

Unravelling the complexities of CO₂ tolerance at PtRu/C and PtMo/C

Andrea E. Russell^{a,b,*}, Sarah C. Ball^b, Stephanie Maniguet^b, David Thompsett^b

^a Southampton University, UK

^b Johnson Matthey Technology Centre, UK

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Abstract

The CO₂ tolerance exhibited by PtRu/C is known to be greater than that of PtMo/C catalysts in contrast to the trend in CO tolerance. In this manuscript the origins of these differences are investigated in a cyclic voltammetric investigation of the potential dependence of the poisoning of Pt/C, PtRu/C and PtMo/C anode catalyst electrodes in a miniature PEM fuel cell when exposed to pure CO, pure CO₂, or 25% CO₂ in H₂. The results show that the difference in the mechanisms of improved CO tolerance, compared to a Pt/C reference catalyst, of PtRu and PtMo explain the decreased CO₂ tolerance of PtMo compared to PtRu; at PtRu the mechanism is intrinsic (water activation at Ru sites), whilst at PtMo the mechanism relies on the turn-over the Mo(IV/VI) redox couple.

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1. Introduction

It has long been recognised that the anode catalysts used in proton exchange membrane fuel cells (PEMFCs) must have a high tolerance to CO when operating with reformate (impure hydrogen derived from the reformation of hydrocarbons), as even low levels of CO severely poison Pt [1]. Reformate typically contains 20–25% CO₂ and 1% CO, and although the latter can be reduced to 10 ppm to 100 ppm by subsequent clean-up steps, it cannot be eliminated.

Considerable effort has been devoted to the development of CO tolerant catalysts, such as PtRu and PtMo bimetallic alloys, with carbon supported PtMo catalysts being identified as particularly promising, with a greater CO tolerance than PtRu [2–5]. It has been shown that the Pt-containing catalysts developed for their CO tolerance can also be poisoned by CO₂ to levels beyond those accounted for by simple dilution [6–8]. However, the trends in CO₂ tolerance of bimetallic alloys do not necessarily follow those for CO tolerance [9–11]. We have previously reported a difference in the CO₂ tolerance exhibited by PtRu/C

and PtMo/C catalysts (operating at 80 °C in 40 ppm CO and 25% CO₂ in H₂) [9]; we found that the PtRu/C catalyst had better CO₂ tolerance than the PtMo/C catalyst.

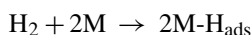
Voltammetric studies in acidic solution have indicated that deactivation of the Pt electrode surfaces in the presence of CO₂ is caused by the build up of a CO-like poison formed by the reduction of CO₂ in the presence of adsorbed hydrogen [12]. The reduction of CO₂ at Pt under PEMFC anode conditions has been ascribed to a reaction analogous to the reverse water gas shift reaction (RWGS);



where M is a surface site on the catalyst. The origins of the adsorbed hydrogen, M-H_{ads}, can either be the electrochemical reaction,



or the non-Faradaic chemical (Tafel) reaction,



Janssen [11] proposed that the chemical mechanism would probably prevail under PEMFC conditions. However, in a recent investigation of CO₂ reduction on carbon supported Pt catalysts

* Corresponding author. Tel.: +44 2380 59 3306; fax: +44 2380 59 6805.
E-mail address: a.e.russell@soton.ac.uk (A.E. Russell).

in acidic solution Smolinka et al. found a potential dependence of the poisoning of the catalyst surface that indicated that the electrochemical mechanism dominated [13]. They also showed that the result was reproduced in the PEMFC environment.

In the following, we will present and discuss a study of the potential dependence of the poisoning of carbon supported Pt, PtRu, and PtMo catalysts by CO and CO₂ in a model PEMFC environment. Results obtained with pure CO₂ and 25% CO₂ in H₂ will be also compared. The results will be interpreted in terms of the role of the electrochemical versus chemical origins of adsorbed hydrogen in the RWGS reaction and the mechanisms of the tolerances of the catalysts to CO and CO₂.

2. Experimental

2.1. Catalysts

Three anode catalysts: 39 wt% Pt, 37 wt%/19 wt% Pt/Ru, and 18 wt%/4 wt% Pt/Mo supported on Cabot XC72R furnace carbons were prepared using proprietary methods. The catalysts were characterised for metal content using inductively coupled plasma-emission spectrometry and Pt crystallite size and degree of intermixing of the binary components by powder X-ray diffraction as summarised in Table 1.

Anode catalyst electrodes were prepared by painting aqueous Nafion containing inks of the anode catalysts onto poly(tetrafluoroethylene) (PTFE)-impregnated Toray TPG-90 and TPG-60 carbon filter papers for the single cell and cyclic voltammetric studies, respectively [14]. The inks were prepared so as to contain 30 wt% Nafion dry weight.

2.2. Single cell studies

For single cell evaluations, electrodes (50 cm² active area) of the three catalysts were prepared using the procedure described above with Pt loadings of 0.24 mg(Pt) cm⁻², 0.24 mg(Pt) cm⁻² and 0.23 mg(Pt) cm⁻² geometric for the Pt, PtRu, and PtMo electrodes, respectively. Membrane electrode assemblies (MEAs) were fabricated from the three electrodes and standard cathodes (40 wt% Pt/XC72R at 0.7 mg(Pt) cm⁻²) using Nafion 115 membrane (DuPont) by hot pressing. The MEAs were conditioned in the single cell overnight, before testing using the different anode feed gasses. All the tests were carried out by measuring the cell voltage at a fixed current density of 500 mA cm⁻², using fuel and oxidant stoichiometries of 1.5 and 2.0, respectively. Gas inlet temperatures and pressures were 80 °C and 30 psi(g), with gases pre-humidified using an external humidifier. Investigation

of the reformat tolerance was performed by switching the anode gas stream from pure H₂ to a reformat mixture, and then monitoring the change in cell voltage. Experiments were performed using 100 ppm CO in H₂ and 25% CO₂ in H₂.

2.3. Cyclic voltammetric studies

Electrodes were prepared using the procedure described above with Pt loadings of 0.219 mg(Pt) cm⁻², 0.218 mg(Pt) cm⁻², and 0.231 mg(Pt) cm⁻² geometric for the Pt, PtRu, and PtMo electrodes, respectively. Membrane electrode assemblies (MEAs) were fabricated from the three anode catalyst electrodes and standard cathodes (60 wt% Pt/Ketjen EC3000J at 0.38 mg(Pt) cm⁻²) using Flemion SH30 membrane (Asahi Glass) by hot pressing. The MEAs were mounted in a miniature single cell PEM fuel cell, 3.14 cm² area, which consisted of acrylic end plates with two graphite flow-field plates with a single serpentine flow field and integral membrane substrate assembly (MSA) humidifiers similar to that previously reported [15] and compressed to 80%. Humidification and heating of the cell was accomplished by circulating water at 80 °C through the MSAs. Gas flow rates were controlled by mass flow controllers (MKS) and the cell back pressure regulated to 10 psi(g) using Equilibar precision back pressure regulators (Insight Process Solutions). H₂ was flowed to the anode and O₂ to the cathode at 60 mL min⁻¹ and the MEAs were conditioned by obtaining polarisation data (steady state current measurements), by poisoning the cell potential in 50 mV increments between the limits of 0.95 V and 0.65 V, holding for 5 s at each step for 10 cycles, followed by holding for 60 s at each step for 2 cycles. Correct mounting of the MEA was confirmed by measurement of the cell current at a cell potential of 0.7 V and the cell resistance by the current interrupt method.

Cyclic voltammetry was performed in the single cell by switching the cathode feed gas to H₂ and using this electrode as a combined counter and reference (RHE) electrode. All voltammograms were obtained using a 10 mV s⁻¹ sweep rate. Base voltammograms were obtained whilst purging the anode with N₂. The effects of exposure to CO, CO₂, and 25% CO₂/balance H₂ as a function of the applied potential were measured by exposing the anode to the selected gas mixture for 3 min followed by flushing the anode with N₂ for 45 min. Stripping voltammograms were obtained by sweeping the potential to the upper limit, 0.8 V for the Pt and PtRu catalysts and 1.0 V for the PtMo catalysts, from the holding potential and then down to a lower limit of 0.1 V for the Pt and PtRu electrodes and 0.075 V for the PtMo. Three complete cycles were recorded.

Table 1
Physical properties of the Pt, PtRu, and PtMo catalysts

Catalyst	Metal assay (wt%)			Atomic ratio of Pt:M	XRD properties	
	Pt	Ru	Mo		Crystallite size (nm)	fcc ^a lattice parameter <i>a</i> (nm)
Pt	38.74			–	3.54	0.391
PtRu	36.8	18.8		51:49	2.50	0.386
PtMo	18.0		4.33	67:33	2.90	0.391

^a fcc is face-centred cubic.

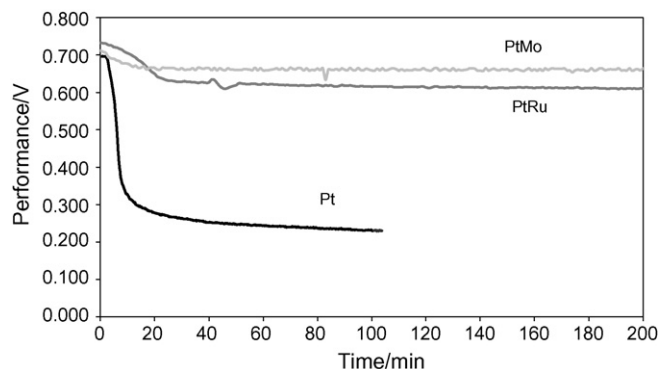


Fig. 1. Change in the cell voltage with time of MEAs containing Pt (black line), PtRu (dark grey line), and PtMo (light grey line) anode electrodes on switching between pure H₂ and 100 ppm CO in H₂ at $t=0$ min, $i=500$ mA cm⁻², 80 °C operation.

3. Results and discussion

The effect of CO in H₂ on the single cell performance is illustrated in Fig. 1, in which the cell voltage as a function of time following switching from H₂ to 100 ppm CO in H₂ is plotted for the three catalysts at a constant current density of 500 mA cm⁻². As previously reported for a similar set of catalysts [9], Pt has the greatest loss in performance, followed by PtRu and PtMo catalysts, both of which suffered much less significant decreases in performance. Similar measurements were conducted by switching to 25% CO₂ in H₂ and the losses in cell voltage for both experiments are reported in Table 2. In contrast to the performance in the presence of CO, the PtRu catalyst has a smaller loss of cell voltage than the PtMo when exposed to CO₂. Thus, PtRu is said to be less CO tolerant than PtMo, but more CO₂ tolerant.

The base voltammograms and those collected after CO adsorption at 0.125 V versus RHE of the three catalysts in the miniature PEM fuel cell are shown in Fig. 2. The data are in general agreement with the voltammograms for a similar set of catalysts as button electrodes obtained as flooded half cell electrodes in 1 mol dm⁻³ H₂SO₄ [9]. One significant difference is the presence of a positive off set in the currents observed in the base voltammograms of the catalysts as shown in Fig. 2. This off set is attributed to H₂ crossover from the cathode side of the cell, resulting in a hydrogen oxidation current. The magnitude of the crossover current, approximately 12 mA, is attributed to the thin membrane. In the case of the Pt electrode this crossover current was almost completely suppressed by the adsorption of CO, with only 14% of the original current remaining. However,

Table 2

Summary of voltage losses on switching from pure H₂ for the Pt, PtRu, and PtMo catalysts, $i=500$ mA cm⁻², 80 °C operation

Catalyst	Voltage loss (mV)	
	100 ppm CO in H ₂	25% CO ₂ in H ₂
Pt	485	31
PtRu	126	16
PtMo	51	45

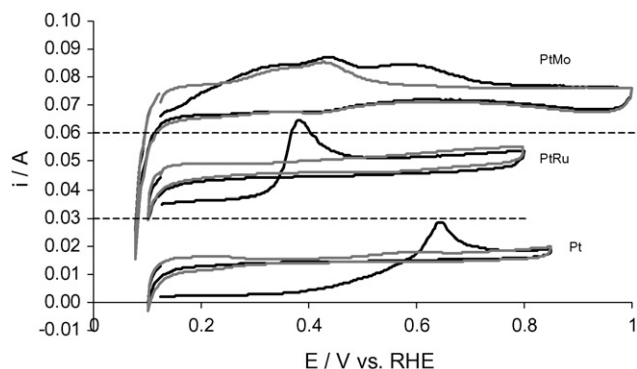


Fig. 2. Cyclic voltammetry of Pt, PtRu, and PtMo anodes after CO adsorption at 0.125 V, as MEA, 80 °C, 10 mV s⁻¹ sweep rate. Black line first cycle after CO exposure; grey line base voltammogram, N₂ purged throughout. The voltammograms have been off-set for clarity and the zero of the current for the PtRu and PtMo electrodes are indicated by dashed lines.

the suppression was not as complete in the case of the PtRu (33% remaining) and PtMo (57% remaining) electrodes. The retained hydrogen oxidation activity of the PtRu and PtMo electrodes may be attributed to either insufficient exposure to CO to obtain a full monolayer at the holding potential of 0.125 V or that some oxidation of CO can take place at potentials as low as the holding potential. The latter explanation may account for the improved CO tolerance of these two alloy catalysts when used as anodes in reformate fuelled PEM fuel cells as illustrated above.

Further examination of the voltammograms shows that the trend in the peak positions for CO electrooxidation for the catalysts is the same as that previously reported in sulphuric acid solution [9]; Pt > PtMo ≫ PtRu. However, the peak positions are shifted approximately -0.12 V compared to the half-cell measurements for the Pt and PtRu catalysts to 0.65 V and 0.39 V, respectively. Identifying the peak potential(s) for CO electrooxidation at the PtMo catalyst is complicated in the miniature PEM fuel cell by the presence of large peaks associated with a Mo redox couple, attributed to Mo(IV/VI) [5], centred at 0.44 V. However, an additional low potential shoulder is observed at 0.34 V and a second peak at 0.59 V. The low potential shoulder is not obvious in the voltammograms of the 35 wt%/5 wt% PtMo half cell electrode (Fig. 1 of reference [9]), but is apparent in the voltammograms of a series of PtMo electrodes of varying Pt:Mo ratio obtained in a fuel cell operating at 70 °C reported by Urian et al. [10]. The improved CO tolerance of PtMo catalysts has been attributed to CO being oxidised at a small number of sites in the 0.15–0.5 V region. The position of the second peak is 0.19 V more negative than that reported for the half cell measurements and 0.05 V more negative than that reported by Urian et al. The negative shift in potentials obtained in the fuel cell environments may be partially accounted for by the increased temperature of operation of the cells (the half cell measurements were conducted at room temperature) and/or a decrease in the coverage of CO on the catalysts in the fuel cell compared to that obtained in flooded electrolyte conditions, reflecting the decreased exposure time (3 min in this work compared to 15 min in the half cell), variations in the efficiency in which the CO contacts the surface of the catalyst particles, or

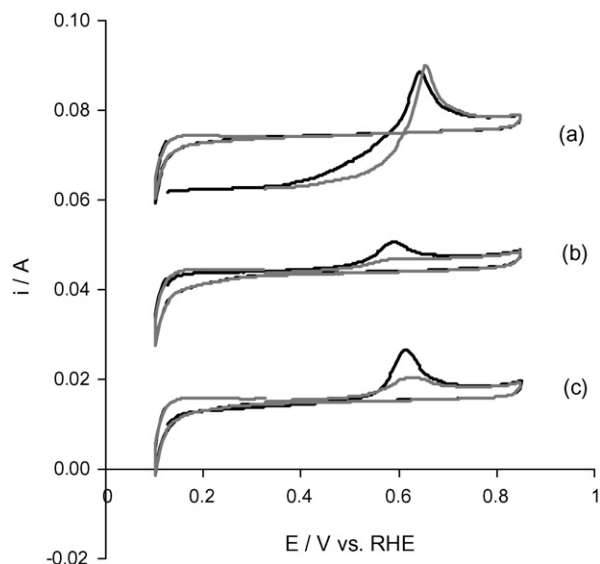


Fig. 3. Cyclic voltammetry of Pt electrode after exposure to (a) CO, (b) CO₂, and (c) 25% CO₂ in H₂ at 0.125 V (black line) and 0.325 V (grey line), as MEA, 80 °C, 10 mV s⁻¹ sweep rate. The voltammograms have been off-set for clarity.

an inherent decrease in the maximum coverage attainable in the presence of H₂, from crossover (this work) or in the gas mixture (Urian's work).

The effects of holding potential and dosing gas (CO, CO₂, or 25% CO₂ in H₂) on the amount of CO-like poisoning species adsorbed on each of the three catalysts are summarised in Figs. 3–5, for the Pt, PtRu, and PtMo catalysts, respectively. The charges associated with the electrooxidation of the CO-like species in the forward/positive going sweep of the voltammograms were determined by baseline correction of the voltammograms, using the currents between 0.15 V and 0.25 V to establish the baseline, and subsequent integration between

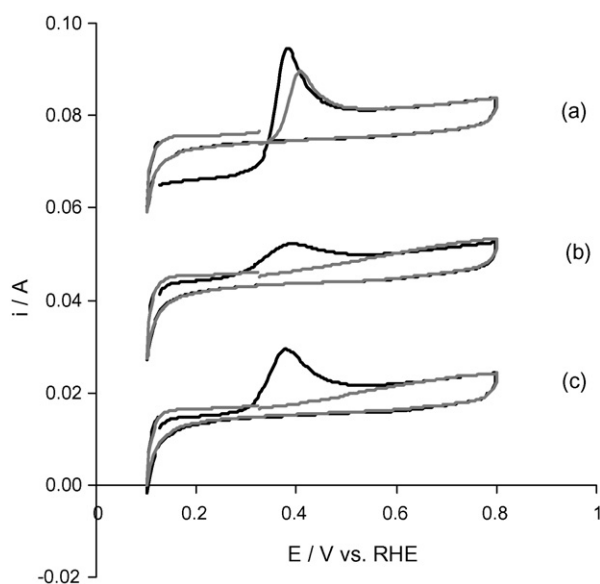


Fig. 4. Cyclic voltammetry of PtRu electrode after exposure to (a) CO, (b) CO₂, and (c) 25% CO₂ in H₂ at 0.125 V (black line) and 0.325 V (grey line), as MEA, 80 °C, 10 mV s⁻¹ sweep rate. The voltammograms have been off-set for clarity.

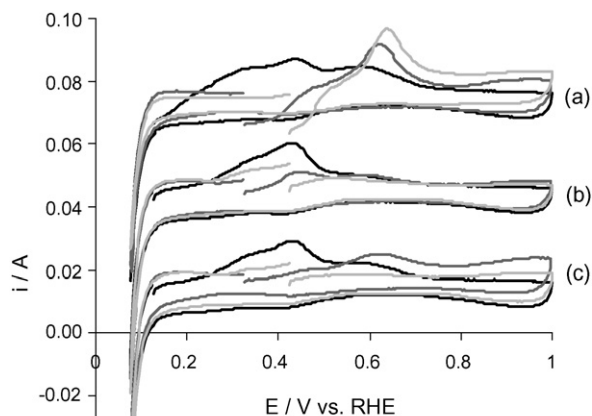


Fig. 5. Cyclic voltammetry of PtMo electrode after exposure to (a) CO, (b) CO₂, and (c) 25% CO₂ in H₂ at 0.125 V (black line), 0.325 V (grey line) and 0.425 V (light grey line) as MEA, 80 °C, 10 mV s⁻¹ sweep rate. The voltammograms have been off-set for clarity.

points that defined the main peak between 0.4 V and 0.7 V for the Pt and 0.3 V and 0.5 V for the PtRu catalysts. The presence of the broad peak associated with oxidation of Mo(IV) to Mo(VI) makes such an analysis more difficult for the PtMo electrode. In this case the voltammogram obtained on the third cycle, in which the peaks associated with the adsorbates were no longer present, was subtracted from the first cycle, followed by integration of any resulting peak in the forward scan of the difference voltammogram. The charges have not been converted to electrochemically active area (ECA cm² g⁻¹(Pt)) or electrochemical platinum surface area (EPSA cm²(Pt) cm⁻² (geometric)) values, as such conversion involves assumptions regarding the adsorption site(s) and identity of the CO-like species. It is likely that the adsorbed species are linearly and multiply bound CO, as recently reported in a combined SEIRAS and DEMS study by Smolinka et al. [13], although alternate species, such as adsorbed COH or COOH have been suggested on the basis of ¹⁴CO radiotracer measurements [16–21] and infrared studies [22,23]. In the discussion below, however, we will refer to the adsorbed species as CO for simplicity.

Exposure of the Pt electrode to CO (Fig. 3a) at 0.125 V approaches a full monolayer of adsorbed CO as evidenced by the near complete suppression of the H₂ crossover current, as described above. Increasing the holding potential to 0.325 V is accompanied by a slight decrease in the coverage (decrease in charge associated with the stripping peak), but this is not sufficient to restore the crossover current. The peak potential shifted to a slightly more positive value, which is the opposite direction expected for a reduced coverage [13,24], but may indicate that the remaining CO adlayer is more compact.

The CO coverages, as evidenced by the peak positions and associated charges, following exposure to CO₂ (Fig. 3b) and 25% CO₂ in H₂ (Fig. 3c) are significantly less than the maximum values obtained with CO. Greater coverages are obtained at 0.125 V than 0.325 V. These results are in excellent agree-

ment with those reported by Smolinka et al. [13]. The increased coverage of CO in the H-upd region suggests that adsorbed H is a key intermediate species in the reduction of CO₂ at Pt. This suggestion is further confirmed by the increased coverage in the presence of H₂, which is oxidised readily at the Pt surface at both potentials. In an experiment similar to that reported here, Urian et al. showed that CO is adsorbed following a 1 h exposure of a Pt/C MEA anode electrode to either CO₂ in H₂ (60 mol/40 mol ratio) or 100 ppm CO in H₂ [10]. However, and in contrast to the results reported here, they did not observe a decrease in coverage when comparing dosing with CO₂ compared to CO containing gas mixtures. The increased exposure time and/or decreased CO concentration used in their experiment may explain the differences with the results reported here. It is not possible to determine whether their results reflect a consistent, complete or partial monolayer coverage that was independent of the composition of the gas mixture. Regardless, the essential role of adsorbed H in the reduction of CO₂ was also confirmed in their work by comparing the CO coverage obtained following purging of the Pt/C electrode with CO₂ at 0.0 V and 0.225 V (see Fig. 6 of reference [10]).

Similar results to those for Pt were obtained for the PtRu electrode at 0.125 V as shown in Fig. 4 and Table 3; the CO coverage was greatest following exposure to pure CO, then the 25% CO₂ in H₂ mixture, and least for exposure to pure CO₂. However, in contrast to the Pt data, the peak potentials for the PtRu electrode are independent of the CO coverage. The rate-limiting step in the electrooxidative removal CO from such catalyst surfaces has been shown to be the activation of water [25]. At PtRu water activation occurs at lower potentials at the Ru sites on the catalyst surface. The surface composition of the 1:1 atomic ratio Pt:Ru catalyst used here has been shown to closely match that of the bulk [26]. Thus, the formation of a compact adlayer of CO adsorbed at Pt sites that are not in close proximity to Ru sites (and therefore more difficult to oxidise) is unlikely. Increasing the holding potential to 0.325 V in pure CO does result in a shift in the peak potential, although the shift is to a more positive potential. The onset of the peak in this voltammogram (Fig. 4a) is at the start of the forward sweep and, therefore, some oxidation of the CO adlayer had occurred during the holding period,

Table 3
Charges associated with electrooxidation of CO-like species derived from the cyclic voltammograms shown in Figs. 3–5 for the Pt, PtRu, and Pt electrodes, electrode area 3.14 cm², catalyst loading as in the text

Dosing gas	Holding potential (V) vs. RHE	Charge (C)		
		Pt	PtRu	PtMo
CO	0.125	0.420	0.345	0.155
	0.325	0.342	0.109	0.405
	0.425	–	–	0.454
CO ₂	0.125	0.085	0.094	0.153
	0.325	0.030	0	0.069
	0.425	–	–	0.007
25% CO ₂ /H ₂	0.125	0.093	0.173	0.313
	0.325	0.057	0	0.171
	0.425	–	–	0

with the more readily oxidised CO molecules being removed first, before the start of the potential sweep.

No evidence of adsorbed CO was found for the PtRu electrode upon exposure to either pure CO₂ or the 25% CO₂ in H₂ mixture at 0.325 V. The on-set potential for CO oxidation at the PtRu electrode, approximately 0.27 V, is such that any CO formed by reduction of CO₂ is removed by the end of the holding period. The increase in the CO coverage derived from CO₂ exposure in the presence of H₂ does continue to suggest that the presence of adsorbed hydrogen is required. Although no H-upd features are observed in the voltammetry of the PtRu electrodes, adsorbed H is likely to be present during H₂ electrooxidation.

As mentioned above, interpretation of the PtMo voltammograms is complicated by the presence of peaks attributed to the Mo(IV/VI) redox couple. These peaks are clearly evident in the voltammograms obtained after holding the potential at 0.125 V for all the dosing gases (the black lines in Fig. 5). In contrast to the results obtained for the Pt and PtRu electrodes, the CO coverage derived from exposure to pure CO at the PtMo electrode increased with increasing holding potential in the potential range investigated in this study. This anomalous behaviour is a reflection of the different mechanism by which alloying with Mo improves the CO tolerance of Pt compared to alloying with Ru. As discussed above, the effect of Ru is to lower the potential at which water is activated, the so-called bifunctional [27] or intrinsic [28] mechanism. The improvement upon alloying with Mo is attributed to a promotion mechanism [28] involving turn over of a Mo redox couple, attributed to Mo(IV/VI) [5], which either reduces the concentration of CO in the gas phase by acting as a water gas shift catalyst, as proposed by Ioroi et al. [29], or provides the activated oxygen species to remove CO from the Pt sites on the electrode surface. Such mechanisms, involving turn-over of the Mo(IV/VI) couple, will only remain active over a limited potential range [30], above which water activation, now at the Pt sites, is once again the source of the activated oxygen species. Thus, the increase in the CO coverage at higher holding potentials is attributed to a decrease in the activity of the Mo species in removing adsorbed CO as the potential is increased.

When the PtMo electrode was exposed to pure CO₂ (Fig. 4b) a decrease in the CO coverage was also observed as the holding potential is increased from 0.125 V to 0.325 V and at 0.425 V very little adsorbed CO is observed. The H-upd region on the PtMo electrode overlaps with Mo(IV/VI) couple and is not well resolved in the voltammogram of the MEA electrode reported here. Reference to voltammograms of a 35 wt%/5 wt% PtMo catalyst in 1 mol dm⁻³ H₂SO₄ reported previously [9] indicates that H is adsorbed in on the PtMo surface over a similar potential region to Pt. Thus, at 0.425 V very little adsorbed H is likely to be present.

When 25% CO₂ in H₂ was used as the dosing gas (Fig. 4c), the coverage of CO also decreased as the holding potential was increased. However, the coverage of CO after exposure at 0.125 V is significantly greater than that obtained when pure CO₂ or CO was used. This result agrees well with those reported by Ioroi et al. [29]. They investigated the effects of gas composition on the poisoning of a carbon supported mixed platinum and molybdenum oxide catalyst [31] and found that

the poisoning effect of 20% CO₂ in H₂ was as great as that obtained with 80 ppm CO in H₂, even though the thermodynamically derived equilibrium composition of the fully hydrated gas mixture would have only contained 11 ppm CO. From this, they surmised that the effect of the molybdenum species was to promote CO₂ reduction at the catalyst surface (the RWGS reaction), although they did not see an increase in the CO content of the gas at the anode outlet. The latter finding was attributed to a self-poisoning of the reaction at the catalyst surface, as the CO formed is effectively trapped on the catalyst surface.

The promotion effects of Mo in enhancing the RWGS reaction, observed as an increase in the CO coverage, are reduced at 0.325 V. Thus, we argue that the enhanced CO coverage obtained at 0.125 V in 25% CO₂ in H₂ may be attributed to suppression of the mechanism by which CO is removed from the surface. Removal of adsorbed CO relies on turn over of the Mo(IV/VI) couple. It appears that the increased concentration of H₂, as compared to that obtained by H₂ crossover, is sufficient to decrease the effectiveness of the Mo species in promoting CO electrooxidation. At 0.425 V no evidence of adsorbed CO was found when 25% CO in H₂ was used, thus confirming the need for adsorbed H to facilitate CO₂ reduction at the PtMo electrode as found above for the Pt and PtRu electrodes.

4. Conclusions

The cyclic voltammetric study presented here has enabled the identification of the origins of the differences in the CO and CO₂ tolerances of carbon supported PtRu and PtMo catalysts. The differences in CO tolerance in the PEMFC environment (PtMo more tolerant than PtRu) are attributed to the difference in mechanism by which the CO tolerance is improved compared to Pt; Ru enabling water activation at lower potentials, the intrinsic mechanism, and Mo serving as a promoter via the turn-over of the Mo(IV/VI) couple of Mo species on the surface of the bimetallic particles. The latter is activated at lower potentials, thereby enabling greater CO tolerance.

Deactivation of the catalysts in the presence of CO₂ occurs via reduction to form CO-like species, which poison the electrode surface. The extent of poisoning when pure CO₂ was used was generally less than that found for a similar exposure to pure CO for all three catalysts investigated, indicating that the rate of CO₂ reduction is not fast, possibly as a consequence of the need for a different initial adsorption site. The exception was the PtMo catalyst exposed to CO or CO₂ at 0.125 V, in which the same coverage was obtained. The potential dependence of the coverage of the CO species at all three catalysts (greater coverage obtained for CO₂ exposure in the H-upd region) indicates that adsorbed H is an important intermediate in the reaction, confirming that the likely mechanism is akin to the reverse water gas shift reaction. The increased coverage in the presence of H₂ supports Janssen's assertion that the non-Faradaic reaction dominates in the supply of adsorbed H under PEMFC conditions, with the potential dependence of the CO coverage reflecting the increased stability of adsorbed H in the H-upd region.

The origins of the decreased CO₂ tolerance of PtMo compared to its CO tolerance are attributed to the effects of H₂ on

the turn-over of the Mo(IV/VI) redox couple, which provides the CO tolerance of this catalyst. In the presence of H₂, turn-over of the redox couple is less facile at low potentials and the CO like species is able to accumulate. Full mitigation of the effect of H₂ was not observed until the potential was increased to 0.425 V, compared to 0.325 V at PtRu, and thus the CO₂ tolerance in reformate fuelled PEMFCs with PtMo is less than that with PtRu anode catalysts.

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