

# Structural studies of electrochemical interfaces with x rays

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(Presented on 31 August 1988)

We have employed x-ray absorption spectroscopy, including surface EXAFS (extended x-ray absorption fine structure) and x-ray standing waves (XSW) in the *in-situ* structural study of electrochemical interfaces. The SEXAFS technique was used to study the structure of half a monolayer of copper underpotentially deposited on a Pt(111) electrode. From analysis of the data a Cu-Cu distance of 2.85 Å and a coordination number of six were determined, strongly suggesting that the deposit is largely composed of clustered sites. The electrosorption isotherm of iodide on a Pt(111) electrode surface was measured *in situ* using x-ray absorption spectroscopy, and it exhibited two plateaus which we ascribe to changes in packing density and surface structure. Using x-ray standing waves, we have studied the potential dependence of the adsorption of iodide onto a Pt/C LSM and have interpreted the results in terms of distributional changes in the vicinity of the electrode surface.

## INTRODUCTION

The study of the structure of the electrode/solution interface represents a problem of both fundamental and practical importance in electrochemistry and many other interfacial disciplines since its properties greatly affect and often control reactivity.<sup>1</sup> Its importance relates to a broad range of problems including corrosion, catalysis, fuel cells, and many others.

In recent years there has been a renewed interest in the study of the electrode/solution interface<sup>2</sup> due in part to the development of new spectroscopic techniques such as surface enhanced Raman spectroscopy,<sup>3</sup> electrochemically modulated infrared reflectance spectroscopy and related techniques,<sup>4</sup> second-harmonic generation,<sup>5</sup> and others which give information about the identity and orientation of molecular species in the interfacial region. Other techniques such as ellipsometry,<sup>6</sup> electroreflectance and differential reflectance spectroscopy,<sup>7</sup> have been used to follow adsorption, film formation, and surface reactions.

These techniques, though powerful, do not reveal the structure and geometric arrangement of atomic species at the interface. Thus, in spite of its importance, our knowledge of the structure 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 (LEED), Auger electron spectroscopy (AES), 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.<sup>8</sup>

However, the fact these techniques require the use of UHV precludes their use for *in situ* studies of the electrode/solution interface. In addition, transfer of the electrode from the electrolytic medium into UHV introduces the very serious 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, of necessity, lost.

X-ray photons, on the other hand, have significant propagation distances even in condensed phases making them suitable probes of the atomic structure of interfacial species. The main difficulty with these measurements has been the low intensities available in conventional x-ray sources. The advent of synchrotron radiation sources<sup>9</sup> based on electron (or positron) storage rings has dramatically changed the outlook by providing continuum sources of x rays at intensities that are five to six orders of magnitude bigger than conventional sources. Thus, EXAFS (extended x-ray absorption fine structure)<sup>10</sup> x-ray absorption near-edge structure (XANES),<sup>10</sup> x-ray standing waves (XSW),<sup>11</sup> and other techniques based on the use of x rays as probes can be applied to the *in situ* study of electrode/solution interfaces. These techniques can be used to obtain information on site symmetry, chemical bonding, interatomic distances, and the coordination number about a species in the interfacial region while the electrode is in contact with an electrolyte solution and under potential control.

We report here on the use of surface EXAFS to study the structure of half a monolayer of copper underpotentially deposited on a Pt(111) electrode and of x-ray absorption spectroscopy and XSW techniques to study the electrosorption isotherm of iodine on platinum.

## 1. EXPERIMENT

Measurements were conducted at the A-3, C-2, and B-cave stations of the Cornell High Energy Synchrotron Source (CHESS). A Si(220) double-crystal monochromator was used to isolate the x-ray wavelength of interest. The incident beam was collimated with a pair of motorized hutch slits and Huber slits just before the sample. The incident beam intensity was monitored with an ionization chamber with flowing nitrogen as fill gas. The characteristic fluores-

cence was monitored using an energy dispersive Si(Li) detector (Princeton Gamma-Tech). The fluorescence and scattering from the sample were reduced by using a thin lead slit directly in front of the detector which reduced the total counts at the detector and enhanced signal to noise.

The electrochemical cell (Fig. 1), contained inside an aluminum housing (not shown), consisted of a cylindrical Teflon body with feedthroughs for electrolytes and electrode connections. A thin layer of solution (of approximately 5  $\mu\text{m}$ ) was trapped between the electrode and a 6- $\mu\text{m}$ -thick polypropylene film, held in place by a Teflon ring. Whenever the applied potential was adjusted, the film was distended by introducing additional electrolyte, so as to allow for adsorption (desorption) from bulk solution. Afterwards, the thin layer configuration was reestablished by the removal of electrolyte. Solutions were introduced into the cell with solution bubblers. The aluminum housing was continuously flushed with prepurified nitrogen gas to minimize oxygen diffusion into the electrochemical cell. The entire cell, with aluminum housing, was mounted on a Huber 410 one-circle goniometer stage. This assembly allowed for very precise angular motion as well as vertical and horizontal translation of the sample.

The applied potential was controlled with a Princeton Applied Research model 173 Potentiostat and model 175 Universal Programmer. Potentials are reported against a silver/silver chloride reference electrode which was separated from the thin-layer cell by a porous Vycor plug.

Solutions were prepared using ultrapure reagents (Alfa) and pyrolytically distilled water (PDW). Prior to injection of electrolyte into the cell, the solution was degassed with helium for at least 2 h.

A Pt(111) crystal ( $11 \times 11 \times 2$  mm) was grown from the melt at the Materials Preparation Facility at Cornell University. It was pretreated by a procedure analogous to that of Hubbard *et al.*<sup>12</sup>

A platinum-carbon layered synthetic microstructure (LSM) of dimensions  $15 \times 20$  mm was obtained from Ovonic Synthetic Materials Co. It had an average  $d$  spacing of 40 Å and consisted of 200 layer pairs of carbon (14 Å) and

Pt(26 Å), deposited on a silicon substrate with platinum as the outermost layer. Subsequent reflectivity measurements of the multilayer showed the first order Bragg reflectivity to be of the order of 50% as compared to a theoretical reflectivity of about 70%.

For the copper underpotential deposition the solution concentration of copper was 50  $\mu\text{M}$ .

In the study of iodide electrosorption, 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. 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.

The surface EXAFS data was analyzed by a modified version of the program obtained from B. Kincaid (AT&T Bell Labs.) whereas the x-ray standing wave experiments were analyzed by a stratified medium formalism.<sup>13</sup>

## II. RESULTS

### A. Surface EXAFS of copper underpotentially deposited on a Pt(111) electrode

Underpotential deposition (UPD)<sup>14</sup> 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. Since subsequent electrodeposition (bulk deposition) will require a significantly different potential, very reproducible monolayer coverages can be routinely obtained.

We have employed the surface EXAFS technique to study the structure of a half-monolayer of copper underpotentially deposited on a platinum (111) bulk single crystal electrode annealed in iodine vapor.<sup>15</sup> The spectrum, shown<sup>12</sup> in Fig. 2(A), 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  $2.88 \pm 0.02$  Å which is very close to the Pt-Pt distance in the (111) direction and suggests that the copper atoms are present at threefold 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 suggests that at half-monolayer coverage, the surface is better represented by one with large copper clusters [Fig. 2(B)] than by a surface that is randomly decorated with copper atoms or covered with a lattice with a large interatomic spacing [Fig. 2(C)]. This is significant since it is a direct experimental documentation of a mechanism where monolayer formation involves clustering and growth rather than random deposition with subsequent coalescence.

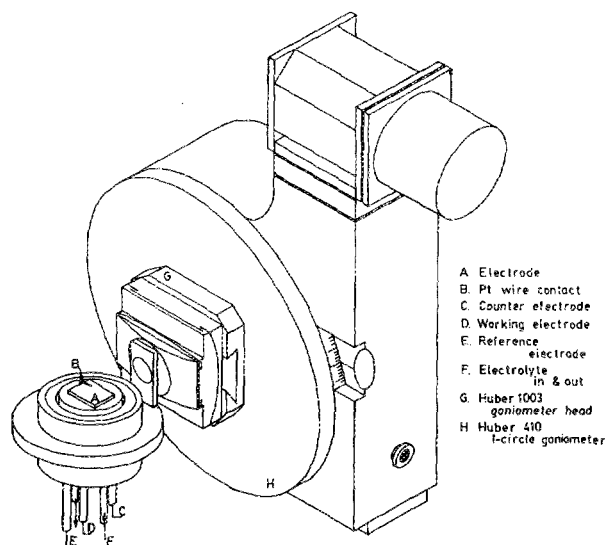


FIG. 1. Electrochemical cell and stage used in the experiments.

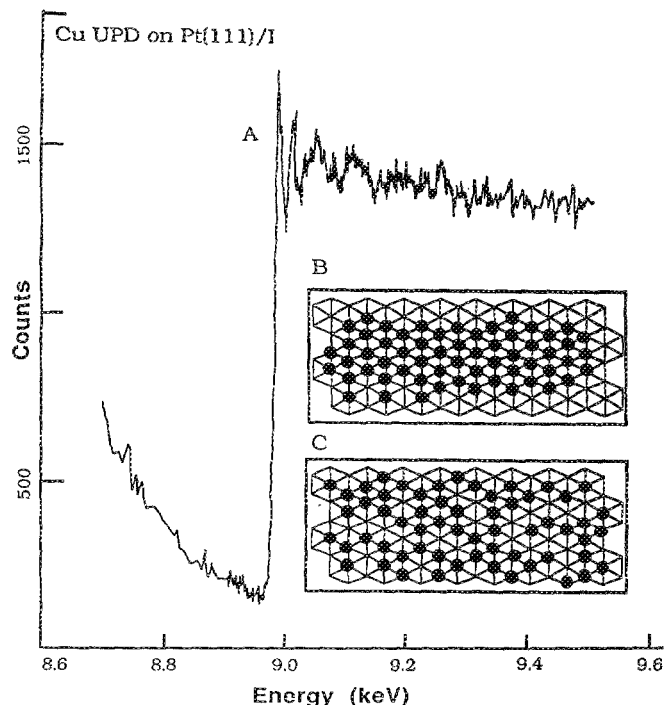


FIG. 2. (A) Fluorescence detected (*in situ*) x-ray absorption spectrum for an underpotentially deposited half-monolayer of copper on a Pt(111) single crystal electrode. Depiction of models involving clustering (B) and random decoration (C) of the surface.

### B. Electrosorption of iodide on a Pt(111) electrode studied *in situ* by x-ray absorption spectroscopy

Since the magnitude of the edge jump in an x-ray absorption spectrum is proportional to the number of absorbers, its potential dependence can be employed to measure potential/surface concentration (electrosorption) isotherms *in situ*. We have carried out such a study on iodide adsorption on a Pt(111) electrode surface. The resulting isotherm, shown in Fig. 3 displayed two plateaus separated by a transition centered at about  $-0.10$  V vs Ag/AgCl. The iodide coverage at the most negative potential studied ( $-1.0$  V) went to an essentially negligible value while that at the positive potential limit ( $+0.50$  V) increased rapidly, suggesting an interfacial accumulation of absorbers.

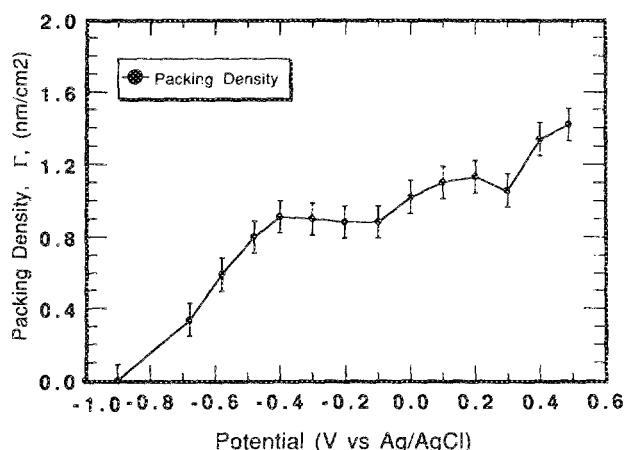


FIG. 3. Electrosorption isotherm for 0.05 mM NaI in 0.1 M  $\text{Na}_2\text{SO}_4/\text{pH} = 6.7$  at a Pt(111) electrode. The lines connect experimental points and do not represent a fit to the data.

The results at the most negative potentials can be interpreted in terms of a model where adsorbed iodine is converted to adsorbed iodide which subsequently shows the behavior expected for a specifically adsorbed anion. That is, there is a marked dependence of the coverage on potential.

The plateaulike features in the isotherm may be explained in thermodynamic terms. For example, we attribute the flatness in the region between  $-0.50$  and  $-0.10$  V to the absence of potential dependence of coverage of a neutral adsorbate (iodine). On the other hand, between  $-0.1$  and  $+0.3$  V, further uptake involves adsorption of iodide. The potential dependence here is due to interaction of the anion with an increasingly positive surface charge. The attainment of a saturation coverage is due to closest packing of iodine species as well as to possible lateral electrostatic interactions. The features in the electrosorption isotherm present at intermediate potentials may also be attributed to the formation of stable structures. Hubbard and co-workers have shown that a transition from a mixed  $\sqrt{3} \times \sqrt{3}$  and  $\sqrt{7} \times \sqrt{7}$  structure to one that is purely  $\sqrt{7} \times \sqrt{7}$  occurs between  $-0.2$  and  $0.0$  V and is accompanied by a change in coverage from  $3/9$  to  $4/9$ .<sup>16</sup> A similar transition is observed here and is assumed, because of the similarity in the packing density change over the transition, to be due to the same structural transition. At the most positive potentials, we believe that the increase in the iodine/iodide concentration is produced by Faradaic

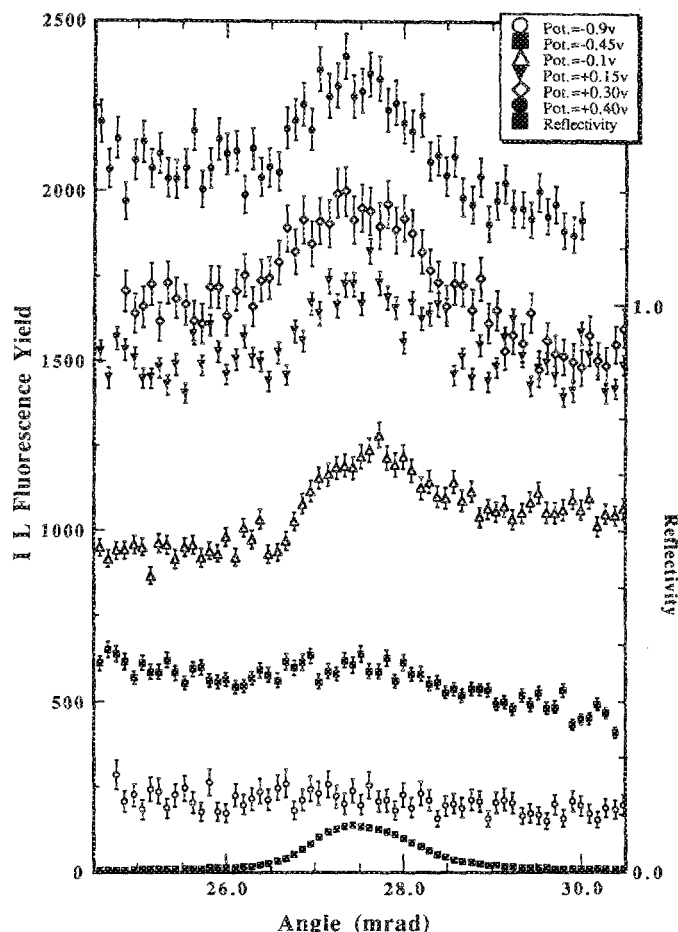


FIG. 4. Normalized iodide fluorescence intensity vs applied potential and reflectivity profile for a Pt/C LSM immersed in an aqueous solution containing 0.05 mM NaI/0.1 M  $\text{Na}_2\text{SO}_4$ .

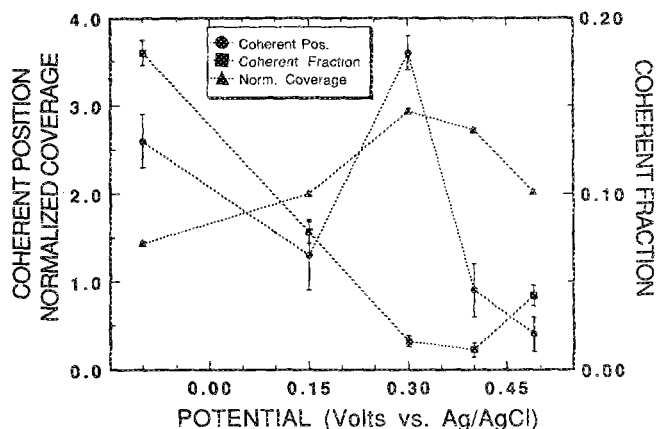


FIG. 5. Plot of coherent position, coherent fraction, and normalized coverage (off-Bragg yield) as a function of electrode potential for a Pt/C LSM immersed in an aqueous solution containing 0.05 mM NaI/0.1M Na<sub>2</sub>SO<sub>4</sub>.

charge flow, followed by association with the adsorbed iodine layer at that potential.

### C. *In situ* x-ray standing wave study of the packing density and potential dependent distributional changes for iodine adsorption at a Pt/C LSM

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 (Fig. 4). From an analysis of the data we were able to determine that at  $-0.90$  V essentially no iodide is present at the Pt/solution 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 towards 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.

Figure 5 shows the potential dependence of the coherent position, the coherent fraction, and the off-Bragg yield, assuming that a model employing these parameters can be invoked. The dependence of the coherent fraction on the applied potential seems to indicate a redistribution of iodide within the diffuse layer as the potential is adjusted. In addition, the minimum in the coherent fraction at about  $+0.35$  V correlates very well with the potential of point of zero charge for this system.<sup>16</sup>

The iodide fluorescence intensity was normalized and

plotted versus potential and the isotherm obtained was in very good agreement to that obtained from x-ray absorption measurements on Pt(111) (*vide-supra*).

### ACKNOWLEDGMENTS

This work was generously supported by the Materials Chemistry Initiative of the National Science Foundation, and the Office of Naval Research. HDA also acknowledges support by the Presidential Young Investigator Award Program at the NSF and the A.P. Sloan Foundation. CHESS is a national facility funded by the National Science Foundation.

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