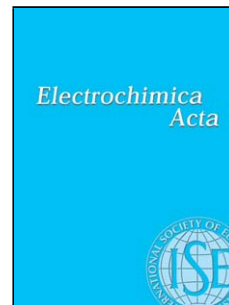


Accepted Manuscript

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

Authors: Abigail Rose, Robert Bilborrow, Colin R. King, M.K. Ravikumar, Yangdong Qian, Richard J.K. Wiltshire, Eleanor M. Crabb, Andrea E. Russell



PII: S0013-4686(09)00445-9
DOI: doi:10.1016/j.electacta.2009.03.060
Reference: EA 14527

To appear in: *Electrochimica Acta*

Received date: 23-11-2008
Revised date: 28-2-2009
Accepted date: 21-3-2009

Please cite this article as: A. Rose, R. Bilborrow, C.R. King, M.K. Ravikumar, Y. Qian, R.J.K. Wiltshire, E.M. Crabb, A.E. Russell, *In situ* Ru K-edge EXAFS of CO adsorption on a Ru modified Pt/C fuel cell catalyst, *Electrochimica Acta* (2008), doi:10.1016/j.electacta.2009.03.060

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

1
2
3 ***In situ* Ru K-edge EXAFS of CO adsorption on a Ru modified Pt/C**
4 **fuel cell catalyst**
5

6 Abigail Rose^{‡a}, Robert Bilsborrow^c, Colin R. King^a, M.K. Ravikumar^b,
7
8 Yangdong Qian^b, Richard J.K. Wiltshire^a, Eleanor M. Crabb^b, and
9
10
11 Andrea E. Russell ^{*a,1}
12

13
14 ^a School of Chemistry, University of Southampton, Highfield, Southampton, SO17
15 1BJ, UK
16

17
18 ^b Department of Chemistry, The Open University, Walton Hall,, Milton Keynes,
19 MK7 6AA, UK
20

21
22 ^c Science and Technology Facilities Council, Daresbury Laboratory, Warrington,
23
24 WA4 4AD, UK
25

26
27 **Abstract**
28

29
30 The Ru-CO bond of CO adsorbed on a Ru modified Pt/C fuel cell catalyst has been
31
32 directly probed by *in situ* EXAFS at the Ru K-edge, providing evidence of a
33
34 CO:metal surface atom ratio greater than 1:1 and that CO is adsorbed at bridging sites
35
36 associated with Ru atoms at the surface of the catalyst nanoparticles.. This result
37
38
39
40
41
42
43

44
45
46
47
48
49
50
51
52
53 ISE member

54
55 * corresponding author, email: a.e.russell@soton.ac.uk, tel: +44 (0)23 8059 3306,
56

57 fax: +44 (0)23 8059 3781
58

59
60 [‡]Present address: Physical Sciences Department, Dstl Porton Down, Salisbury
61 SP4 0JQ, UK
62
63
64
65

1 illustrates the limitations of single crystal models as representations of the bonding of
2 adsorbed species at nanoparticle surfaces.
3

4 5 **1. Introduction**

6
7
8
9 Assessment of the intrinsic activities of carbon supported fuel cell catalysts relies on
10 the *in situ* measurement of the true/accessible surface area of the metal nanoparticles
11 when formulated into an ionomer bound electrocatalyst layer. *In situ* measurements
12 are essential, as variations in the preparation method and ionomer content as well as
13 hydration of the electrocatalyst layer will determine the fraction of the particles that
14 are electrochemically accessible.
15
16
17
18
19
20
21
22
23

24 For Pt catalysts measurement of the charge associated with the adsorption of a
25 monolayer of hydrogen atoms is routinely used, with one H atom corresponding to
26 one surface Pt atom and an associated charge of $210 \mu\text{C cm}^{-2}$ being used to calculate
27 the Pt surface area [1]. As discussed by Green and Kucernak [2], H adsorption and
28 stripping is not suitable for the assessment of the area of many alloy catalysts such as
29 PtRu, as the charge associated with H and other oxidation processes overlap or the H
30 adsorption reaction is more complex due to the formation of bronzes or the absorption
31 of H into the metal lattice. Thus, the electrooxidation of an adsorbed monolayer of
32 CO is used as the preferred method for the *in situ* measurement of the surface area of
33 such electrocatalysts [3]. It is generally assumed that the CO is bonded linearly to a
34 single metal surface atom and, therefore, a 1:1 ratio between the number of adsorbed
35 CO molecules and metal surface atoms exists with a charge of $420 \mu\text{C cm}^{-2}$ being
36 used which is double that of the adsorbed H monolayer. This assumption has recently
37 been called into question by Green and Kucernak [2] and ourselves [4], with a higher
38 site occupancy of CO at the Ru surface atoms being suggested.
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 In this paper *in situ* EXAFS is used to directly probe the bonding of CO to Ru surface
2 atoms on a Ru modified Pt/C electrocatalyst to probe the validity of the 1:1 CO to
3
4 surface metal atom assumption.
5
6

7 **2. Experimental**

8
9
10 Preparation of the Ru modified Pt/C catalyst by the reaction of reduced 19.5 wt% Pt/C
11 catalyst powder with a solution of ruthenocene in *n*-heptane was conducted, as has
12
13 been described previously [4, 5], to provide a coverage equivalent to 1.5 monolayers
14
15 of Ru on the Pt surface. Briefly, the 19.5 wt% Pt/C catalyst powder was reduced by
16
17 heating in H₂ at 200 °C for 3 hours and then exposed to the required amount of
18
19 ruthenocene dissolved in *n*-heptane to yield a coverage of 0.75 monolayers of Ru
20
21 based on the known dispersion (fraction of surface atoms) of the base Pt/C catalyst.
22
23 H₂ was then purged through the resulting dispersion for 24 hrs at room temperature,
24
25 followed by 8 hrs at 98 °C. The mixture was filtered, washed with clean *n*-heptane,
26
27 and then dried in air. The process was repeated to give a final (theoretical) coverage
28
29 of 1.5 monolayers of Ru on the Pt/C. The final ruthenium modified catalysts
30
31 composition was determined by ICP-AES and found to be 17.86 wt% Pt, 5.29 wt%
32
33 Ru, which corresponds to a coverage of 1.4 monolayers and a Pt:Ru atomic ratio of
34
35 1:0.59.
36
37

38 The resulting catalyst and the base Pt/C were characterised by XRD, TEM, and CO
39
40 chemisorption. The XRD patterns corresponded to an fcc structure, characteristic of a
41
42 PtRu alloy. No evidence of a separate amorphous or crystalline Ru phase was found.
43
44 Sherrer analysis of the XRD pattern, corrected for the instrumental broadening, of the
45
46 Ru/Pt/C catalyst yielded an average crystallite size of 4.9 nm based on the arithmetic
47
48 mean from four reflections, compared to a diameter of 3.8 nm for the Pt/C. The
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 average particle sizes, determined by analysis of the TEM images (not shown), were
2 4.2 and 2.8 nm for the Ru/Pt/C and Pt/C catalysts, respectively. The CO
3
4 chemisorption measurements were conducted as follows. A quantity of the dry
5
6 catalyst powder was loaded into a quartz tube and precisely weighed; 0.0607 g of the
7
8 Pt/C and 0.0584 g of the Ru/Pt/C catalyst was used. The tubes were loaded into the
9
10 CO chemisorption apparatus, purged with He for a minimum of 30 minutes and then
11
12 pretreated by heating to 50 °C whilst purging with H₂ for 30 minutes followed by
13
14 cooling to room temperature whilst maintaining the H₂ flow to remove any surface
15
16 oxidation of the metal nanoparticles, which occurs upon exposure and subsequent
17
18 storage of the catalysts in air. CO was then introduced and the uptake measured
19
20
21 volumetrically.
22
23
24
25

26
27 Electrodes were prepared from an ink containing the catalyst powder (either the 19.5
28
29 wt% Pt/C base catalyst or the Ru modified Pt/C) and an alcoholic solution of Nafion
30
31 as a binder (to provide 15 wt% Nafion in the final electrode and a loading of 5 mg Pt
32
33 cm⁻² of prepared electrode area) which was spread onto wet proofed carbon paper (E-
34
35 TEK TGPH-90), and the resulting sheet pressed at 10 kg cm⁻² for 3 minutes at 100°C.
36
37 Circular electrodes were cut from the compressed sheet and boiled in triply distilled
38
39 water to ensure a fully flooded state prior to both the electrochemical and EXAFS
40
41 measurements.
42
43
44
45

46
47 The cells and methods used for collection of cyclic voltammograms (CVs) and *in situ*
48
49 EXAFS measurements (station 16.5 of the SRS, Daresbury), as well as the data
50
51 analysis techniques have been described previously [4, 6]. Both CVs and the EXAFS
52
53 measurements were conducted in 1 mol dm⁻³ H₂SO₄ solution. The EXAFS data was
54
55 collected in fluorescence mode using a 30-element Ge solid-state detector. CO
56
57 monolayer oxidation CVs were obtained by bubbling CO through the electrolyte for
58
59
60
61
62
63
64
65

1 30 minutes at 0.05 V, followed by purging with N₂ for a further 30 minutes before the
2 CV was collected. EXAFS data were obtained prior to CO exposure in un-purged
3 electrolyte, with CO adsorbed in the presence of CO saturated solution, and after
4 oxidative stripping of the adsorbed CO in un-purged solution by exchanging the
5 electrolyte in the EXAFS cell.
6
7
8
9
10

11 **Results and Discussion**

12
13
14
15
16 Cyclic voltammograms of both the Pt/C and the modified, Ru/Pt/C, catalyst electrodes
17 in 1 mol dm⁻³ H₂SO₄ are shown in figure 1. As reported in an earlier study of such a
18 Ru/Pt/C catalyst, the CV of the modified catalyst is dominated by a relatively large
19 capacitive current compared to that of the Pt/C catalyst [5]. The hydrogen
20 adsorption/desorption peaks between 0.0 and 0.25 V are also much less distinct in the
21 Ru/Pt/C CV and the peak associated with oxide stripping is shifted to 0.45 V from the
22 0.75 V observed in the Pt/C CV (compare the black lines in figures 1 b and a). As
23 discussed in the introduction, this loss of resolution in hydrogen region is
24 characteristic of PtRu alloy catalysts. The shift in the oxide stripping peaks is also
25 indicative of the presence of Ru at the surface of the catalyst particles. The position of
26 the CO stripping peak (maximum) provides further evidence of the surface
27 composition of the Ru/Pt/C catalyst; 0.62 V for Ru/Pt/C and 0.79 V for Pt/C. In a
28 recent study of the effects of the composition of conventionally prepared
29 monometallic Ru/C and Pt/C catalysts and a series of bimetallic PtRu/C catalysts, we
30 have shown that the peak potential for CO monolayer oxidation decreases from 0.57
31 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].
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 surface of the metal particle following reduction of the modified surface, either
2 electrochemically or during the reduction steps in the two deposition steps. This result
3 is not surprising, as it has been shown by Ruban, Skriver, and Norskov [8] that the
4 surface segregation energy for a Ru overlayer on a Pt substrate is such that the Ru will
5 preferentially move away from the surface, and is in agreement with our earlier study
6 of the effects of reduction on the composition of the Ru modified Pt/C catalysts [4, 5].
7

8
9
10
11
12
13
14
15 The CO monolayer oxidation CVs were used to determine the surface areas of the
16 catalyst electrodes by subtraction of the second cycle CVs (black lines in figures 1 a
17 and b) from the first cycle (red lines in figures 1 a and b), in which the monolayer of
18 adsorbed CO was oxidised, thereby reducing the effects of anion adsorption and
19 capacitance, which have been commented on by Jusys *et al* [9]. A charge of $420 \mu\text{C}$
20 $\text{cm}_{\text{Pt}}^{-2}$ was assumed. The surface area normalised to the mass of Pt on the electrode of
21 the Pt/C base catalyst was $102 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ and $154 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ for the Ru modified Pt/C
22 catalyst, which corresponds to $110 \text{ m}^2 \text{ g}_{\text{Pt+Ru}}^{-1}$. The surface areas were also determined
23 by CO chemisorption. A value of $92.3 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ was found for the Pt/C, corresponding
24 to a value of CO:M of 0.37. For the Ru/Pt/C catalyst a value of $180.4 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$,
25 corresponding to a CO:M value of 0.66 based on the Pt content, which equates to
26 $128.8 \text{ g}_{\text{Pt+Ru}}^{-1}$ or a value of 0.47 based on the Pt+Ru content. Both results indicate a
27 greater dispersion/decrease in particle size following modification of the parent Pt/C
28 catalyst by Ru, which is opposite to increase in particle or crystallite size observed in
29 both TEM and XRD data, respectively. Previously we have interpreted this
30 discrepancy as evidence of a breakdown of the assumption of a 1:1 CO:metal surface
31 atom ratio which is commonly employed in the analysis of both the CO monolayer
32 oxidation CVs and chemisorption data [5], an assumption that has also been
33 questioned by Green and Kucernak, in a study of unsupported PtRu catalyts [2] where
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 they attributed the increase in surface area/dispersion to the adsorption of more than
2 one CO per Ru surface atom.
3

4
5 The coordination of CO to Ru in the Ru/Pt/C catalysts was further investigated using
6 *in situ* EXAFS measurements. Figure 2 shows the Ru K-edge XAS data collected at
7 0.0 V vs. RHE before purging the solution with CO, in the presence of a saturated CO
8 solution, and after removing the adsorbed CO from the electrode surface by oxidative
9 stripping. The inset highlights the differences in the relative amplitudes of the edge
10 peak, at 22150 eV, and the peak of the first oscillation, at 22175 eV, as the conditions
11 were varied. The increase in the relative amplitude of the peak at 22175 eV in the
12 presence of CO agrees well with an increase in the number of neighbours with low
13 atomic mass in the first coordination shell of the Ru, such as the C of adsorbed CO
14 and is in excellent agreement with the Ru K-edge XANES study of CO adsorbed on a
15 Pt₅₀Ru₅₀ catalyst electrode surface by Aberdam *et al.* [10].
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31

32
33 The isolated Ru K-edge EXAFS data and the corresponding Fourier transforms are
34 shown in figure 3. The data collected before CO exposure and following the removal
35 of the adsorbed CO yield EXAFS and Fourier transforms that are identical within
36 experimental error, indicating that no significant restructuring of the catalyst particles
37 accompanied the adsorption and removal of CO. Analysis of the data, shown in table
38 1, indicates that the average coordination surrounding the Ru atoms is composed of
39 3.1 Ru atoms at 2.63 Å and 2.1 Pt atoms at 2.70 Å in the first coordination shell. The
40 presence of Ru and Pt neighbours in the first coordination shell and the absence of O
41 or other neighbours of low atomic mass in the EXAFS of the electrochemically
42 reduced catalyst demonstrates that the Ru is selectively deposited onto the supported
43 Pt particles during the preparation of the catalyst and is not present as a separate
44 amorphous Ru oxide phase within the experimental error [4].
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

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, which 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 can not 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

1 bridging coordination is typical of metal carbonyl clusters [12], where a combination
2 of linear and bridging CO ligands encapsulate the metal cluster. Such bridging CO
3 ligands, in particular, stabilise the formation of M-M bonds. The metal nanoparticles
4 comprising the Ru/Pt/C catalyst in the current study are considerably larger than the
5 cores of such cluster compounds and it is hard to envisage a surface covered by bridge
6 bound CO species. However, if the adsorbed CO molecules at the Ru atoms at the
7 edges of the faces of the particles were to be bridge bound, this would make up a
8 considerable fraction of the total number of Ru-C interactions. Additionally, more
9 than one CO molecule may be bound to the individual Ru atoms at the vertices of the
10 nanoparticles, as is the case for the cluster compounds. Such a high coverage of CO is
11 likely to have an effect on the metal-metal distance of the outermost layer of metal
12 atoms in the nanoparticle and, indeed, we observe a slight increase in the Ru-Ru and
13 Ru-Pt distances compared to those obtained in the absence of adsorbed CO.
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30

31 **4. Conclusions**

32
33
34
35
36 The surface areas obtained using either CO chemisorption or the electrochemical
37 stripping of an adsorbed CO monolayer are commonly used to characterise carbon
38 supported Pt and Pt based alloy electrocatalysts and the results are often used to
39 normalise electrocatalytic activity to obtain specific activities. In calculating the
40 surface areas from such measurements assumptions are made regarding the adsorption
41 site and/or site occupancy of adsorbed CO and the coverage that constitutes a full
42 monolayer. The numbers employed are based on careful studies of the adsorption of
43 CO on single crystal surfaces, both in UHV and in the electrochemical environment.
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

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

1 may provide inaccurate determinations of the surface area and/or the size of the
2 nanoparticles comprising the catalyst. In the case of the Ru/Pt/C catalyst described
3 above, the areas determined from both CO chemisorption and the CO stripping
4 voltammogram are likely to be over-estimations of the electrochemically active area
5 of the catalyst.
6
7
8
9
10

11 **Acknowledgements**

12
13 The EPSRC are thanked for funding studentships for AR, CRK, and RJKW and
14 postdoctoral fellowship for MKR, and CLRC for access to the SRS. The Open
15 University is thanked for funding the studentship for YQ. Johnson Matthey is also
16 thanked for their financial support. The technical assistance of Chris Corrigan at the
17 SRS is also appreciated.
18
19
20
21
22
23
24
25
26
27
28

29 **5. References**

- 30
31
32
33 1. A. Essalik, K. Amouzegar, O. Savagogo, *J. Appl. Electrochem.*, 25 (1995) 404.
34
35
36 2. C.L. Green, A. Kucernak, *J. Phys. Chem. B.*, 106 (2002) 1036.; C.L. Green, A.
37 Kucernak, *J. Phys. Chem. B.*, 106 (2002) 11446.
38
39
40
41 3. F.C. Nart, W. Vielstich, "Normalisation of porous active surface areas," in
42 Handbook of Fuel Cells, Volume 2 Electrocatalysis, W. Vielstich, A. Lamm, H.A.
43 Gasteiger, Eds., John Wiley and Sons, N.Y. USA, 2003, pages 302-315.
44
45
46
47
48
49 4. E.M. Crabb, M.K. Ravikumar, D. Thompsett, M. Hurford, A. Rose, A.E. Russell,
50 *Phys. Chem. Chem. Phys.*, 6 (2004) 1792.
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

- 1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
5. A. Rose, E.M. Crabb, Y. Qian, M.K. Ravikumar, P.P. Wells, R.J.K. Wiltshire, J. Yao, R. Bilsborrow, F. Mosselmans, A.E. Russell, *Electrochim. Acta*, 52 (2007) 5556.
 6. S. Maniguet, R.J. Mathew, A.E. Russell, *J. Phys. Chem. B.*, 104 (2000) 1998.
 7. R.J.K. Wiltshire, C.R. King, A. Rose, P.P. Wells, H. Davies, M.P. Hogarth, D. Thompsett, B. Theobald, F.W. Mosselmans, M. Roberts, A.E. Russell, *Phys. Chem. Chem. Phys.*, submitted.
 8. A.V. Ruban, H.L. Skriver, J.K. Norskov, *Phys. Rev. B.*, 59 (1999) 15990.
 9. Z. Jusys, J. Kaiser, R.J. Behm, *Electrochim. Acta.*, 47 (2002) 3693.
 10. D. Aberdam, R. Durand, R. Faure, F. Gloaguen, J.L. Hazemann, E. Herrero, A. Kabbabi, O. Ulrich, *J. Electroanal. Chem.*, 398 (1995) 43.
 11. J. Evans, G. Jingxing, H. Leach, A.C. Street, *J. Organomet. Chem.*, 372 (1989) 61.
 12. See for example, the review, C. Femoni, M.C. Iapalucci, F. Kaswalder, G. Longoni, S. Zacchini, *Coord. Chem. Rev.*, 250 (2006) 1580, and references therein.

Figure Captions:

1
2
3 Figure 1. Cyclic voltammograms of (a) Pt/C and (b) Ru/Pt/C electrodes recorded
4
5 at 10 mV s^{-1} in $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ at $25 \text{ }^\circ\text{C}$. Black solid line before
6
7 CO adsorption, red dashed line CO stripping voltammogram and blue
8
9 dotted line second cycle after CO stripping.
10
11

12
13 Figure 2. Ru K edge XAS for Ru modified Pt/C at 0.0 V vs. RHE in 1 mol dm^{-3}
14
15 H_2SO_4 . (a) before CO exposure, (b) with adsorbed CO, (c) after CO
16
17 stripping.
18
19

20
21 Figure 3. k weighted Ru K edge EXAFS (a, c, and e) and the corresponding
22
23 Fourier transforms (b, d, and f) for Ru modified Pt/C at 0.0 V vs. RHE
24
25 in $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. (a, b) before CO exposure, (c,d) with adsorbed
26
27 CO, (e, f) after CO stripping. Data shown as thin solid lines and fits as
28
29 dotted lines.
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

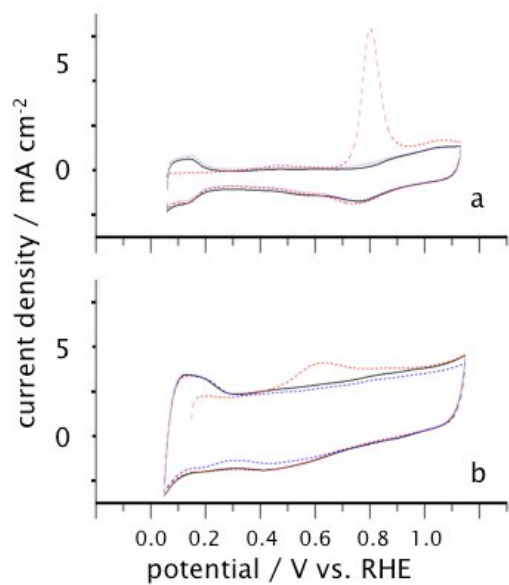


Figure 1.

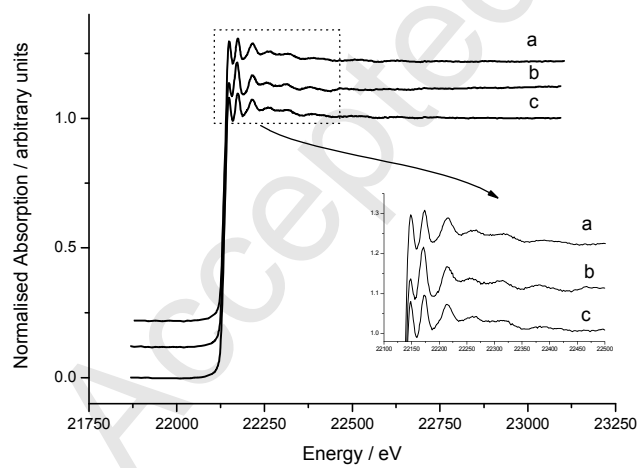


Figure 2.

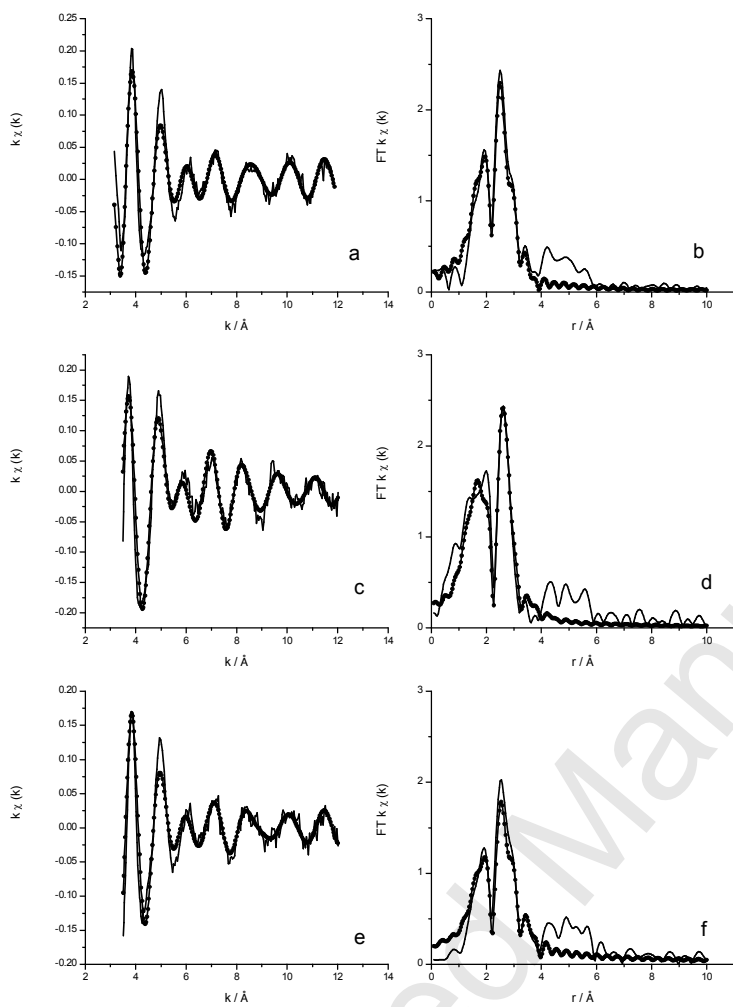


Figure 3.

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 H₂SO₄. Standard deviations of the parameters given in brackets.

CO exposure	Neighbour	<i>N</i>	<i>R</i> / Å	$2\sigma^2$ / Å ²	<i>E_f</i> / eV	<i>R_{exafs}</i> / %
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