 ± 0.05 | 0.27 ± 0.26                    |
| PtRu black (4E) | 7.47                   | 145 ± 1                       | 0.251 ± 0.002                | 96 ± 11         | 0.67 ± 0.08 | 150 ± 100                     |
| 70% Pt/C (9E)   | 1.0–3.25               | 110 ± 15                      | 0.19 ± 0.03                  | 105 ± 9         | 0.61 ± 0.06 | 6.5 ± 3.2                     |

Table 1. Parameters from least squares fits of Eq. 3 to polarization curves at 50 °C for the oxidation of 1.0 M methanol at various electrodes.
I. For Pt black, the 4E cell gave somewhat higher mass transport limiting currents would depend on the electrode material and potential. The background current was not reproducible, and so could not be accurately corrected. Although variations in the background current should lead to random errors, and these can be seen to be very large for $k_0$ in Table I, there does appear to be some bias. This illustrates the difficulties in obtaining meaningful kinetic parameters for fuel cell catalysts, and the importance of testing multiple electrodes.

When the parameters for Pt and PtRu black in the 4E cell are compared (Table I), only the difference in $k_0 \pm 0.5$ is statistically significant. The much earlier onset of methanol oxidation at the PtRu electrodes can therefore be attributed to the ca. 200 fold increase in $k_0$ relative to Pt black (based on the average $k_0$ for Pt black in the 4E and 9E cells). This is explained by the well known bifunctional mechanism in which the adsorbed CO intermediate in methanol oxidation is oxidized to CO$_2$ at sites adjacent to surface Ru-OH sites. These are formed at lower potentials than Pt-OH sites.

Polarization curves for the oxidation of 1 M methanol were also obtained for a series of anodes prepared with various loadings of a commercial carbon supported Pt catalyst (HiSPEC 13100, 70% Pt). Two anodes with each nominal loading were used in the 9E cell, with a Pt black electrode as a control. Figure 4 shows $m$ and $k_0$ values obtained by fitting to Eq. 3 to each data set, as a function the nominal Pt loading. Although there is significant scatter in the data due to difficulty in controlling the loading and compression of each electrode, there was not a significant dependence of either parameter, or the Tafel slope (not shown), on the Pt loading. Consequently, average parameters for the 8 Pt/C anodes are reported in Table I. It can be seen that the uncertainties were similar to those obtained for Pt and PtRu electrodes with constant loadings, again indicating a lack of loading dependence for the Pt/C anodes. Comparison of the data for Pt/C and Pt black in the 9E cell (Table I) shows that the Tafel slopes were not significantly different, while $k_0$ was significantly higher for the Pt/C anodes (based on a $t$ test at 95% confidence). Clearly Pt/C was the better catalyst for methanol oxidation, even at a much lower Pt loading (1 mg cm$^{-2}$ for Pt/C vs. 4 mg cm$^{-2}$ for Pt black). The $m$ values obtained for the Pt/C anodes were lower and more variable than for the Pt black anodes. This was most likely due to uneven and variable compression of the cathode.

Overall, the Tafel slopes reported in Table I do not show any clear differences between the three catalyst types. The average slope of 95 mV is much lower than the value of 166 mV at 300 K calculated from first principles for methanol oxidation at Pt(111), with the first C-H bond breaking as the rate determining step. Experimental Tafel slopes reported in the literature for a variety of electrode types and conditions cover a wide range that encompasses these two values. Literature Tafel slopes for methanol oxidation at Pt black, Pt/C and PtRu/C range from 80–195 mV$^{27,47–54}$ and do not show significant correlation with the temperature (22–80°C), catalyst, or electrolyte (HClO$_4$, H$_2$SO$_4$, or NaF$^{11−35}$). The slopes reported in Table I are at the low end of this range, and this is most likely due to the correction for resistance and mass transport effects employed in the analysis.

Since Tafel slopes do not currently appear to be useful for discriminating between catalysts, $k_0$ is a crucial parameter. The data in Table I...
show that it qualitatively reflects the differences in activities of the Pt black, PtRu black, and 70% Pt/C catalysts. However, extrapolation of the kinetic current to $E^\circ$ can lead to large uncertainties and inaccuracies. Furthermore, there are only a few literature reports that provide data for comparison. Wang et al. reported an exchange current of 9.4 mA cm$^{-2}$ for the oxidation of 1 M methanol at PtRu in a DMFC at 80°C. This corresponds to $k^0 \sim 5 \times 10^{-6}$ cm s$^{-1}$ at 50°C, which is much larger than the value of $(1.5 \pm 1.0) \times 10^{-8}$ cm s$^{-1}$ for PtRu in Table I. This can be attributed mainly to the much higher Tafel slope of 293 mV obtained for the DMFC. Fitting parameters to a model for a DMFC provided $k^0 \sim 3 \times 10^{-7}$ cm s$^{-1}$ at 50°C for PtRu/C for an assumed Tafel slope of 118 mV. However, this was based on fitting of polarization curves with only one data point in the Tafel region.

This brief survey of kinetic parameters for methanol oxidation highlights the need for a standardized methodology to provide characteristic parameters that can be compared across research groups. Steady-state measurements in a PEM electrolysis cell in crossover mode appear to be well suited for comparing the activities of DAFC catalysts. This conjecture was explored further with ethanol as the fuel, which brings the added complication of variations in $n_{av}$, with potential.

**Ethanol oxidation.—** A comparison of ethanol polarization curves with methanol polarization curves is shown in Fig. 3. It can be seen that the currents were much higher for ethanol at all potentials, with the difference more pronounced for Pt than PtRu. Inspection of the data in Fig. 3 reveals that the half-wave potentials are similar for ethanol and methanol at ca. 0.44 V for PtRu and 0.61 V for Pt, indicating that the kinetics ($i_k$), are similar. Consequently, the main differences in the currents are due to differences in the mass transport coefficient ($m$) and stoichiometry ($n_{av}$). These are most obvious and illuminating in the mass transport region, above ca. 0.6 V for PtRu and ca. 0.7 V for Pt. Whereas methanol oxidation produced an almost constant current in this region, that was essentially the same for PtRu and Pt, the currents for ethanol oxidation varied significantly with potential, and were very different for PtRu vs. Pt. Since $m$ cannot vary with potential or the electrode material, the variations in the ethanol oxidation current in the mass transport region indicate that $n_{av}$ depends on the potential and the electrode material. This is consistent with numerous studies of product distributions for ethanol oxidation.16,17

Quantitative analysis of the ethanol polarization curves in Fig. 3 can be achieved by application of a Tafel analysis (Eq. 2) at low potentials, where $j$ is less than ca. 10% of $j_{lim}$, followed by application of Eq. 3 to determine how $n_{av}$ varies with potential in the high potential region. Fig. 5 shows Tafel plots of the low potential data from Fig. 3. Average values of $k^0 n_{av}$, the Tafel slope, and $\alpha$ for the two Pt and two PtRu electrodes are reported in Table II. $k^0$ cannot be accurately determined here because $n_{av}$ is unknown for the Tafel region.

The $k^0 n_{av}$ and $\alpha$ values from the Tafel plots were subsequently used in Eq. 3 to calculate $j_{lim}$ as a function of potential. Results are shown in Fig. 6 for one of the PtRu electrodes, where the measured current is compared with the calculated kinetic and mass transport limited currents. The variation of the calculated $j_{lim}$ with potential is most likely due to changes in $n_{av}$, although it could be an artifact caused by extreme deviation from the Tafel relationship at high potentials. Deviations from the low potential Tafel behavior have generally been observed for ethanol oxidation, and it was shown in a rotating disc study that the mass transport limit could not be reached due to oxide formation on the Pt surface. However, the very thick catalyst layers used here together with restriction of mass transport by the membrane and cathode have clearly allowed the mass transport limit to be reached for methanol oxidation in Figs. 2 and 3, with no effect of oxide formation over the potential range employed. It therefore does not appear to be reasonable to attribute the decreasing $j_{lim}$ seen in Fig. 6 to changes in the kinetic current.

In order to explore this interpretation further, and to quantify $n_{av}$, the flow rate ($u$) dependence of the ethanol oxidation current ($i$) was measured in a normal 5 cm$^2$ cell. This allows $n_{av}$ to be determined with reasonable accuracy56 by use of Eq. 4:

$$i = n_{av}FC_{in}u \left(1 - \exp\left(-\frac{j_{lim}}{n_{av}FC_{in}u}\right)\right) \quad [4]$$

where $C_{in}$ is the concentration of ethanol entering the cell and $j_{lim}$ is the current at high flow rates. The polarization curve and $n_{av}$ versus potential are shown in Fig. 7. It can be seen that the polarization curve shows a similar decrease in the current at potentials above 0.55 V to that seen in Fig. 3 for ethanol oxidation at PtRu, and that this can be attributed to the parallel decrease in $n_{av}$ observed in Fig. 7. The $n_{av}$

![Figure 5](image.png)  
**Figure 5.** Tafel plots for the low potential data in Fig. 3 for oxidation of 1.0 M ethanol at Pt (■, △) and PtRu black (●, □) anodes.

![Figure 6](image.png)  
**Figure 6.** Experimental current densities ($j$) and calculated kinetic ($j_k$) and mass transport limited ($j_{lim}$) current densities for oxidation of 1.0 M ethanol at a PtRu black anode in a 4E cell at 50°C.

| Catalyst (cell) | Loading (mg cm$^{-2}$) | $Tafel$ slope (mV decade$^{-1}$) | $\alpha$ | $k^0 n_{av}$ (cm s$^{-1}$) |
|----------------|------------------------|-------------------------------|---------|-------------------------|
| Pt black (4E)  | 4.0                    | 154 ± 11                      | 0.42 ± 0.03 | (9.5 ± 7.1) x 10$^{-8}$ |
| PtRu black (4E)| 5.47                   | 116 ± 5                       | 0.55 ± 0.03 | (3.6 ± 0.9) x 10$^{-7}$ |

Table II. Parameters from Tafel analysis of polarization curves for the oxidation of 1.0 M ethanol at Pt black and PtRu black electrodes.
values in Fig. 7 are close to the $n_{av}$ of 3 previously determined for a Pt black electrode at 0.7 V under these conditions. They indicate that the ethanol was oxidized primarily to acetaldehyde ($n = 2$) and acetic acid ($n = 4$), with little formation of CO$_2$ ($n = 12$), which is consistent with product yields at ≤ 50°C measured by DEMS.

The mass transport coefficient for ethanol in the 4E cell can be estimated from Eq. 1 by using the $j_{lim}$ values in Fig. 6 with the $n_{av}$ values in Fig. 7 at the same potentials. An average $m$ of $(2.0 \pm 0.2) \times 10^{-4}$ cm s$^{-1}$ was obtained, which is somewhat lower than the value of $(2.7 \pm 0.1) \times 10^{-4}$ cm s$^{-1}$ obtained for methanol under the same conditions (Table I). This is as expected based on the larger size of the ethanol molecule. This value of $m$ was then used with Eqs. 1 and 3 to calculate $n_{av}$ vs. potential from the data in Fig. 3, for both the PtRu and Pt anodes. The results are shown in Fig. 8. The values for PtRu are similar to those in Fig. 7 for the 5 cm$^2$ cell because they were used for determining $m$. The Pt black anodes gave similar $n_{av}$ values at high and low potentials, but significantly lower values at intermediate potentials. The higher $n_{av}$ values at low potentials are consistent with the potential dependence of CO$_2$ formation reported in a DEMS study. However, the very low values of $n_{av}$ for the Pt anodes at intermediate potentials in Fig. 8 (0.6 to 0.85 V) indicate that they are not accurate, and that these anodes were not operating under mass transport controlled conditions. The values below $n_{av} = 2$ are not possible because ethanol cannot be oxidized to a stable product by less than two electrons. Clearly, $i_2$ deviated from the low potential Tafel relationship at potentials above 0.6 V (or lower) and accurate values of $j_{lim}$ and $n_{av}$ were not obtained from Eq. 3.

0.1 M methanol and ethanol.—Previous work in the 5 cm$^2$ cell has shown that the mass transport limit can be reached at Pt electrodes when 0.1 M ethanol is employed, and that $n_{av}$ is increased by decreasing the ethanol concentration and increasing the temperature. Consequently, further experiments were conducted with 0.1 M methanol (for calibration) and 0.1 M ethanol at 80°C. In addition, a thicker membrane (Nafion 117 instead of Nafion 115) was employed to decrease the mass transport current relative to the kinetic current. A 9E cell was used to simultaneously collect polarization curves for three electrodes each of three different types of anode: Pt/C, PtRu/C, and a 50:50 mixture by mass of these two catalysts (Fig. 9).

The data for methanol in Fig. 9 show a significant difference in the half wave potential between the Pt/C and PtRu/C anodes, while the mixed anode shows the same half wave potential as PtRu/C. Although the limiting current for PtRu/C appears to be lower than for the other two types of anode, the difference is only statistically significant (95% confidence t-test) relative to the mixed anodes. The low limiting current for PtRu/C implies that methanol oxidation did not proceed to completion at these anodes (i.e. $n_{av} < 6$). Consequently, the PtRu/C results were not used in the estimation of $m$ for methanol for these conditions. Averaging the limiting currents for the Pt and mixed anodes gave $m = (4.0 \pm 0.4) \times 10^{-4}$ cm s$^{-1}$ for the Nafion 117 membrane at 80°C. If it is assumed that the ratio of $m$ for methanol and ethanol is the same as for Nafion 115 at 50°C, then $m$ for ethanol with Nafion 117 at 80°C can be estimated to be ca. $3.0 \times 10^{-4}$ cm s$^{-1}$. This can then be used to estimate $n_{av}$ vs. potential for ethanol oxidation from the data in Fig. 9B.

From a visual comparison of the data sets in Fig. 9, it can be seen that the half-wave potentials showed a similar trend for methanol and ethanol, while the limiting current region showed a much stronger dependence on the catalyst for ethanol than for methanol. This indicates
that $n_{av}$ was influenced more by the catalyst, with Pt producing up to twice as many electrons as PtRu. This is in agreement with measurements of product distributions and ethanol consumption for these two catalysts under similar conditions in a 5 cm$^2$ cell. It can also be seen from the data in Fig. 9B that the mixture of the two catalysts gave a similar half-wave potential to PtRu/C, while $n_{av}$ values were closer to those for Pt/C. There was clearly a significant synergistic effect between the two catalysts, and this is being investigated in further work.

Quantitative analysis of the polarization curves in Fig. 9B to determine the potential dependent $n_{av}$ values was conducted by fitting to Eq. 3, as described for Fig. 6. Fig. 10 shows the $n_{av}$ vs. potential plots that were obtained for each type of anode. For comparison, $n_{av}$ values obtained by measuring the amount of ethanol consumed in a 5 cm$^2$ cell are included. These were measured with 0.1 M ethanol supplied to the anode and N$_2$ at the cathode, and verified by simultaneously measuring the product distribution. It can be seen that there is a remarkable agreement between the two data sets in Fig. 10 for the Pt/C anodes. However, the voltamograms in Fig. 9 for the PtRu/C anodes gave $n_{av}$ values that were significantly higher than those from Ref. 60 at most potentials. This may have been due to the difference (relative to cyclic voltammetry or chronoamperometry) is the use of apparent that is well suited for understanding the kinetics of these reactions in fuel cells.

Conclusions

Operation of fuel cell hardware in crossover mode can produce steady-state polarization curves with mass transport regions that provide stoichiometric information in addition to the kinetic data obtained at low potentials. Polarization curves for methanol oxidation were accurately modelled by a normal first order electrochemical rate expression coupled with steady state mass transport (Eq. 3). However, the limiting current can vary from the value expected for complete oxidation to CO$_2$ ($n = 6$). Polarization curves for ethanol oxidation can also be modelled with a first order electrochemical rate expression, although the mass transport limited current varies with potential due to variation in the product distribution with potential, which causes the number of electrons transferred to vary. In the mass transport region, the current is proportional to $n_{av}$ (Eq. 1), while $n_{av}$ can be estimated from Eq. 3 in the mixed kinetic-mass transport region. The accuracy of this methodology is good for ethanol oxidation at PtRu catalysts, but further assessment is required for Pt catalysts. Nevertheless, steady-state polarization curves obtained in crossover mode provide excellent data for the preliminary evaluation of catalysts for methanol and ethanol oxidation in PEMFC hardware, and kinetic data that is well suited for understanding the kinetics of these reactions in fuel cells.

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