THE INCLUSION OF Mo, Nb AND Ta IN Pt AND PtRu CARBON SUPPORTED ELECTROCATALYSTS IN THE QUEST FOR IMPROVED CO TOLERANT PEMFC ANODES

D.C. Papageorgopoulos
M. Keijzer
F. A. de Bruijn

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Abstract

The effect of the inclusion of Mo, Nb and Ta in Pt and PtRu carbon supported anode electrocatalysts on CO tolerance in proton exchange membrane fuel cells (PEMFC) has been investigated by cyclic voltammetry and fuel cell tests. CO stripping voltammetry on binary Pt_\text{M} / C (M: Mo, Nb, Ta) reveals partial oxidation of the CO adlayer at low potential, with PtMo(4:1) / C exhibiting the lowest value. At 80 °C, the operating temperature of the fuel cell, CO oxidation was observed at potentials close to 0 V vs. RHE. No significant difference for CO electro-oxidation at the lower potential limit, compared to PtRu / C, was observed for PtRuM_y / C (M: Mo, Nb). Fuel cell tests demonstrated that while all the prepared catalysts exhibited enhanced performance compared to Pt / C, only the addition of a relatively small amount of Mo to PtRu results in an electrocatalyst with a higher activity, in the presence of carbon monoxide, to PtRu / C, the current catalyst of choice for PEM fuel cell applications.

Keywords

PEMFC, CO, tolerance, Electrocatalysts, PtMo.
1. INTRODUCTION

The development of new electrocatalyst materials, with significantly lower affinity for carbon monoxide, is essential in the further advancement of polymer electrolyte membrane fuel cell (PEMFC) technology. An ideal catalyst for the anode would be fully tolerant to CO poisoning, while maintaining its activity for the oxidation of hydrogen. Platinum, the most active material for the hydrogen oxidation reaction, is unfortunately extremely susceptible to CO.

It is well established that bimetallic systems, with Pt as one of the components, can give substantial tolerance to the presence of CO in the fuel stream. One known example is that of PtRu, where enhanced tolerance could be ascribed to a decrease in CO binding energy on platinum due to electronic substrate effects [1], and to the oxidation of chemisorbed CO being catalyzed at low potentials by the activation of H$_2$O [2]. The latter is due to the facile formation of the oxygen containing species, in the form of adsorbed hydroxyl species (OH$_{ads}$), on oxophilic ruthenium.

Water induced oxide formation has been attributed to metals situated in the early transition series and a high water dissociation capability has been predicted for these [3]. Quite recently, a two- to threefold enhancement of CO tolerance in a PEM fuel cell was reported to be exhibited by carbon supported alloy nanocrystalline PtMo(4:1)/C, as compared to PtRu/C [4,5]. The increased CO tolerance was related to the ability of PtMo to promote the CO oxidation process at very low electrode potentials. This was attributed to oxygen transfer from Mo oxyhydroxide species with only the OH species of the oxyhydroxide states (predominantly MoO(OH)$_2$) being reactive with adsorbed CO [6,7]. Since this reactive state, due to its size, has the potential of reducing the availability of adjacent Pt sites for molecular hydrogen
dissociation, a PtMo catalyst with an atomic ratio of 4:1 was shown to give the best performance. Additionally, the formation of a molybdenum hydrogen bronze $\text{H}_2\text{MoO}_x$ that could be formed by the ‘spillover’ of hydrogen from Pt sites to Mo, has been suggested as a possible explanation for enhanced catalytic activity towards CO [8].

There has also been an effort to improve the behavior of the PtRu binary catalyst by incorporation of a third metal exhibiting facile oxide formation characteristics. In the case of PtRuMo, promising results were attained for PEMFC operation on methanol [9,10] or reformate gas [10]. The inclusion of W was also found to be beneficial [10,11], while partial substitution of Ru in PtRu by Cr, Zr, or Nb, resulted in a decrease in activity for $\text{H}_2$ oxidation in the presence of 10 or 100 ppm CO [11].

In the present study, binary and ternary catalyst formulations of one of Mo, Nb and Ta with Pt and PtRu respectively, supported on high-surface area carbon, doped with Nafion were prepared and tested for their applicability as CO tolerant anode electrocatalysts in the PEMFC. The metals chosen to modify both Pt and PtRu have been predicted to activate water dissociation, as mentioned previously. For the bimetallic systems, only Pt rich electrocatalysts were made, in accordance to previous results for PtMo alloys. The preparation method was such that alloying, to an extent at least, was avoided. Thus, both the effects of the metals included in the binary and ternary systems and of the preparation method were examined.
2. EXPERIMENTAL

Catalyst preparation and characterization

All catalysts, supported on carbon Vulcan XC-72 with a 20 wt% metal loading, were prepared by a process relative to the one claimed by Degussa AG for PtRu [12]. Deposition of the metals from aqueous solution took place by chemical reduction of their corresponding salts, with platinum nitrate (Merck), ruthenium chloride hydrate (Aldrich) and the respective chlorides for the other metals (Aldrich) used as precursors and formaldehyde as the reducing agent. The catalysts were dried at 80 °C. For PtRu, the lack of high temperature annealing, during the preparation, leads to the noble metals being present in highly dispersed form on the support material without being alloyed to each other, as verified by X-ray diffraction analysis (XRD) [12].

Pt_{4}M_{1} and Pt_{6}Ru_{9}M_{2} (M: Mo, Nb, Ta) ratios were calculated and the bulk composition of each of the prepared catalysts was evaluated by Energy Dispersive X-ray analysis (EDX, Thermo NORAN) in a Scanning Electron Microscope (SEM, JEOL JSM-6330F). Furthermore, PtMo(4:1) / C and PtNb(3:1) / C were examined by Transmission Electron Microscopy (TEM, Phillips 301). The images revealed very similar particle size (< 3 nm) and distribution characteristics. For the cyclic voltammetry and fuel cell test experiments, propanol based catalyst inks were prepared with Nafion (5%, EW 1100). For comparison, E-TEK Pt and E-TEK PtRu (1:1), all 20 wt% on Vulcan XC-72, were also used.

Cyclic voltammetry

Cyclic voltammetry experiments were conducted in 1N H_{2}SO_{4} (Merck) prepared with Millipore super Q water. The setup consisted of a standard
electrochemical cell, with the usual three electrode arrangement, on a computer controlled Autolab PGSTAT 20 potentiostat / galvanostat (Ecochemie). The working electrode was prepared by the deposition of the catalyst ink under investigation on both sides of a platinum foil (1.5 cm²), followed by drying in ambient conditions. A platinized Pt square foil (1.5 cm²) was used for counter electrode. Hg / Hg₂SO₄ (K₂SO₄ saturated) was used as a reference electrode, which has a potential of E = +0.658 V versus the Reversible Hydrogen Electrode (RHE) and all potentials were referred to the RHE.

The samples were electrochemically cleaned in solution by continuous cycling between 18 and 1260 mV and nitrogen purging, which was found to ensure stability in terms of surface area response to potential cycling. No dissolution effects for any of the samples tested were observed after this treatment. 10% CO in Argon gas (Scott Specialty Gases) was employed. The solution was saturated with the gas, in each case, while the electrode was held at the adsorption potential, which was 18 mV versus RHE. This adsorption potential is representative for the interaction of CO with a hydrogen saturated surface in a PEM fuel cell. Solution saturation occurred after dosing for about 35 minutes. After each dose, bulk CO was removed by bubbling nitrogen through it. Stripping voltammograms were collected between 18 mV (starting potential) and 1.26 V with a scan rate of 5 mV / s, for 25 and 80 °C respectively. Complete oxidation of adsorbed species was accomplished in a single scan; no oxidation was monitored during the second scan.

**Fuel cell MEA preparation and experiments**

In all fuel cell experiments reported in this paper, Nafion 105 (Du Pont) was used as a membrane, and prefabricated 0.35 mg Pt / cm² single sided ELAT gas diffusion electrodes from E-TEK were used as cathode. For the anode, the catalyst ink
was applied on to a E-TEK single sided ELAT gas diffusion backing resulting in an electrode with a low precious metal loading (~ 0.35 mg / cm²). The electrodes that were used were impregnated with a 5% Nafion solution resulting in a Nafion loading of ~1 mg / cm². Membrane Electrode Assemblies (MEAs) were prepared by hot-pressing the Nafion membrane and the two 7 cm² electrodes together at a temperature of 130 °C and a pressure of 40 bar(g) for 1.5 min.

The MEAs were clamped between two serpentine-machined graphite blocks and connected to the test station. At start-up, a constant voltage of 0.5 V was applied for 18 h, using air (cathode) and hydrogen (anode) humidified at cell temperature by membrane humidification and at a pressure of 1.5 bar. All experiments were performed at 80 °C. To examine CO tolerance, the fuel cells voltage drop over the electronic load was kept constant at 0.5 V, while the current density was measured for several CO concentrations in pure H₂, with performance data obtained in the steady state.
3. RESULTS AND DISCUSSION

PtM / C (M: Mo, Nb, Ta)

The electrochemical and CO electro-oxidation characteristics of carbon supported PtM, with M one of Mo, Nb, Ta, were examined by cyclic voltammetry. Figure 1 compares the voltammograms of supported PtMo(4:1) and PtNb(3:1) to Pt in pure 1 N H₂SO₄ at 25 °C. For the bimetallic catalysts, the hydrogen region from 0 to ~0.33 V vs. RHE, corresponding to the reductive adsorption of protons in the cathodic scan and the subsequent oxidation of the hydrogen adatoms in the anodic scan, exhibits distinct peaks which are characteristic of platinum. A smaller oxidation

![Graph of cyclic voltammetry](image)

**Figure 1:** Cyclic voltammetry of carbon supported Pt, PtMo(4:1) and PtNb(3:1) in 1 N H₂SO₄ at 25 °C. Scanning rate v = 5 mV / sec.
charge, in this region, for PtMo(4:1) and especially PtNb(3:1), for an equal amount of material applied on the electrode, implies a smaller electrochemical surface area for these catalysts compared to Pt/C. This decrease in hydrogen oxidation charge, is much stronger, especially for Nb, than would be expected from the lower amount of Pt in the bimetallic system compared to the platinum only catalyst. Since TEM image yielded particles, for PtMo(4:1) / C and PtNb(3:1) / C, with comparable size and distribution characteristics, particle size effects can be excluded. Electronic effects could be postulated as a possible cause. However, these should lead to a shift in adsorption potential, which was clearly not seen, rather than in a change in the peak.

**Figure 2:** Cyclic voltammetry of carbon supported Pt and PtMo(4:1) after CO saturation, in 1 N H₂SO₄ at 25 °C. The clean spectrum for PtMo(4:1) / C is also depicted for comparison. Scanning rate v = 5 mV / sec.
height at the same potential. The observed inhibition of hydrogen adsorption and subsequent oxidation seems to be due, most possibly, to surface segregation of Nb. Given that surface enrichment in Pt has been predicted for these alloys [13], the segregation would be a result of the preparation process, where annealing was avoided. Oxide reduction proceeds via a single peak, as evident in the cathodic scan. This indicates the formation of an alloy phase, at least under cycling conditions. What is particular though for PtMo(4:1) is that its voltammogram shows a redox behavior at potentials of ~0.4V vs. RHE, which has been suggested to be due to $\text{Mo}^{4+} \leftrightarrow \text{Mo}^{6+}$ oxidation states [4,6], in comparison with the Pourbaix diagram for Mo [14]. Finally, it should be noted that no dissolution effects have been observed, due to repeated cycling, for any of the binary systems tested.

Figure 2 shows the CO stripping voltammetry on PtMo(4:1) / C and Pt / C, following carbon monoxide saturation at 18 mV vs. RHE and subsequent purging of the solution with N$_2$, at 25 °C. The voltammogram for PtMo(4:1) / C without any CO adsorption is also depicted. The hydrogen coverage is unity at the adsorption potential of 18 mV. Upon CO saturation of the solution, CO displaces virtually all of the hydrogen from the surface, as seen by the suppression of the adsorption – desorption charges in the respective region. There is a distinct similarity of the main CO oxidation peak of PtMo(4:1) / C to that of Pt / C, assigned to strongly, linear, bonded carbon monoxide [15]. This resemblance has been observed elsewhere [4,16] and has lead to the suggestion that it is a result of the reaction proceeding on Pt sites between CO and Pt-OH [4]. The predicted weakening of CO adsorption due to mixing of Pt by Mo [17] does not manifest in a lowering of the saturation coverage. Apart from this main peak, there is a small ‘pre-wave’ oxidation peak, at low potentials, for both systems, with that for PtMo (4:1) / C shifted to an even lower
value (~0.2 V). It has been proposed that at this low potential the electro-oxidation of CO is consistent with a mechanism where adsorbed carbon monoxide on Pt sites is oxidized by OH activated at neighboring Mo atoms [4]. Only a small number of sites seem to be active for this reaction, as the majority of CO is oxidized at potentials typical of pure Pt, suggesting a high degree of heterogeneity for the PtMo catalyst’s surface [16].

**Figure 3:** Cyclic voltammetry of CO saturated carbon supported PtMo(4:1) at 25 and 80 °C, in 1 N H₂SO₄. Scanning rate v= 5 mV / sec.

With increasing temperature, the CO electro-oxidation peak shifts negatively, as seen in Figure 3 for PtMo(4:1) / C, in accordance with the general trend. More significantly, the low potential peak shifts also in a similar fashion, with oxidation evident at potentials close to 0 V vs RHE at 80 °C, the operating temperature of the PEM fuel cell. This is in agreement with studies on a bulk
PtMo(77:23) alloy which showed that 2% CO in Ar was oxidized at potentials as low as 50 mV at 60 °C [18].

Figure 4: Cyclic voltammetry of carbon supported PtMo(4:1), PtNb(3:1) and PtTa(6:1) after CO saturation, in 1 N H₂SO₄ at 25 °C. The inset depicts a blow up of the anodic scan from 18 to 600 mV vs. RHE. Scanning rate ν= 5 mV / sec.

Table 1: Main peak potentials $E_p$ for CO electro-oxidation at 25 and 80 °C, for carbon supported PtM (M: Mo, Nb, Ta and Ru).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$E_p$ at 25 °C (mV)</th>
<th>$E_p$ at 80 °C (mV)</th>
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<tbody>
<tr>
<td>Pt (E-TEK)</td>
<td>718</td>
<td>557</td>
</tr>
<tr>
<td>PtMo(4:1)</td>
<td>712</td>
<td>516</td>
</tr>
<tr>
<td>PtNb(3:1)</td>
<td>727</td>
<td>528</td>
</tr>
<tr>
<td>PtTa(6:1)</td>
<td>734</td>
<td>520</td>
</tr>
<tr>
<td>PtRu (E-TEK)</td>
<td>466</td>
<td>341</td>
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The cyclic voltammetry after CO adsorption at 18 mV vs. RHE, of carbon supported PtNb(3:1), PtTa(6:1) and PtMo(4:1) in 1N H₂SO₄ at 25 °C, is shown in Figure 4. As in the case of PtMo(4:1) / C and Pt / C, CO tends to fully saturate both PtNb(3:1) / C and PtTa(6:1) / C by displacing adsorbed hydrogen. Similar electro-oxidation characteristics are also observed, with the majority of molecules in the CO adlayer depleted in a single peak at a potential which resembles that seen on Pt, which is preceded by a ‘pre-wave’ oxidation peak. While a similar mechanism seems to be in place, it is evident, as depicted in the inset of Figure 4, that the peak at lower potential, most likely associated with CO oxidation at Pt-M interfacial sites, is delayed for PtTa(6:1) / C and PtNb(3:1) / C compared to PtMo(4:1) / C. Although not shown, this holds true for the stripping voltammograms at 80 °C as well, where both peaks shift to lower values. These results imply a greater significance for Mo as a co-catalyst in systems applied to CO tolerant anodes.

The values for the main peak potentials Eₚ for all three catalysts, at 25 and 80 °C, are given in Table 1. It is worth noticing that at 80 °C the shift is more pronounced in the case of the bimetallic catalysts. This could additionally be a result of an electronic modification of carbon monoxide chemisorption and water dissociation on Pt atoms, due to bimetallic particle formation. Also given, are the Eₚ values from the oxidation of CO form carbon supported alloyed PtRu, where a cathodic shift of more than 200 mV is observed, compared to Pt / C.

Since a typical fuel cell anode operates near +50 mV, at a temperature of 80 °C, it would be interesting to see how the cyclic voltammetry results correlate with the influence of CO on MEAs with PtM / C (M: Mo, Nb, Ta) anodes directly under PEMFC conditions. The latter can be seen in Figure 5, where current density is plotted against CO concentration, with the cell voltage set at 0.5 V at 80 °C.
Figure 5: Current density versus CO concentration for cells operated with anode catalysts consisting of carbon supported Pt (E-TEK), PtRu (E-TEK), PtMo(4:1), PtNb(3:1) and PtTa(6:1) at a pressure of 1.5 bar and a cell voltage of 0.5 V. $T_{\text{cell}} = T_{\text{hum}} = 80^\circ$C.

Additionally, the percentage of current density to CO concentration is plotted in Figure 6. The performance for carbon supported alloyed PtRu (E-TEK) is also exhibited for comparison. With pure hydrogen as the fuel, the highest current is attained by Pt / C with a somewhat lower current observed for PtMo(4:1) / C, in agreement to what was observed elsewhere [19]. On the other hand, PtNb(3:1) / C gives a surprisingly low hydrogen oxidation current density. The addition of CO in the fuel stream leads to a drop in activity for all catalysts tested, with Pt exhibiting its established susceptibility to carbon monoxide poisoning. While better than Pt/C, the
Figure 6: Current density ratios $j / j_o$, where $j_o$ is the current density obtained in pure H$_2$, versus CO concentration for cells operated with anode catalysts consisting of carbon supported Pt (E-TEK), PtRu (E-TEK), PtMo(4:1), PtNb(3:1) and PtTa(6:1) at a pressure of 1.5 bar and a cell voltage of 0.5 V. $T_{cell} = T_{hum} = 80\, ^\circ C$.

The performance of the prepared catalysts does not meet the standard set by PtRu, the current choice for tackling reformate poisoning in the PEMFC. PtMo(4:1) / C gives better results than both PtNb(3:1) / C and PtTa(6:1) / C, as was implied by cyclic voltammetry in terms of the respective catalyst’s ability to oxidize CO at very low anode overpotentials.

For PtTa(6:1) / C, only a small improvement to Pt is detected, in contrast to what has been previously claimed for PtTa alloys comprising of between about 2 and 10 a.% Ta with Pt in a phosphoric acid fuel cell [20]. Niobium is better than tantalum.
in this respect, but it is seriously hindered by its inability to satisfactorily oxidize hydrogen. This seems to be a reflection of the lower electrochemical surface area observed in cyclic voltammetry, compared to Pt/C. While surface segregation effects could be a cause, as was postulated earlier, an additional contribution could arise from a possible screening of adjacent platinum sites by the formation of niobium hydroxyoxide species, in a fashion similar to what has been proposed for PtMo [6]. It should be noted that Nb is at a +V oxidation state at 0 V [14] enabling the formation of such species. Enriching the catalyst in platinum should alleviate the effect. Figure 7 shows a bar diagram for the comparison of the performance of PtNb(3:1) / C to

![Bar Diagram](image)

**Figure 7**: A comparison of the current density for cells operated with anode catalysts consisting of carbon supported PtNb(3:1) and PtNb(9:1) operated with pure hydrogen at the anode and with the inclusion of 40 and 100 ppm CO, at a pressure of 1.5 bar and a cell voltage of 0.5 V. \( T_{\text{cell}} = T_{\text{hum}} = 80 \, ^\circ\text{C} \).
PtNb(9:1) / C in pure H₂ and in fuel streams of hydrogen with 40 and 100 ppm CO. Higher current densities are attained with PtNb(9:1) / C, without the relative ability of the bimetallic catalyst to handle CO being hindered in the process.

Although the state of the ‘as prepared’ catalysts was not determined, the inferior performance, of PtMo(4:1) / C in particular, compared to results reported elsewhere [4,5], could be a result of poor alloying induced by the lack of an annealing step in the preparation method. Good proximity and mixing of the atoms is essential for the tolerance mechanism, in the case of PtMo, in contrast to what has been claimed for PtRu [12]. It has been suggested that a key factor correlating with good PtMo anode performance in the presence of CO is the particle size of the supported catalyst [21], with catalysts revealed to be poorly alloyed showing relatively poor tolerance. The best tolerance was achieved with PtMo samples of larger particle sizes, possibly linked to more complete alloying. The preparation method currently deployed has been shown to produce catalysts with a small particle size (<2nm), in the case of PtRu / C [12] and PtPd / C [22]. For PtMo(4:1) / C, particles smaller than 3 nm were observed in the TEM images. Furthermore, the avoidance of any surface segregation phenomena associated with thermal pre-treatment, which would not be extensive due to the finite size of the nanoparticles, with Pt the segregating element in the Pt-Mo system, does not result in any improvement in activity.
PtRuM / C (M: Mo, Nb)

In order to examine whether the oxophilicity of Mo and Nb could be beneficial in further improving CO tolerance in PtRu, supported catalysts consisting of ternary formulations of Pt and Ru with small amounts of Mo and Nb were prepared and studied. The CO electro-oxidation characteristics of these catalysts were examined by cyclic voltammetry in 1N H₂SO₄. Figures 8 and 9 show the CO stripping voltammetry on Pt / C, PtRu / C and Pt₆Ru₉Mo₂ / C, following carbon monoxide saturation at 18 mV vs. RHE and subsequent purging of the solution with nitrogen, at 25 and 80 °C respectively. The voltammogram of clean Pt₆Ru₉Mo₂ / C is

Figure 8: Cyclic voltammetry of carbon supported Pt, PtRu and PtRuMo(9:9:2) after CO saturation, in 1 N H₂SO₄ at 25 °C. The clean spectrum PtRuMo(9:9:2) / C is also depicted for comparison. Scanning rate \(\nu= 5 \text{ mV} / \text{sec} \).
also depicted and exhibits a broad hydrogen region with two oxidation peaks faintly distinguishable and an oxide reduction peak that is situated at a higher cathodic potential compared to PtRu / C. It has to be added that, similar to the binary systems, no dissolution effects were observed due to repeated cycling, for up to at least ten cycles, in this potential range. As seen in Figure 8, CO saturation leads to total

![Cyclic voltammetry of carbon supported Pt, PtRu and PtRuMo(9:9:2) after CO saturation, in 1 N H₂SO₄ at 80 °C. Scanning rate ν= 5 mV / sec.](image)

**Figure 9:** Cyclic voltammetry of carbon supported Pt, PtRu and PtRuMo(9:9:2) after CO saturation, in 1 N H₂SO₄ at 80 °C. Scanning rate ν= 5 mV / sec.

displacement of hydrogen from the particle surfaces and to the creation of a stable CO adlayer for all three catalysts. For PtRu / C, the CO electro-oxidation peak is shifted to a considerably lower potential (466 mV) compared to Pt / C (718 mV), which is characteristic of this system [15,16]. CO evolves in a single broad peak from the ternary catalyst, at a higher value than that of PtRu / C, with oxidation contributions
Table 2: Main peak potentials $E_p$ for CO electro-oxidation at 25 and 80 °C, for carbon supported PtRuM (M: Mo, Nb). The values for Pt/C and PtRu are also listed for comparison.

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<td>557</td>
</tr>
<tr>
<td>Pt$_9$Ru$_9$Mo$_2$</td>
<td>580</td>
<td>381</td>
</tr>
<tr>
<td>Pt$_9$Ru$_9$Nb$_2$</td>
<td>555</td>
<td>381</td>
</tr>
<tr>
<td>Pt$<em>9$Ru$<em>9$Mo$</em>{1.5}$Nb$</em>{0.5}$</td>
<td>550</td>
<td>372</td>
</tr>
<tr>
<td>PtRu (E-TEK)</td>
<td>466</td>
<td>341</td>
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The minor oxidation feature, at low potential, associated with Pt-Mo has vanished for the ternary system. The main peak shifts to a lower value, becoming narrower in the process, at 80 °C, as seen in Figure 9. It is still broader and at a higher value than that for PtRu / C, but the onset for oxidation appears to coincide with that for the binary Pt-Ru system. The difference between PtRuMo and PtRu at the very low potential range is extremely small. The ability Mo exhibits in activating water dissociation, as was discussed in the previous section, seems to be overshadowed, in the stripping voltammetry, by the cocatalytic effect of Ru. Similar characteristics have also been seen for the other catalysts tested, namely Pt$_9$Ru$_9$Nb$_2$ / C and Pt$_9$Ru$_9$Mo$_{1.5}$Nb$_{0.5}$ / C, whose values for the main peak potentials for CO electro-oxidation at 25 and 80 °C are given in table 2.
Figure 10: Current density versus CO concentration for cells operated with anode catalysts consisting of carbon supported Pt (E-TEK), PtRu (E-TEK), PtRuNb(9:9:2), PtRuMoNb(9:9:1.5:0.5) and PtRuMo(9:9:20) at a pressure of 1.5 bar and a cell voltage of 0.5 V. T_{cell} = T_{hum} = 80 °C.

The results in Figures 10 and 11 show the effects of CO on cell performance with the prepared catalysts used in anodes and compared to PtRu / C prepared at ECN with the same method; to commercially available Pt / C and to two samples of alloyed PtRu / C. The results clearly elucidate whether systems with Mo and / or Nb in a ternary formulation with Pt and Ru could potentially improve CO tolerance in PEMFC anodes. Neither the addition of Mo nor that of Nb hinders, at any significant level, the oxidation currents achieved when pure hydrogen is used as the fuel. With CO in the stream, niobium has a negative effect in PtRu by promoting CO poisoning. Mo, on the other hand, has exactly the opposite effect. The catalyst with 10 a% of
Mo shows a noticeable improvement in performance, in the presence of carbon monoxide, compared not only to PtRu / C prepared with the same method, but also to the alloyed E-TEK system. This is a reflection of the fact that fewer Mo atoms are needed to obtain the same adsorbed H\textsubscript{2}O as Ru. The prepared PtRu / C constituting of non-alloyed particles \cite{12} seems to be affected to a somewhat lesser extent to CO poisoning to the PtRu supported catalyst with the alloyed particles. For Pt\textsubscript{9}Ru\textsubscript{9}Mo\textsubscript{2} / C, the co-catalytic effect of Mo becomes more advantageous at higher CO

**Figure 11:** Current density ratios \( j / j_0 \), where \( j_0 \) is the current density obtained in pure H\textsubscript{2}, versus CO concentration for cells operated with anode catalysts consisting of carbon supported Pt (E-TEK), PtRu (E-TEK), PtRuNb(9:9:2), PtRuMoNb(9:9:1.5:0.5) and PtRuMo(9:9:2) at a pressure of 1.5 bar and a cell voltage of 0.5 V. \( T_{\text{cell}} = T_{\text{hum}} = 80 \, ^\circ\text{C} \).
concentrations with an improvement of ~15% in current density ratio \((j/j_0)\) at and above 100 ppm of CO, at a cell voltage of 0.5 V. Duplicate experiments have shown these results to be reproducible.

The extent to which the different metals that compose the ‘as prepared’ catalysts are in contact with each other is not known. It is highly possible that separate islands on the carbon surface are formed, as was suggested for PtRu / C prepared with the same method, wherein the crystallite size of the platinum is less than 2 nm and that of Ru less than 1 nm [12]. In contrast to what was observed for the binary system, this has no affect on the performance of the system, as also seen for the prepared PtRu / C. Previous studies on PtRuMo / C, with a 1:1:1 molar ratio, prepared by an impregnation method, showed that while PtRuMo / C was more active than the prepared PtRu, the PtRu catalyst supplied by E-TEK is more active for \(\text{H}_2/\text{CO}\) oxidation to both of them [10]. In the same study, PtRuMo / C was also prepared using a colloid method, but still found to be less active than the E-TEK PtRu / C.

While optimization of the molar ratio of the constituents may yet yield further improvement, it was demonstrated that the addition of molybdenum to PtRu could positively modify the catalysts ability to tolerate carbon monoxide, and should be considered as an alternative to PtRu / C for PEMFC applications.
4. CONCLUSIONS

The effects of CO poisoning of carbon supported anode electrocatalysts consisting of binary formulations of one of Mo, Nb and Ta with Pt and ternary formulations of Mo, Nb with Pt and Ru, were examined by cyclic voltammetry and fuel cell tests. In agreement with previous reports in the literature, CO stripping voltammograms for the binary catalysts revealed that while the majority of molecules in the CO adlayer were depleted in a single peak at a potential which closely resembles that seen on Pt, there was also a minor peak at lower potentials, with the lowest observed for carbon supported PtMo with an atomic ratio of 4:1 (PtMo(4:1) / C). At 80 °C, the operating temperature of the fuel cell, CO oxidation was observed at potentials close to 0V vs. RHE. No significant change was observed, in the stripping voltammetry, at the low potential limit for the ternary systems compared to PtRu.

Fuel cell anodes consisting of carbon supported PtMo(4:1) exhibit enhanced CO tolerance compared to Pt / C and the other binary systems tested, but do not outperform PtRu / C. This is most likely due to the very poor alloying, induced by the lack of an annealing step in the preparation process, of the catalyst particles. The inclusion of 10 a% Mo in PtRu, on the other hand, gives an electrocatalyst with a higher activity, in the presence of CO, to PtRu / C. This renders it a promising candidate in replacing binary PtRu / C, the current catalyst of choice for PEM fuel cell applications.
5. REFERENCES


