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REAL TIME STRUCTURAL ELECTROCHEMISTRY OF PLATINUM CLUSTERS USING DISPERSIVE XAFS

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ABSTRACT

Chemical reference tables state that the standard potential for the reaction of Pt with water, $\text{Pt} + 2\text{H}_2\text{O} \rightarrow \text{Pt}(\text{OH})_2 + 2\text{H}^+ + 2\text{e}^-$, is 0.98 V, and electrochemical studies propose that this reaction may occur at potentials as low as 0.8 V [1-5]. Using dispersive x-ray absorption fine-structure (XAFS) spectroscopy [6], we have directly probed the structural evolution of a Pt catalyst operating in-situ in a polymer electrolyte [7] fuel cell during cyclic voltammetry. The changes in the number of Pt and O nearest-neighbors and the Pt charge demonstrate a close correspondence with features in the voltammogram. Because dispersive XAFS is very sensitive to detecting structural changes, we have been able to detect the presence of chemisorbed oxygen at potentials of 0.6-0.9 V in the anodic sweep. Since double-layer charging is regarded as the only process in this region for bulk Pt [3-5], these results may reflect a limitation of previous (indirect) studies on Pt electrochemistry, or they may indicate that these clusters are different from their bulk metal counterparts. Exploiting the time-resolving capability of dispersive XAFS, we also monitored changes in the Pt charge and the number of O and Pt nearest-neighbors during the electrochemical oxidation and reduction of the Pt clusters in real-time. The results are inconsistent with those expected from the place-exchange mechanism [8-11] for the formation of the surface oxide on bulk Pt electrodes in aqueous solution;

Our current model for understanding these behaviors is that, relative to bulk Pt, unusual types of surface sites play a major role in determining the reactivity of these clusters.

EXPERIMENTAL

E-TEK carbon-supported, platinum catalyst (~20 Å dia. Pt particles) was incorporated into the cathode (7.7 mg Pt/cm²) of a polymer electrolyte membrane fuel cell [7]. Pt L_{III}-edge XAFS spectra were measured in dispersive mode [6] on beam line 2-2 at the Stanford Synchrotron Radiation Laboratory. XAFS data reduction was performed by standard methods [12], defining the first inflection point of the Pt edge as 11572.2 eV and the ionization threshold as 11585 eV. Cyclic voltammetry was performed with the cell operating at +80°C and water-saturated N₂ and H₂ flowing over the cathode and anode sides, respectively. An EG&G model 273 potentiostat was used to control the applied potential and a Soltec model VP-6424S X-Y recorder recorded the current as a function of voltage. After the completion of two full cycles which included the anodic and cathodic sweeps between 0.025 V to 1.200 V (versus the hydrogen side of the fuel cell) at a scan rate of 5mV/sec, XAFS data acquisition was initiated as the anodic portion for the third cycle commenced. 100 spectra were measured

sequentially at 5 second exposures while the potential was swept, with each spectrum corresponding to a voltage increment of 25 mV. Under these conditions, 94 spectra were required to complete a full cycle.

The oxidation kinetics were studied on an identical composition cathode (2.6 mg Pt/cm²) by first equilibrating the cathode at 0.10 V (vs the hydrogen side), measuring a spectrum, and then jumping the applied voltage to 1.20 V. At this point, 30 consecutive spectra were measured at 10 sec intervals. The reduction was monitored identically, with 1.20 V and 0.10 V as the initial and final potentials, respectively.

RESULTS AND DISCUSSION

The Fourier-Transform moduli ($k=2-10 \text{ \AA}^{-1}$) depict the structural evolution of the catalyst between the reduced and oxidized forms (figure 1). The continuous changes in the Pt—Pt ($R=2.24 \text{ \AA}$) and Pt—O ($R=1.50 \text{ \AA}$) peaks are readily visible as the applied potential is varied. The anodic sweep of the cyclic voltammogram (figure 2a) shows the features commonly seen for bulk Pt in acid solution [3-5]. The shoulder at ca. 100 mV and the peak at 250 mV represent the desorption of weakly and strongly bound hydrogen atoms, respectively [13]. The broad feature around 600 mV originates from the oxidation of the carbon support [14]. The rise in current indicative of the Pt surface oxidation process begins at ca. 900 mV and continues up to 1200 mV. Nonlinear least-squares curve-fits of the Fourier-filtered XAFS data [12] at 25 mV give a single shell of 9.6 Pt atoms (N_{Pt}) at $2.76 \text{ \AA}$. At 1200 mV, there are 0.6 O atoms (N_O) at $2.01 \text{ \AA}$, and $N_{Pt} = 8.5$ at $2.76 \text{ \AA}$.

Figure 2 also shows N_{Pt} (inverted), N_O , and $\mu(E)$ —each versus the applied potential. Since $\mu(E)$, the magnitude of the L_{III} absorption edge at 11575 eV, is known to increase with the positive charge on the Pt atom [15], its increase indicates that the Pt is gradually oxidizing in the double-layer region between 300–900 mV. Above 900 mV, $\mu(E)$ increases more rapidly, correlating well with the oxidation wave seen in the voltammogram. N_O follows $\mu(E)$, showing that at 600 mV, a finite amount of oxygen is chemisorbed onto the surface. Between ca. 300–900 mV, N_{Pt} is unaffected by the presence of oxygen. This suggests that oxygen adsorption is primarily a surface effect in this region. If it were to involve Pt rearrangement, N_{Pt} would also be changing.

While the N_O and $\mu(E)$ plots indicate a continuous transformation between two states—oxidized and reduced, the N_{Pt} plot demonstrates the existence of the hydrogen adsorbed state seen in the voltammogram. In figure 2, N_{Pt} changes from 9.7 at 75 mV to 9.5 at 300 mV, with no change in the Debye-Waller factor. Although the accuracy in XAFS coordination numbers is typically 15-30%, the dispersive mode allows for high *precision* (estimated to be ± 0.08 Pt atoms here). Since $N_O \approx 0$ at these potentials, this decrease in N_{Pt} probably results from the desorption of hydrogen. The increased Pt—Pt bonding (i.e., ordering) in the presence of adsorbed hydrogen is an effect which is opposite to that observed on bulk Pt [16].

Above 900 mV, N_{Pt} decreases concomitantly with the increases in N_O and $\mu(E)$, indicating that rearrangement of the Pt lattice [17] is coupled to the surface oxide formation. The value of $N_O=0.60$ at 1200 mV requires (assuming an average structure between $\text{Pt}(\text{OH})_4$ and $\text{Pt}(\text{OH})_6$) that ca. 14% of the Pt is oxidized. This is consistent with the 15% oxidized calculated for the change in $\mu(E)$ using Pt and PtO_2 as Pt^0 and Pt^{4+} models. It also agrees with the change in Pt coordination which gives $1 - (8.5/9.6) = 12\%$. Thus ca. 14% of the Pt leaves the metallic domain of the particle and becomes an amorphous oxide or hydrous oxide layer.

Using the values of N_O obtained between 25–300 mV as the noise level (assuming no chemisorbed oxygen), the result is a *precision* of ± 0.04 atoms. Thus the values of $N_O=0.10$, 0.30 at 600 and 900 mV represent an amount which is above the noise level. Since O atoms

can adsorb onto 3-fold [111] or 4-fold [100] faces in addition to the 5 and 6-fold hollow vacancies on edges and corners [18], each surface Pt atom will coordinate to ca. 4-5 oxygens. With the observed coordination of 0.10-0.30, approximately 2-6% of all the Pt atoms are oxidized. This is readily accommodated by involving only surface atoms (which compose 30% of the particle's total Pt). Analysis of the changes in $\mu(E)$ using PtO₂ and Pt metal as fully oxidized and reduced references gives 3-8% Pt oxidized over the 600-900 mV region.

A model for Pt oxidation below 900 mV may be envisioned in terms of the properties of small particles. These nominally 20 Å diameter particles possess a significant number of surface atoms (30%) occupying a variety of low-coordination sites (i.e., highly exposed edges and corners) [18]. With lower coordination, the binding energies are smaller so that these sites can be oxidized at lower potentials [19]. It is known that different crystalline faces (i.e., [111] or [100]) of bulk Pt electrodes have different potentials for oxidation [20,21]. Therefore, it may be the case that these sites, representing a minority of the total surface area on bulk Pt, are revealed only when there are a substantial number of them, e.g., in highly dispersed particles.

The kinetics of surface oxide formation are demonstrated in figure 3a by the increase in the Fourier transform amplitude of the O contribution at $R=1.50$ Å and the decrease in the amplitude of the Pt nearest-neighbor contribution [17] at $R=2.24$ Å. Similarly, the loss of Pt-O bonds and the restructuring of the Pt near-neighbor shell into the higher amplitude form in figure 3b clearly demonstrate the removal of the surface oxide. Nonlinear least-squares curve-fits of the Fourier-filtered XAFS data at 0.10 V give a single shell of 9.9 Pt atoms at 2.76 Å. After 5 minutes at 1.20 V, $N_O=1.0$ at 2.01 Å, and $N_{Pt}=8.3$ at 2.76 Å, with no significant change in the Debye-Waller factor of the Pt shell. The absence of any changes in the shapes of the Fourier transform features for $R=2.7-3.5$ Å argues against the formation of any significant numbers of O-bridged Pt-Pt distances. Together with the low value of N_O , these data suggest that O is restricted to the surface and has not been inserted below the Pt surface layer.

In comparing N_O , N_{Pt} , and $\mu(E)$, it is apparent that the time dependencies of these three parameters are similar during oxidation (figure 4a). During the reduction, the rate of Pt restructuring appears to be conserved, whereas N_O and $\mu(E)$ change more rapidly (figure 4b). That N_O and $\mu(E)$ follow each other closely in the oxidation and reduction indicates that the charge on the Pt is directly coupled to the number of Pt-O bonds.

The oxidation kinetics were best fit with a logarithmic function [11], which accounts for the initial, rapid change followed by the relatively constant slow change out to long times. The reduction kinetics were easily fit with a single exponential, indicative of a pseudo first-order, one step reaction (on this time scale). The rates of 0.044 sec^{-1} for changes in N_O and 0.045 sec^{-1} for changes in $\mu(E)$ are twice as fast as the 0.022 sec^{-1} constant for the change in N_{Pt} . That N_{Pt} does not change at the same rate as N_O and $\mu(E)$ in the reduction suggests an amount of decoupling for the Pt restructuring.

If the microsecond scale, reversible chemisorption of oxygen [1,2] observed on bulk Pt, had also occurred on these clusters, an offset between the values of N_{Pt} , N_O , and $\mu(E)$ at $t=0$ and those obtained from extrapolation of the time dependence would be present. Using the standard deviation of the fit as the noise level, the extrapolated values are always within 2σ of the baseline values and are not consistent in direction. The extent of surface coverage resulting from any reaction faster than those tracked here is thus estimated at $0 \pm 7\%$.

In the context of the two-step reaction sequence proposed for the surface oxide formation on bulk Pt [11], none of the structural signatures for place-exchanged PtO_x are found in the XAFS spectra of these clusters. In addition, the oxidation involves only a single, slow step that resembles the slow step in bulk Pt oxidation both in its logarithmic growth [11] and its overall rate. The formation of surface oxide on bulk Pt and on the clusters may thus be distinct, resulting in different products but possessing similar rates and mechanisms. The irreversibility observed in electrochemical measurements is accounted for in these results by

the observation of different kinetics (and therefore different mechanisms) for the oxidation and reduction processes.

One model that can account for these results is a labile surface for the cluster, where the Pt atoms reconstruct to sites of lower coordination during the oxidation, increasing the effective surface area and number of sites accessible to O in the process. Once open surface sites are created during the reduction, the chemisorbed oxygen may diffuse across this surface, leaving patches of bare surface that can then reconstruct at their intrinsic rate to minimize the total surface area. The ability to develop this type of detailed model, based on direct structural data rather than indirect measures of structure (i.e., current), demonstrates the advantages of dispersive XAFS in this type of application.

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Figure 1. Fourier-transform moduli of Pt EXAFS ($k=2-10 \text{ \AA}^{-1}$) as a function of applied potential during cyclic voltammetry. The increase in the amplitude of the peak at $1.50 \text{ \AA}$ demonstrates the adsorption of oxygen onto the Pt, while the reduction in amplitude of the peak at $2.3 \text{ \AA}$ indicates a rearrangement of the Pt lattice.

Figure 2. Evolution of XAFS features during the anodic sweep of cyclic voltammetry. Values for each plot are given at 0 and 1.2 volts, respectively. (A) current trace from -35 mA to 30 mA; (B) N_{Pt} from 9.6 to 8.5; (C) $\mu(E)$ from 1.152 to 1.264; and (D) N_O from 0.0 to 0.6.

Figure 3. (At left) Fourier transform moduli of the Pt EXAFS ($k=2-10 \text{ \AA}^{-1}$) acquired during the oxidation (A) and reduction (B).

Figure 4. (Above) XAFS structural features as a function of time during the oxidation (A), and reduction (B): N_O (long dash), N_{Pt} (short dash), $\mu(E)$ (solid).

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