Electrochemical deposition of copper onto Pt(111) in the presence of (bi)sulfate anions

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Using *in situ* x-ray diffraction we have studied the underpotential deposition (UPD) of copper onto a Pt(111) electrode in sulfuric acid. Deposition occurs in a two-stage process; close to a full monolayer of Cu being preceded by a $(\sqrt{3} \times \sqrt{3})R30°$ structure that consists of both Cu and (bi)sulfate anions and is similar to the structure observed on the Au(111) electrode. Utilizing anomalous scattering methods we can accurately determine the Cu coverage during UPD and propose structural models based on crystal truncation rod measurements. [S0163-1829(97)01332-5]

Modifying the atomic structure at the electrode-electrolyte interface by the underpotential deposition (UPD) of a monolayer of another metal can have important consequences for the catalytic reactions and charge-transfer processes that take place at the interface. *In situ* probes, such as x-ray-based techniques and scanning tunneling microscopy (STM) are well suited to the study of the electrode-electrolyte interface during the UPD process as is evident by the numerous recent publications.[1] Due, in part, to these studies it has been realized that the presence of other adsorbing species in solution can alter the UPD process. For example, we have shown that the presence of halide anions splits the Cu UPD onto Pt(111) into a two-stage process whereby formation of a full Cu monolayer is preceded by an incommensurate Cu-halide bilayer.[2] The presence of coadsorbed structures complicates interpretation of the measurements which can be insensitive to the chemical nature of the adsorbed species. This has been illustrated by studies of Cu UPD onto Au(111) in sulfuric acid where a $(\sqrt{3} \times \sqrt{3})R30°$ adlayer was originally assigned to 1/3 of a monolayer of Cu atoms[3] but more recently was shown to consist of 2/3 of a monolayer of Cu and 1/3 of a monolayer of (bi)sulfate anions.[4] Such inconsistencies also highlight the problems of accurately determining surface coverages in an electrochemical environment.

In this report, we present x-ray-scattering measurements during the UPD of Cu onto Pt(111) in the presence of (*bi*)sulfate anions. By monitoring the scattered intensity at particular reciprocal-lattice points as the electrode potential is changed, it is apparent that the UPD process is a two-stage process, completion of a Cu monolayer being proceeded by a $(\sqrt{3} \times \sqrt{3})R30°$ structure. Although the scattering from the superlattice structure is too weak to perform a full structural analysis, we attempt to deduce the structure by measurement of the specular x-ray reflectivity. The sensitivity of this measurement to the Cu adatoms is enhanced by the use of anomalous scattering methods in which the incident x-ray energy is tuned close to the Cu K adsorption edge. The results indicate that the UPD of Cu in the presence of (bi)sulfate is similar on both Pt(111) and Au(111) electrodes.

The experimental procedures and methods have been described in detail in our previous publications.[2,5] In this experiment the electrolyte consisted of $10^{-3}M$ Cu in 0.25M H_2SO_4. All potentials are quoted versus a saturated calomel electrode. The x-ray measurements were made on beamline 7-2 at the Stanford Synchrotron Radiation Laboratory using focused monochromatic x-ray radiation. The Pt(111) surface is indexed to the hexagonal unit cell where the surface normal is along the $(0,0,l)_{hex}$ direction, $(h,0,0)_{hex}$ and $(0,k,0)_{hex}$ lie in the plane of the surface and subtend 60° and the units for h, k, and l are $a^* = b^* = 4\pi/\sqrt{3}a_{Pt}$ and $c^* = 2\pi/\sqrt{6}a_{Pt}$.

Figure 1 shows the Cu adsorption isotherm obtained from electrochemical measurements utilizing a rotating ring disk electrode (RRDE) technique in our laboratory.[6] The filled circles correspond to the Cu coverage obtained by potentiostatic measurements, in which the amount of Cu deposited on the disk electrode in a potential step from E_i (indicated in the figure) is assessed from the corresponding change in the constant Cu^{2+} flux to the ring electrode. This is known as a shielding experiment (see Ref. 6 for more details) and enables separation of the charge corresponding to copper deposition from the total charge (including the charge due to coadsorption of anions and charging of the double layer) which would be obtained by integrating the voltammetric curve. For reference purposes the lower curve in Fig. 1 shows the cathodic sweep of the cyclic voltammogram (CV) measured on the disk electrode. The presence of (bi)sulfate anions in solution causes a splitting of the voltammetric Cu deposition peak. This result is in agreement with previous studies which, depending on the solution concentrations and sweep rates can show single peaks or double peaks in both sweep directions.[7]

The CV measured in the x-ray cell was very similar to the one shown in Fig. 1 and this indicates that the x-ray system was free of detectable contaminants. Structural changes at the Pt electrode surface during Cu deposition can be observed by measuring the scattered intensity at particular reciprocal-lattice points on the Pt(111) crystal truncation rods (CTR's) as the electrode potential is changed. Such a
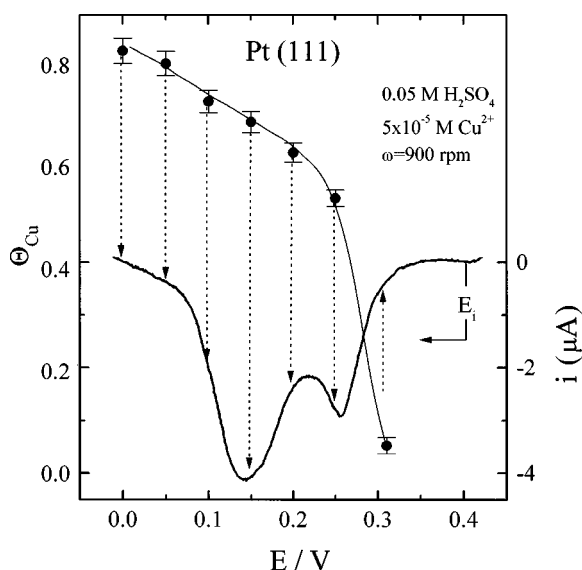
FIG. 1. The lower curve shows the cathodic sweep of the cyclic voltammogram (CV) for a Pt(111) disk electrode in a RRDE configuration in 0.05 M $H_2SO_4 + 10^{-5}$ M Cu at a rotation rate of 900 rpm potential sweep rate of 10 mV/s. The closed circles represent the Cu coverage (atoms per surface Pt atom) assessed from changes in the ring current during Cu deposition onto the disk electrode as the potential is stepped (for each point) from E_i (see Ref. 6). The solid line is a guide to the eye.

measurement, at (0,0,3.9) on the specular CTR and at (0,1,2.5), a position on a nonspecular CTR, are shown in Fig. 2. The specular CTR is sensitive to the electron density profile at the Pt surface averaged over the surface plane and so the measurement at (0,0,3.9) is capable of detecting the potential regions where different adsorbing structures are present. In this case the results clearly indicate that UPD
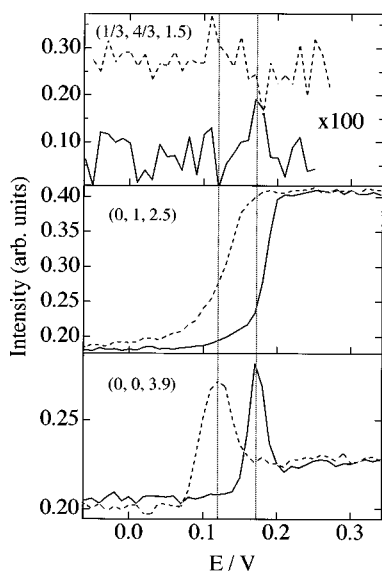

FIG. 2. Changes in the x-ray scattering at (0, 0, 3.9), lower panel, (0, 1, 2.5), middle panel, and (1/3, 4/3, 1.5), top panel, as the electrode potential is swept at 2 mV/s in 0.25 M $H_2SO_4 + 10^{-3}$ M Cu. The solid lines and dashed lines are for the positive-going (anodic) and negative-going (cathodic) sweep directions, respectively. The dotted vertical lines are guides to the eye.

occurs in a two-stage process (i.e., there are three different intensity levels) and the sharpness of the peak implies that the structure formed in the middle potential region is present over a very narrow potential range. The results at (0,1,2.5) are less dramatic although the presence of a kink in the data can be detected (note that in some ways, this result mirrors the Cu coverage measured by RRDE and shown in Fig. 1).

Having identified the three structural regions of interest we held the electrode potential at 0.0 V (where nominally a monolayer of Cu is expected to be adsorbed), at 0.15 V (where it was found that no significant decay from the peak intensity at the (0,0,3.9) position was observed) and at 0.4 V [where the surface is expected to be covered by (bi)sulfate anions] and searched for in-plane x-ray scattering which would be associated with an ordered interface superstructure. No scattering peaks were observed at 0.0 V which is not surprising as Cu is expected to be adsorbed into a (1×1) pseudomorphic Cu overlayer. No peaks were observed at 0.4 V either, although STM and low-energy electron-diffraction studies have shown that $(\sqrt{3} \times \sqrt{3})R30°$ and $(\sqrt{3} \times \sqrt{7})$ structures of ordered (bi)sulfate anions can be formed.[8] We presume that if such structures are present then they possess only short-range order and are thus undetectable by x-ray scattering.[9] At 0.15 V we were also unable to detect any in-plane peaks for small values of the out-of-plane momentum transfers, i.e., at $l = 0.1$ where survey scans were performed. At higher l, however, weak peaks which could be indexed to a $(\sqrt{3} \times \sqrt{3})R30°$ superlattice diffraction pattern were observed. For example, rocking scans through the (2/3, 2/3, 2), (1/3, 1/3, 1.5), and (1/3, 4/3, 1.5) positions showed broad peaks, with full width at half maximum (FWHM) of 0.84°, 0.49°, and 1.72°, respectively, which gives an ordered domain size in the range 30–60 Å.[10] This correlation length is at the limit of detection by x-ray scattering and the weak intensities coupled with the narrow stable potential range certainly preclude a detailed structural analysis as was recently performed for the $Au(111)/Cu/H_2SO_4$ system by Toney *et al.*[4] In the top part of Fig. 2 is shown the x-ray scattering intensity at (1/3, 4/3, 1.5) as the potential is swept at the same rate as the data in the lower figures. Although the signal to noise is poor, it can clearly be seen that the scattering from the $(\sqrt{3} \times \sqrt{3})R30°$ structure is only present in the same narrow region highlighted by the changes at (0, 0, 3.9). This was confirmed by measurements of the rocking scan through (1/3, 4/3, 1.5) at discrete potentials over the range 0.0–0.3 V.

To gain more insight into the nature of the Cu UPD structures we measured the (0,0,l), (1,0,l), and (0,1,l) CTR scattering at 0.0 and 0.15 V in order to derive structural models. Such results are relatively insensitive to the orientation of any adsorbed (bi)sulfate molecules (at least within the accuracy of deriving structural parameters) and so we approximated the (bi)sulfate anion to be that of a single molecule (i.e., single ion core) consisting of one sulfur and two oxygen atoms ($Z = 64$). Additional sensitivity to the coverage and location of the Cu atoms was obtained by performing the CTR measurements with incident x-ray energies of 8.78 keV (200 eV below the Cu K adsorption edge) and 8.94 keV (5 eV below the Cu K adsorption edge). In simulating the CTR
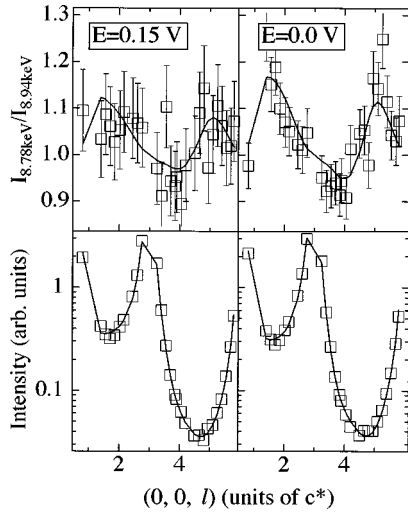
FIG. 3. The measured specular CTR scattering for an incident x-ray energy of 8.78 keV (lower panels) and the ratio between a similar data set measured at 8.94 keV (upper panels) at electrode potentials of 0.15 V (left) and 0.0 V (right). The solid lines are fits to the data to a single structural model and the ratio data set is calculated by fixed changes in the Cu atomic form factor (see text for details).

data, the Cu atomic form factor in the scattering equations (for detailed scattering equations, see Refs. 5 and 11) is then replaced by

$$f_{Cu} = f_0(Q) - f' - if'',$$

where the values of $f_0(Q)$ are obtained by polynomial fits to the values given in Ref. 12 and f' and f'' are calculated according to Ref. 13. At each electrode potential a simultaneous fit to the CTR data ($E = 8.78$ keV) and the ratio data set ($R = I_{8.78\,keV}/I_{8.94\,keV}$) was performed. The structural parameters allowed to vary were the Cu coverage, Pt-Cu surface normal spacing, (bi)sulfate coverage and Cu- (bi)sulfate surface normal spacing, along with their respective enhanced Debye-Waller-type roughness.[14] Results of fits to the specular CTR data and ratio data at electrode potentials of 0.0 and 0.15 V are shown in Fig. 3 by the solid lines. For the specular CTR, the scattering is insensitive to the in-plane order of the adsorbed species. The parameters to the fits are listed in Table I. Use of the anomalous scattering techniques enhances the accuracy of the Cu coverage determination.

TABLE I. Fit parameters to the CTR data. The coverages θ are atoms per surface Pt atom. The surface normal spacings are defined in Fig. 4 (cf $d_{Pt(111)} = 2.27$ Å). Results from Ref. 4 for UPD onto Au(111) are shown for comparison.

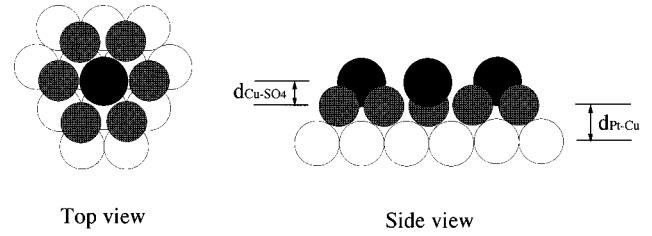|	0.15 V	(Au results)	0.0 V
θ_{Cu}	0.60±0.04	(0.66)	0.81±0.04
$d_{Pt\text{-}Cu}$	2.08±0.05 Å	(2.27 Å)	2.09±0.05 Å
σ_{Cu}	0.09±0.05 Å		0.14±0.04 Å
θ_{SO_4}	0.22±0.05	(0.28)	0.21±0.05
$d_{Cu\text{-}SO_4}$	1.5±0.1 Å	(1.49 Å)	1.8±0.1 Å
σ_{SO_4}	0.55±0.2 Å		0.55±0.2 Å

FIG. 4. Schematic illustration of the proposed $(\sqrt{3} \times \sqrt{3})R30°$ structure formed at 0.0 V. The open circles correspond to surface Pt atoms, the shaded circles to Cu atoms and the black circles to (bi)sulfate molecules [the orientation of the (bi)sulfate molecule is not determined]. The surface normal spacings which are derived from the fits to the data (solid lines in Fig. 3) are indicated.

The results in Table I show that at 0.15 V, the Cu coverage is 0.60 with an adsorbed (bi)sulfate layer of coverage 0.22 on top of the Cu layer. By comparison with the structural model derived from the $(\sqrt{3} \times \sqrt{3})R30°$ Cu- (bi)sulfate structure on Au(111) we can see that our CTR results are in good agreement with that study (the structural parameters derived in Ref. 4 are also listed in Table I for comparison). As the l dependence of our $(\sqrt{3} \times \sqrt{3})R30°$ reflections showed a similar trend to the results from the system, i.e., too weak to be measured at small l and strongest at $l \sim 1.5$,[4] we propose that Cu UPD in the presence of (bi)sulfate anions proceeds by the same structural pathway on both Pt(111) and Au(111). Figure 4 shows a schematic of the proposed $(\sqrt{3} \times \sqrt{3})R30°$ structure. Ideal coverages for the structure are $\theta_{Cu} = 2/3$ and $\theta_{SO_4} = 1/3$. The bond lengths we obtain for the Cu-(bi)sulfate bilayer are in good agreement with the Au study where it was proposed that the (bi)sulfate is chemically bonded to the hexagonal Cu layer. As the Cu adatoms are adsorbed into hollow sites (see below), the Pt-Cu spacing gives a Pt-Cu bond length of 2.63 Å which is slightly smaller than the calculated metallic bond (2.67 Å). The fact that we have approximated the (bi)sulfate molecule to a single ion core leads to the large Debye-Waller roughness which presumably represents the spatial extent of the molecule.

At 0.0 V our results give a Cu coverage of 0.81 monolayers per Pt surface atom with 0.21 monolayers of (bi)sulfate anions still adsorbed on top of the Cu layer. Due to the increase in Cu coverage, the (bi)sulfate anions are located at an increased height above the Cu adlayer presumably as the hollow sites in the hexagonal Cu adlayer have been filled by Cu adatoms. It is interesting that the Cu coverage we derive by the CTR measurement are in good agreement with those obtained from the RRDE experiments and it appears, therefore, that it is not possible to complete a full Cu monolayer on the Pt(111) surface.[15] Fits to the nonspecular CTR data at both potentials (0.0 and 0.15 V), again to both raw data and ratio data sets, gave occupation of both types of threefold hollow sites, face-centered-cubic (fcc) and hexagonal close-packed (hcp), although the fcc sites are favored (fcc/hcp = 0.51/0.09 at 0.15 V and 0.67/0.16 at 0.0 V). The data is not shown but the quality of the fits was similar to that in Fig. 3. In contrast to the Au(111) system where the Cu adatoms occupied only the fcc sites[4] it appears that on Pt(111) the energy difference between these sites may be smaller. We cannot rule out the fact that the $(\sqrt{3} \times \sqrt{3})R30°$ structure

may only be formed on the fcc sites, i.e., it is quite possible that patches of (1×1) Cu and $(\sqrt{3}\times\sqrt{3})R30°$ coexist at 0.15 V. Occupation of both types of threefold hollow site may be responsible for the weak ordering of the intermediate Cu-(bi)sulfate bilayer phase and for the inability to complete the Cu monolayer at 0.0 V. It might be possible to complete the Cu monolayer at slightly more negative potential. On Pt(111), however, completion of the monolayer is proceeded immediately by bulk Cu deposition, i.e., they are separated by ~10 mV.[6]

In summary we have shown that Cu UPD in the presence of (bi)sulfate anions follows the same structural pathway on both the Pt(111) and Au(111) electrode surfaces. The mechanism is also similar to that for Cu UPD onto Pt(111) in the presence of halide anions. Adsorption of Cu into both the fcc and hcp threefold hollow Pt sites prevents the formation of structures with significant long-range order in both the Cu monolayer regime and the $(\sqrt{3}\times\sqrt{3})R30°$ Cu-(bi)sulfate bilayer. Our interpretation of the CTR results is aided by the use of anomalous scattering methods which allow accurate determination of the Cu coverage and Pt-Cu surface normal spacings.

[1] For example, see O. R. Melroy *et al.*, Phys. Rev. B **38**, 10 962 (1988); O. M. Magnussen *et al.*, J. Vac. Sci. Technol. B **9**, 969 (1991); T. Hachiya, H. Honbo, and K. Itaya, J. Electroanal. Chem. **315**, 275 (1991); M. F. Toney *et al.*, Phys. Rev. B **45**, 9362 (1992); H. S. Yee and H. D. Abruna, J. Phys. Chem. **97**, 6278 (1993); R. R. Adzic, J. Wang, C. M. Vitus, and B. M. Ocko, Surf. Sci. **293**, L876 (1993); G. J. Edens, X. Gao, and M. J. Weaver, J. Electroanal. Chem. **375**, 357 (1994).

[2] I. M. Tidswell, C. A. Lucas, N. M. Marković, and P. N. Ross, Phys. Rev. B **51**, 10 205 (1995); N. M. Marković *et al.*, Surf. Sci. **335**, 91 (1995).

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[5] I. M. Tidswell, N. M. Marković, C. A. Lucas, and P. N. Ross, Phys. Rev. B **47**, 16 542 (1993).

[6] For more details of the RRDE technique, see N. M. Marković, H. A. Gasteiger, and P. N. Ross, Langmuir **11**, 4098 (1995).

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[8] H. Ogasawara, J. Inukai, and M. Ito, Surf. Sci. **311**, L665 (1994); A. M. Funtikov, U. Linke, U. Stimming, and R. Vogel, *ibid.* **324**, L343 (1995).

[9] We should also note that we found no ordered anion structures at any potential in sulfuric acid solutions that were free of Cu.

[10] Calculated as domain size, $D = 2/\Delta Q$, where ΔQ is the FWHM in Å^{-1}.

[11] For example, A. R. Sandy *et al.*, Phys. Rev. B **43**, 4667 (1991).

[12] *The International Tables for X-ray Crystallography, Vol. 3* (Kynoch, Birmingham, England, 1968).

[13] S. Brennan and P. L. Cowan, Rev. Sci. Instrum. **63**, 850 (1992).

[14] Included in addition to the thermal Debye-Waller factor in the form $\exp(-q^2\sigma^2/2)$, where q is the surface normal momentum transfer.

[15] The lower limit of potential (0.0 V) was chosen to avoid the formation of Cu^+ via one electron reduction of Cu^{2+} without further reduction to metallic copper.