

was taken at the same time. The OWG electrode had sheet resistance of ca. 500 Ω/cm^2 and donor density of ca. $10^{20}/\text{cm}^3$ ($[\text{SbCl}_3]$ in the spray solution = 2.5 wt %); the optical path length was 1 cm.

It is apparent from Figure 3 that I_{OWG} increased when MB was reduced to the colorless form, and reoxidation of reduced MB caused a decrease in I_{OWG} . It should be noted that almost the same result was obtained when the dye solution was replaced with a 0.1 mol/dm³ KCl solution to leave the adsorbed dye on the electrode surface. This shows that the change in I_{OWG} shown in Figure 3 is mainly due to the redox reaction of the adsorbed dye molecules. In addition, O₂ evolution at higher potential regions and H₂ evolution at lower potential regions did not affect I_{OWG} . This is because these reactions do not give color changes at the electrode surface.

The sensitivity factor² of this system was estimated by comparing absorption spectra of adsorbed MB taken with a spectrophotometer and attenuation of the guided light due to adsorbed MB; typical values of sensitivity factor were 20–40 depending on the mode number. These values compare well with those for glass OWGs. This shows that the guided light has sufficiently large electric field in the SnO₂ layer as well as at the surface of SnO₂ as expected. The sensitivity values obtained here is similar to those for a carefully designed internal multireflection measurement.⁸

We can, however, increase the sensitivity of the OWG electrodes further by increasing the optical path length and by changing the OWG parameters, e.g., refractive indexes of the OWG materials.

In order to make accurate and fast electrochemical measurements using the OWG electrodes, the conductivity of the conductive film should be as high as possible. However, an increase in the conductivity of the film causes attenuation of the guided light. We therefore will have a practical limit of the conductivity. However, we can avoid this problem by optimizing the design of the OWG electrodes. For instance, we can coat the surface of the SnO₂ film with metal except for the OWG region to reduce the total resistance of the electrode; the metal part should be covered with an inert material in order to avoid direct contact with the electrolyte solution. It is rather easy to make such an OWG electrode having an OWG region of 1 mm width and of 1 cm length. This electrode will give a resistance of 50 Ω when the resistivity of the SnO₂ film is 500 $\Omega\text{ cm}$.

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FEATURE ARTICLE

Is There Any Beam Yet? Uses of Synchrotron Radiation in the in Situ Study of Electrochemical Interfaces

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The advantages of employing synchrotron radiation for the in situ study of electrochemical interfaces are discussed with emphasis on the techniques of surface EXAFS (extended X-ray absorption fine structure) and X-ray standing waves. The principles behind the techniques are briefly considered followed by a discussion of recent experimental results. Examples include the study of underpotentially deposited metallic monolayers, polymer films on electrodes, and in situ measurement of adsorption isotherms. We conclude with an assessment of future directions.

Introduction

The central goal of electrochemical research is to understand and control electrochemical reactivity at the atomic and molecular levels. Such control and understanding, if achieved, would profoundly affect many areas of scientific, technological, and economic importance. The establishment of understanding of structure/reactivity correlations are critical to the achievement of these goals.

The interfacial nature of electrochemical reactions makes their study particularly difficult since they involve the coupling of a multitude of processes including transport rates and the nature and form of the reactant(s) and product(s) as well as the electron-transfer event itself. In addition, the nature of the electrode surface, including its crystallographic orientation, can profoundly affect reactivity. Furthermore, the very high electric fields present

will distort the electronic clouds of species in the vicinity of the electrode and will give rise to gradients in potential and ionic distributions.¹ Finally, since only the region proximal to the electrode/solution interface itself will be affected, we need to develop techniques that will allow us to probe only this region. All of these aspects have, thus far, presented some formidable obstacles to the structural characterization of electrode/solution interfaces.

In recent years,² however, there has been a renewed interest in the study of the electrode/solution interface due in part to the

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development of new spectroscopic techniques such as surface-enhanced Raman spectroscopy,³ electrochemically modulated infrared reflectance spectroscopy and related techniques,⁴ second-harmonic generation,⁵ and others that give information about the identity and orientation of molecular species in the interfacial region. Other techniques such as ellipsometry,⁶ electroreflectance spectroscopy, and differential reflectance spectroscopy⁷ have been used to follow adsorption, film formation, and surface reaction.

The major limitation of these techniques is that the information extracted relates only indirectly to microscopic structural details, and hence, the accuracy of the conclusions rests on the appropriateness of the assumptions made in the models employed. As a result, our knowledge of the electrode/solution interface at the atomic level is still very rudimentary.

This can be attributed, in part, to the lack of structure-sensitive techniques that can operate in the presence of a condensed phase. Ultrahigh-vacuum (UHV) surface spectroscopic techniques such as low-energy electron diffraction, Auger electron spectroscopy, and others have been applied to the study of electrochemical interfaces, and a wealth of information has emerged from these ex situ studies on well-defined electrode surfaces.⁸ However, the fact that these techniques require the use of UHV precludes their use for in situ studies. In addition, transfer of the electrode from the electrolytic medium into UHV introduces the question of whether the nature of the surface examined ex situ has the same structure as the surface in contact with the electrolyte and under potential control. Furthermore, any information on the solution side of the interface is lost.

Because of their short wavelengths and significant penetration depths, X-rays represent a unique tool with which to study atomic and molecular details of electrochemical interfaces. The main difficulty with these measurements has been the low intensities available in conventional X-ray sources. The advent of synchrotron radiation sources of high-energy and high-intensity X-rays⁹ has dramatically changed the outlook. As a result, a number of experiments can now be employed in the in situ study of electrochemical interfaces including EXAFS (extended X-ray absorption fine structure), X-ray standing waves (XSW), and surface diffraction. It is clear that the application of these techniques to the study of electrochemical interfaces will allow a much deeper understanding of structure-reactivity correlations.

In this article we present an overview of the uses of synchrotron radiation in the study of electrochemical interfaces with emphasis on surface EXAFS and XSW. In addition, we project a view to some of the future applications.

Synchrotron Radiation

No single development has influenced the use of X-ray-based techniques more than the development of synchrotron radiation sources based on electron (or positron) storage rings. These provide a continuum of photon energies at intensities that can be from 10^3 to 10^6 higher than those obtained with conventional X-ray tubes, thus dramatically decreasing data acquisition times as well as making other experiments feasible. In the present context, the most attractive features of synchrotron radiation are the high

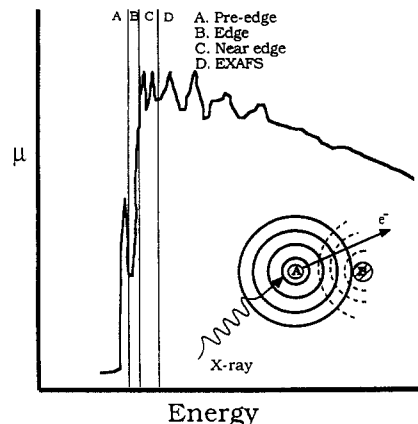


Figure 1. Depiction of the various regions in an X-ray absorption spectrum. Inset: Interference between outgoing (solid lines) and backscattered waves (broken lines) giving rise to EXAFS.

intensities, broad spectral range, and high degree of linear polarization.¹⁰

Synchrotron radiation is based on the emission of electromagnetic waves by accelerated charged particles, orbiting electrons, or positrons, in this case, at relativistic speeds. The angular distribution of the radiation pattern is highly peaked in the tangential forward direction, and this natural collimation effect gives rise to very high fluxes on small targets.

The spectral distribution of synchrotron radiation is continuous and depends on a number of factors. Two that are particularly important are the electron energy (E) (expressed in gigaelectronvolts; 10^9 eV) and the bending radius R (in meters) of the orbit. These are related by the critical energy, E_c , given by

$$E_c \text{ (keV)} = 2.21 E^3 / R \quad (1)$$

The fact that E_c is inversely proportional to the bending radius is used in so-called insertion devices such as wiggler and undulator magnets.¹¹ Although a description of these is beyond the scope of this article, the basic principle behind these is to make the electron beam undergo sharp serpentine motions, thereby having a very short radius of curvature. The net effect is to increase the flux and the critical energy.

Another very important property of synchrotron radiation is its very high degree of polarization. The radiation is predominantly polarized with the electric field vector parallel to the acceleration vector. Thus, in the plane of the orbit, the radiation is 100% plane polarized.

The properties and uses of synchrotron radiation have been reviewed, and the interested reader is referred to the monograph by Winick and Doniach.⁹

EXAFS and X-ray Absorption Spectroscopy

Introduction. EXAFS refers to the modulations in the X-ray absorption coefficient beyond an absorption edge¹² (Figure 1). Such modulations can extend up to about 1000 eV beyond the edge and have a magnitude of typically less than 15% of the edge jump. Experimentally, it involves the measurement of the ab-

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sorption coefficient (or any parameter that can be related to it) as a function of photon energy. The absorption coefficient is a measure of the probability that a given X-ray photon will be absorbed and therefore depends on the initial and final states of the electron. The initial state is very well-defined and corresponds to the localized core level. The final state is represented by the photoionized electron which can be visualized as an outgoing photoelectron wave that originates at the center of the absorbing atom. In the presence of near neighbors (at distances less than 5 Å; EXAFS is sensitive only to short-range order), this photoelectron wave can be backscattered (Figure 1, inset) so that the final state will be given by the sum of the outgoing and backscattered waves. It is the interference between the outgoing and backscattered waves that gives rise to the EXAFS oscillations.

The frequency of the EXAFS oscillations will depend on the distance between the absorber and its near neighbors, whereas the amplitude of the oscillations will depend on the numbers and type of neighbors as well as their distance from the absorber. From an analysis of the EXAFS one can obtain information on near-neighbor distances, numbers, and types. A further advantage of EXAFS is that it can be applied to all forms of matter and that one can focus on the environment around a particular element by employing X-ray energies around an absorption edge of the element of interest.

The simple description of EXAFS given above is based on the single electron, single scattering formalism¹³ where it is assumed that, for sufficiently high energies of the photoelectrons, one can make the plane wave approximation and in addition only single backscattering events will be important. This is the reason why the EXAFS is typically considered for energies higher than 50 eV beyond the edge since in this energy region the above approximations hold well.

In addition to the EXAFS region, Figure 1 shows that there are also three other regions; the pre-edge, edge, and near-edge regions. Below or near the edge, there can be absorption peaks due to excitations to bound states. As a result, the pre-edge region is rich in information pertaining to the energetic location of orbitals, site symmetry, and electronic configuration.

The position of the edge contains information concerning the effective charge of the absorbing atom. Thus, its location and change can be correlated with the oxidation state of the absorber in a way that is analogous to XPS measurements.

Finally, in the near-edge region (generally termed XANES; X-ray absorption near-edge structure), the photoelectron wave has very small momentum, and as a result the plane wave as well as the single electron, single scattering approximations is no longer valid. Instead, one must consider a spherical photoelectron wave as well as the effects of multiple scattering. Because of multiple scattering, the photoelectron wave can sample much of the environment around the absorber. Thus, this region of the spectrum is very rich in structural information. However, the theoretical modeling is very complex.^{12e,f,i}

Theory of EXAFS. The EXAFS can be expressed as the normalized modulation of the absorption coefficient as a function of energy:

$$\chi(E) = [\mu(E) - \mu_0(E)] / \mu_0(E) \quad (2)$$

Here $\mu(E)$ is the total absorption coefficient at energy E and $\mu_0(E)$ is the smooth atomlike absorption coefficient. In order to be able to extract structural information from the EXAFS, we need to use a wave vector (k) formulation given by

$$k = ([2m(h\nu - E_0)] / \hbar)^{1/2} \quad (3)$$

where E_0 is defined as the threshold energy which is typically close to but not necessarily congruent with the energy at the absorption edge.

In wave vector form the EXAFS can be expressed as a summation over the various coordination (near neighbor) shells and is given by

$$\chi(k) = \sum_j \frac{1}{k r_j^2} N_j F_j(k) S_j(k) e^{-\sigma_j^2 k^2} e^{-2r_j/\lambda(k)} \sin(2kr_j + \phi_j(k)) \quad (4)$$

where k represents the wave vector, r is the absorber-backscatterer distance, and N_j is the number of scatterers of type j with backscattering amplitude $F_j(k)$. The product of these last two terms gives the maximum amplitude. There are also amplitude reduction factors. $S_j(k)$ takes into account many-body effects such as electron shake-up and shake-off processes, whereas the term $e^{-\sigma_j^2 k^2}$ (known as the Debye-Waller factor) accounts for thermal vibration and static disorder. Finally, the term $e^{-2r_j/\lambda(k)}$ takes into account inelastic scattering effects where $\lambda(k)$ is the mean free path of the photoelectron.

The oscillatory part of the EXAFS ($\sin(2kr_j + \phi_j(k))$) takes into account the relative phases between the outgoing and backscattered waves and as a result includes the interatomic distance between absorber and scatterer. Since the accuracy of the determination of interatomic distances depends largely on the appropriate determination of the relative phases, a great deal of attention has been given to this aspect. This can be achieved by ab initio calculation of the phases involved,¹⁴ or alternatively they can be determined experimentally through the use of model compounds and the concept of phase transferability.¹⁵

Data Analysis. The basic aim of an EXAFS data analysis is to be able to extract information related to interatomic distances, numbers, and types of backscattering neighbors. The first step in the analysis is the background subtraction which is typically done by employing polynomial splines. The EXAFS oscillations are also normalized to a single-atom value by normalizing the data to the edge jump. Afterward, they are converted to wave vector form.

At this stage, the data are multiplied by a power of k , typically k^2 or k^3 . Such a factor cancels the $1/k$ factor in eq 4 as well as the $1/k^2$ dependence of the backscattering amplitude at large values of k . This step is important in that it prevents the large-amplitude oscillations (typically present at low k) from dominating over the smaller ones (typically at high k).

Fourier transform and filtering techniques are then employed, and the resulting data are fitted for phase and amplitude to yield values for interatomic distances and number of near neighbors which are typically accurate to ± 0.02 Å and $\pm 20\%$, respectively.

Surface EXAFS. EXAFS is fundamentally a bulk technique due to the large penetration depth of high-energy X-rays. In order to make it surface sensitive, one can take one of two general approaches. In the first case, if one knows a priori that the specific element of interest is present only at the surface, then a conventional EXAFS measurement will necessarily give surface information. Alternatively, one can employ detection techniques or geometries such that the detected signal arises predominantly from the surface or near-surface region.¹⁶ These include electron detection and operating at angles of incidence that are below the critical angle of the particular material (i.e., grazing incidence). For studies on single-crystal surfaces, surface EXAFS offers an additional experimental handle, and this refers to the polarization dependence of the signal since only those bonds whose interatomic vector has a projection that lies in the plane of polarization of the beam will contribute to the observed EXAFS. Thus, polarization dependence studies can provide a wealth of information concerning adsorption sites and near-neighbor geometries. For a near-neighbor shell of atoms (N_i) whose interatomic vector with the

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absorber makes some angle θ_j relative to the plane of polarization, one can relate the effective coordination number (N_j^*) and the true coordination number through¹⁷

$$N_j^* = 3 \sum_j \cos^2 \theta_j \quad (5)$$

Polarization-dependent surface EXAFS measurements have provided some of the best defined characterizations of adsorbate structures. Other aspects of surface EXAFS have been thoroughly reviewed by Citrin.¹⁸

EXAFS Studies on Electrochemical Systems

The discussion to follow will focus on the study of underpotentially deposited monolayers as well as polymer films on electrodes.

Surface EXAFS Studies of Underpotentially Deposited Metal Monolayers. The study of electrochemically deposited monolayers poses the strictest experimental constraints since the signals are very low. On the other hand, these studies can provide much detail on interfacial structure at electrode surfaces as well as the effects of solvent and supporting electrolyte ions.

Underpotential deposition (UPD)¹⁹ refers to the deposition of metallic layers on an electrode of a different material. The first monolayer is deposited at a potential that is less negative (typically by several hundred millivolts) than the expected thermodynamic potential, hence the term underpotential deposition. This occurs over a somewhat narrow range of potentials where the coverage varies from zero to a monolayer. A distinct advantage of this approach is that it allows for the precise control of the surface coverage from a fraction of a monolayer up to a full monolayer. Since subsequent electrodeposition (bulk deposition) will require a significantly different potential, very reproducible monolayer coverages can be routinely obtained. Thus, this represents a unique family of systems with which to probe electrochemical interfacial structure in situ.

We, and others, have been involved in the study of such systems including Cu/Au(111),²⁰ Ag/Au(111),²¹ Pb/Ag(111),²² and Cu/Pt(111)/I.²³ The first three systems involved the use of epitaxially deposited metal films on mica as electrodes²⁴ which gives rise to electrodes with well-defined single crystalline structures. In the last case a bulk platinum single crystal was employed. Because of the single crystalline nature of the electrodes, polarization dependence studies could be used to ascertain surface structure.

In order to minimize background scattering and attenuation of incident and emitted beams, thin-layer cells were employed in all of these studies, and although very slow sweep rates had to be employed, well-defined voltammetric responses were obtained. For example, Figure 2A,B shows voltammograms for the underpotential deposition of copper on an epitaxial film of gold (111 orientation) on mica and on a bulk Pt(111) single-crystal electrode that had been pretreated with a layer of adsorbed iodine.

The best characterized system to date is the underpotentially deposited copper on gold. In this case we were able to obtain EXAFS spectra of a deposited monolayer with the polarization of the X-ray beam being either perpendicular (Figure 3A) or

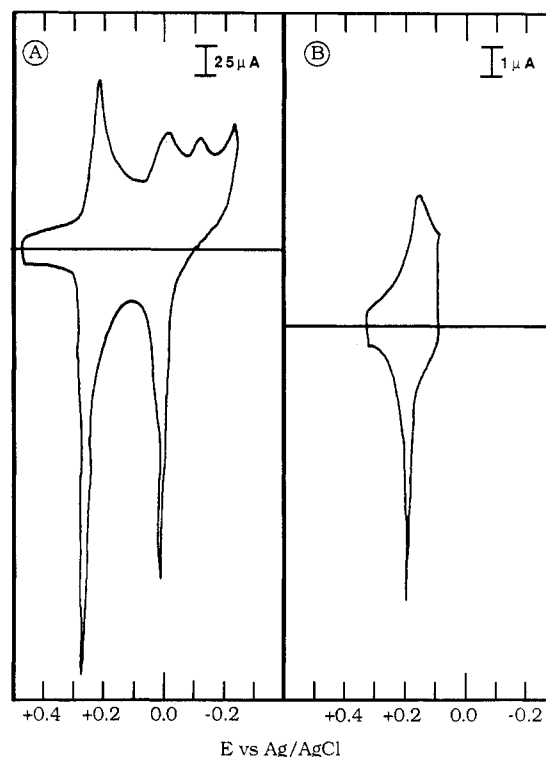


Figure 2. Voltammetric scans for the underpotential deposition of copper on (A) an epitaxial film of gold (111 orientation) on mica and on (B) a bulk Pt(111) single-crystal electrode coated with a layer of iodine. Experimental conditions: (A) 1 M H₂SO₄ containing 5×10^{-5} M Cu²⁺, sweep rate 1 mV/s; (B) 0.1 M H₂SO₄ containing 5×10^{-5} M Cu²⁺, sweep rate 1 mV/s.

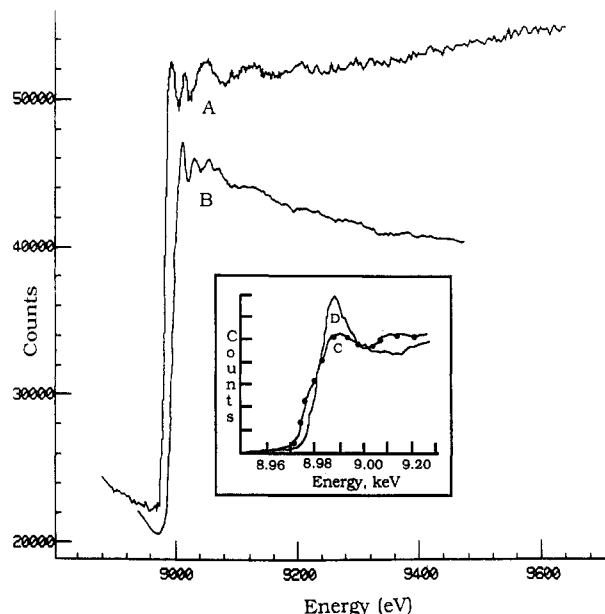


Figure 3. Fluorescence detected (in situ) X-ray absorption spectrum for an underpotentially deposited (UPD) monolayer of copper on a gold(111) electrode with the plane of polarization of the X-ray beam being perpendicular (A) or parallel (B) to the plane of the electrode. Inset: Edge region of the X-ray absorption spectrum for a copper UPD monolayer before (C) and after (D) stripping.

parallel (Figure 3B) to the plane of the electrode. From analysis of the data, a number of salient features can be pointed out. First of all, the copper atoms appear to be located at 3-fold hollow sites (i.e., three gold near neighbors) on the gold (111) surface with six copper near neighbors. The Au-Cu and Cu-Cu distances obtained were 2.58 and 2.91 ± 0.03 Å, respectively. This last number is very similar to the Au-Au distance in the (111) direction, suggesting a commensurate structure. Most surprising,

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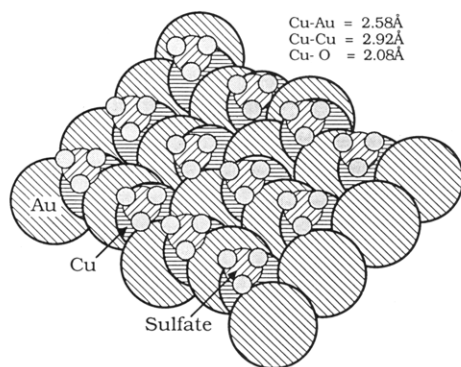


Figure 4. Structure of a copper UPD monolayer on a gold(111) electrode surface.

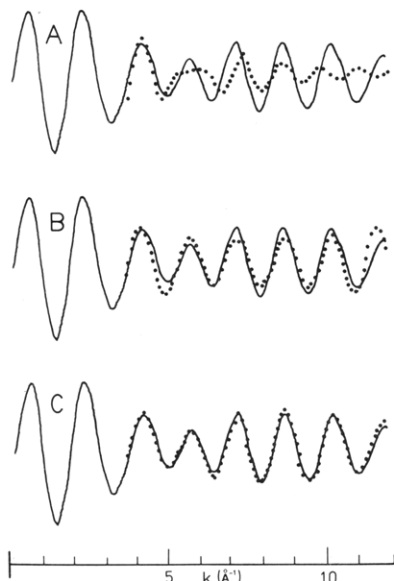


Figure 5. Fourier filtered EXAFS (solid lines) and fits for a silver UPD monolayer on a gold(111) electrode with only gold (A) or oxygen (B) or both gold and oxygen (C) as backscatterers.

however, was the presence of oxygen as a scatterer at a distance of $2.08 \pm 0.02 \text{ \AA}$. From analysis and fitting of the data we obtained that the surface copper atoms are bonded to an oxygen from either water or sulfate anion from the electrolyte. That there might be water or sulfate in contact with the copper layer is not surprising. However, such interactions generally have very large Debye-Waller factors so that typically no EXAFS oscillations (or heavily damped oscillations) are observed. The fact that the presence of oxygen (from water or electrolyte) at a very well-defined distance is observed is indicative of a significant interaction and underscores the importance of in situ studies.

A pictorial representation of this system is shown in Figure 4 where the source of oxygen is presented as sulfate anions since recent experiments by Kolb and co-workers²⁵ indicate that at the potential for monolayer deposition the electrode is positive of the potential of zero charge, E_{PZC} , so that sulfate would be present to counterbalance the surface charge. We could also follow the edge features to ascertain changes in oxidation state. Figure 3C shows the edge region for the deposited monolayer while Figure 3D shows the spectrum after stripping of the copper monolayer. The appearance of the characteristic "white" line (resonance near the edge) as well as the edge shift to higher energies is fully consistent with an oxidation-state change from zero to two.

Studies of Ag on Au(111)²¹ yield very similar results in terms of the structure of the deposited monolayer with the silver atoms being bonded to three surface gold atoms and located at 3-fold hollow sites forming a commensurate layer. Again, strong in-

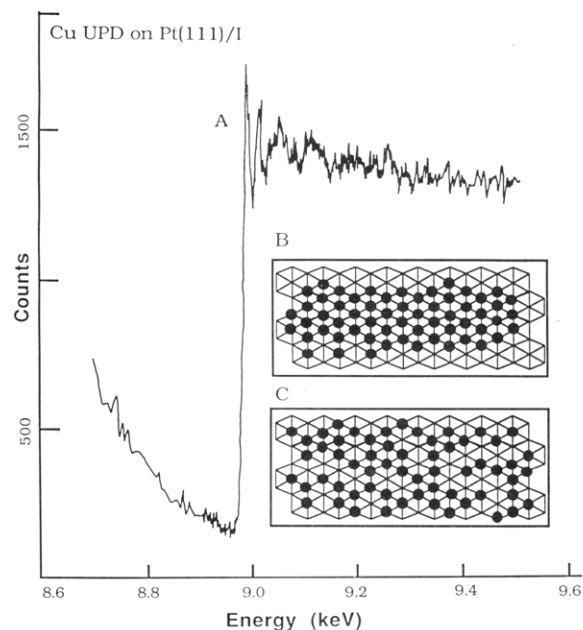


Figure 6. (A) Fluorescence-detected (in situ) X-ray absorption spectrum for an UPD half-monolayer of copper on a Pt(111) single-crystal electrode. Depiction of models involving clustering (B) and random decoration (C).

teraction by oxygen from water or electrolyte (perchlorate) was present. Figure 5A–C shows the Fourier filtered EXAFS as well as the fits obtained when considering scattering by gold (A) or oxygen (B) alone and by both gold and oxygen (C). Whereas in the first two cases there were significant deviations in different parts of the spectrum, the fit with both gold and oxygen backscatterers is excellent over the entire range of k values. Again this underscores the importance of in situ structural determination.

Most recently, we have studied the structure of a half-monolayer of copper underpotentially deposited on a platinum(111) bulk single-crystal electrode annealed in iodine vapor.^{23,26} The spectrum, shown in Figure 6A, although a bit noisy (data acquisition was limited because of problems with the synchrotron), exhibits five well-defined oscillations. It should be mentioned that the plane of polarization of the X-ray beam was parallel to the electrode surface so that the experiment is most sensitive to in-plane scattering of copper by other copper neighbors. From analysis of the data we determined a Cu–Cu distance of $2.85 \text{ \AA}$, which is very close to the Pt–Pt distance in the (111) plane and suggests that the copper atoms are present at 3-fold hollow sites and that they form a commensurate layer with the platinum substrate. More important, however, was the finding that the average number of Cu near neighbors was six. This strongly suggests that at half-monolayer coverage the surface is better represented by large clusters of copper atoms (Figure 6B) than by a surface that is randomly decorated with copper atoms or covered with a lattice with a large interatomic spacing (Figure 6C). This is significant since it is a direct experimental documentation of a mechanism where monolayer formation involves clustering rather than random deposition with subsequent coalescence.

Polymer Films on Electrodes. Although the field of chemically modified electrodes²⁷ has seen a tremendous growth in the recent past, there is very limited information on the structure of these layers. In an effort to bridge this gap, we have performed some in situ EXAFS measurements on chemically modified electrodes.²⁸ Specifically, we have studied films of $[\text{M}(\text{v-bpy})_3]^{2+}$ (v-bpy is

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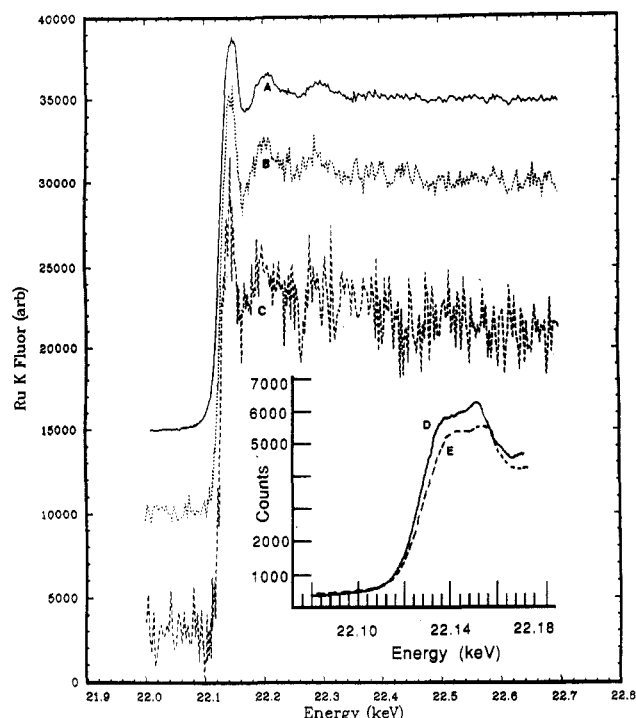


Figure 7. Fluorescence-detected X-ray absorption spectrum for (A) bulk $[\text{Ru}(\text{bpy})_3]^{2+}$ and for platinum electrodes modified with one (C) and five (B) monolayers of poly $[\text{Ru}(\text{v-bpy})_3]^{2+}$. Inset: Changes in the edge location for a platinum electrode modified with a polymeric film of $[\text{Ru}(\text{v-bpy})_3]^{2+}$ as a function of oxidation state. Curves D and E are for Ru(II) and Ru(III), respectively.

4-vinyl-4'-methyl-2,2'-bipyridine; $\text{M} = \text{Ru}, \text{Os}$) and $[\text{Os}(\text{v-bpy})_2(\text{phen})]^{2+}$ electropolymerized onto a platinum electrode and in contact with an acetonitrile/0.1 M TBAP (tetra-*n*-butyl ammonium perchlorate) solution and under potential control. We have focused on determining the lower limit of detection as well as trying to ascertain any differences in the metal-ligand bond distances for the electropolymerized films as a function of surface coverage when compared to the parent complex. Figure 7C,B shows spectra for electrodes modified with one and five equivalent monolayers of the ruthenium complex whereas Figure 7A shows the spectrum for bulk $[\text{Ru}(\text{bpy})_3]^{2+}$. In Figure 7C one can ascertain that only the most prominent features of the spectrum of the parent compound (Figure 7A) are present. (It should be mentioned that a monolayer of $[\text{Ru}(\text{v-bpy})_3]^{2+}$ represents about 5.4×10^{13} molecules/cm², which is about 5% of a metal monolayer. This is mentioned since it is the metal centers that give rise to the characteristic fluorescence employed in the detection.) However, at a coverage of five monolayers (Figure 7B) the spectrum is essentially indistinguishable from that of the bulk material. Upon fitting of the data for phase and amplitude, we obtain a Ru-N distance of 2.01 Å and a coordination number of six. This correlates very well with the known values of 2.056 Å²⁹ and six, respectively. In addition, it is also clear that there is little difference between the electrodeposited polymer and the monomeric parent compound in terms of the near-edge spectral features, pointing to a similar geometric disposition of scatterers. Furthermore, changes in oxidation state can be monitored by the shift in the position of the edge. For example, upon oxidation of the polymer film (at +1.60 V) from Ru(II) (Figure 7D) to Ru(III), the edge position shifts to higher energy by about 1.5 eV (Figure 7E). Thus, one can determine the oxidation state of the metal inside a polymer film on an electrode surface.

Similar results were obtained for the osmium complexes in terms of the local structure around the metal center and changes in the position of the edge as a function of oxidation state. In addition, we were able to correlate changes in the near-edge features with

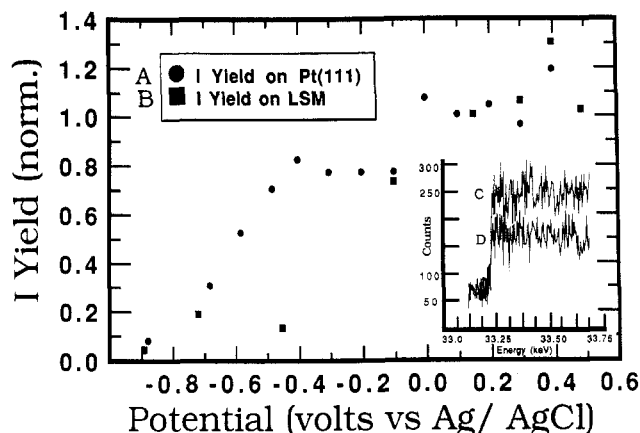


Figure 8. Normalized iodide fluorescence intensity vs applied potential for a Pt(111) single-crystal electrode (A) and a Pt/C LSM (B) immersed in an aqueous solution containing 50 μM NaI/0.1 M Na_2SO_4 . Inset: Changes in the edge jump for the Pt(111) electrode mentioned above at potentials of -0.2 V (D) and +0.2 V (C).

the coordination environment around the osmium metal center.

These results indicate that the structure of electroactive polymer films and the oxidation state of the metal center can be obtained at relatively low coverages, and this should have important implications in trying to identify the structure of reactive intermediates in electrocatalytic reactions at chemically modified electrodes.

In Situ Measurement of Potential/Surface-Concentration Isotherms

Since the magnitude of the edge jump is proportional to the number of absorbers, its potential dependence can be employed in constructing potential/surface-concentration isotherms in situ. We have carried out such a study on iodide adsorption on a Pt(111) electrode surface.³⁰ (The adsorption of iodide was carried out from a solution containing 0.05 mM NaI, 0.1 M sodium sulfate, and 5 mM phosphoric acid at a pH of 6.7 obtained by the addition of sodium hydroxide. Prior to adsorption of iodide from solution, the adsorbed iodine layer (present from the pretreatment) was electrochemically removed by hydrogenation at -1.0 V. The electrode was then allowed to contact the NaI solution for 10 min at the applied potential under study. Scans across the iodine K edge were obtained, and typically 35 scans, each of about 10 min, were obtained at each potential.)

Hubbard and co-workers³¹ recently reported an isotherm obtained ex situ by monitoring the iodine Auger electron intensity from electrodes that were emersed from iodide-containing solutions at different potentials. Their data show that at potentials negative of -0.60 V there is no adsorption. The iodine coverage then increases as the emersion potential is made progressively less negative, and there is a significant change in coverage from $1/3$ to $4/9$ in going from -0.20 to +0.20 V. The coverage remains essentially constant and then decreases at about +0.60 V due to competitive adsorption of oxygen on the platinum surface.

Our results, shown in Figure 8A, are in very good agreement with those mentioned above for potentials negative of +0.40 V. Especially gratifying was the fact that we could monitor (in situ) (Figure 8, inset) the change in coverage from $1/3$ to $4/9$ by changing the applied potential from -0.2 (Figure 8D) to +0.3 V (Figure 8C).

Our data, however, differ significantly from theirs at potentials positive of +0.40 V. In our case the iodine fluorescence intensity increases whereas in their case it remains constant and then decreases at potentials positive of +0.60 V due to faradaic oxidation. It needs to be pointed out that for this system the potential of point of zero charge, E_{PZC} , is estimated to be at about +0.40

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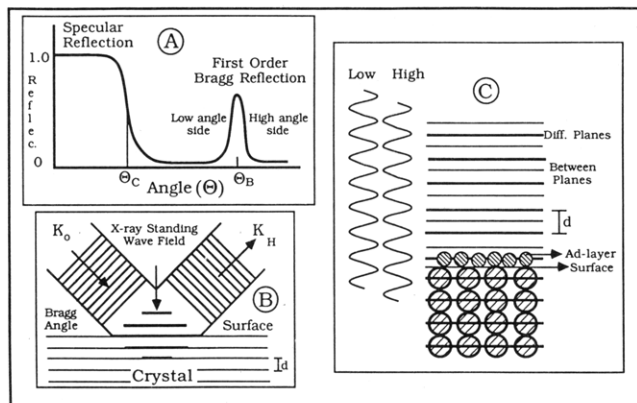


Figure 9. (A) Depiction of specular and first-order Bragg reflection from a surface. (B) Generation of an X-ray standing wave field. (C) Movement of an X-ray standing wave field in the $-H$ direction upon advancing the angle of incidence across a Bragg reflection.

V.³⁰ Very little faradaic current was observed in this potential region, and we are tentatively interpreting our data as indicating that the increase in the iodine fluorescence intensity at potentials positive of +0.40 V is due to the association of iodide or its oxidation products with the electrode surface. However, the point to be made is that the potential dependence of the surface concentration of a species can be followed in situ.

X-ray Standing Waves

Introduction. The X-ray standing wave technique represents an extremely sensitive tool for determining the position of impurity atoms within a crystal^{32a,b} or adsorbed onto crystal surfaces.^{32c} This technique is based on the X-ray standing wave field that arises as a result of the interference between the coherently related incident and Bragg diffracted beams from a perfect crystal. In the vicinity of a Bragg reflection (Figure 9A,B), an incident plane wave (with wave vector k_0) and a reflected wave (with wave vector k_H) interfere to generate a standing wave with a periodicity equivalent to that of the (h,k,l) diffracting planes. The standing wave not only develops in the diffracting crystal but also extends well beyond its surface with the nodal and antinodal planes of the standing wave being parallel to the diffracting planes. As the angle of incidence is advanced through the strong Bragg reflection, the relative phase between the E -field amplitudes of the incident and reflected plane waves changes by π radians. As a result, the antinodal planes of the standing wave field move in the $-H$ direction by $1/2$ of a d spacing, from a position halfway between the (h,k,l) diffracting planes (on the low angle side of the Bragg reflection) to a position that coincides with them (on the high angle side of the Bragg reflection) (Figure 9C). Thus, the standing wave can be made to sample an adsorbate or overlayer at varying positions above the substrate interface and normal to its diffraction planes.

For an atomic overlayer that is positioned parallel to the diffracting planes, the nodal or antinodal planes of the standing wave will pass through the atom plane as the angle is advanced. Since the photoelectric effect is (by the dipole approximation) proportional to the E -field intensity at the center of an atom, the fluorescence emission yield will be modulated in a characteristic fashion as the substrate is tilted in angle. The phase and amplitude of this modulation (or so-called coherent position and coherent fraction) are a measure of the mean position $\langle Z \rangle$ and width $(\langle Z^2 \rangle)^{1/2}$ of the distribution of atoms in the overlayer. The Z scale is mod d and points in the direction normal to the diffraction planes. Standing wave measurements of $\langle Z \rangle$ and $(\langle Z^2 \rangle)^{1/2}$ can be accurate to within 1% and 2% of the d spacing, respectively.³³

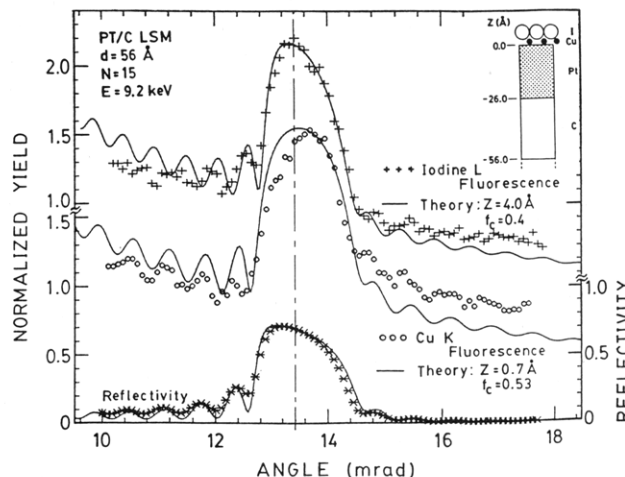


Figure 10. Normalized fluorescence yield for I and Cu and reflectivity profile for a Pt/C LSM with an electrodeposited copper layer and adsorbed iodide. Discrete points: experimental data. Solid lines: theoretical fits.

One of the problems associated with the implementation of the standing wave technique is the fact that it requires the use of perfect or nearly perfect crystals. This presents a problem especially for relatively soft materials such as copper, gold, silver, and platinum which are not only very difficult to grow in such high quality but are also very difficult to maintain in that state. Thus, most experiments have been performed on silicon or germanium single crystals.

An alternative to the use of perfect crystals is the use of layered synthetic microstructures (LSM).³⁴ These devices are prepared by the sequential deposition of alternate layers of materials, typically of high and low electron density elements such as W/C, Mo/C, W/Si, and Pt/C, onto a smooth substrate material such as silicon or cleaved mica. The number of layer pairs is such that the d spacing of the synthetic multilayer dictates the diffracting properties of the interface. The advantages that accrue from the use of LSM are manifold. Firstly, these devices are physically robust and can be handled without undue provisions. They can be tailored to contain materials of interest and, furthermore, one can vary the d spacing of the diffracting planes (20–100 Å), thus varying that the probing distance of the technique. Their use also simplifies experimental design since the angular reflection widths for the LSM's are of the order of milliradians as opposed to microradians for crystals.

We have employed a Pt/C (Pt as the outermost layer) LSM in the investigation of the adsorption of iodide followed by the electrodeposition of a layer of copper.³⁵ Initially, a layer of iodide was adsorbed onto the platinum surface of the LSM (electrode), and it was then studied by the XSW technique. The characteristic iodine L fluorescence could be detected, and its angular dependence was indicative of the fact that the layer was on top of the platinum surface layer. A well-developed reflectivity curve (collected simultaneously) was also obtained. Following this, the LSM was placed in an electrochemical cell and half a monolayer of copper was electrodeposited. The LSM (now with half a monolayer of copper and a monolayer of iodide) was again analyzed by the XSW technique. Since the incident X-ray energy (9.2 keV) was capable of exciting fluorescence from both the copper and the iodide, the fluorescence intensities of both elements (as well as the reflectivity) were obtained simultaneously. The results presented in Figure 10 show the reflectivity curve and the modulation of the iodide and copper fluorescence intensities. The most important feature is the noticeable phase difference between the iodide and copper modulations, i.e., the location of the iodide and copper fluorescence maxima with the copper maximum being

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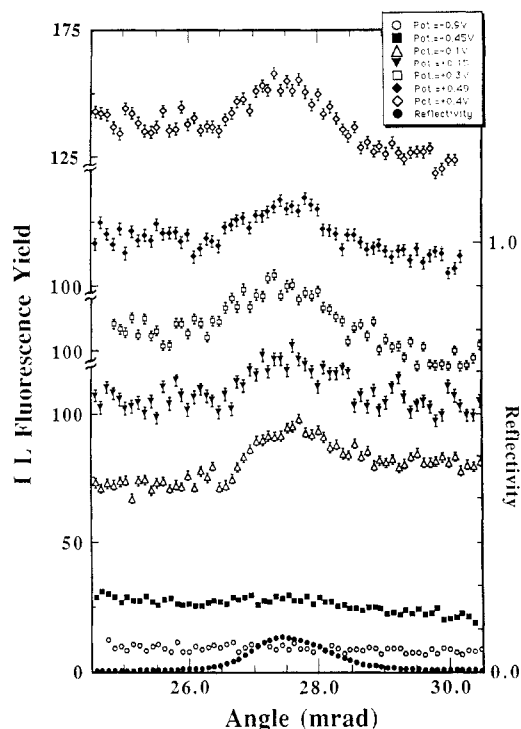


Figure 11. Normalized iodide fluorescence intensity vs applied potential and reflectivity profile for a Pt/C LSM immersed in an aqueous solution containing 50 μM NaI/0.1 M Na_2SO_4 .

to the right of the iodide maximum. Since the antinodes move inward as the angle increases, the order in which these maxima occur can be unambiguously interpreted as meaning that the copper layer is closer than the iodide layer to the surface of the platinum. Since the iodide had been previously deposited on the platinum, this represents unequivocal evidence of the displacement of the iodide layer by the electrodeposited copper. Similar findings based on Auger intensities and LEED patterns have been previously reported by Hubbard and co-workers.²⁶ In addition, from an analysis of fluorescence yields, we were able to determine that the electrodeposited copper layer had a high degree of coherence with the underlying substrate.

Most recently, we have studied the potential dependence of the adsorption of iodide onto a Pt/C LSM. In this experiment we simultaneously monitored the reflectivity across the first order Bragg reflection as well as the characteristic iodine fluorescence intensity. Figure 11 shows data for the normalized iodide fluorescence intensity as a function of potential, and it can be seen that at -0.90 V essentially no iodide is present at the interface. As the potential is made progressively positive, the iodide fluorescence intensity increases and the peak maximum shifts to lower angles up to a potential of $+0.40$ V. At $+0.49$ V, the fluorescence intensity decreases and the peak maximum again moves toward higher angles. Qualitatively, these data appear to indicate that at -0.90 V there is no iodide adsorbed and that the coverage increases as the potential is made progressively positive. The movement of the peak maximum to lower angles indicates that, on average, the interfacial iodine density is moving away from the electrode surface.

The iodide fluorescence intensity was normalized and plotted vs potential, and, except for one point, the results (Figure 8B) are

in excellent agreement with those from our previously mentioned study.

In addition to our studies, Materlik and co-workers have studied the underpotential deposition of thallium on single-crystal copper electrodes under both ex situ³⁶ and in situ³⁷ conditions. In general, these studies are of great significance since they demonstrate the applicability of the X-ray standing wave technique to the in situ study of UPD monolayers, even employing metallic single-crystal electrodes.

As mentioned in the Introduction, one of the limitations of the XSW technique is that it requires the use of perfect crystals. Although LSM's can be employed, the layers within an LSM are amorphous and therefore not well-defined. It would be most desirable to be able to perform XSW studies on single-crystal surfaces without having to resort to perfect or nearly perfect crystals.

An alternative is offered by employing a backscattering geometry on a single crystal rather than the conventional shallow angle incidence. The dynamical theory of X-ray diffraction predicts that in a backscattering geometry the reflection widths for a single-crystal surface will be of the order of milliradians as opposed to microradians under conventional incidence. This means that single crystals with a larger mosaic spread (such as those encountered in typical good quality though not perfect single crystals) could be employed in such measurements. We have performed such an experiment on a locally grown and cut bulk Pt(111) single crystal and found the reflectivity width of 6 mrad to be very close to that predicted by theory.³⁸ Thus, this approach may allow a more widespread use of this technique.

Conclusions and Future Directions

The use of X-rays as probes is providing a rare glimpse at the in situ structure of electrochemical interfaces. Although these studies are still in very early stages of development, it is clear that their use will become more widespread and other applications and techniques that will complement and augment our understanding will be explored. Of particular note are the recent reports on surface diffraction³⁹ and time-resolved measurements.⁴⁰ We are confident that these studies will provide the basis for a better understanding and control of electrochemical reactivity.

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