Electrochimica Acta 54 (2009) 5262–5266

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

In situ Ru K-edge EXAFS of CO adsorption on a Ru modified Pt/C fuel cell catalyst

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ARTICLE INFO

Article history:
Received 23 November 2008
Received in revised form 28 February 2009
Accepted 21 March 2009
Available online 28 March 2009

Keywords:
PtRu
Fuel cell catalysts
CO adsorption
Surface area
EXAFS

ABSTRACT

The Ru–CO bond of CO adsorbed on a Ru modified Pt/C fuel cell catalyst has been directly probed by *in situ* EXAFS at the Ru K-edge, providing evidence of a CO:metal surface atom ratio greater than 1:1 and that CO is adsorbed at bridging sites associated with Ru atoms at the surface of the catalyst nanoparticles. This result illustrates the limitations of single crystal models as representations of the bonding of adsorbed species at nanoparticle surfaces.

1. Introduction

Assessment of the intrinsic activities of carbon supported fuel cell catalysts relies on the *in situ* measurement of the true/accessible surface area of the metal nanoparticles when formulated into an ionomer bound electrocatalyst layer. *In situ* measurements are essential, as variations in the preparation method and ionomer content as well as hydration of the electrocatalyst layer will determine the fraction of the particles that are electrochemically accessible.

For Pt catalysts measurement of the charge associated with the adsorption of a monolayer of hydrogen atoms is routinely used, with one H atom corresponding to one surface Pt atom and an associated charge of 210 μC cm^{-2} being used to calculate the Pt surface area [1]. As discussed by Green and Kucernak [2], H adsorption and stripping is not suitable for the assessment of the area of many alloy catalysts such as PtRu, as the charge associated with H and other oxidation processes overlap or the H adsorption reaction is more complex due to the formation of bronzes or the absorption of H into the metal lattice. Thus, the electrooxidation of an adsorbed monolayer of CO is used as the preferred method for the *in situ* measurement of the surface area of such electrocatalysts [3]. It is generally assumed that the CO is bonded linearly to a single metal surface atom and, therefore, a 1:1 ratio between the number of adsorbed CO molecules and metal surface atoms exists with a charge of 420 μC cm^{-2} being used which is double that of the adsorbed H monolayer. This assumption has recently been called into question by Green and Kucernak [2] and ourselves [4], with a higher site occupancy of CO at the Ru surface atoms being suggested.

In this paper *in situ* EXAFS is used to directly probe the bonding of CO to Ru surface atoms on a Ru modified Pt/C electrocatalyst to probe the validity of the 1:1 CO to surface metal atom assumption.

2. Experimental

Preparation of the Ru modified Pt/C catalyst by the reaction of reduced 19.5 wt% Pt/C catalyst powder with a solution of ruthenocene in *n*-heptane was conducted, as has been described previously [4,5], to provide a coverage equivalent to 1.5 monolayers of Ru on the Pt surface. Briefly, the 19.5 wt% Pt/C catalyst powder was reduced by heating in H_2 at 200 °C for 3 h and then exposed to the required amount of ruthenocene dissolved in *n*-heptane to yield a coverage of 0.75 monolayers of Ru based on the known dispersion (fraction of surface atoms) of the base Pt/C catalyst. H_2 was then purged through the resulting dispersion for 24 h at room temperature, followed by 8 h at 98 °C. The mixture was filtered, washed with clean *n*-heptane, and then dried in air. The process was repeated to give a final (theoretical) coverage of 1.5 monolayers of Ru on the Pt/C. The final ruthenium modified catalysts composition was determined by ICP-AES and found to be 17.86 wt% Pt, 5.29 wt% Ru,

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0013-4686/$ – see front matter
doi:10.1016/j.electacta.2009.03.060

which corresponds to a coverage of 1.4 monolayers and a Pt:Ru atomic ratio of 1:0.59.

The resulting catalyst and the base Pt/C were characterised by XRD, TEM, and CO chemisorption. The XRD patterns corresponded to an fcc structure, characteristic of a PtRu alloy. No evidence of a separate amorphous or crystalline Ru phase was found. Sherrer analysis of the XRD pattern, corrected for the instrumental broadening, of the Ru/Pt/C catalyst yielded an average crystallite size of 4.9 nm based on the arithmetic mean from four reflections, compared to a diameter of 3.8 nm for the Pt/C. The average particle sizes, determined by analysis of the TEM images (not shown), were 4.2 and 2.8 nm for the Ru/Pt/C and Pt/C catalysts, respectively. The CO chemisorption measurements were conducted as follows. A quantity of the dry catalyst powder was loaded into a quartz tube and precisely weighed; 0.0607 g of the Pt/C and 0.0584 g of the Ru/Pt/C catalyst was used. The tubes were loaded into the CO chemisorption apparatus, purged with He for a minimum of 30 min and then pretreated by heating to 50 °C whilst purging with H_2 for 30 min followed by cooling to room temperature whilst maintaining the H_2 flow to remove any surface oxidation of the metal nanoparticles, which occurs upon exposure and subsequent storage of the catalysts in air. CO was then introduced and the uptake measured volumetrically.

Electrodes were prepared from an ink containing the catalyst powder (either the 19.5 wt% Pt/C base catalyst or the Ru modified Pt/C) and an alcoholic solution of Nafion as a binder (to provide 15 wt% Nafion in the final electrode and a loading of 5 mg Pt cm^{-2} of prepared electrode area) which was spread onto wet proofed carbon paper (E-TEK TGPH-90), and the resulting sheet pressed at 10 kg cm^{-2} for 3 min at 100 °C. Circular electrodes were cut from the compressed sheet and boiled in triply distilled water to ensure a fully flooded state prior to both the electrochemical and EXAFS measurements.

The cells and methods used for collection of cyclic voltammograms (CVs) and *in situ* EXAFS measurements (station 16.5 of the SRS, Daresbury), as well as the data analysis techniques have been described previously [4,6]. Both CVs and the EXAFS measurements were conducted in 1 mol dm^{-3} H_2SO_4 solution. The EXAFS data was collected in fluorescence mode using a 30-element Ge solid-state detector. CO monolayer oxidation CVs were obtained by bubbling CO through the electrolyte for 30 min at 0.05 V, followed by purging with N_2 for a further 30 min before the CV was collected. EXAFS data were obtained prior to CO exposure in un-purged electrolyte, with CO adsorbed in the presence of CO saturated solution, and after oxidative stripping of the adsorbed CO in un-purged solution by exchanging the electrolyte in the EXAFS cell.

3. Results and discussion

Cyclic voltammograms of both the Pt/C and the modified, Ru/Pt/C, catalyst electrodes in 1 mol dm^{-3} H_2SO_4 are shown in Fig. 1. As reported in an earlier study of such a Ru/Pt/C catalyst, the CV of the modified catalyst is dominated by a relatively large capacitative current compared to that of the Pt/C catalyst [5]. The hydrogen adsorption/desorption peaks between 0.0 and 0.25 V are also much less distinct in the Ru/Pt/C CV and the peak associated with oxide stripping is shifted to 0.45 from 0.75 V observed in the Pt/C CV (compare the black lines in Fig. 1a and B). As discussed in the introduction, this loss of resolution in hydrogen region is characteristic of PtRu alloy catalysts. The shift in the oxide stripping peaks is also indicative of the presence of Ru at the surface of the catalyst particles. The position of the CO stripping peak (maximum) provides further evidence of the surface composition of the Ru/Pt/C catalyst; 0.62 V for Ru/Pt/C and 0.79 V for Pt/C. In a recent study of the effects of the composition of conventionally prepared monometallic Ru/C and Pt/C catalysts and a series of bimetallic PtRu/C catalysts, we have shown that the peak potential for CO monolayer oxidation decreases from 0.57 V for Ru/C to 0.48 V for 1:1 PtRu/C and then increases again to 0.79 V for Pt/C [7]. The large capacitative current and the 0.62 V peak potential for the oxidation of the CO monolayer observed in the CVs of the Ru/Pt/C catalyst are, therefore, indicative of a Ru rich PtRu surface. This suggests that some of the Ru is driven below the surface of the metal particle following reduction of the modified surface, either electrochemically or during the reduction steps in the two deposition steps. This result is not surprising, as it has been shown by Ruban et al. [8] that the surface segregation energy for a Ru overlayer on a Pt substrate is such that the Ru will preferentially move away from the surface, and is in agreement with our earlier study of the effects of reduction on the composition of the Ru modified Pt/C catalysts [4,5].

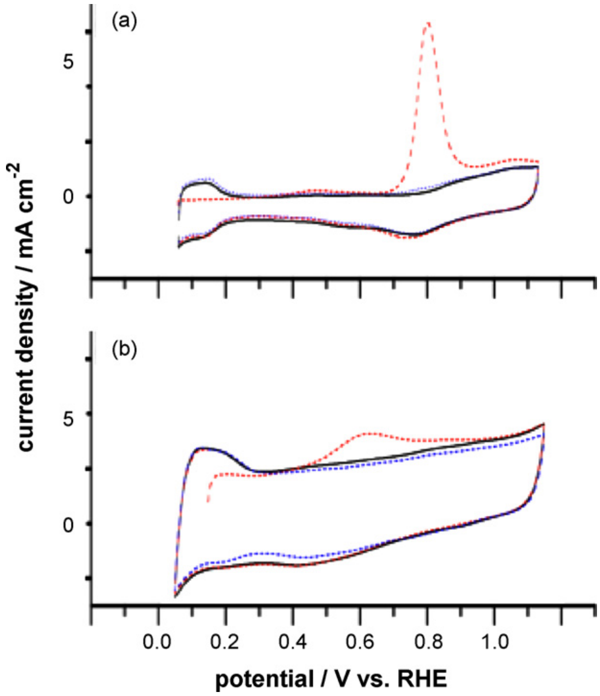

Fig. 1. Cyclic voltammograms of (a) Pt/C and (b) Ru/Pt/C electrodes recorded at 10 mV s^{-1} in 1.0 mol dm^{-3} H_2SO_4 at 25 °C. Black solid line before CO adsorption, red dashed line CO stripping voltammogram and blue dotted line second cycle after CO stripping. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article)

The CO monolayer oxidation CVs were used to determine the surface areas of the catalyst electrodes by subtraction of the second cycle CVs (black lines in Fig.1 a and b) from the first cycle (red lines in Fig. 1a and b), in which the monolayer of adsorbed CO was oxidised, thereby reducing the effects of anion adsorption and capacitance, which have been commented on by Jusys et al. [9]. A charge of 420 °C cm_{Pt}^{-1} was assumed. The surface area normalised to the mass of Pt on the electrode of the Pt/C base catalyst was 102 $m^2\,g_{Pt}^{-1}$ and 154 $m^2\,g_{Pt}^{-1}$ for the Ru modified Pt/C catalyst, which corresponds to 110 $m^2\,g_{Pt+Ru}^{-1}$. The surface areas were also determined by CO chemisorption. A value of 92.3 $m^2\,g_{Pt}^{-1}$ was found for the Pt/C, corresponding to a value of CO:M of 0.37. For the Ru/Pt/C catalyst a value of 180.4 $m^2\,g_{Pt}^{-1}$, corresponding to a CO:M value of 0.66 based on the Pt content, which equates to 128.8 g_{Pt+Ru}^{-1} or a value of 0.47 based on the Pt + Ru content. Both results indicate a greater dispersion/decrease in particle size following modification of the parent Pt/C catalyst by Ru, which is opposite to increase in particle or crystallite size observed in both TEM and XRD data, respectively. Previously we have interpreted this discrepancy as

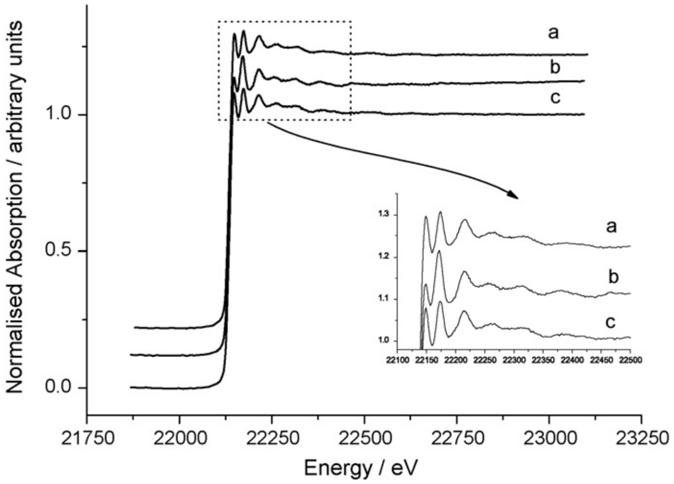

Fig. 2. Ru K edge XAS for Ru modified Pt/C at 0.0 V vs. RHE in 1 mol dm^{-3} H_2SO_4. (a) before CO exposure, (b) with adsorbed CO, (c) after CO stripping.

evidence of a breakdown of the assumption of a 1:1 CO:metal surface atom ratio which is commonly employed in the analysis of both the CO monolayer oxidation CVs and chemisorption data [5], an assumption that has also been questioned by Green and Kucernak, in a study of unsupported PtRu catalyts [2] where they attributed the increase in surface area/dispersion to the adsorption of more than one CO per Ru surface atom.

The coordination of CO to Ru in the Ru/Pt/C catalysts was further investigated using *in situ* EXAFS measurements. Fig. 2 shows the Ru K-edge XAS data collected at 0.0 V vs. RHE before purging the solution with CO, in the presence of a saturated CO solution, and after removing the adsorbed CO from the electrode surface by oxidative stripping. The inset highlights the differences in the relative amplitudes of the edge peak, at 22,150 eV, and the peak of the first oscillation, at 22,175 eV, as the conditions were varied. The increase in the relative amplitude of the peak at 22,175 eV in the presence of CO agrees well with an increase in the number of neighbours with low atomic mass in the first coordination shell of the Ru, such as the C of adsorbed CO and is in excellent agreement with the Ru K-edge XANES study of CO adsorbed on a $Pt_{50}Ru_{50}$ catalyst electrode surface by Aberdam et al. [10].

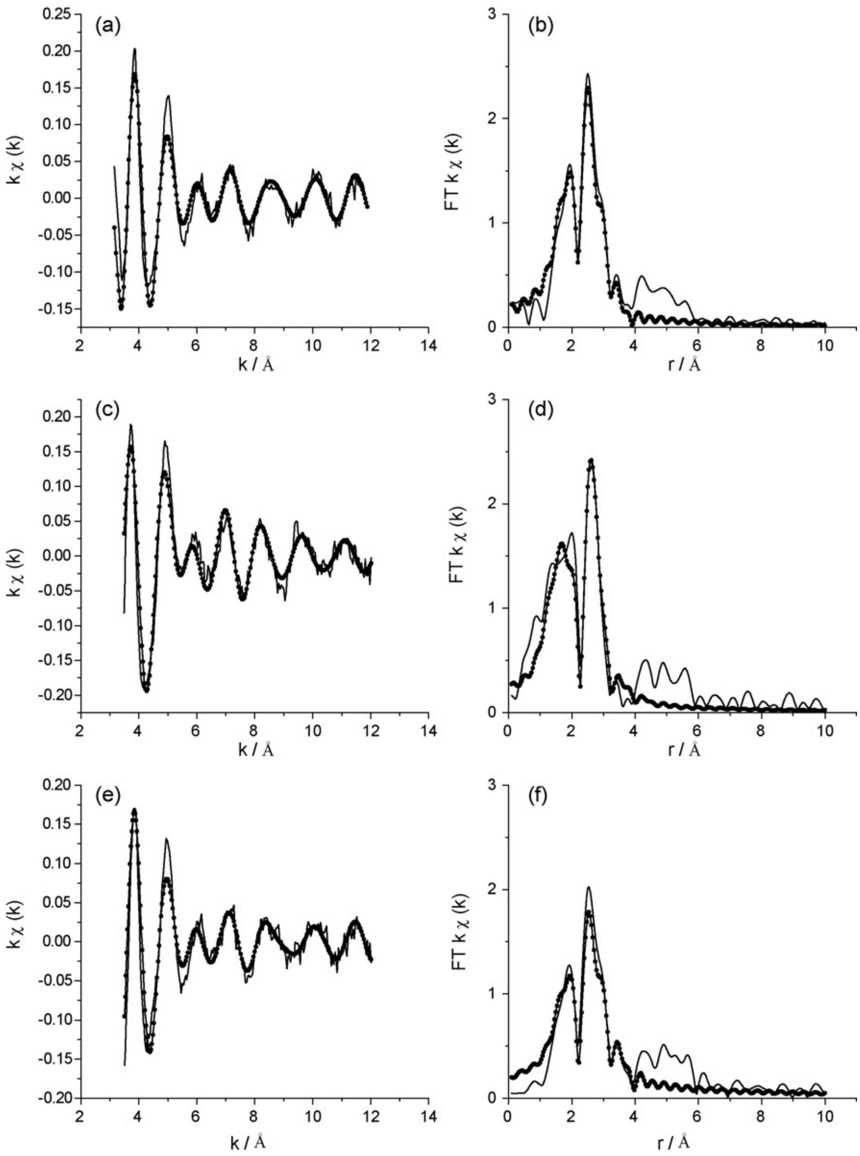

Fig. 3. *k* weighted Ru K edge EXAFS (a, c, and e) and the corresponding Fourier transforms (b, d, and f) for Ru modified Pt/C at 0.0 V vs. RHE in 1 mol dm^{-3} H_2SO_4. (a and b) before CO exposure, (c, d) with adsorbed CO, (e, f) after CO stripping. Data shown as thin solid lines and fits as dotted lines.

Table 1
EXAFS fitting parameters for the Ru modified Pt/C catalyst electrode at 0.0 V vs. RHE as a function of the CO exposure. Data collected at the Ru K edge *in situ* in 1 mol dm^{-3} H_2SO_4. Standard deviations of the parameters given in brackets.

CO exposure	Neighbour	*N*	*R* (Å)	$2\sigma^2$ (Å)^2	*Ef* (eV)	R_{exaf} (%)
Before	Ru–Ru	3.1 (0.2)	2.63 (0.01)	0.015 (0.002)		
	Ru–Pt	2.1 (0.2)	2.69 (0.01)	0.010 (0.002)		
	Ru–Pt	0.5 (0.9)	3.83 (0.16)	0.018 (0.033)		
					−12.1 (0.5)	37
Solution saturated with CO	Ru–C	1.4 (0.3)	2.04 (0.02)	0.024 (0.008)		
	Ru–Ru	3.7 (0.3)	2.71 (0.01)	0.015 (0.001)		
	Ru–Pt	2.0 (0.3)	2.74 (0.01)	0.010 (0.002)		
	Ru–Pt	3.2 (1.6)	3.91 (0.04)	0.024 (0.008)		
					−1.5 (0.9)	39
After CO stripping	Ru–Ru	3.1 (0.2)	2.64 (0.01)	0.017 (0.001)		
	Ru–Pt	2.2 (0.2)	2.70 (0.01)	0.010 (0.002)		
	Ru–Pt	1.0 (1.1)	3.80 (0.07)	0.019 (0.015)		
					−2.1 (0.6)	43

The isolated Ru K-edge EXAFS data and the corresponding Fourier transforms are shown in Fig. 3. The data collected before CO exposure and following the removal of the adsorbed CO yield EXAFS and Fourier transforms that are identical within experimental error, indicating that no significant restructuring of the catalyst particles accompanied the adsorption and removal of CO. Analysis of the data, shown in Table 1, indicates that the average coordination surrounding the Ru atoms is composed of 3.1 Ru atoms at 2.63 Å and 2.1 Pt atoms at 2.70 Å in the first coordination shell. The presence of Ru and Pt neighbours in the first coordination shell and the absence of O or other neighbours of low atomic mass in the EXAFS of the electrochemically reduced catalyst demonstrates that the Ru is selectively deposited onto the supported Pt particles during the preparation of the catalyst and is not present as a separate amorphous Ru oxide phase within the experimental error [4].

In the presence of CO, the coordination numbers of the Ru and Pt neighbours remain unchanged within the experimental error from those in the absence of CO. In addition, 1.4 low atomic number neighbours, whom we have attributed to C of adsorbed CO, are found at 2.04 Å. The structural parameters obtained from the analysis of EXAFS data provide the average, per atom, coordination environment surrounding the absorber atoms. Thus, a full monolayer of linearly bound CO adsorbed on particles with a surface of equal numbers of Pt and Ru atoms should have a C coordination number equal to the fraction of metal atoms on the surface based on the assumption that there is one linearly bound CO per surface metal atom; for example a M–C coordination number equal to 0.5 is expected for a catalyst with a dispersion of 50%, as we found previously for CO adsorbed on a Pt/C catalyst [6]. As indicated by the CO monolayer oxidation peak, the surface of the Ru/Pt/C catalyst is enriched in Ru compared to 1:1 PtRu/C alloy catalyst and, thus, the predicted coordination number is expected to be slightly greater than the CO:M ratios determined from the CO chemisorption measurements. Even if all the Ru atoms were segregated to the surface (an assumption not supported by the metal coordination numbers obtained by analysis of the EXAFS data) the Ru–C coordination number cannot be greater than 1 for a full monolayer of linearly adsorbed CO molecules.

The distances obtained from the EXAFS analysis provide further insights into the coordination of CO to the catalyst surface. In our previous study of CO adsorption on a Pt/C catalyst, a Pt–C distance of 1.85 Å was found and attributed to linearly bound CO. The 2.04 Å distance for the Ru–C shell found in the current study is more indicative of bridge bound than linearly bound CO. In an EXAFS study of a ruthenium carbonyl hydroformylation catalyst, Evans et al. obtained Ru–C distances of 1.94 Å for linearly bound CO and 2.17 Å for the bridge bound species [11]. Such bridging coordination is typical of metal carbonyl clusters [12], where a combination of linear and bridging CO ligands encapsulate the metal cluster. Such bridging CO ligands, in particular, stabilise the formation of M–M bonds. The metal nanoparticles comprising the Ru/Pt/C catalyst in the current study are considerably larger than the cores of such cluster compounds and it is hard to envisage a surface covered by bridge bound CO species. However, if the adsorbed CO molecules at the Ru atoms at the edges of the faces of the particles were to be bridge bound, this would make up a considerable fraction of the total number of Ru–C interactions. Additionally, more than one CO molecule may be bound to the individual Ru atoms at the verticies of the nanoparticles, as is the case for the cluster compounds. Such a high coverage of CO is likely to have an effect on the metal–metal distance of the outermost layer of metal atoms in the nanoparticle and, indeed, we observe a slight increase in the Ru–Ru and Ru–Pt distances compared to those obtained in the absence of adsorbed CO.

4. Conclusions

The surface areas obtained using either CO chemisorption or the electrochemical stripping of an adsorbed CO monolayer are commonly used to characterise carbon supported Pt and Pt based alloy electrocatalysts and the results are often used to normalise electrocatalytic activity to obtain specific activities. In calculating the surface areas from such measurements assumptions are made regarding the adsorption site and/or site occupancy of adsorbed CO and the coverage that constitutes a full monolayer. The numbers employed are based on careful studies of the adsorption of CO on single crystal surfaces, both in UHV and in the electrochemical environment. The combined electrochemical and EXAFS results presented above provide direct evidence that the picture of adsorbed CO derived from such single crystal studies may not be directly translatable to the realm of supported nanoparticle electrocatalysts and may provide inaccurate determinations of the surface area and/or the size of the nanoparticles comprising the catalyst. In the case of the Ru/Pt/C catalyst described above, the areas determined from both CO chemisorption and the CO stripping voltammogram are likely to be over-estimations of the electrochemically active area of the catalyst.

Acknowledgements

The EPSRC are thanked for funding studentships for AR, CRK, and RJKW and postdoctoral fellowship for MKR, and CLRC for access to the SRS. The Open University is thanked for funding the studentship for YQ. Johnson Matthey is also thanked for their financial support. The technical assistance of Chris Corrigan at the SRS is also appreciated.

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