

Surface Resonance X-Ray Scattering Observation of Core-Electron Binding-Energy Shifts of Pt(111)-Surface Atoms during Electrochemical Oxidation

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Surface resonance x-ray scattering, sensitive to the monolayer-level change of an oxidation state of a *buried* interface, is used for the investigation of electrochemical oxidation of Pt(111) single crystal surface. The strongly \mathbf{Q} -dependent energy scans through the L_{III} resonance energy of Pt atoms were accounted for by a large increase of the electron binding energy of the surface atoms as a result of surface *anodic* oxidation.

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The use of x-ray techniques based on resonance scattering phenomena has been rapidly increasing ever since continuously tunable monochromatic x rays became available at synchrotron sources. While the imaginary part of the scattering factor was widely used in the x-ray absorption fine structure spectroscopy and related techniques, recently more attention has been given to the use of its *real* part. Examples are the diffraction anomalous fine structure (DAFS) technique for site-sensitive local structure measurements [1,2], the multiple anomalous dispersion phasing technique for structural biology applications [3], and resonance scattering on crystal truncation rods from a dissimilar buried interface [4] and on reflectivity for multilayer interfaces [5]. The objective of our study is to demonstrate that monolayer or submonolayer level chemical *changes* occurring at a buried *single crystal* surface (not overlayer) can be studied by the resonance surface scattering in a manner similar to Ref. [4]. Specifically, we will show that the *chemically sensitive* core binding-energy shifts, resulting from anodic surface oxidation of a platinum single crystal, can be determined from \mathbf{Q} -dependent, energy-dispersive surface x-ray scattering measurements at a deep-core-level resonance energy.

Platinum has been a model system used for many fundamental studies in electrochemistry including anodic oxidation, due to its importance in electrocatalysis and possible similarity to oxidation and corrosion of other metals. It is also an appropriate model system for this study because the surface structure of oxidized platinum has been recently well established by x-ray scattering studies [7]. Experimental details, such as cell geometry [6], electrochemical procedures, and sample preparations, have been described previously [7].

The x-ray measurements were performed at the X25A wiggler beam line, with a platinum-coated toroidal mirror and a standard Si(111) monochromator ($\Delta E \sim 4$ eV), of the National Synchrotron Light Source (NSLS) and at the 12-ID-B undulator beam line, with a rhodium-coated flat mirror and a cryogenically cooled Si(111) monochromator ($\Delta E \sim 2$ eV), of the Basic Energy Sciences Synchrotron Radiation Center (BESSRC), Advanced Photon Source

(APS). The signal from thermoelectrically cooled silicon or the CdZnTe PIN diodes detector was fed through an amplifier, with $0.25 \mu\text{sec}$ pseudotriangular shaping and base-line restoration, to a pulse height analyzer (PHA). Consequently, we were able to eliminate the fluorescence contamination by counting only the peak near channel 150 (see the inset of Fig. 1) and the elastic diffuse background by subtracting counts measured with 0.3° offset.

The atomic elastic x-ray scattering factor may be divided into two terms near a resonance condition of a ground state A (L_{III} level in our case) of an atom: R and f . R represents the difference between the x-ray scattering amplitude of the electron in the ground state A and the Thompson scattering amplitude (resulting in the resonance contribution only), and f represents the sum of all other scattering amplitudes (nonresonance contributions). Then, the resonance scattering amplitude

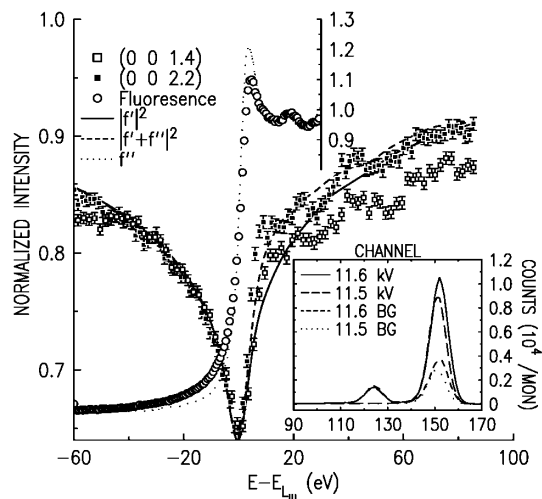


FIG. 1. Surface scattering intensity and bulk fluorescence intensity through L_{III} resonance. f' and f'' are normalized to their respective maximum values. In the inset, the counts vs the PHA channel for four cases are shown: (i) surface scattering intensity at (0 0 1.4) below the edge (long dashed line) and (ii) above the edge (solid line); (iii) background scattering intensity below the edge (dotted line) and (iv) above the edge (short dashed line).

of polarization-conserving scattering for the n th atom, R_n , can be written in the well-known form of the sum over all the available intermediate states (denoted with I) in the system following the notation of Ref. [8],

$$R_n \approx \frac{r_0}{m_e \hbar} \sum_I \frac{|\mathcal{M}_{IA}|^2 [2\omega_{IA}^n (\omega_{IA}^n - \omega) + (\frac{\Gamma_I}{2\hbar})^2]}{(\omega_{IA}^n + \omega) [(\omega_{IA}^n - \omega)^2 + (\frac{\Gamma_I}{2\hbar})^2]} + i \frac{r_0}{m_e \hbar} \sum_I \frac{\frac{\Gamma_I}{2\hbar} (\mathcal{M}_{IA})^2}{[(\omega_{IA}^n - \omega)^2 + (\frac{\Gamma_I}{2\hbar})^2]}, \quad (1)$$

where $\hbar\omega_{IA}^n$ is the binding-energy *difference* between the ground and intermediate levels for the n th atom whose ground state energy may slightly differ from other like atoms due to their different oxidation states either because they are in a different sublattice [2] or because, as in our case, they are oxidized. Note that the real part of R_n exhibits a negative singularity and the imaginary part exhibits a step-wise jump at $\omega_{IA}^n \approx \omega$ after integration over the available continuum intermediate states. Such integration (with more elaborate relativistic corrections) by Cromer and Liberman [9] is numerically available for Pt atoms and it was used in our data analysis by adjusting the binding energies and instrumental energy resolutions.

We will treat the x-ray scattering from the surface of a monoatomic single crystal limited to a one-dimensional half-infinite sum [10], which is sufficient for the purpose of our discussion. The surface scattering amplitude per surface atom can be written in the ordinary way as

$$S_z(\mathbf{Q}, \omega) = \sum_{n=1}^{-\infty} f_n e^{i\mathbf{Q} \cdot \mathbf{r}_n} + \sum_{n=1}^{-\infty} R_n e^{i\mathbf{Q} \cdot \mathbf{r}_n}, \quad (2)$$

where the first and the second terms are the nonresonance and resonance scattering factors, respectively. The term, $\mathbf{Q} \cdot \mathbf{r}_n$, is the usual phase delay of the scattered x rays as in the classical theory of x-ray scattering, and the scattering amplitudes are coherently summed over every atom in the system for both the resonance scattering amplitude [11] and the nonresonance scattering amplitude.

First, we consider the scattering from a clean unoxidized platinum surface; for this case, all the layers are identical ($R_n = R_0$), and the scattering intensity is directly proportional to $|f_0 + R_0|^2$ whose resonance behavior is *independent* of \mathbf{Q} . Indeed, the surface scattering intensity vs x-ray energy measured at various points along the (0 0 L) rod looks identical, except for the absolute value of the intensity as expected from a clean Pt(111). Energy scans made at (0 0 1.4) and at (0 0 2.2), normalized to their corresponding intensities measured far from the resonance, are shown in the main panel of Fig. 1. The solid line represents $|f'|^2$ (f' being the real part of $f_0 + R_0$ calculated with the Cromer-Liberman method) and the dashed line represents $|f' + f''|^2$ (f'' being the experimentally observed standard values [12] shown as the dotted line). The dashed line agrees well with the data (squares) and we use these f' and f'' values in the data analysis described below. Note also that the mea-

sured fluorescence (open circles in the main panel), used for our scan-by-scan energy calibration, agrees well with the standard (dotted line) [12].

Now we consider a simplified model where only the atoms in the first layer ($n = 1$) are oxidized. The second term of Eq. (2) can then be rewritten as $e^{iq}(R_1 e^{iq} + \frac{R_0}{2i \sin q})$, where $q = \pi L/3$ ($L = 2c \sin \theta / \lambda$ is the unit of the c -axis reciprocal lattice in a hexagonal-index scheme). When $q = \pi/2$ (anti-Bragg condition, $L = 1.5$) this becomes $-R_1 + \frac{R_0}{2}$ and the scattering amplitude from the rest of the atomic layers is opposite in phase to that from the first layer alone. Therefore if the core binding energy of the atoms in the first layer is sufficiently different from that of the rest of the layers ($\omega_{IA}^1 - \omega_{IA}^{n < 1} \gg \hbar^{-1}$), the surface scattering intensity can have a *positive* singularity in addition to the usual negative one. We observe this positive singularity in our measurement for the essentially same reason, although the platinum surface oxidation involves two partial layers of platinum [7].

The cyclic voltammogram (CV, a set of repeated I - V curves) of the single crystal Pt(111) surface is partly shown in Fig. 2(a). The current spike at ~ 1.1 VHE (volt from hydrogen evolution) is the result of the top layer oxidation to form a layer of Pt-O. An approximately 0.3 monolayer, however, *place exchanges* to O-Pt in a staggered configuration [7] to minimize the dipole-dipole interaction energy between the nearest neighbors [13] as schematically shown in the upper right corner of Fig. 2. Note that the electron density profile of this structure has two partial monolayers on top of the virtually undisturbed

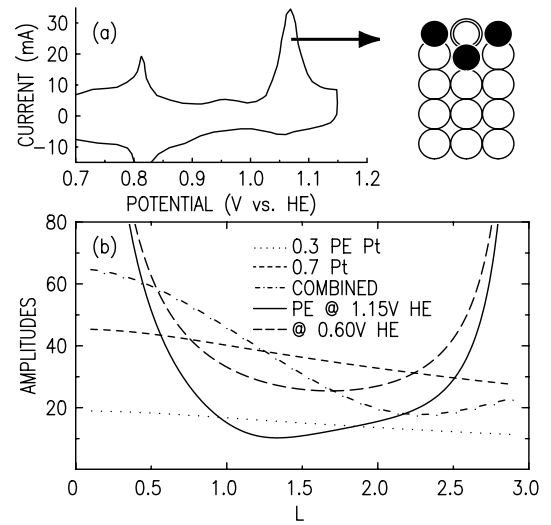


FIG. 2. (a) The current anomaly in CV for the surface oxidation and a schematic model for the oxidized surface. The open circles, filled circles, and double circles represent platinum atoms, oxygen atoms, and the platinum atom that exchanged its place with oxygen, respectively. (b) The scattering amplitudes from the layers of the double circles (dotted line) and the first layer (dashed line), their combined amplitude (dot-dashed line), the total amplitude (solid line), and the amplitude from a clean surface (long dashed line).

Pt(111) surface [7]. Since the scattering factor of oxygen is much smaller than that of platinum, we will ignore it in our discussion although it is included in our calculations as a small correction.

The x-ray scattering intensity of such a structure can be modeled simply as a coherent sum of three components using the previously determined structure parameters [7]; scattering amplitudes from (i) the undisturbed half-infinite platinum layers ($z_0 = 0$ and $-\infty < n \leq 0$), (ii) the first 0.7 monolayer of oxidized platinum atoms ($z_1 = 1$), and (iii) 0.3 monolayer of oxidized and place-exchanged (PE) platinum atoms ($z_2 = 0.7$) where z represents the position of the layers in the unit of layer spacing. The nonresonance scattering amplitudes for each layer and their combinations are shown in Fig. 2(b). Here we can see that individual amplitudes for the two partial layers change only slightly over the range of L shown but the combined amplitude is substantially decreased for $1.5 < L < 3$ because the relative phases of the two layers are *opposite*. Since the scattering amplitude from the rest of the layers ($n \leq 0$) sharply increases, the effect of the *positive* singularity will become less detectable as L approaches 3. Therefore we expect that the presence of the positive singularity can be clearly demonstrated only for a narrow range within $1.5 \leq L \leq 2.6$ if the L_{III} -edge binding energy for the PE second-layer platinum is sufficiently larger than that for the first layer.

The scans measured at 12-ID-B (open circles) are shown in Figs. 3(a) and 3(b). A pronounced positive spike just above the resonance energy is clear for $L = 2.2$ and a somewhat less pronounced feature at $L = 2.6$ can also be seen. The solid line is the fit made with the aforementioned f' and f'' for the discussed oxidation model of two partial platinum layers on an ideal platinum substrate. Only two parameters were adjusted in our fit after the monochromator resolution was fixed at 2 eV: the overall scale factor and the binding-energy shift of the PE second-layer atoms. We found that the binding-energy shift of the first layer (0.7 monolayer) was not needed in our fit, therefore was set to zero. The fit value of the energy shift was a surprisingly large value of 9(2) eV. Considering that no other adjustable parameters were used in the calculation, the agreement is excellent for both L values. The minimum near 20 eV and subsequent oscillations at a higher energy in the fit are essentially due to f'' .

In Fig. 3(c) the data taken at X25A for several L values are shown by the connected open circles. These data are compared to the essentially same calculations with the 9 eV shift but with 4 eV monochromator resolution shown as smooth solid lines in Fig. 3(d). The individual agreement may not seem impressive. However, the overall qualitative agreement is very good. Note that the qualitative features of the energy scans were all reproduced near the edge. In particular, the intensities for $L = 1.55, 1.8,$ and 2.2 (three scans from the bottom) demonstrate that the features are clearly different from

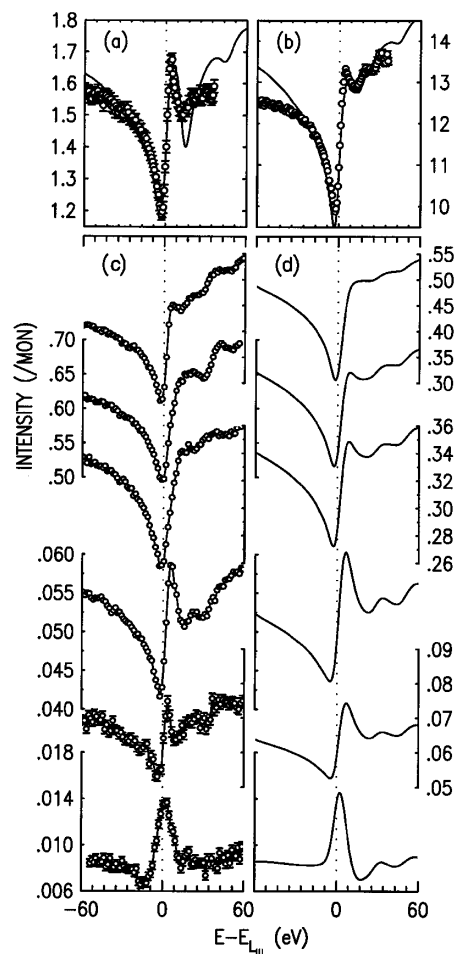


FIG. 3. Upper panels: Energy scans at $L = 2.2$ (a) and 2.6 (b) measured at the 12-ID-B beam line, APS. The solid lines are fits to the data. Lower panels: (c) The scans measured for several L values at the X25 beam line, NSLS (open circles are connected by solid lines for clarity), and (d) the corresponding calculations using the fit parameters of (a) and (b). The values of L are 0.8, 2.6, 0.9, 2.2, 1.8, and 1.55, respectively, from the top. The intensity axes of (c) and (d) are shown staggered, at right for the top scan, at left for the next, and so forth.

the usual shape of single negative singularity expected for a resonance scattering factor, and that the calculations reproduce all the unusual features at least qualitatively. The measurements were performed at two different beam lines on three different Pt(111) single crystals, and all the main characteristics of the results were reproduced numerous times.

The anodic surface oxidation is different from surface oxidation in a UHV environment. The surface is under water and in an extremely high electric field since an anodic potential is applied across a double layer region of only tens of angstroms. Under this electric field, the electrons will be *pulled* toward the surface. In addition, the PE second-layer platinum atoms are surrounded by nearest neighbor oxygen atoms [7] which tend to further deprive the platinum atoms of electrons. In fact, the measured charge transfer is as large as $1.7 e^-/\text{Pt}$ [7]

and we expect that those atoms are at a higher oxidation state and have higher binding energies of core electrons than the atoms in the rest of the layers. This is why we see the large 9 eV shift of the L_{III} edge of the second-layer platinum atoms but we see no observable amount of shift for the first-layer platinum even though platinum atoms in both layers are expected to have formed Pt-O. The large shift of the core binding energy (much larger than any surface studies done under UHV condition) is not unreasonable compared to an ionized isolated atom where the core-electron binding energies can shift as much as one Ry per one-electron loss [14]. Since the Pt-O involves nearly two electrons, the 9 eV shift is yet smaller than the shift expected for a doubly ionized, isolated platinum atom. However, it is possible that a part of the shift may originate from a higher intermediate quantum state [see Eq. (1)] for the PE platinum atoms. This can happen if the oxide monolayer forms a band structure very different from the rest of the metallic layers thereby pushing up the available unoccupied state compared to the Fermi level. But this effect cannot be larger than the work function. Therefore, the majority of the 9 eV shift must come from the core-level binding-energy shift.

Although our modeling and understanding of the data are narrowly limited to the shift of the Pt L_{III} -edge binding energy due to the change in the oxidation state, our results essentially prove the thesis of the paper. We ignored the potentially important DAFS effects in our data analyses. However, we have sufficiently proven the most basic feature of the x-ray resonance surface scattering, namely, that surface scattering can deliver monolayer or submonolayer sensitive measurements of the oxidation state through highly sensitive Q -dependent energy-dispersive measurements due to the *interferences* between the scattering amplitudes from the individual surface layers. From an electrochemical stand point, we have shown directly that the long-proposed place exchange of surface platinum and oxygen indeed accompanies a substantial electron loss of the PE platinum atoms. Theoretical studies for charge distribution around Pt-O and O-Pt under anodic oxidation conditions will be extremely valuable for comparison with our results.

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