

Effect of Redox State of PtRu Electrocatalysts on Methanol Oxidation Activity

Aislinn H. C. Sirk,[†] Josephine M. Hill,[‡] Sherman K. Y. Kung,[†] and Viola I. Birss*,[†]

Department of Chemistry and Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive, N.W., Calgary, AB, Canada T2N 1N4

Received: September 1, 2003; In Final Form: October 15, 2003

PtRu is a promising catalyst for methanol oxidation in direct methanol fuel cells. However, the most active Pt:Ru ratio and oxidation state of the Ru component are still under investigation. PtRu black was obtained from Johnson Matthey, and the as-received catalyst was treated with either hydrogen or oxygen at elevated temperatures to alter the oxidation state. The samples were characterized by cyclic voltammetry (CV), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and X-ray diffraction (XRD) to confirm their redox states and for correlation with their methanol oxidation activity. All of the characterization techniques support successful oxidation and reduction of the PtRu catalyst. The methanol oxidation activity was measured, and the sequence at 25 °C was found to be reduced > as-received > oxidized >> strongly oxidized. The effect of the drying regime and the dispersing agent for the catalysts was also investigated, and it was found that samples supported using acetic acid were more active than those supported by Nafion, but were less stable and more susceptible to change in catalyst state from heat gun drying.

Introduction

Direct methanol fuel cells (DMFCs) show great promise as high-efficiency, low-emission future power sources. However, there are several barriers to their implementation, including methanol crossover through the Nafion membrane¹ causing poisoning of the cathode, as well as substantial power losses due to the relatively low activity of the methanol oxidation catalysts currently in use. Improvements are needed in both of these areas before DMFCs can enter the market on a competitive basis.²

Although many different electrocatalysts have been investigated, such as PtRe, PtMo, and PtSn³ and ternary compounds such as PtRuW, PtRuMo, and PtRuSn⁴ as well as Pt/metal phthalocyanines,⁵ the benchmark anode catalyst is still PtRu. There are difficulties with direct comparisons between these catalyst materials as characterization is not facile and other factors, such as surface area, particle size,^{6,7} homogeneity of the alloy,⁸ crystal plane,⁹ preparation technique,¹⁰ pretreatment, and the particular experimental conditions employed, affect the observed activity. Despite this, it has been conclusively shown that the addition of Ru to Pt increases the anode activity by greatly reducing the effects of CO poisoning. CO oxidation on PtRu catalysts occurs at a significantly lower overpotential compared to that at pure Pt catalysts,¹¹ and thus, the methanol oxidation activity is much higher. This is due to both ligand and bifunctional effects,¹² with one study showing that the bifunctional effect of Ru to activate water to OH is about 4 times larger than the ligand effect.¹³

The optimum ratio of Pt to Ru in these catalysts is still unknown. Many groups use a 50/50 atomic ratio, but Gasteiger et al. found that values as low as 10 at. % Ru are optimum at room temperature and that the pretreatment involving cycling

to higher potentials dissolves Ru and leads to the belief that a higher ratio than this is necessary.¹⁴ An optimum ratio of 10–30% Ru for room temperature methanol oxidation has also been reported.¹⁵

There is also debate in the literature as to whether a PtRu bimetallic alloy¹⁶ or a Pt and Ru oxide mixture¹⁷ is the most effective methanol oxidation catalyst. It has been postulated that the mixed electronic and protonic conductivity of hydrous Ru oxide makes it the more desirable form of Ru (versus metallic Ru) and that Pt metal mixed with Ru oxide may have been incorrectly identified as a bimetallic alloy through X-ray diffraction patterns.¹⁸ It is possible that some of these different views arise from experimental differences in the measurement of methanol oxidation activity. For example, Gottesfeld et al. used membrane electrode assemblies (MEA) in a full cell configuration¹⁶ to determine activity, while Rolison et al.¹⁷ have employed sticky carbon rotating disk electrodes in a half-cell configuration.

The primary goal of the present work has been to conclusively establish the relative methanol oxidation activity of PtRu catalysts in well-characterized reduced, as-received, oxidized, and strongly oxidized states, using a consistent experimental approach. It has been found, in all cases, that the reduced PtRu yields the highest methanol oxidation activities and the strongly oxidized the lowest. Also, the role of Nafion, as compared to other binding agents, has been examined in half-cell experiments, to determine if the presence or absence of the binder contributes to some of the confusion in the literature. All catalysts were characterized using cyclic voltammetry (CV), thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and powder X-ray diffraction (XRD), to confirm their redox states and to correlate the properties of the catalysts with their methanol oxidation activity.

Experimental Section

Catalyst Preparation. PtRu (Johnson Matthey catalysts; 50% Pt, 50% Ru (weight percent)) catalysts were studied in four

* To whom correspondence should be addressed. Telephone: (403) 220-6432. Fax: (403) 284-1372. E-mail: birss@ucalgary.ca.

[†] Department of Chemistry.

[‡] Department of Chemical and Petroleum Engineering.

forms: as-received, reduced, oxidized, and strongly oxidized. Reduction was carried out by heating the sample to 100 °C in a tube furnace over 2–3 h under pure hydrogen at 100 mL/min and then remaining at 100 °C for 1 h. (If the slow heating was not carried out during reduction, then sintering, loss of surface area, and loss of methanol oxidation activity occur.) Catalyst oxidation was also achieved in the tube furnace by placing the PtRu powder under a stream of pure, humidified oxygen at 100 mL/min for 1 h at 100 °C. The oxygen was humidified by passing through a bubbler filled with deionized water and then over the sample. The strongly oxidized samples were heated for 2 h at 200 °C under flowing humidified oxygen.

The catalysts were deposited on glassy carbon (GC) electrodes to determine their methanol oxidation activity. For the Nafion dispersed catalyst, the catalyst was mixed with aqueous Nafion solution (1100 equivalent weight). The solution was sonicated for 15 min, and then the catalyst solution was applied by micropipet to the GC electrode surface, with a target loading of 2.6 mg/cm². Catalyst samples were also dispersed using acetic acid, followed by sonication of the solution and then application by micropipet to the GC surface. To purify the acetic acid, it was first refluxed for 3 h with 2 wt % potassium permanganate and then distilled. After the catalysts were applied to the GC electrodes, they were air-dried for 30 min at room temperature, or dried for 1 min using a heat gun. The drying procedure removed the excess water from the Nafion and all of the acetic acid.

Experiments were carried out using sticky carbon (SC) electrodes with a 1:1 wt ratio of beeswax to graphite powder to reproduce results previously reported in the literature.¹⁷ SC electrodes have been used for characterization of various electroactive materials,¹⁹ but unfortunately, it was found that our electrodes gave very irreproducible results for methanol oxidation activity for a given catalyst sample, possibly due to a variable resistance within the electrodes.

Electrochemical Assessment of Catalysts and Determination of Methanol Oxidation Activity. All experiments were carried out at room temperature (23 ± 2 °C) using rotating disk GC electrodes (7 mm diameter) at 500 rpm in nitrogen purged 0.5 M H₂SO₄ solution. After electrochemical characterization and stabilization (2 h), methanol was added to the cell solution to bring its total concentration to 0.25 M MeOH. The methanol oxidation activity was monitored over time and the activity after 2 h was compared. The counter electrode was a Pt gauze, and the reference electrode was a reversible hydrogen electrode (RHE). An EG&G PARC 175 function generator was used in conjunction with a Hokuto Denko HA-301 potentiostat. The electrochemical data were recorded concurrently on an X/Y chart recorder (Linseis LY 14100-11 X-Y) and by computer (Chart4 by PowerLab).

Catalyst Characterization. The catalysts were characterized using thermogravimetric analysis (TGA) to determine the extent of oxidation of the metals and transmission electron microscopy (TEM) to determine the particle size and morphology. The TGA (Netzsch STA 449C) analyses were performed at a heating rate of 4 °C/min from 20 to 800 °C and a flow rate of 30 mL/min, using argon or air as the carrier gas. The samples were prepared for TEM analysis using ultramicrotomy. The samples were embedded in epoxy (Araldite, Electron Microscopy Sciences) and then cut into thin sections with a diamond knife (Diatome U.S.). The thin sections were supported on Cu grids with a carbon film. The samples were analyzed via TEM (Phillips Tecnai F20 with a field emission gun) using an accelerating voltage of 200 kV.

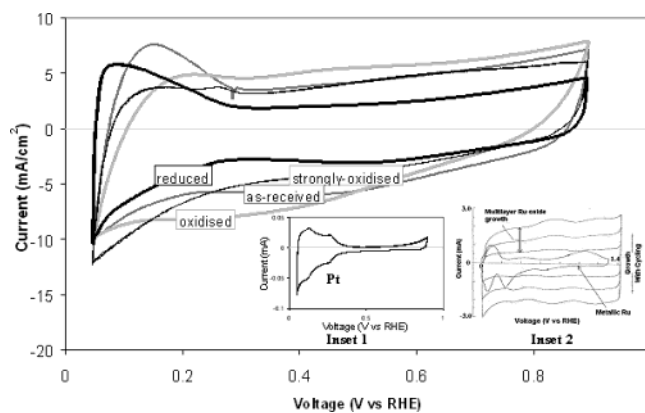


Figure 1. CVs (20 mV/s) of as-received, reduced, oxidized, and strongly oxidized Nafion dispersed PtRu catalysts deposited on glassy carbon electrodes in 0.5 M H₂SO₄. Insets: inset 1, CV of Pt metal in 1 M H₂SO₄ at 25 °C; inset 2, CV of Ru metal in 1 M H₂SO₄ at 25 °C. Irreversible oxidation to hydrous ruthenium oxide occurs with cycling.

Results and Discussion

Catalyst Characterization. Cyclic Voltammetry. Cyclic voltammograms (CVs) were collected for each electrocatalyst in nitrogen purged 0.5 M H₂SO₄ (Figure 1) to electrochemically characterize and stabilize the catalyst materials, before methanol oxidation was undertaken. It can be seen that, as the PtRu becomes more oxidized, the shape of the CVs changes notably. For comparison, inset 1 in Figure 1 demonstrates the CV response of pure Pt, while inset 2 shows the transition of the CV response from that of a bulk metallic Ru electrode to hydrous Ru oxide,²⁰ brought about by electrochemical cycling over an extended range of potential. In the case of Ru metal, hydrogen adsorption/desorption peaks (H up peaks) are seen centered at ca. 0.1 V; anodic current due to compact Ru oxide formation is also seen, commencing already at 0.3 V, with its reduction occurring in a peak at 0.25 V under these conditions. Hydrous Ru oxide (inset 2) displays large pseudocapacitive currents throughout the potential range, while Pt shows only the H up peaks up to 0.9 V (inset 1).

As can be seen by comparison of the CV responses for metallic Pt and Ru and for hydrous Ru oxide (Figure 1 insets) with those of the catalysts, the method employed to reduce or oxidize the samples appears to have resulted in the desired change in state. That is, the oxidized PtRu catalyst shows the more capacitive features of hydrous Ru oxide, while the reduced PtRu sample displays more of the distinct H up region, typical of the metallic Pt and Ru states. The strongly oxidized sample has CV features that are consistent with RuO₂·xH₂O, where *x* is less than 0.5.²¹

While the appearance of the CVs yields only a qualitative measure of the degree of oxidation or reduction of the catalysts, a more quantitative method of estimating the degree of oxidation or reduction of the catalyst was also employed by ratioing the current in the CVs at 0.2 V to that at 0.5 V. Figure 2 shows a plot of the ratio of current in the CVs at 20 mV/s at 0.2 V (at which the H up reaction would be expected to occur at the metallic, but not oxidized, surfaces) to that at 0.5 V (where the pseudocapacitive electrochemistry of hydrous Ru oxide electrochemistry should yield larger currents vs at Pt and Ru). It can be seen from Figure 2 that the more reduced the state of the PtRu catalysts, the higher this ratio is. This is as predicted, despite the fact that there may have been some differences expected between the CV responses of the bulk vs powdered specimens. As the strongly oxidized sample is not composed of hydrous ruthenium oxide, but mainly RuO₂, the ratio for that

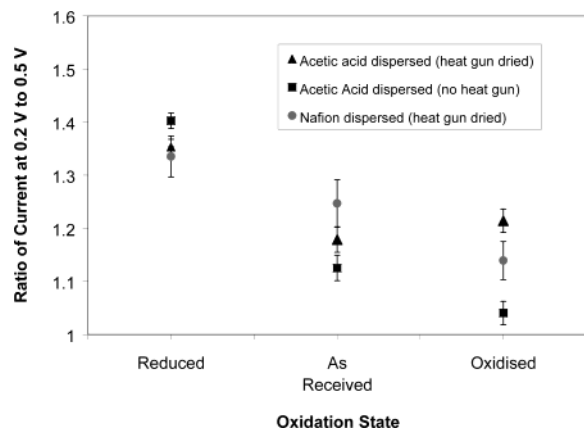


Figure 2. Ratio of currents at 0.2 and 0.5 V as a function of catalyst pretreatment (20 mV/s).

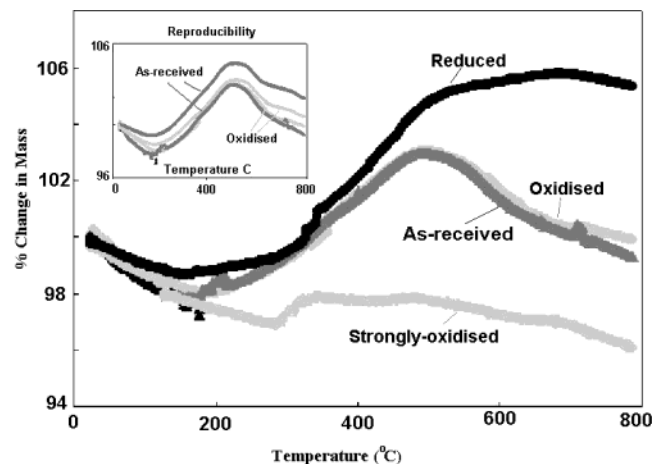


Figure 3. Thermogravimetric analysis of reduced, as-received, oxidized, and strongly oxidized PtRu samples heated at 4 °C/min in flowing air. Inset: TGA of as-received and oxidized samples in air showing reproducibility of results.

sample cannot be added to the graph to determine the degree of oxidation.

In Figure 2, the Nafion dispersed catalysts show a clear relationship between the degree of catalyst oxidation or reduction and the electrochemical response. The acetic acid dispersed catalysts, when dried using a heat gun, have a less defined relationship. While the reduced sample has the highest ratio, as expected, the as-received and oxidized samples have similar ratios. However, Figure 2 also shows that, when the acetic acid catalysts were dried at room temperature using no additional heating or drying steps, a clear correlation between the extent of catalyst oxidation and the ratio of currents can be observed. It can be therefore seen that the acetic acid dispersed catalyst (room temperature dried) shows the greatest degree of oxidation and reduction of the catalysts. It would be reasonable to expect the methanol oxidation activity of this catalyst to also show the greatest extremes, which as will be demonstrated later is indeed the case.

Thermogravimetric Analysis (TGA) of Catalysts. TGA was employed to provide a more quantitative measure of the extent of oxidation or reduction of the catalysts. Figure 3 shows the TGA results for the four catalyst samples under study here. All of the samples exhibit a small initial decrease in mass, likely due to a loss of water. The reduced, oxidized, and as-received samples all demonstrate an increase in mass at 200–500 °C, probably reflecting oxide formation, suggesting that even the oxidized sample may not have been fully oxidized by our

treatment. However, the reduced sample shows a larger mass gain than the other samples, supporting the CV results. The strongly oxidized sample shows almost no mass gain, indicating that the sample was already fully oxidized and could not undergo any further oxidation. The decrease in mass between 500 and 600 °C, seen in the oxidized and as-received samples, is not fully understood, but may be due to a PtO_xH_y species decomposing to Pt.¹⁷ However, it is not clear why this is not also seen for the reduced or strongly oxidized samples.

If all of the Pt in these catalysts were oxidized to PtO, this would give a 5.4% mass gain of the entire sample, while oxidizing both the Ru and Pt to RuO and PtO would result in a 9.7% mass gain. The total mass gain for the reduced sample was approximately 7%, consistent with these predictions.

The as-received, oxidized, and reduced samples appeared to be identical when TGA was run under an argon atmosphere. Also, the reproducibility of the TGA data was quite good, as demonstrated in the inset to Figure 3.

TEM Analysis. The TEM images shown in Figure 4 also demonstrate differences between the oxidized, reduced, as-received, and strongly oxidized catalysts. The reduced PtRu catalyst is crystalline and shows the lattice fringes of the alloy structure (Figure 4A). The particles have a diameter of 8–15 nm for the reduced PtRu, vs 3–7 nm for the as-received PtRu material, as can be discerned from a comparison of Figure 4A and Figure 4B. It is likely that the reduced catalyst is sintered during the reduction process. The as-received and oxidized materials are very similar in appearance to each other, consistent with the TGA data (Figure 3), especially when compared to the reduced catalyst. The strongly oxidized sample has the largest particle size, being in the 10–20 nm diameter range. Sintering still occurred for the strongly oxidized sample, likely due to the longer time and higher temperature of this treatment.

XRD Analysis. The XRD data (Figure 5) show that only the strongly oxidized sample contains significant amounts of Ru oxide, consistent with the features observed in the cyclic voltammogram. All other samples reveal only metallic Pt signals. However, these signals are slightly shifted, which is consistent with alloying to the Ru metal or with the presence of Ru oxide. The as-received, reduced, and oxidized samples may contain very small crystals of Ru oxide. Consistent with the TEM results, the strongly oxidized sample has the largest crystal size, as shown by the narrowest peak, and the as-received sample has the smallest crystal size.

Determination of Methanol Oxidation Activity. Development of Overall Experimental Protocol. Figure 6 shows the CV response of a reduced PtRu catalyst, before and after the addition of methanol to the solution. It can be seen that the redox activity above 0.5 V, which would normally be associated with compact Ru oxide formation and reduction (Figure 1), largely disappears in the presence of methanol, as the forward and reverse currents are almost identical. For some samples, the reverse scan during methanol oxidation yields slightly lower currents than during the forward scan, but never to the same extent as in the absence of methanol, also indicating suppression of oxide formation. Overall, the oxidation of PtRu appears to be suppressed by the presence of methanol or by the methanol oxidation reaction, as is clearly demonstrated in Figure 6. This result is consistent with EXAFS data showing that Ru oxide is unstable during MeOH oxidation and that the catalyst may exist predominantly as metallic PtRu under fuel cell operation after conditioning (running for over 3 days).²²

To determine whether methanol oxidation activity should be measured on the forward or reverse scan, the potential was held

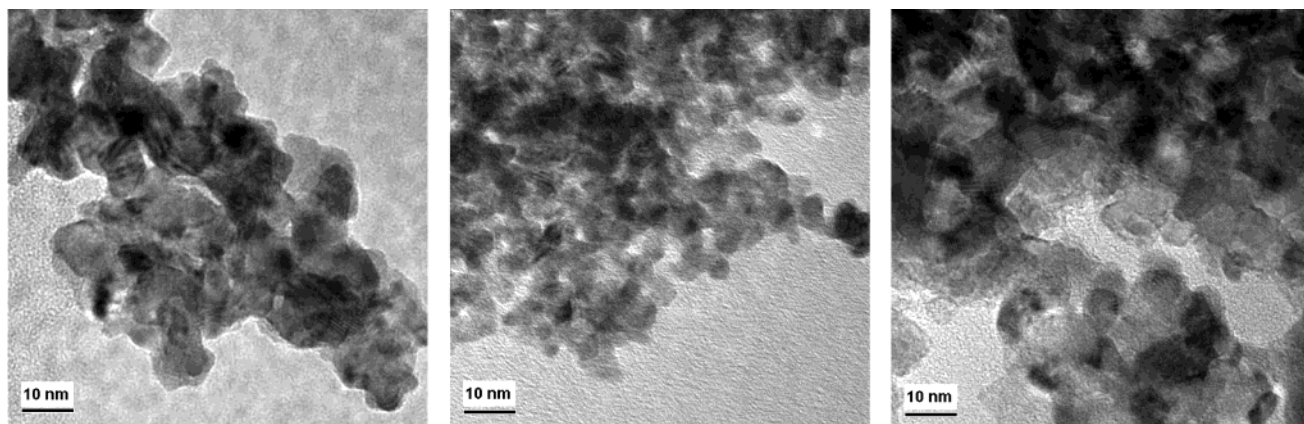


Figure 4. TEM images of reduced (A, left), as-received (B, middle), and strongly oxidized (C, right) PtRu samples at 340000 \times magnification.

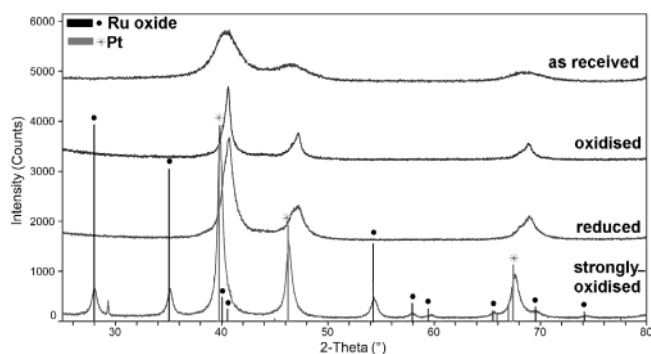


Figure 5. XRD data for PtRu catalysts. The vertical lines correspond to the JCPDS lines for Pt metal and Ru oxide.

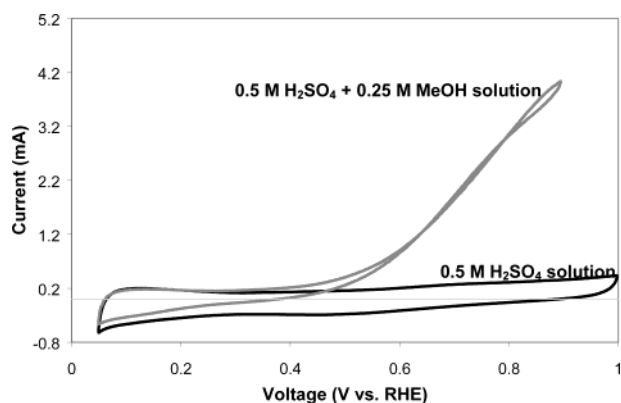


Figure 6. CVs of Nafion dispersed reduced PtRu catalyst (0.5 M H_2SO_4 , 500 rpm, 20 mV/s) before and after addition of methanol (0.25 M).

at various values between 0.4 and 0.9 V, in both the anodic and cathodic sweeps. Figure 7 shows that, in the absence of methanol, the current drops rapidly to zero with time, as oxide growth essentially ceases after ca. 10 s. In the presence of methanol (Figure 8), it is important to note that, when the potential is held, the current rapidly drops to the value measured during the cathodic scan. Therefore, the current measured in the cathodic scan can be assumed to be entirely due to methanol oxidation and was therefore used to compare the methanol oxidation activity of the various catalysts in this work.

Another factor that had to be controlled in this work was the loading of the catalyst on the GC surface, so that the methanol oxidation currents could be compared validly. Despite the application of the same volume of dispersed catalyst suspension of equal concentrations to each GC electrode by micropipet, there were some still differences in the amount of catalyst

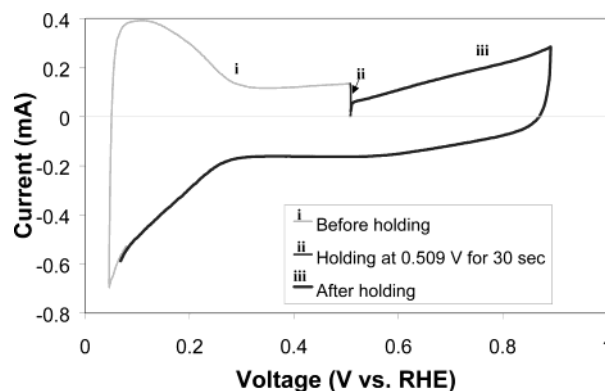


Figure 7. Effect of holding at constant potential on CV of Nafion dispersed reduced PtRu (0.5 M H_2SO_4 , 20 mV/s).

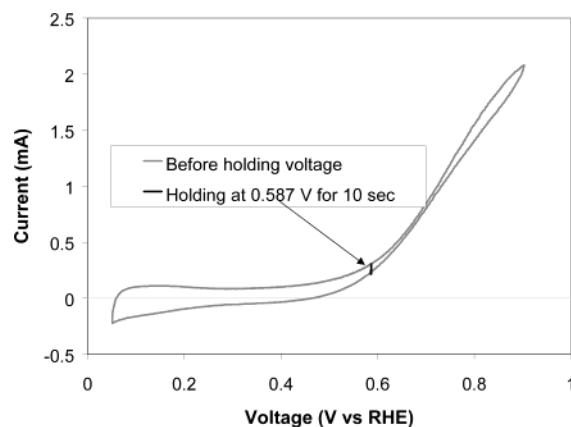


Figure 8. Effect of holding at constant potential on CV of Nafion dispersed reduced PtRu (0.5 M H_2SO_4 , 0.25 M methanol, 500 rpm, 20 mV/s).

applied to the electrode. This discrepancy was due to occasional inhomogeneities of the suspensions and the risk of settling of the dispersed catalyst, thus diluting the solution phase. To account for these inhomogeneities, the total current passed at 0.2 V in a CV sweep at 20 mV/s was assumed to be proportional to the real surface area of catalyst. To compare the methanol oxidation activities of the samples, all of the data were therefore corrected for their loading by dividing the methanol oxidation current by the current passed at 0.2 V. When the data were corrected using the currents passed at 0.1 V, the trends reported here remained the same, thus validating this approach.

An interesting observation was also made in the experiments shown in Figure 9. With prolonged holding of the potential in the methanol oxidation range, the currents slowly but continu-

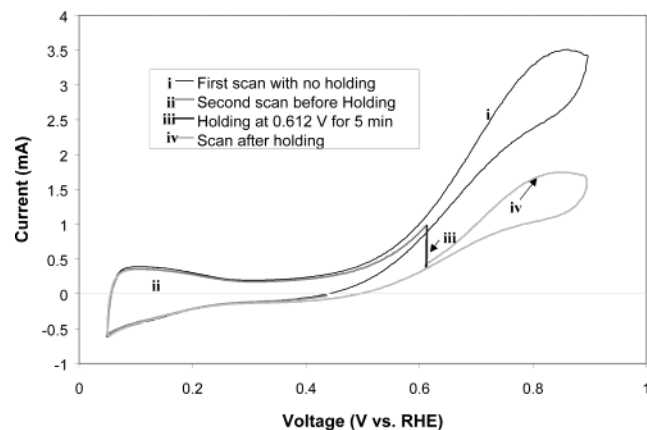


Figure 9. Deactivation of acetic acid dispersed reduced PtRu catalyst by holding at constant potential (0.5 M H_2SO_4 , 0.25 M methanol, 500 rpm, 20 mV/s).

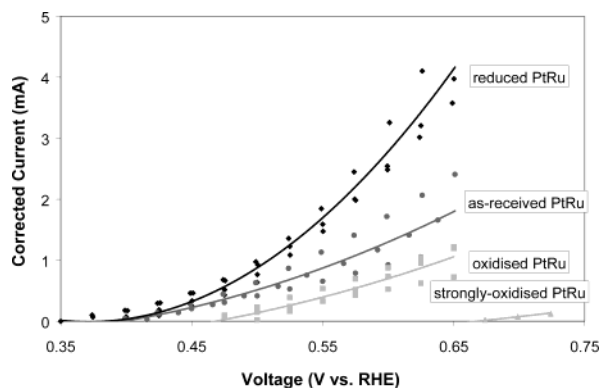


Figure 10. Methanol oxidation activity of Nafion supported catalysts (0.5 M H_2SO_4 , 0.25 M MeOH, 500 rpm, 20 mV/s).

ously drop with time. This apparent deactivation appears to be reversible, as the original activity could be regained by cycling back to lower potentials. It is not known what causes this deactivation, as the potential is too high for this to be due to CO poisoning. It could be caused by a buildup of other products, such as CO_2 (the buildup of CO_2 gas may block the pores of the catalyst) or H^+ , causing a localized decrease in pH, which would shift the equilibrium potential of the methanol oxidation reaction positively. This form of catalyst deactivation was not a factor in this work, as the methanol activity was obtained strictly from the cathodic scan CV data.

Methanol Oxidation Activity at Nafion Dispersed PtRu Catalysts. Up to three of each of the as-received, reduced, and oxidized samples were investigated in order to determine their methanol oxidation activity, as is shown in Figure 10. The strongly oxidized sample was run once to confirm that the activity was much lower than any other sample. It is clear that the reduced catalyst is the most active, followed by the as-received and then the oxidized sample, which is the same sequence as reported by Gottesfeld et al.²³ with regard to the reduced and as-received catalysts, although they did not investigate an oxidized sample in their work. In our experiments, the methanol oxidation activity was clearly related to the degree of oxidation or reduction of the sample. This relationship is confirmed further by the very low activity observed at the strongly oxidized specimen, which showed no methanol oxidation currents until potentials greater than 0.65 V (Figure 10).

As the degree of oxidation and reduction of the samples has been confirmed using several analytical techniques (Figures 2–5), it is possible now to correlate the methanol oxidation

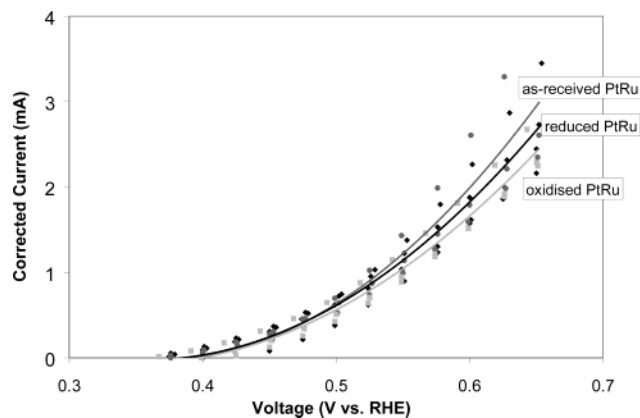


Figure 11. Methanol oxidation activity of acetic acid dispersed PtRu catalysts, dried for 1 min using a heat gun (0.5 M H_2SO_4 , 0.25 M MeOH, 500 rpm, 20 mV/s).

activity directly with the redox state of the catalyst. It is interesting to note that, even though the as-received and oxidized samples were indistinguishable by TEM and TGA, they still exhibit markedly different methanol oxidation activities. Their activities were consistent with the differences between the oxidized and the as-received samples that were measured from the ratios of the current at 0.2 and 0.5 V (Figure 2). It appears that the electrochemical measurements are the most appropriate for determining the degree of oxidation of these PtRu catalysts.

Methanol Oxidation at Acetic Acid Dispersed PtRu Catalysts. There were two issues that had to be addressed when acetic acid was used as a dispersing agent, namely purity and drying temperature, as both of these were found to affect the methanol oxidation activity of the catalysts. Acetic acid was used to disperse the PtRu catalysts, partly to establish the effect of the presence of Nafion on methanol oxidation activity. Although the nondistilled acetic acid data are not shown here, the use of distilled acetic acid gave an enhancement in methanol oxidation activity and overall higher activities, suggesting the presence of impurities in acetic acid which poison and block active sites.

Even after distillation, Figure 11 shows that there is still no clear trend in the methanol oxidation activity for the various acetic acid dispersed catalysts. Therefore, we looked more closely at the method of preparation of these acetic acid dispersed catalysts to determine if there were other factors that might be affecting their state. Notably, the samples had been dried for 1 min with a heat gun and, upon investigation, it was found that the electrode surface could reach temperatures of up to 400 °C, potentially altering the catalyst. Therefore, a set of acetic acid dispersed catalysts were dried in air at room temperature. Figure 12 demonstrates that, when dried at low temperatures, the same relative activities that were observed for the Nafion dispersed catalyst, i.e., reduced is more active than as-received is more active than oxidized, is seen. This confirms that too high of a drying temperature overcomes the original differences in catalyst oxidation state. However, the Nafion supported catalysts were also dried by heat gun, but the change in activity could still be determined as the Nafion film would surround the catalyst particles and protect them from the direct effect of the hot air.

Comparison of Distilled Acetic Acid and Nafion Supported PtRu Catalysts. A full comparison of the activity of the three catalysts supported in these two ways is shown in Figure 13, indicating that the acetic acid dispersed reduced PtRu is the best catalyst, overall. The Nafion dispersed as-received and oxidized catalysts perform better than the acetic acid dispersed only at lower current densities. Changing the Nafion content

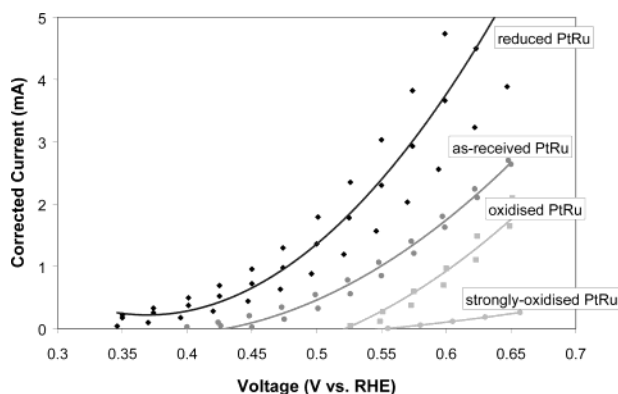


Figure 12. Methanol oxidation activity of acetic acid dispersed PtRu catalysts, dried at room temperature (0.5 M H₂SO₄, 0.25 M MeOH, 500 rpm, 20 mV/s).

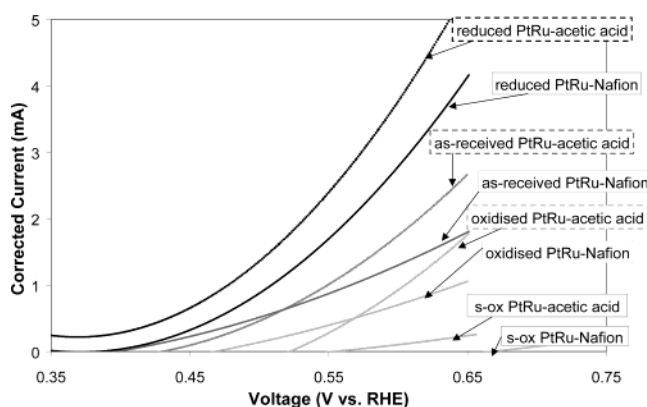


Figure 13. Comparison of methanol oxidation activity of acetic acid and Nafion dispersed catalysts (0.5 M H₂SO₄, 0.25 M MeOH, 500 rpm, 20 mV/s).

of catalysts in PEM fuel cells is known to affect the methanol oxidation activity (giving a greater activity with lower Nafion content).¹⁶ However, in a fuel cell, it is not possible to remove the Nafion, as it is required for both proton conductivity and stabilization of the catalyst.

In the present work in 0.5 M H₂SO₄, it is interesting to note that Nafion does exhibit an inhibiting role on the catalytic activity of our most active catalyst by comparison with the acetic acid dispersed catalysts. It may be possible that the Nafion limits the transport of reactants through the electrode or blocks or isolates some of the active sites.¹⁶ The blocking effect is likely the reason that both the oxidized and as-received catalyst perform better in the absence of Nafion than in its presence at higher potentials (where mass transport is more likely to be rate limiting than kinetics), as can be seen in Figure 12. This result may support the hypothesis that hydrous Ru oxide can act successfully as an ionic conductor.

When using Pt as a methanol oxidation catalyst, Ru or another promoting material must be present, as otherwise CO poisoning of the Pt will greatly lower all methanol oxidation activity. Ru by itself is even more inactive toward methanol oxidation and aids methanol oxidation only by promoting the removal of the adsorbed CO intermediate from Pt. To catalyze the methanol oxidation reaction in an MEA, both an active catalytic site (reduced PtRu) and an ionically conducting pathway (Nafion or hydrous Ru oxide) are required.

The as-received catalyst is initially not in its most active fully reduced form, but instead appears to be slightly oxidized. This oxidation may have occurred with time, simply by contact of the small metallic particles with air. The electrochemistry

confirmed that the oxidation and reduction of the catalysts was successful, while the TGA indicated that the reduction was successful.

It should be noted that heat treatment in H₂ or O₂ does not merely influence the oxidation state of the catalysts, but can also affect the Pt or Ru surface distribution of the metal, with heating in H₂ resulting in a Pt-rich surface environment and heating in O₂ resulting in a Ru-rich surface distribution.²⁴ However, with the TGA results providing the bulk material analysis and the electrochemistry yielding the surface analysis, our work is an investigation of the effect of catalyst oxidation and reduction, rather than of metallic ratios. It must be noted that, from preliminary EDX results, varying ratios of Pt:Ru were observed for the reduced catalyst, which was the most active.

Conclusions

Four states of PtRu catalyst were examined for their methanol oxidation activity in this work: as-received, reduced, oxidized, and strongly oxidized. The relative oxidation states were confirmed by electrochemistry, TGA, TEM, and XRD analysis. Reduction of as-received PtRu catalysts at a slow heating rate minimized the loss of surface area. As-received and oxidized catalysts are similar in their physical properties. By oxidizing the sample more thoroughly, it was possible to greatly reduce the catalytic activity of both Nafion and acetic acid supported catalysts. Overall, the relative activities were reduced > as-received > oxidized >> strongly oxidized.

Each of the catalysts was dispersed using acetic acid and Nafion to determine the effect of the proton conducting polymer on the PtRu catalyst. In sulfuric acid solutions, acetic acid dispersed catalysts are more active than Nafion dispersed samples, especially at higher current densities, as when larger currents are flowing, mass transport through the catalyst will have a greater influence on the reaction rate. However, activity loss with time was most pronounced with acetic acid dispersed samples (ca. 25% over 2 h), as compared to the Nafion supported samples (ca. 10% loss over 2 h), so while the lack of ionomer may enhance activity, a nonsupported MEA is not suitable for practical fuel cell applications. Distillation of the acetic acid gives an enhanced catalytic activity of acetic acid supported catalysts due to removal of impurities. Finally, heat gun drying of the PtRu catalysts altered their original oxidation state and should be avoided.

Of all the catalysts tested, acetic acid supported reduced PtRu gives the best methanol oxidation activity, due to an optimum combination of catalytic activity and active site accessibility.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council of Canada for the overall support of this work and also for the postgraduate scholarship support of A.H.C.S. We also thank Adrien Cote, Leslie May, and Guohui Li for their assistance with the TGA experiments and Rick Humphrey at the Microscopy and Imaging Facility at the University of Calgary for TEM assistance.

References and Notes

- (1) Ramya, K.; Dhathathreyan, K. S. *J. Electroanal. Chem.* **2003**, 542, 109.
- (2) Wasmus, S.; Küver, A. *J. Electroanal. Chem.* **1999**, 461, 14.
- (3) Grgur, B.; Markovic, N.; Ross, P. N. *Electrochim. Acta* **1998**, 43 (24), 3631.
- (4) Gotz, M.; Wendt, H. *Electrochim. Acta* **1998**, 43 (24), 3637.
- (5) Bett, J.; Kunz, H.; Aldykiewicz, A., Jr.; Fenton, J.; Bailey, W.; McGrath, D. *Electrochim. Acta* **1998**, 43 (24), 3645.

- (6) Mukerjee, S.; McBreen, J. *J. Electroanal. Chem.* **1998**, *448*, 163.
- (7) Rice, C.; Tong, Y.; Oldfield, E.; Wieckowski, A.; Hahn, F.; Gloaguen, F.; Léger, J.; Lamy, C. *J. Phys. Chem. B* **2000**, *104*, 5803.
- (8) Iwasita, T.; Hoster, H.; John-Anacker, A.; Lin, W.; Vielstich, W. *Langmuir* **2000**, *16*, 522.
- (9) Tremiliosi-Filho, G.; Kim, H.; Chrzanowski, A.; Wieckowski, A.; Grzybowska, B.; Kulesza, P. *J. Electroanal. Chem.* **1999**, *467*, 143.
- (10) Denis, M.; Gouérec, P.; Guay, D.; Dodelet, J.; Lalande, G.; Schulz, R. *J. Appl. Electrochem.* **2000**, *30*, 1243.
- (11) Davies, J.; Hayden, B.; Pegg, D.; Rendall, M. *Surf. Sci.* **2002**, *496*, 110.
- (12) Lui, P.; Nørskov, J. *Fuel Cells* **2001**, *1* (3–4), 192.
- (13) Lu, C.; Rice, C.; Masel, R.; Babu, P.; Waszczuk, P.; Kim, H.; Oldfield, E.; Wieckowski, A. *J. Phys. Chem. B* **2002**, *106*, 9581.
- (14) Gasteiger, H. A.; Markovic, N.; Ross, P. N., Jr.; Cairns, E. J. *J. Electrochem. Soc.* **1994**, *141* (7), 1795.
- (15) Lamy, C.; Léger, J.; Hahn, F.; Beden, B. *Electrochem. Soc. (Electrode Processes)* **1996**, 96–8, 356.
- (16) Thomas, S.; Ren, X.; Gottesfeld, S. *J. Electrochem. Soc.* **1999**, *146* (12), 4354.
- (17) Long, J.; Stroud, R.; Swider-Lyons, K.; Rolison, D. *J. Phys. Chem. B* **2000**, *104*, 9772.
- (18) Rolison, D.; Hagans, P.; Swider, K.; Lo, J. *Langmuir* **1999**, *15*, 774.
- (19) Long, J.; Ayers, K.; Rolison, D. *J. Electroanal. Chem.* **2002**, *522*, 58.
- (20) Birss, V. I.; Myers, R.; Angerstein-Kozłowska, H.; Conway, B. E. *J. Electrochem. Soc.* **1984**, *131* (7), 1502.
- (21) Long, J. W.; Swider, K. E.; Merzbacher, C. I.; Rolison, D. R. *Langmuir* **1999**, *15* (3), 780.
- (22) Viswanathan, R.; Hou, G.; Liu, R.; Bare, S.; Modica, F.; Mickelson, G.; Segre, C.; Leyarowska, N.; Smotkin, E. *J. Phys. Chem. B* **2002**, *106*, 3458.
- (23) Dinh, H.; Ren, X.; Garzon, F.; Zelany, P.; Gottesfeld, S. *J. Electroanal. Chem.* **2000**, *491*, 222.
- (24) McNicol, B.; Short, R. *J. Electroanal. Chem.* **1977**, *81*, 249.