

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.

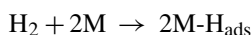
Voltammetric studies in acidic solution have indicated that deactivation of the Pt electrode surfaces in the presence of CO₂ is caused by the build up of a CO-like poison formed by the reduction of CO₂ in the presence of adsorbed hydrogen [12]. The reduction of CO₂ at Pt under PEMFC anode conditions 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 reformate tolerance was performed by switching the anode gas stream from pure H₂ to a reformate 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.

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