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Shape resonances and EXAFS scattering in the Pt $L_{2,3}$ XANES from a Pt electrode

W.E. O'Grady^a and D.E. Ramaker^{a,b}

^aChemistry Division, Naval Research Laboratory, Washington, DC 20375

^bChemistry Department, George Washington University, Washington, DC 20052

Atomic hydrogen and oxygen adsorption on a platinum electrode in H_2SO_4 and $HClO_4$ electrolytes were studied by Pt $L_{2,3}$ XANES. The Pt electrode was formed of highly dispersed 1.5–3.0 nm particles supported on carbon. A difference procedure utilizing the L_2 and L_3 spectra at various applied voltages was used to isolate the electronic and geometric effects in the XANES spectra. At 0.54 V (relative to RHE) the Pt electrode in $HClO_4$ is assumed to be "clean". By taking the difference between the spectra at 0.0 and 0.54 V, the Pt-H antibonding state (electronic effect) is isolated and found to have a Fano-resonance line shape. In addition, a significant Pt-H EXAFS scattering (geometric effect) was found for photon energies 0 to 20 eV above the edge. The difference between the spectra at 1.14 and 0.54 V allows isolation of the Pt-O antibonding state and the Pt-O EXAFS scattering.

Keywords: EXAFS, XANES, electrochemistry, platinum electrode, shape resonances

1. Introduction

The determination of detailed information about the structure and electronic state of bonds and interactions at solid liquid interfaces and their role in electrocatalytic reactions has not been accomplished in spite of the use of a wide variety of powerful surface analytical techniques including both *in situ* and *ex situ* techniques (Abruna, 1991; Kolb, 1987). The kinetic measurements for the oxygen reduction reaction on the low index planes of Pt have only recently been successfully carried out (Markovic, 1997). At the present time we know that the rate of the reaction is modified by the adsorption of anions but we do not know how the interaction of these species bound to the surface interact or how they effect the mechanism of the oxygen reduction reaction. In earlier work (O'Grady, 1997), we have shown that atomic XAFS can provide information on the surface charge and the interatomic potential of the surface atoms providing insight into the electronic structure at an electrode surface. In this work we introduce the discovery of shape resonances in the XAS spectra to provide information on the electronic structure of the Pt-O and Pt-H bonds and how they are affected by the potential. At the same time the Pt-O and Pt-H EXAFS data provide bond distances for these species.

2. Experimental

Teflon bonded Pt/C electrodes were fabricated as reported earlier (McBreen, 1987) for the *in situ* XAS experiments. The cell used in these measurements was similar to that described for *in situ* nickel

oxide electrode studies (McBreen 1987). Nafion was used as the separator and the Pt/C electrode was flooded with 0.5M H_2SO_4 and held in a PTFE gasket. The counter electrode was an uncatalyzed high-surface-area carbon electrode flooded with 0.5M H_2SO_4 and held in a PTFE gasket. The reference electrode was a Pd/H electrode. The Pt L_3 edge XAFS was collected at room temperature in the transmission mode on beamline X-11A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The NSLS storage ring operated at 2.52 GeV beam energy with ring currents between 40 and 200 mA. Gas flow ionization chambers were used to monitor the intensities of the incident and transmitted X-rays. The Si(111) double crystal monochromator was detuned by 30% at the Pt L_3 edge (11564 eV) to minimize the presence of higher harmonics in the beam.

3. Results

Figure 1 shows a current vs. voltage (I-V) curve for a Pt electrode. We have labeled the regions where H, O, H_2 and anion direct adsorption will dominate, and we have indicated the potentials where data were taken in H_2SO_4 and $HClO_4$. The advantage of having both the L_2 and L_3 edge will be clear from the analysis below, but unfortunately this data is not available for H_2SO_4 . Nevertheless, the greater number of applied voltages for H_2SO_4 provides other new insights.

A difference procedure utilizing the L_2 and L_3 spectra at various applied voltages was used to isolate the electronic and geometric effects of the adsorption in the XANES spectra. At 0.54 V (relative to RHE) the Pt electrode in $HClO_4$ is assumed to be "clean". By taking the difference, ΔL_3 or ΔL_2 , between the spectra at 0.0 and 0.24 or 0.0 and 0.54 V, the Pt-H effects are isolated and the difference between 1.14 and 0.54, that due to the oxygen adsorption. An important alignment procedure to be described elsewhere (Ramaker, 1999) is performed before taking the difference. The changes in the spectra due to adsorption are attributed to changes in the EXAFS scattering (ΔXAS , the additional Pt-Ad [adsorbate] scattering and possible changes in the Pt-Pt scattering) and to an electronic contribution. This

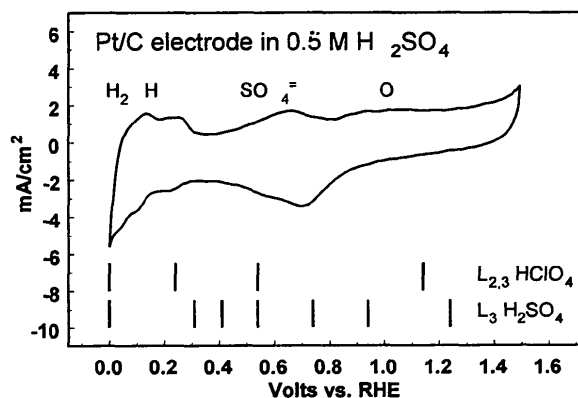


Figure 1

Current vs. voltage curve for a Pt electrode in 1 M H_2SO_4 . Also shown are the expected regions where H, O, SO_4^- direct anion adsorption, and H_2 adsorption would dominate. Finally the applied voltages where the L_2 and L_3 absorption edges were measured in perchloric acid, and the L_3 edges in sulfuric acid electrolyte are indicated.

latter contribution arises from the antibonding Pt-Ad orbital [AS] which appears as a result of the adsorption. The AS contribution appears only in the ΔL_3 spectra, because at the L_2 edge, the spin orbit splitting of the 5d band causes the AS state to be nearly filled (Ramaker, 1999). This same spin orbit splitting causes a valence band difference (ΔVB) to appear in the L_3 spectra. The anti-bonding state is degenerate with the continuum and is therefore a "shape" resonance exhibiting the usual Fano-resonance spectral line shape (Ramaker, 1999). These contributions are summarized in Table 1.

The Fano-resonance spectral line shape can be described by the expression (Ramaker, 1999):

$$\text{AS}(E) = 1/k A \sin \phi [(1-q\varepsilon)/(1+\varepsilon^2)], \quad (1)$$

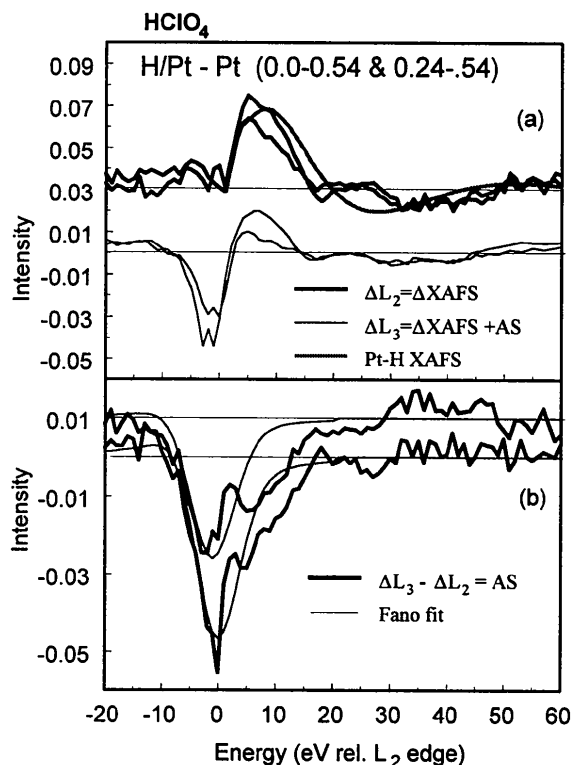


Figure 2

a) Comparison of the difference spectra H/Pt - Pt at potentials 0.0-0.54 V and 0.24-0.54 V for a Pt electrode in HClO_4 electrolyte. These difference spectra highlight the effects of H chemisorption. Both the $\Delta L_2 = \Delta \text{XAFS}$ (light solid) and $\Delta L_3 = \Delta \text{XAFS} + \text{AS}$ (heavy solid) differences are shown and compared with the Pt-H XAFS (dashed line) calculated with the FEFF code using the Hedin Lundquist potential and a Pt-H distance of 1.9 Å. Both difference spectra are shown with the same line selection, since the more intense difference in each case obviously comes from the larger voltage difference. The ΔL_2 data and Pt-H XAFS have been offset by 0.03 for clarity. b) Comparison of the Fano resonance lineshape obtained from the experimental difference $\Delta L_3 - \Delta L_2 = \text{AS}$ (heavy solid lines for both potential differences) and the least squares fit of the Fano expression in eq. (1) (light solid). The data and fit for 0.24-0.54 have been offset by 0.01 for clarity.

Table 1
Summary of additional contributions present in each spectrum relative to reference clean L_2 spectrum (REF)

	L_3	L_2
Ad/Pt	AS + ΔVB + ΔXAFS + REF	ΔXAFS + REF
Pt	ΔVB + REF	REF

where ε is the normalized energy scale [$\varepsilon = (E - E_{\text{res}})/\Gamma$] relative to the resonance energy, E_{res} , with resonance width Γ , q is the "shape" parameter which accounts for the interference between the resonant and non-resonant waves [$q = \cot 2\delta$], δ is the total phase of the non-resonant cross-section, A is a normalization constant, and k is the momentum of the photoelectron. Here 2δ is the usual phase found in EXAFS containing the $2kr$ term and the phase from the absorber and back-scatterer (i.e., $2\delta = 2kr + 2\delta_a + \delta_b$). A least squares fit of Eq. 1 to the experimentally observed lineshape allows a characterization of the resonance in terms of the parameters 2δ , E_{res} and Γ . The resultant profile was Gaussian broadened by the indicated amount to account for lifetime and Debye-Waller effects (Table 2).

Figures 2a and 3a show the ΔL_2 and ΔL_3 difference spectra for H and O adsorption in HClO_4 . After comparing the ΔL_2 and ΔL_3 difference spectra with the calculated Pt-H and Pt-O XAFS functions obtained with the FEFF code, it is clear that at larger energies, the difference spectra are dominated by additional Pt-Ad scattering. Because of the different backscattering phases, the Pt-H and Pt-O XAFS functions are very different. Agreement between theory and experiment is reasonable, considering the sensitivities of the XAFS function to the chosen

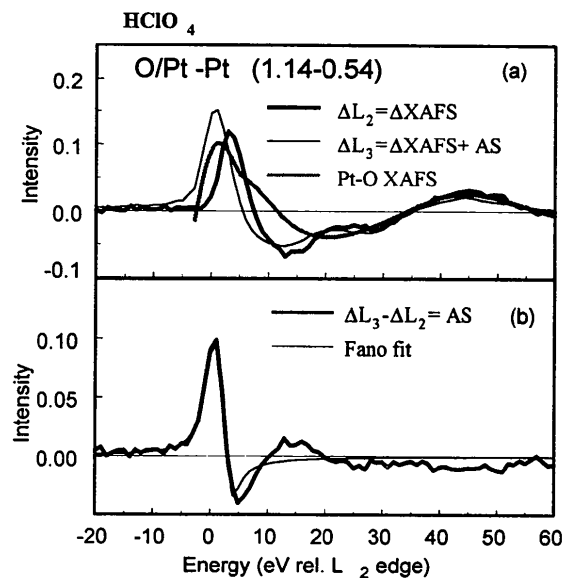


Figure 3

Similar spectra as in Fig. 2a, but O/Pt-Pt data showing the effect of O adsorption from the potential region 1.14-0.54 V RHE. b) Similar spectra as in Fig. 2b, but for the O/Pt case.

potential parameters in FEFF, and the inaccuracy of the FEFF code at these low energies.

Within 5 eV of the edge, the shape resonance or AS contribution dominates. The AS contribution can be isolated by taking the difference, $\Delta L_3 - \Delta L_2$, as shown in Figs. 2b and 3b. For both the H and O adsorbates, the shape resonance appears very close to and even below zero energy.

The most significant disagreement between theory and experiment above 10 eV comes around 25 eV for both O and H adsorption. This feature arises from the change in the Pt-Pt distance as O or H is adsorbed (i.e. it is the second component in the ΔXAS contribution). It is known that the Pt-Pt distance near the surface decreases due to the lack of full coordination about the surface Pt atoms (Koningsberger, 1986). This distance relaxes back to normal when the H or O is adsorbed. This feature can be used to monitor the change in Pt-Pt distance with adsorption.

In Figs. 2b and 3b, we show the fit of the Fano line shape to the experimental line shape. The Fano parameters obtained from the fits are indicated in Table 2. The Fano line shapes for O and H have a totally different shape because the background scattering is very different, as mentioned above. This is indicated in the fit parameters by the totally different 2δ parameters for H and O. Another significant point is the large difference in the Gaussian broadening required for H compared to O. We attribute this to the much larger Debye-Waller factor expected for the very light H atom compared to the much heavier O atom. The amplitude parameter of course increases with the coverage, and the Pt-H widths remain relatively constant. The much smaller width for Pt-O could result from the loss of metallic character as the oxide layer is formed. This resonance width primarily reflects escape of the electron into the valence band, and in the case of the Pt-O the position of the resonance high above the valence band makes this escape probability small.

Table 2

Summary of Fano fit parameters obtained by the fit of eq. (1) to the Pt data in $HClO_4$.

	A (± 0.03)	E_{res} (eV) (± 0.03)	Γ (eV) (± 0.4)	2δ (± 0.1)	GB* (eV)
H/Pt (0.0-0.54)	0.07	-2.0	3.0	-0.71	5
H/Pt (-0.24-0.54)	0.05	-1.6	2.9	-0.90	5
O/Pt (1.14-0.54)	0.21	2.2	0.8	0.06	1.5

*Gaussian Broadening

The resonance energies for the H adsorption are negative, which is expected for the rather large Pt particles in this work. We have shown elsewhere (Ramaker, 1999), that the resonance energy changes with the size of the cluster, and the nature of the particle support in supported metal catalysts. In general, as the metallic nature of the particles increases (either by increasing the particle size, placing it on a more basic support, or applying less anodic potentials as in this work) the resonance energy goes more negative. Thus the more negative resonance energy at 0.0 V compared to 0.24 V is totally consistent with this previous data.

4. Summary

In summary, unprecedented detail on the adsorption of H, O, H_2 , and SO_4^- (the latter two reported elsewhere (Ramaker, 1999)) on a Pt electrode *in situ* in an electrochemical cell, has been obtained. This detailed new information includes the following:

1. The Pt-O and Pt-H resonance energies are found to move upward exactly as expected with increasing applied potential. The resonance energy for the Pt-H bond is found to be negative, similar to that found elsewhere for H chemisorbed on large Pt clusters supported on zeolites or amorphous supports. The Pt-O resonance energy is positive reflecting the stronger Pt-O bond.
2. The $Pt-SO_4^-$ interaction reveals a Pt-O bond length of around 2.2 Å. This sulfate interaction allows the Pt surface to relax, so that the usual Pt-Pt contraction at the surface does not occur.
3. The Pt- H_2 interaction (not discussed here, but reported in Ramaker, 1999) in a similar electrochemical environment involves H_2 bonded with its internuclear axis perpendicular to the surface with a Pt-H distance of 1.9 Å and its internuclear bond distance nearly unchanged from that in the gas phase.

The techniques utilized here are quite generally applicable. These techniques can be utilized to study all types of atomic adsorption and molecular adsorption if relatively strong bonding and antibonding orbitals are formed. It is anticipated that the resonance state, as well as the Pt-adsorbate EXAFS scattering, can be used as new *in situ* tools to study other systems in electrochemistry, catalysts, and biological systems.

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