

Mo oxide modified catalysts for direct methanol, formaldehyde and formic acid fuel cells

CHAOJIE SONG, MOHAMMAD KHANFAR and PETER G. PICKUP*

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7 Canada
(*author for correspondence, tel.: +1-709-737-8657, fax: +1-709-737-3702, e-mail: ppickup@mum.ca)

Received 11 May 2005; accepted in revised form 13 September 2005

Key words: electrocatalysis, formaldehyde, formic acid, fuel cell, methanol, molybdenum oxide, platinum

Abstract

Pt black and PtRu black fuel cell anodes have been modified with Mo oxide and evaluated in direct methanol, formaldehyde and formic acid fuel cells. Mo oxide deposition by reductive electrodeposition from sodium molybdate or by spraying of the fuel cell anode with aqueous sodium molybdate resulted in similar performance gains in formaldehyde cells. At current densities below ca. 20 mA cm⁻², cell voltages were 350–450 mV higher when the Pt catalyst was modified with Mo oxide, but these performance gains decreased sharply at higher current densities. For PtRu, voltage gains of up to 125 mV were observed. Modification of Pt and PtRu back catalysts with Mo oxide also significantly improved their activities in direct formic acid cells, but performances in direct methanol fuel cells were decreased.

1. Introduction

Although fuel cells have great potential as clean and efficient sources of electricity, their adoption is still severely hampered by supply and storage issues for hydrogen, which is by far the preferred fuel. This has created interest in the use of other fuels, and methanol has emerged as the second best choice. Besides being easily produced from widely available fuels (particularly natural gas), methanol can be conveniently transported, handled, and stored, and therefore, it can be supplied from distribution points for daily consumption. However, there are some serious obstacles hindering the application of direct methanol fuel cells (DMFC) [1]. The oxidation of methanol is still kinetically slow, even on state-of-the-art catalysts, and methanol crossover through the fuel cell membrane significantly decreases the efficiency of the cell due to loss of fuel and poisoning of the cathode catalyst.

Other fuels that have been considered include trimethoxymethane [2], dimethyl ether [3], aliphatic alcohols [4], acetals [5], isopropanol [6], and formic acid [7], but none provide compelling characteristics for commercialization. Formaldehyde does not seem to have been seriously considered, presumably because of its risks to human health. However, its performance is important from a scientific point of view and there may be commercial opportunities in specialized applications and in formaldehyde sensors. There has been significant

interest in the electrochemical oxidation of formaldehyde for many years [8–11].

Of particular interest are comparisons within the methanol, formaldehyde, formic acid series. All of these compounds can produce adsorbed CO as an intermediate (see below), and it is poisoning of the anode catalyst by this species that leads to the ubiquitously poor anode activity of organic fuel cells. This is one of the main factors inhibiting commercialization of the DMFC. However, it does not appear to be such a serious problem with formic acid, for which a pathway that does not produce adsorbed CO is more significant [12]. Such a pathway may also be important for formaldehyde. Furthermore, since formaldehyde and formic acid are possible intermediates in the electrochemical oxidation of methanol, studies of formaldehyde and formic acid fuel cells will be important in arriving at a full understanding of the mechanisms of oxidation of methanol and help to guide catalyst development for the DMFC.

The work reported here was motivated by Shropshire's observation [8] that addition of Na₂MoO₄ to methanol and formaldehyde solutions in H₂SO₄(aq) could promote their electrochemical oxidation at Pt black electrodes. This effect was much more pronounced for formaldehyde than for methanol. Li et al. [13] have recently reported similar results for methanol oxidation in the presence of Na₂MoO₄, and Wang [14] has shown that Mo(VI) is catalytically active for the oxidation of

weakly adsorbed CO, formaldehyde and methanol. Codeposited mixtures of Pt and Mo oxide have also shown enhanced activity for methanol oxidation [15]. Mo–Pt alloys have also been investigated [16, 17], but although these exhibit good tolerance to CO [17, 18] they have not been very effective for methanol oxidation. It has been suggested that metallic Mo is only effective for the removal of weakly bound CO and not the proposed strongly bound form(s) produced during methanol oxidation [17]. Theoretical work has also indicated that Mo could be an effective co-catalyst for the oxidation of CO containing (or producing) fuels [19]. Lamy and coworkers [20] have reported that a PtRuMo ternary catalysts showed higher catalytic activity toward methanol oxidation than a PtRu binary catalyst prepared in the same way.

The goal of the work described in this paper was initially to develop high surface area Mo oxide modified gas diffusion electrodes for direct methanol fuel cells. However, modification of Pt and PtRu black electrodes with Mo oxide was found to decrease their activity for methanol oxidation. Attention was therefore focused on formaldehyde and formic acid cells, in which the modified electrodes did show enhanced performance. This validates the catalyst modification procedures, and provides insight into differences between methanol, formaldehyde, and formic acid oxidation.

2. Experimental

2.1. Modification of gas diffusion electrodes

2.1.1. Electrodeposition method

A gas diffusion electrode consisting of 4.0 mg cm^{-2} Pt black on PTFE treated Toray 9 mil carbon fiber paper (donated by Ballard Power Systems) was sprayed with deionized water to wet the catalyst layer, and then placed in a cell containing $1 \text{ mM Na}_2\text{MoO}_4$ in $3.7 \text{ M H}_2\text{SO}_4(\text{aq})$. A potential of -0.15 V vs. Ag/AgCl was applied for a certain time, and then the electrode was removed from the cell, rinsed with water and dried in air.

2.1.2. Solvent evaporation method

One ml of $1\% \text{ Na}_2\text{MoO}_4(\text{aq})$ was sprayed onto the electrode and allowed to dry in air. Electrodes with 4.0 mg cm^{-2} Pt black (from Ballard) or 4.4 mg cm^{-2} PtRu black (donated by H Power Corp.) on carbon paper were used.

2.2. Fuel cell measurements

Nafion115 membranes (DuPont) were cleaned in $10\% \text{ H}_2\text{O}_2(\text{aq})$, $1 \text{ M H}_2\text{SO}_4(\text{aq})$ (1 h at $60\text{--}80 \text{ }^\circ\text{C}$ in each solution) and water. Cathodes consisting of 4.0 mg cm^{-2} Pt and $14\% \text{ PTFE}$ on Toray carbon fiber paper, were donated by Ballard Power Systems.

Anodes were evaluated at $60 \pm 1 \text{ }^\circ\text{C}$ in commercial (Fuel Cell Technologies or Electrochem.) 5 cm^2 active area cells fed with 1 M aqueous formaldehyde, methanol or formic acid at 0.15 ml min^{-1} and dry air at a fixed flow rate of 75 ml min^{-1} , corresponding to a stoichiometry ($\text{mol O}_2/4 \text{ mol electrons}$) of 3.8 at 200 mA cm^{-2} . The electrodes and membranes were put into the cell without prior pressing [21]. The pressure of ca. 15 kg cm^{-2} exerted during cell assembly was found to be sufficient to provide good contact between the electrodes and the membrane.

Polarization data were recorded using a Princeton Applied Research PARC model 273 electrochemical analysis system. The voltage at each current density was allowed to stabilize for 30–60 s before measurement. Anode polarization curves were obtained by passing H_2 through the cathode compartment of the fuel cell. Under these conditions the cathode evolves H_2 and behaves as a dynamic hydrogen electrode (DHE). Its potential remains approximately constant at a value close to that of a reversible hydrogen electrode.

Fuel (methanol, formaldehyde, or formic acid) crossover was measured by using a steady state electrochemical method similar to that described by Ren et al. [22]. The cathode compartment of the fuel cell was flushed with nitrogen to remove O_2 , and the fuel cell cathode (now the anode in the experiment) was set at a potential of 0.7 V relative to the fuel cell anode (containing aqueous fuel; and now acting as a DHE) for 50 s to oxidize fuel that had accumulated within the cathode. The potential was stepped to 0.9 V for 100 s, and then to 0.8 V for 100 s. The steady state currents at these potentials were always very close, confirming that they represent the limiting current. Their average was taken as the fuel crossover current, which is proportional to the flux of fuel across the membrane. A correction for electro-osmotic drag was not applied.

3. Results

3.1. Modified Pt and PtRu black gas diffusion electrodes in DMFCs

Figure 1 shows polarization curves of direct methanol fuel cells with Pt black and Mo oxide modified Pt black anodes. Mo oxide was deposited on the pre-made Pt black gas diffusion electrodes either by spraying them with a $\text{Na}_2\text{MoO}_4(\text{aq})$ solution or by electrodeposition of a molybdenum bronze (H_xMoO_3) from $\text{Na}_2\text{MoO}_4(\text{aq})$. One of the sprayed electrodes was reduced before use by passing H_2 through the anode compartment of the fuel cell.

It is clear from the results in Figure 1 that none of the Mo modified electrodes performed any better in the fuel cell than unmodified Pt black, and that Mo can actually poison the Pt catalyst if it is not reduced before use. When PtRu black anodes were modified by spraying or

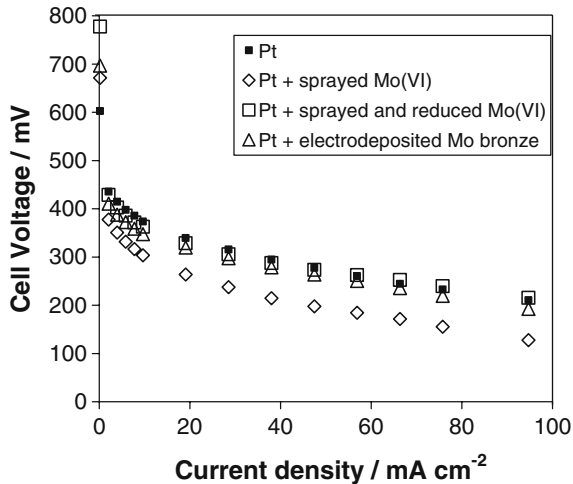


Fig. 1. Polarization curves for direct methanol fuel cells with Pt black (solid points) and Mo oxide modified Pt black (open points) anode catalysts. The anode Pt loading was 4.0 mg cm^{-2} in all cases.

electrodeposition, they showed inferior DMFC performances to unmodified PtRu black (not shown).

3.2. Modified Pt and PtRu black gas diffusion electrodes in direct formaldehyde fuel cells

Figure 2 shows polarization curves for direct formaldehyde fuel cells with Pt black catalyzed gas diffusion electrodes modified by the electrodeposition of H_xMoO_3 , and by spraying with Na_2MoO_4 solution. The presence of the Mo species greatly increased the performance of the fuel cell at low current densities ($< 20 \text{ mA cm}^{-2}$). At 19 mA cm^{-2} , the potential was 400 mV higher for the best modified electrode than for Pt black alone. The Mo bronze deposition time did not influence the performance of the modified anodes strongly (not shown), although a 30 min deposition did produce a slightly larger enhancement in performance than both shorter (10 s or 10 min) and longer

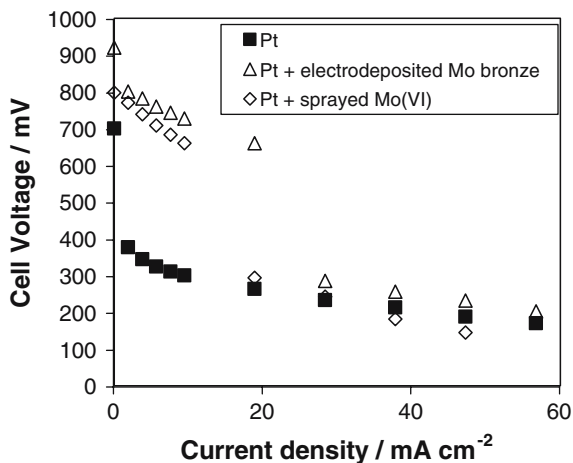


Fig. 2. Polarization curves for direct formaldehyde fuel cells with Pt black (solid points) and Mo oxide modified Pt black (open points) anode catalysts. The anode Pt loading was 4.0 mg cm^{-2} in all cases.

(2 h) deposition times. The modification method did not greatly affect the performance of the modified anodes either. The performance of the anode modified by spraying with a Na_2MoO_4 solution was similar to anodes modified by electrodeposition for shorter (10 s) and longer times (2 h), while somewhat inferior to those modified by electrodeposition at 10 min and 30 min.

Figure 3 shows anode polarization curves obtained by using the fuel cell cathode as a DHE. These clearly show that Mo oxide greatly decreases the overpotential for formaldehyde oxidation at low current densities.

The effects of Mo oxide modification were long lived. Figure 4 shows polarization curves recorded over a period of 2 days for a cell with a Mo oxide modified anode. The performance on the second day was not significantly different from that on the first day.

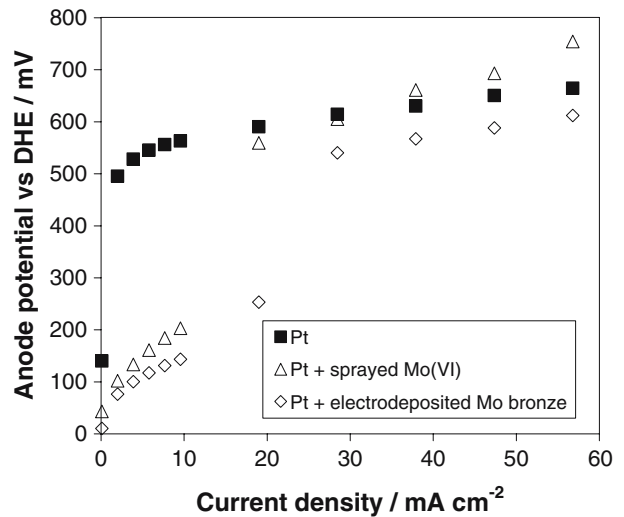


Fig. 3. Anode polarization curves for the direct formaldehyde fuel cells of Fig. 2.

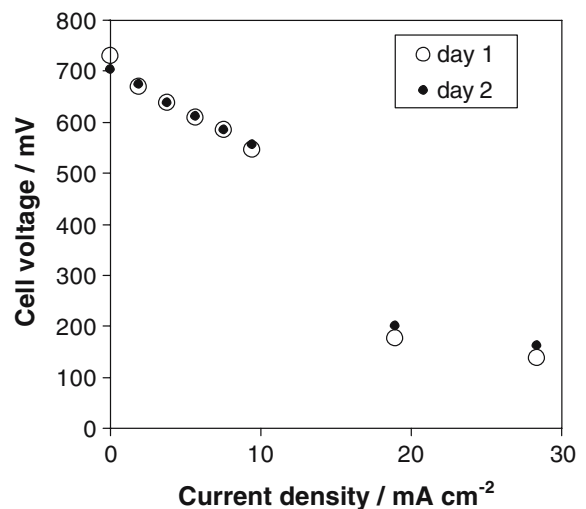


Fig. 4. Polarization curves on consecutive days for a direct formaldehyde fuel cell with a Pt black anode that had been sprayed with $\text{Na}_2\text{MoO}_4(\text{aq})$.

Figure 5 shows polarization curves and anode polarization curves for a direct formaldehyde fuel cell with a PtRu black anode, and with a similar electrode that had been modified simply by spraying it with a $\text{Na}_2\text{MoO}_4(\text{aq})$ solution. Modification with Na_2MoO_4 improves the performance of the PtRu catalyst at low current densities, while at higher current densities, catalytic activity promotion by Mo oxide disappears. The anode polarization curves show that modification of PtRu with Mo oxide decreases formaldehyde oxidation overpotentials significantly. For example, the anode potential was 60 mV lower at a current density of 7.5 mA cm^{-2} .

Comparison of the curves for the unmodified electrodes (Pt and PtRu) in Figures 2 and 5 clearly shows the superiority of the PtRu alloy, which shows $> 200 \text{ mV}$ higher cell potentials at all current densities. The effect of modification with Mo oxide is much more pronounced for Pt than for PtRu. Nonetheless, the best overall direct formaldehyde fuel cell performance was obtained with the Mo oxide modified PtRu catalyst.

3.3. Modified Pt and PtRu black gas diffusion electrodes in direct formic acid fuel cells

Figure 6 compares polarization curves for direct formic acid fuel cells with Pt black and PtRu black anodes, and with similar electrodes that had been modified by electrodeposition of H_xMoO_3 from Na_2MoO_4 solution for 30 min (Pt), or by simply spraying with Na_2MoO_4 solution (PtRu). Comparison of the curves shows that unmodified Pt and PtRu gave similar performances, while modification with Mo oxide improved the performance of both catalysts. The improvement is not as significant as observed for direct formaldehyde fuel cells.

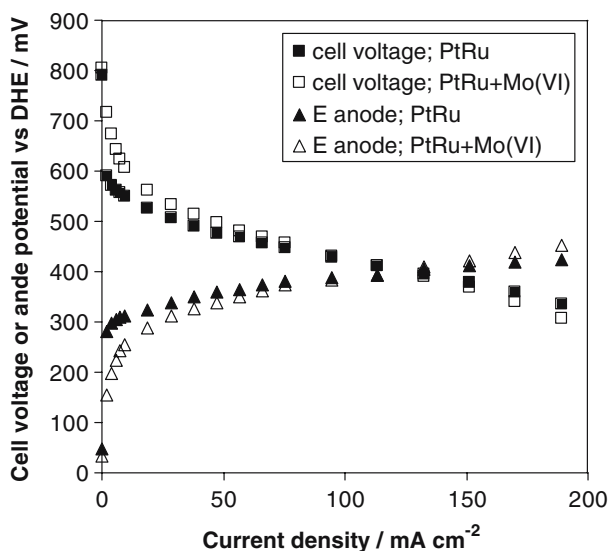


Fig. 5. Polarization curves (squares) and anode polarization curves (triangles) for direct formaldehyde fuel cells with a PtRu black anode catalyst (solid points) and a similar anode that had been sprayed with $\text{Na}_2\text{MoO}_4(\text{aq})$. The Pt + Ru loadings were 4.4 mg cm^{-2} .

The best direct formic acid fuel cell performance was obtained with the modified PtRu catalyst.

Anode polarization curves for the direct formic acid fuel cells with Pt, PtRu and Mo oxide modified Pt and PtRu catalysts are shown in Figure 7. As was observed for formaldehyde, modification with Mo oxide decreased the formic acid oxidation potentials for both catalysts. The effects were more pronounced at very low current densities, but quite large ($> 50 \text{ mV}$) for Pt at current densities as high as 30 mA cm^{-2} . PtRu and Mo oxide modified PtRu exhibited significantly smaller overpotentials for formic acid oxidation than did Pt and Mo oxide modified Pt. These results are qualitatively similar to those for the cell voltage (Figure 6), but there are significant quantitative differences, particularly when the unmodified catalysts are compared. For

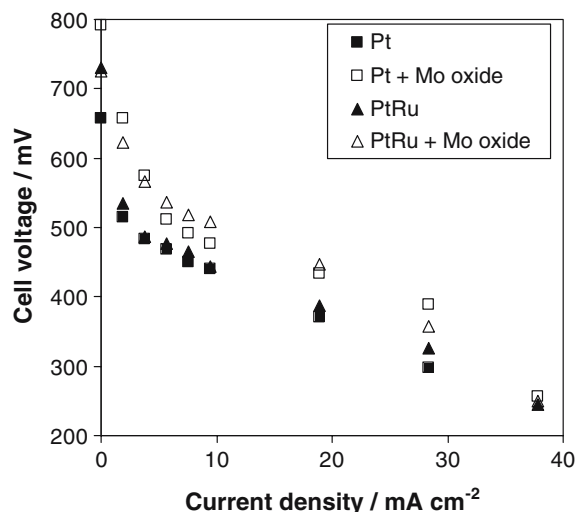


Fig. 6. Polarization curves for direct formic acid fuel cells with Pt black (solid squares), PtRu black (solid triangles), Mo oxide modified Pt black (open squares), and Mo oxide modified PtRu black (open triangles) anode catalysts. The anode Pt and Pt + Ru loadings were 4.0 and 4.4 mg cm^{-2} , respectively.

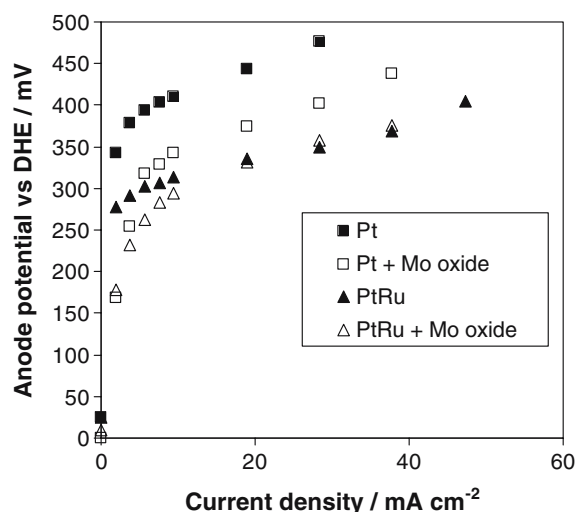


Fig. 7. Anode polarization curves for the direct formaldehyde fuel cells of Fig. 6.

example, Pt and PtRu gave similar fuel cell performances, while PtRu gave significantly lower anode overpotentials than Pt. Clearly, the cell potentials are influenced by variations in the cathode performance and that can lead to misleading conclusions regarding changes in anode performance. This illustrates the importance of recording anode polarization curves as well as cell polarization curves.

3.4. Formaldehyde and formic acid crossover

Methanol crossover through the Nafion membrane is one of the main problems in DMFCs. The use of other fuels may reduce fuel crossover. Rhee et al. [23] have reported that formic acid crossover is two orders of magnitude lower than methanol crossover, although the comparison data cited for methanol crossover appears to be too high (see below).

The crossover of formaldehyde and formic acid in our direct formaldehyde and formic acid cells were measured as the limiting currents required to oxidize formaldehyde or formic acid reaching the cathode compartment of the fuel cell. The anode compartment contained 1 M formaldehyde or 1 M formic acid, while N₂ was passed through the cathode compartment. At 60 °C, the average formaldehyde flux for five MEAs with different anode catalysts was $(1.06 \pm 0.15) \times 10^{-7}$ mol cm⁻² s⁻¹ (crossover current = 41 mA cm⁻²), the average formic acid flux for seven MEAs with different anode catalysts was $(1.24 \pm 0.24) \times 10^{-7}$ mol cm⁻² s⁻¹ (crossover current = 24 mA cm⁻²), while methanol crossover in the same cell under the same conditions was $(1.69 \pm 0.10) \times 10^{-7}$ mol cm⁻² s⁻¹ (97 mA cm⁻²) [21]. Clearly, there are not significant differences in the crossover rates of the three fuels, although the currents needed to oxidize the fuel crossing to the cathode do vary significantly because of the different numbers of electrons involved ($n=2, 4,$ and 6 for formic acid, formaldehyde and methanol, respectively).

4. Discussion

The results presented here clearly show that Mo oxo species deposited on Pt or PtRu can catalyze the electrochemical oxidation of formaldehyde and formic acid, and improve the performances of direct formaldehyde and formic acid fuel cells. However, contrary to some literature reports [13, 15, 24], we have not found any evidence that the promotion of methanol oxidation by Mo oxo species produces significant improvements in the performance of direct methanol fuel cells.

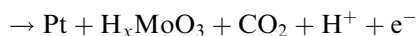
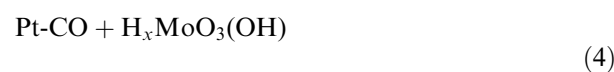
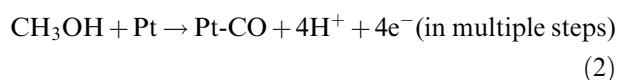
The performance gains seen in direct formaldehyde and formic acid cells were similar for catalysts modified by reductive electrodeposition of H_xMoO₃, and evaporative deposition of Na₂MoO₄. The higher oxidation state of such species, obtained at anode potentials above ca. +500 mV vs. SHE, is widely accepted to be Mo(VI),

while there is considerable uncertainty regarding the lower oxidation state(s) [17]. Mo(0), Mo(III), Mo(IV), and Mo(V) all appear to be possibilities [13, 17, 25–28]. Under the acidic conditions of a PEM fuel cell, the reduced species is probably best represented as H_xMoO₃. The Mo redox process commonly observed at $E^o \sim 0.4$ V vs. SHE (or DHE) (e.g. ref. 17) can then be represented as:



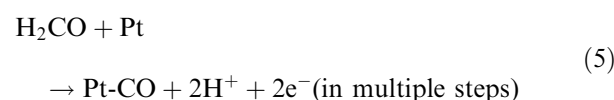
At the potentials at which the Mo oxide deposit shows catalytic activity towards formaldehyde oxidation (>0.3 V vs. DHE; see Figure 3), it is still in a partially reduced state (i.e. $x > 0$). Its activity disappears when it is fully oxidized ($E_{\text{anode}} > 500$ mV vs. DHE in Figure 3). Shropshire [8] attributed this effect to irreversible loss of Mo(VI) from the Pt surface. In the work reported here, the apparent reversibility of this effect may be due to the presence of excess Mo oxide and/or the lack of an acidic solution to facilitate rapid removal of desorbed species. Thus desorbed species may re-adsorb when the cell is at open circuit or be replaced by new H_xMoO₃ species from nearby Mo oxide particles. It is also possible that the Mo(VI) remains on the surface of the Pt and that it is only the reduced species that is catalytically active.

A number of authors have discussed the mechanism of methanol oxidation at Pt in the presence of Mo oxide species [8, 10, 13, 15, 28]. It appears likely that Mo hydroxy species promote oxidative removal of adsorbed CO intermediates. The “bifunctional” mechanism that has been well established for methanol oxidation on PtRu alloys [29] can be written for Pt–Mo oxide as follows.



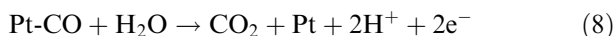
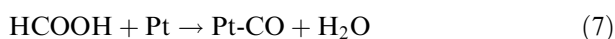
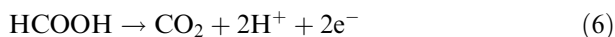
Thus H_xMoO₃ type species on the Pt surface promote the formation of OH groups adjacent to CO poisoned Pt sites, and these combine with the adsorbed CO to strip it from the surface as CO₂. The clean Pt surface then becomes available for further oxidation of methanol.

The oxidation of formaldehyde on Pt follows a similar mechanism to that for methanol oxidation, again leading to poisoning of the electrode by adsorbed CO [10]:



Presumably, the activating effect of Mo oxide is similarly due to stripping of CO through the “bifunctional” mechanism described in equations (3) and (4).

The oxidation of formic acid on Pt is thought [12] to involve both a direct pathway (equation 6) that does not involve adsorbed CO and an indirect pathway involving adsorbed CO (equations 7 and 8).



The activating effect of Mo oxide through the “bifunctional” mechanism will only affect the indirect pathway. The less significant effect observed in formic acid cells, relative to formaldehyde cells, may therefore reflect the lower impact of the CO-pathway in formic acid oxidation.

A key question that arises from the postulation that the role of the Mo oxide is the same in methanol and formaldehyde oxidation is why its effect is so much more pronounced in the formaldehyde case? There are a number of possible reasons for this.

Shropshire [8] suggested that the rate limiting step was the oxidation of the organic species in solution by an Mo(VI) species on the Pt surface. The rate of this chemical step would be increased by the lower redox potential of formaldehyde vs methanol.

Another difference between formaldehyde and methanol oxidation may be the nature of the adsorbed CO intermediate that is formed. It has been reported that Mo is only active for stripping of weakly adsorbed CO [17] and so it is possible that CO from formaldehyde is more weakly adsorbed than CO from methanol.

A third possibility is that Mo is only active in its reduced state [17], and that methanol does not adsorb rapidly enough on Pt at potentials at which there is sufficient reduced Mo to be effective [17]. Since formaldehyde adsorbs on Pt more strongly than methanol [8], it would exhibit more effective catalysis by H_xMoO_3 .

Proper assessment of a new catalyst for practical systems requires comparison with a PtRu alloy catalyst, which is the current state-of-the-art for methanol oxidation, and this is done in Figures 5, 6, and 7. Significantly, the Mo oxide modified Pt catalysts (Figures 2 and 3) outperform the PtRu catalyst (Figure 5) for formaldehyde oxidation at very low current densities, indicating that Mo can promote formaldehyde oxidation at lower potentials than can Ru. However, at the current densities required in a fuel cell, the activity of Mo is insufficient and PtRu is far superior. Combination of Mo with PtRu is synergistic, and provides the best overall performance, as reported by Lamy and coworkers for methanol oxidation [20] and Baltruschat and coworkers for CO oxidation [17]. The results are similar

for formic acid oxidation, with Mo oxide modified Pt being better than PtRu at low current densities and Mo oxide modified PtRu providing the best performance (Figures 6 and 7)

Formaldehyde and formic acid crossover rates measured in this work were not significantly different from methanol crossover rates, and this is expected given the similar sizes of the molecules and that fact that formic acid should not be significantly ionized in the strongly acidic Nafion membrane. Surprisingly, Rhee et al. [23] have reported that formic acid crossover is two orders of magnitude lower than methanol crossover. They reported a formic acid crossover rate of $0.2 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ for 1 M formic acid permeation through Nafion 117 at room temperature, while we have obtained a value of $1.2 \times 10^{-7} \text{ mol cm}^{-2} \text{ s}^{-1}$ with a 29% thinner Nafion 115 membrane (127 vs. 178 μm) at 60 °C. Assuming an approximate doubling of the flux between 25 °C and 60 °C [22], Rhee et al.’s formic acid crossover result is only a factor of two lower than ours, and is consistent with the conclusion that formic acid crossover is not greatly lower than methanol crossover. Wang et al. [30] have reported that formic acid crossover is approximately half as fast as methanol crossover over a range of temperatures.

5. Conclusions

Modification of Pt and PtRu catalysts with Mo oxides significantly improves their catalytic activity toward formaldehyde and formic acid oxidation. This provides greatly enhanced low current density performances in direct formaldehyde fuel cells, but the effect becomes less significant at high current densities. Enhanced cell performances at low current densities were also observed in direct formic acid fuel cells, although the effects were not as significant as for formaldehyde. The performances of direct methanol cells were not improved by modification of the anode with Mo oxide.

The observation of catalytic activity at potentials significantly lower than observed with Ru points to the possibility of achieving high efficiencies and high current densities for the oxidation of formaldehyde, formic acid, and perhaps methanol. The modification procedures have not yet been optimized, and the nature of the catalytic species and mechanism are largely unknown. Further work is likely to result in an increase in the current that the Mo oxide co-catalyst can sustain at low potential.

Acknowledgement

This work was supported by a Natural Sciences and Engineering Research Council of Canada (NSERC) Strategic Projects Grant, by Memorial University and by H Power Corp.

References

1. C. Lamy, J.M. Leger and S. Srinivasan, in *Modern Aspects of Electrochemistry*, **34** (2001) pp. 53–118.
2. J.T. Wang, W.F. Lin, M. Weber, S. Wasmus and R.F. Savinell, *Electrochim. Acta* **43** (1998) 3821.
3. J.T. Muller, P.M. Urban, W.F. Holderich, K.M. Colbow, J. Zhang and D.P. Wilkinson, *J. Electrochem. Soc.* **147** (2000) 4058.
4. C. Lamy, E.M. Belgsir and J.M. Leger, *J. Appl. Electrochem.* **31** (2001) 799.
5. O. Savadogo and X. Yang, *J. Appl. Electrochem.* **31** (2001) 787.
6. Z.G. Qi, M. Hollett, A. Attia and A. Kaufman, *Electrochem. Solid State Lett.* **5** (2002) A129.
7. C. Rice, R.I. Ha, R.I. Masel, P. Waszczuk, A. Wieckowski and T. Barnard, *J. Power Sources* **111** (2002) 83.
8. J.A. Shropshire, *J. Electrochem. Soc.* **112** (1965) 465.
9. P. Olivi, L.O.S. Bulhoes, J.-M. Leger, F. Hahn, B. Beden and C. Lamy, *J. Electroanal. Chem.* **370** (1994) 241.
10. S. Nakabayashi, I. Yagi, N. Sugiyama, K. Tamura and K. Uosaki, *Surf. Sci.* **386** (1997) 82.
11. M.V. ten Kortenaar, Z.I. Kolar, J.J.M. de Goeij and G. Frens, *J. Electrochem. Soc.* **148** (2001) E327.
12. C. Rice, S. Ha, R.I. Masel and A. Wieckowski, *J. Power Sources*, **115** (2003) 229.
13. W.S. Li, L.P. Tian, Q.M. Huang, H. Li, H.Y. Chen and X.P. Lian, *J. Power Sources*, **104** (2002) 281.
14. H.S. Wang, *Acta Chimica Sinica*, **60** (2002) 606.
15. Y. Wang, E.R. Rachjini, G. Cruz, Y. Zhu, Y. Ishikawa, J.A. Colucci and C.R. Cabrera, *J. Electrochem. Soc.* **148** (2001) C222.
16. S.A. Lee, K.W. Park, J.H. Choi, B.K. Kwon and Y.E. Sung, *J. Electrochem. Soc.* **149** (2002) A1299.
17. G. Samjeske, H.S. Wang, T. Löffler and H. Baltruschat, *Electrochim. Acta* **47** (2002) 3681.
18. S. Ball, A. Hodgkinson, G. Hoogers, S. Maniguet, D. Thompson and B. Wong, *Electrochem. Solid State Lett.* **5** (2002) A31.
19. A.B. Anderson, E. Grantscharova and S. Seong, *J. Electrochem. Soc.* **143** (1996) 2075.
20. A. Lima, C. Coutanceau, J.M. Leger and C. Lamy, *J. Appl. Electrochem.* **31** (2001) 379.
21. C. Song and P.G. Pickup, *J. Appl. Electrochem.* **34** (2004) 1065.
22. X.M. Ren, T.E. Springer, T.A. Zawodzinski and S. Gottesfeld, *J. Electrochem. Soc.* **147** (2000) 466.
23. Y.W. Rhee, S.Y. Ha and R.I. Masel, *J. Power Sources* **117** (2003) 35.
24. T.H.M. Housmans and M.T.M. Koper, *J. Phys. Chem. B.* **107** (2003) 8557.
25. K. Machida and M. Enyo, *J. Electrochem. Soc.* **137** (1990) 1169.
26. B. Wang and S. Dong, *J. Electroanal. Chem.* **379** (1994) 207.
27. L. Kosminsky and M. Bertotti, *J. Electroanal. Chem.* **471** (1999) 37.
28. S. Mukerjee and R.C. Urian, *Electrochim. Acta* **47** (2002) 3219.
29. T. Iwasita, *Electrochim. Acta* **47** (2002) 3663.
30. X. Wang, J.M. Hu and I.M. Hsing, *J. Electroanal. Chem.* **562** (2004) 73.