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Research has involved the use of x-rays as in-situ probes of electrochemical interfaces in an attempt to gain some insights as to how interfacial structure affects electrochemical reactivity. X-rays provide an ideal tool for these studies because of their short wavelength and significant propagation distances even in the presence of a condensed phase. The areas that have been emphasized are:

1. Surface EXAFS
2. X-ray standing waves

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Surface EXAFS and Standing Wave Measurements

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We have been involved in the use of x-rays as in-situ probes of electrochemical interfaces in an attempt to gain some insights as to how interfacial structure affects electrochemical reactivity. X-rays provide an ideal tool for these studies because of their short wavelength and significant propagation distances even in the presence of a condensed phase. The areas that we have emphasized are:

1. Surface EXAFS
2. X-ray standing waves

1. Surface EXAFS:

Our work on surface EXAFS has centered on the study of the structure of underpotentially deposited metal monolayers and redox polymer films on electrodes.

a. UPD metal monolayers:

Underpotential deposition (UPD) 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 up to a full monolayer. Since subsequent electrodeposition (bulk deposition) requires a significantly different potential, very reproducible monolayer coverages can be routinely obtained.

We have studied the structure of Cu on Au(111), Ag on Au(111) (both a full monolayer coverage) and that of Cu on Pt(111)/I at half a monolayer coverage.

For the Cu/Au system, we have been able to determine that the copper atoms appear to be located at three fold hollow sites (i.e.; 3 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 $2.91 \pm 0.03 \text{ \AA}$, respectively. This last number is very similar to the Au-Au distance in the (111) direction, suggesting a commensurate structure. Most surprising, 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 determined 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 vibrational amplitudes (Debye Waller factor) 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.

Studies of Ag on Au(111) 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 three-fold hollow sites forming a commensurate layer. Again, strong interaction by oxygen from water or electrolyte (perchlorate) was present. In this case the Ag-Au and Ag-O distances were 2.75 and 2.42 ± 0.05 Å, respectively.

We have also studied the structure of a half-monolayer of copper underpotentially deposited on a platinum (111) bulk single crystal electrode annealed in iodine vapor. From analysis of the data we determined a Cu-Cu distance of 2.80 Å which is very close to the Pt-Pt distance in the (111) direction and suggests that the copper atoms are present at three-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 6. This suggests that at half-monolayer coverage the surface is better represented by one with large clusters of copper atoms than by a surface that is randomly decorated with copper atoms or covered with a lattice with a large interatomic spacing. 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.

b. Polymer films on electrodes:

We have performed surface EXAFS studies of redox polymer films on electrode surfaces. Specifically, we have studied films of $[\text{Ru}(\text{v-bpy})_3]^{2+}$ (v-bpy is 4-vinyl,4'-methyl-2,2'-bipyridine) electropolymerized onto a platinum electrode and in contact with an acetonitrile/0.1M TBAP (tetra-n-butyl ammonium perchlorate) solution and under potential control. We were able to obtain good quality spectra (indistinguishable from that of the bulk material) for coverages of about 5 monolayers. (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.) 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. These correlate very well with the known values of 2.056 Å and six, respectively. In addition, changes in oxidation state could 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) to Ru(III), the edge position shifts to

higher energy by about 1.5 eV. Thus, one can determine the oxidation state of the metal inside a polymer film on an electrode surface.

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.

2. X-Ray Standing Waves

The X-ray standing wave (XSW) technique represents an extremely sensitive tool for determining the position of impurity atoms within a crystal or adsorbed onto crystal surfaces. 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, incident and reflected plane waves (K_O and K_H) interfere to generate a standing wave with a periodicity equivalent to that of the (h,k,l) diffracting planes. The standing wave develops not only in the diffracting crystal, but also extends well beyond its surface (about 1000\AA) with the nodal and antinodal planes of the standing wave being parallel to the diffracting planes. As the angle of incidence is advanced across the strong Bragg reflection, the relative phase between the incident and reflected plane waves (at a fixed point relative to the crystal's diffraction planes) changes by π and as a result, the antinodal planes of the standing wave field move into the crystal in a direction normal to the diffraction planes by $1/2$ of a d-spacing, from a position half-way 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). 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. The key to the use of the standing wave technique as an atomic positional probe is the proportionality between the standing wave's electric field intensity and photoelectric effects. Thus, measurement of the fluorescence yield for a particular adsorbate or overlayer corresponds to a direct measurement of the standing wave's electric field intensity at the center of that adsorbate or overlayer.

We have employed a PVC LSM (layered synthetic microstructure) (Pt as the outermost layer) with a 56\AA d-spacing in the study of the adsorption of iodide followed by the electrodeposition of a layer of copper. A layer of iodide was adsorbed onto the platinum surface of the LSM (electrode) followed by the electrodeposition of half a monolayer of copper and subsequently studied by the XSW technique. Since the incident

X-ray standing wave technique
Poly Electrodeposition

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 most significant result 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 to the right of the iodide maximum. Since the antinodes in the electric field of the standing wave move inward as the angle of incidence 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 adsorbed on the platinum this represents unequivocal evidence of the displacement of the iodide layer by the electrodeposited copper. Similar findings based on Auger intensities have been previously reported by Hubbard and coworkers. In addition, from an analysis of fluorescence yields, we were able to determine that the electrodeposited copper layer had a high degree of coherence (54% coherent fraction) with the underlying substrate.

Most recently we have studied the potential dependence of the adsorption of iodide onto a Pt/C LSM (consisting of 200 layer pairs of carbon (14Å) and platinum (26Å), respectively with platinum as the top-most layer). In this experiment we simultaneously monitored the reflectivity across the first order Bragg reflection as well as the characteristic iodine fluorescence intensity. 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.

We recently began an electrochemical study of the effects of adsorbates on Cu UPD on Pt(111). In these studies we have studied the electrochemical response of Cu UPD on Pt(111) in the presence of halides and pseudo-halides including Cl^- , Br^- , I^- , CN^- , SCN^- and S^{2-} . We find that the voltammetric responses are very sensitive to the nature of the competing adsorbates which cause significant shifts (relative to sulfate media) in the potentials of the the UPD processes. We also find an excellent correlation between the reduction potentials for the CuX species (i.e. $\text{CuX} + \text{e}^- \rightarrow \text{Cu} + \text{X}^-$) and the potential

for the first copper UPD process in the presence of the respective halide (or pseudohalide). This suggests a significant interaction between the copper ad-layer and the halide which could be ascribed to partial charge transfer and is fully consistent with our above-mentioned results for Cu UPD on Pt(111)/I.

We have also found some evidence concerning the dynamics of the deposition. For example, whereas the voltammetric traces in the presence of chloride or bromide did not change with time, in the case of cyanide, dramatic differences were noted between the first and second scans with a wave at +0.228 V growing at the expense of those at +0.311 and +0.332 V with the latter being typical of those in sulfate media alone. This suggests the presence of a barrier to surface diffusion of adsorbed cyanide and the concomitant formation of islands of this adsorbate leading to deposition of Cu in discrete domains of cyanide and sulfate. It is interesting to note that the growth of the new voltammetric feature was at the expense of the waves typical of voltammetry in sulfate media and that both were in coexistence, suggesting a smooth transition in the metal ad-layer structure.

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