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BEHAVIOR OF CuP AND OFHC Cu ANODES UNDER ELECTRODEPOSITION CONDITIONS

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Films formed on CuP (with 0.05 wt% P) and OFHC Cu anodes in electroplating solutions were studied by X-ray Photoelectron Spectroscopy, X-ray Absorption Spectroscopy, electrochemical methods, and a newly developed gravimetric technique. The black film formed on CuP in Cl-containing solutions was found to resemble a porous sponge composed of CuCl but laden with concentrated CuSO₄ solution. The difference between the buoyancy-corrected measured mass change and the charge-equivalent mass change was found to have two components: a reversible part that comes and goes as the current is turned on and off, and an irreversible part that remains on the surface and increases in mass with time. The irreversible part results from the anodic film, which increases linearly with charge density but independent of current density. The reversible part of the mass change arises from the weight of the diffusion layer. In contrast to CuP, OFHC Cu releases much more Cu⁺ during anodic polarization and forms a poorly-adherent anodic film that is considerably heavier than the black film for a given charge density.

INTRODUCTION

Anodes used in electrodeposition of Cu from acid sulfate baths typically contain about 0.05 wt % P. This small amount of P has been shown to have a large effect in promoting the formation of an adherent black film on the anode surface during plating (1, 2). In contrast, pure Cu forms a brownish film (sometimes called slime), which is not adherent and can migrate by electrophoresis to the cathode and degrade the plated film.

Copper is commonly electroplated from solutions containing H₂SO₄ and CuSO₄ with small amounts of Cl⁻, which has a strong influence on the depo-

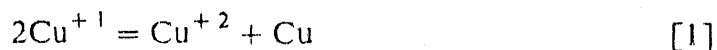
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sition kinetics and deposit morphology (3). Whereas classic studies of Cu dissolution and deposition in solutions of H_2SO_4 and CuSO_4 have determined that the reaction involves two consecutive charge-transfer steps with Cu^{+1} as an intermediate (4, 5), some reports have indicated that the second step of the dissolution process might involve disproportionation of Cu^{+1} (6) :



The slime formed on pure Cu anodes in plating solutions containing Cl^- has in fact been attributed to disproportionation of some amount of Cu^{+1} (1, 2). It is well known that Cl^- stabilizes Cu in the 1+ oxidation state by forming various cuprous chloride complexes (7-10). It has been suggested that the role of P is to promote oxidation of Cu directly to cupric ion, thereby avoiding the deleterious consequences of cuprous ion disproportionation (1, 2). The goal of the present work is to improve the understanding of the role of P and of the behavior of the black anodic film. It should be emphasized that the plating reaction at the cathode was not studied in this investigation.

EXPERIMENTAL

The electrolyte was a typical acid sulfate plating solution consisting of 0.27 M CuSO_4 + 1.7 M H_2SO_4 + 2 mM HCl . In certain experiments, the CuSO_4 or HCl was omitted. Samples of Cu-0.05 wt% P and OFHC Cu were anodically polarized, usually at constant current in the range of 15-30 mA/cm². This range is typical for anodic current density during electrodeposition of Cu from acid sulfate baths.

Anodic films formed on OFHC Cu and CuP were examined by X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS). Samples for XPS analysis were prepared by anodic polarization at a constant current of 30 mA/cm² for 90 min. Following this treatment, the CuP samples were gently washed with water and dried with N_2 . The OFHC Cu samples were just left to dry, since washing with water resulted in complete removal of the brown film.

XAS was done in transmission on samples prepared by two different methods. In the first approach, a CuP sheet was anodically polarized for several hours in a beaker containing the complete plating solution. The sample was removed, and black film was immediately scraped off the anode surface with no prior rinsing. This material was then sealed in polyimide tape and analyzed.

In the second approach, the XAS analysis was performed *in situ* without removing the sample from the cell. CuP and OFHC Cu pieces were first thinned to 0.01 cm by rolling. A 300 Å thick film of Pt was evaporated on one side of each sample to assure conductivity. Each was then totally converted to anodic film by electro-dissolution in a solution containing H₂SO₄ and HCl only (with no CuSO₄). The plastic cell had a narrow (0.07 cm) crevice region, attached on one side, in which the sample was dissolved, Figure 1. In this configuration, the x-ray beam only needed to pass through a small amount of solution. Furthermore, the force of gravity caused the dense copper-containing solution generated by dissolution of the anode to drop down to the bottom of the cell. This technique allowed analysis of the copper in the anodic film with no contributions from underlying copper metal or copper in solution. The x-ray energy was scanned in steps of 5, 0.5, and 5 eV in the ranges -100 to -10, -10 to +50, and +50 to +200 eV, respectively, where the ranges are given relative to the Cu K 1s edge at 8982 eV. The absorption coefficient was taken to be $\ln(I_0/I_T)$, where I_0 and I_T are the incident and transmitted beam intensities as measured by ionization chambers. The background decay of each edge was subtracted out by fitting a line to the region below the edge. The edges were then normalized to a step height of unity using the data from 100 to 200 eV.

Rotating ring-disk electrode (RRDE) experiments were performed with both Cu and CuP disks in an assembly that allowed for removal and exchange of the disk. The Pt ring was potentiostated at 0.3 V vs. a saturated mercurous sulfate electrode (MSE) so as to monitor the rate of Cu⁺¹ release from the disk by its oxidation to Cu⁺². The disks were 0.5 cm in diameter, and the collection efficiency at the ring was 22%. The disks were abraded to 1200 grit prior to measurement. The rotation rate was 350 rpm. A Pine Instruments rotator and potentiostat were used for the RRDE experiments. The disk current was turned on for repeated periods of 100 s, which were separated by periods of 100 s with the disk current off.

Potentiodynamic polarization curves were measured with the Cu and CuP disks in the RRDE assembly. The rotation rate was 350 rpm. A PAR 273 potentiostat was used with the current-interrupt IR compensation option. The reference electrode was a MSE electrode capacitively coupled to a Pt wire. The potential was scanned anodically from open circuit at a rate of 0.1 mV/s.

The mass of the anodic film during dissolution was determined with a gravimetric technique that is a modification of previously described methods (11-14). Hurlen suspended samples from a quartz helix and monitored the mass change, as determined by the helix contraction, during exposure to solutions with a range of oxidizing power (11-13). In this work, the samples were

suspended from a hanging balance, and current was provided to the sample by means of an electrical connection, Figure 2. A similar technique has been used to determine potentials of zero charge of a gold foil in various electrolytes (14). The balance used in this work was a Cahn DCA-312, which has automatic data acquisition, a minimum time resolution of 1 sec, and a sensitivity of 0.1 mg. The samples were 2.5 x 5 x .25 cm³ sheets (with total area of about 28 cm²) that were abraded to 600 grit and suspended in the solution by a 0.025 cm diameter Au wire passing through a small hole drilled in the samples. The Au wire intersected the water line and was connected to the balance by a Cu S-hook. Electrical connection was made with a 0.012 cm diameter Cu wire that was attached to a second S-hook. This thin Cu lead did not influence the measured weight change. Two Cu counter-electrodes equal in area to the sample were used. A PAR 273 potentiostat was used for these experiments, and the current was recorded by a PC/AT. The current was turned on for repeated periods of 5, 15, or 60 min, which were separated by periods of 5 min with the current off. The 100 ml cell was glass and had a cover with a hole allowing passage of the Au wire and connections for deaeration and blanketing of the electrolyte with wet Ar gas.

In most gravimetric experiments, the solution was agitated by bubbling wet Ar at a rate of 50 sccm through a 3 mm diameter open-ended glass tube immersed in the cell. The solution separated for large current densities and large charge densities in the absence of such agitation, for dark solution settled to the bottom and clear solution collected at the top of the cell. Bubbling with Ar eliminated this artifact while introducing minimal noise in the measured mass. The diffusion-layer thickness for these conditions of Ar bubbling in the gravimetric cell was determined to be about 120 μ m from the limiting current density at a Ni electrode in a solution of 1.5 M NaOH + 0.15 M K₃Fe(CN)₆ + 0.15 M K₄Fe(CN)₆ (15). For stagnant experiments, the solution was blanketed with wet Ar to prevent evaporation.

ANALYSIS OF GRAVIMETRIC DATA

During anodic dissolution, the anode may be assumed to be a two-phase composite consisting of a metallic phase and a homogeneous anodic film phase. The measured mass change will be a sum of the mass changes of the two phases corrected for buoyancy effects:

$$\Delta m_{\text{meas}} = \Delta V_m(\rho_m - \rho_s) + \Delta V_f(\rho_f - \rho_s) \quad [2]$$

where ΔV_m and ΔV_f are the volume changes of the metal and anodic film phases, respectively, and ρ_m , ρ_f , and ρ_s are the densities of the metal, film, and

solution, respectively. The anodic film thickness, $\Delta x_f = \Delta V_f/A$ where A is the total electrode area, can be shown by rearrangement of Eqn. 2 to be:

$$\Delta x_f = \frac{1}{A} \left(\frac{\rho_m - \rho_s}{\rho_f - \rho_s} \right) \left[\frac{\Delta m_{\text{meas}}}{(\rho_m - \rho_s)} - \Delta V_m \right] \quad [3]$$

However, from Faraday's Law the volume change of the metal is proportional to the charge passed, Q :

$$\Delta V_m = \frac{M_m}{\rho_m n F} \int_0^t I(\tau) d\tau = \frac{M_m Q(t)}{\rho_m n F} \quad [4]$$

where M_m is the atomic weight, n is the number of electrons per atom of dissolved copper, and F is Faraday's constant. No side reactions such as gas evolution take place at the anode surface. The value of n was determined for each experiment from the total charge and total mass loss, which was measured at the end of the experiment after removing the anodic film by ultrasonic cleaning in water. This approach determines an average value of n , which is assumed to be constant during the entire experiment (an assumption that may be in error).

It is now convenient to define two area-normalized masses: the measured mass change corrected for buoyancy, $\Delta m_D = \rho_m \Delta m_{\text{meas}} / A(\rho_m - \rho_s)$, and the charge-equivalent mass change, $\Delta m_E = M_m Q(t) / A n F$. The anodic film thickness (and also film mass, since $\Delta m_f = A \Delta x_f \rho_f$) is thus proportional to the difference between the buoyancy-corrected measured mass change and the charge-equivalent mass change:

$$\Delta x_f = \frac{1}{\rho_m} \left(\frac{\rho_m - \rho_s}{\rho_f - \rho_s} \right) [\Delta m_D - \Delta m_E] \quad [5]$$

The solution density was measured to be 1.131 g/cm³, and ρ_m was taken to be that of copper, 8.96 g/cm³. The apparent black-film density was determined by scraping the anodic film off a CuP sample that had been freshly anodized in a Cl⁻-containing solution, filling a known length of 0.76 mm diameter teflon tube, and measuring the mass change. The average value of several measurements was 1.4 g/cm³. Using these values, the factor in Eqn. 5 relating anodic film thickness to the difference between buoyancy-corrected measured mass and current-equivalent mass is 32.5 $\mu\text{m}\cdot\text{cm}^2/\text{mg}$. It was not possible to measure the density of the brown film formed on pure Cu because of its lack of cohesion. Additionally, the densities for the thin anodic films formed on both Cu and CuP in solutions without Cl⁻ were not determined.

RESULTS

Potentiodynamic Polarization Experiments

The polarization curve for CuP in the full electrolyte is shown in Figure 3. The fluctuations in the current are probably caused by a noisy brush contact to the rotating disk. At -270 mV, a current drop resulting from salt film precipitation is exhibited. The exchange current density for the Cu/Cu^{+2} reaction is 0.3 mA/cm^2 . Two Tafel slopes are seen: 21 mV/dec at low overpotentials and 83 mV/dec at higher overpotentials. If the direction of the potential scan is reversed before salt film precipitation occurs, the current traces back almost exactly along the same curve with little hysteresis, indicating that the two Tafel slopes represent two activation-controlled regions. The black film forms during the anodic polarization but does not impede the dissolution process.

XPS and XAS Experiments

XPS analysis of a black film formed on CuP in Cl-containing solution showed the presence of the following elements in the respective oxidation states: Cu, +1; O, -2; Cl, -1; P, 0 and +3. The P/Cu ratio was 9 at% after 160 C/cm^2 and increased with increasing charge; this is an increase of 100x over that in the metal. The Cl/Cu ratio was 25%. The energy of the Cu LVV Auger line indicated that CuCl was the major component. Additionally, there was evidence of some Cu_2O , which may result from reaction with air during sample transfer.

X-ray absorption spectra at the Cu 1s edge are given in Figure 4 for metallic Cu and several different Cu-containing compounds. The edge moves to higher energies as the oxidation state increases. A pronounced peak at the edge is seen for CuSO_4 . Similar absorption edges of Cu-containing compounds have been previously reported (16, 17). The absorption edge for black film scraped off of an anode is shown in Figure 5; it appears to be a combination of CuCl and CuSO_4 edges. The absorption edge of a black film formed in the cell shown in Figure 1 using the method described above is given in Figure 6. This film, which has been totally converted from a thin CuP foil in a solution without CuSO_4 , exhibits an absorption edge very similar to CuCl. The rather large amount of P in the film may be responsible for the variations from the CuCl edge. These observations indicate that the black film is similar to a porous sponge that is composed of CuCl and saturated with concentrated CuSO_4 solution. The difference between the samples of Figs. 5 and 6 is that the black film scraped off of a sample polarized in the full plating bath is actually a combination of the film and the solution. By dissolving a thin foil in

a solution without CuSO_4 , however, only the substance of the black film, or a CuCl -like material, is present.

Brown film formed by a similar treatment of a thin OFHC Cu foil in a solution with no CuSO_4 appeared to be a combination of Cu and CuO . This XAS observation is in agreement with XPS analysis of the brown film on Cu, which also found metallic Cu in the anodic film. Since the sample was not rinsed prior to XPS analysis and thus dried CuSO_4 was present on the surface, Cu^{+2} and S were also observed. In the absence of P, Cu^{+1} likely disproportionates to result in a fine mixture of Cu in the 0 and +2 oxidation states. The P acts in some way by either binding the Cu^{+1} into the black film or decreasing Cu^{+1} formation.

Gravimetric Experiments

The gravimetric experiments provided further information on the nature of the anodic films. In Figure 7, both the buoyancy-corrected measured mass change, Δm_D , and the charge-equivalent mass change, Δm_E , are shown for the first part of an experiment during which a current of 30 mA/cm^2 was periodically applied to a CuP electrode in Cl-containing solution. If the current causes faradaic dissolution of Cu, the metal should lose mass at a constant rate when the current is on, and the mass should be constant when the current is off. This behavior is displayed by Δm_E in Figure 7. As seen from Δm_D , however, the sample mass actually increases when the current is first turned on (at the 5 min mark). After about 30 s, a maximum mass is achieved and the sample then loses mass at a constant rate, with a slope close to that exhibited by Δm_E . When the current is turned off 15 min later, the sample continues to lose weight for several minutes. The difference between Δm_D and Δm_E , shown above to be proportional to the anodic film mass, is given in Figure 8 for the entire experiment. The mass change is seen to be composed of two parts: a reversible part, Δm_{Rev} , that comes and goes as the current is turned on and off, and an irreversible part, Δm_{Irr} , that remains on the electrode surface. The reversible mass change is relatively constant with time, but the irreversible mass change increases almost linearly with time. This behavior has been observed for experiments lasting up to 17 h.

The effects of both current density and charge density on the reversible and irreversible mass changes are shown in Figure 9 for CuP in Cl-containing solution. The reversible mass change increases almost linearly with current density and is relatively constant with time or charge. The irreversible mass change increases linearly with charge density and is almost independent of current density. The total mass change shows some dependence on current density but is more strongly dependent on charge density.

A comparison of stagnant and agitated experiments is shown in Figure 10 for the lowest current density studied, 15 mA/cm². Whereas both the reversible and irreversible mass changes decrease with agitation, the irreversible mass change is more strongly affected. This occurs despite the increase in transport of Cl⁻ to the electrode surface with agitation.

Similar experiments (with agitation) were performed using CuP in solutions without Cl⁻ and using OFHC Cu anodes in solutions both with and without Cl⁻. The reversible mass changes were similar for all cases, also varying at the end of the first 15 min period between 0.2 and 0.4 mg/cm² for current densities between 15 and 30 mA/cm². The films formed on both Cu and CuP in Cl⁻-containing solutions exhibited reversible mass changes that increased weakly with charge density. The irreversible mass changes were also similar for all cases except Cu in Cl⁻-containing solutions. The slopes of the Δm_{irr} vs charge density curves are given in Table 1. For Cu in Cl⁻-containing solutions, the irreversible film mass was found to increase about 10 times faster than for the other cases.

The physical nature of the anodic films for the various cases was found to be vastly different. In contrast to the thick, viscous black film formed on CuP in the presence of Cl⁻, the brown film formed on OFHC Cu adhered poorly to the electrode surface. As soon as the electrode was handled, the brown film would easily dislodge from the surface. A light stream of water was sufficient to completely remove the film. In solutions without Cl⁻, the anodic films formed on both Cu and CuP were much thinner, and the underlying metallic grains could be seen through the films. The film formed on Cu washed off easily, but the film on CuP was difficult to remove completely even by ultrasonic cleaning in water.

The values of n determined after the gravimetric experiments are given in Table 1. The values for CuP may be somewhat high as a result of incomplete removal of the anodic film by the ultrasonic cleaning. This likely explains the apparent n slightly larger than 2 for dissolution of CuP in the solution without Cl⁻. The one case with an n much less than 2 was Cu in the Cl⁻-containing solution. The Cl⁻ stabilizes the cuprous ion by complexation, but it does not prevent the disproportionation reaction that results in thick slime formation on Cu anodes.

RRDE Experiments

In the RRDE experiments, the current monitored at the ring, divided by the collection efficiency, measures the rate of Cu⁺¹ release from the disk. Figure 11 shows the ring current for CuP and OFHC Cu disks in solutions

with and without Cl^- . In these experiments, the disk current was alternately switched from 0 to 15 mA/cm^2 (2.85 mA) and back to 0 for periods of 100 s. There is a finite background ring current when the disk current is 0. This is the result of etching of Cu by Cu^{+2} . Gravimetric experiments show that CuP loses weight in the plating solution at open circuit, even in deaerated solutions, at a rate equivalent to $4 \times 10^{-5} \text{ A/cm}^2$.

The largest changes in ring current occurred when the disk current was switched on for the first cycle, which began at 600 s. The increases during subsequent cycles were lower, indicating that the growing anodic films blocked the release of Cu^{+1} . The presence of Cl^- increased both the background Cu^{+1} current and the amount of Cu^{+1} emitted when the disk current was on. The ring current was higher for a Cu disk than for a CuP disk, both with and without Cl^- . Even for a Cu disk, however, the amount of Cu^{+1} was not large, and it decreased with time. After a few cycles, the change in the ring current when the disk current was turned on was about 0.1 and $0.05 \mu\text{A}$ for the Cu disk in the solutions with and without Cl^- , respectively. These ring currents are equivalent to Cu^{+1} currents at the disk of 0.45 and $0.23 \mu\text{A}$, values which are far below the 310 and $155 \mu\text{A}$ calculated from the values of n determined for Cu in these solutions. Larger ring currents would also be expected for the CuP disk if the Cu^{+1} calculated from the measured n all reached the ring. After the first cycle, current at the CuP disk in the Cl^- -containing solution generated practically no change in the ring current. Interestingly, the CuP disk in the Cl^- -free solution switched to an inverse behavior in which the ring current was lower when a current was passed at the disk than when the disk was at open circuit.

The differences between the measured and expected ring currents are caused either by trapping of Cu^{+1} in the surface film or by disproportionation. Apparently, the Cu^{+1} that does not further oxidize to Cu^{+2} is bound into the black film on CuP but disproportionates in the case of Cu.

DISCUSSION

Each of the different experiments described above reveals an aspect of the nature of the anodic films formed on Cu and CuP. The current densities and potentials used in this study are well below the values at which salt film precipitation is observed as shown in Figure 3. These films are therefore not salt films that precipitate on account of mass transport limitations. In fact, some black film forms during prolonged exposures at open circuit.

The XPS and XAS experiments provide information on the composition of the anodic films. The black film on CuP is enriched in P and Cl with Cu

in the +1 oxidation state. There is no evidence that the black film acts as an impediment to current flow. Dissolved cupric ions can clearly pass through the black film at very high rates. The black film may be viewed as a porous structure made up of a CuCl-like material that is enriched with P. This notion is supported by the very low apparent density of the film compared to the density of 4.14 g/cm³ for solid CuCl (18). The cupric ions will attract sulfate anions to maintain charge neutrality, and this dissolved cupric sulfate permeates the film. The measured *n* for CuP in Cl-containing solutions is only slightly less than 2. It is possible to convert this *n* using Faraday's Law to a rate of Cu⁺¹ production. Even the small amount of Cu⁺¹ formed during anodic dissolution is retained in the anodic film and never reaches the ring in the RRDE experiments. The fate of the Cu⁺¹ that does not further oxidize to Cu⁺² is strongly influenced by the presence of P. The role of P is to promote the retention of Cu⁺¹ in the thickening black film. In the absence of P, Cu⁺¹ disproportionates or is released into the solution. Cl⁻ also plays a vital role in the formation of black film, because the black film network is made of CuCl. Without Cl⁻, the thick black film network cannot form.

The gravimetric experiments show that the mass change has two parts: the reversible part that comes and goes as the current is turned on and off and the irreversible part that continually increases. Interestingly, this behavior was observed for anodic films on Cu and CuP in solutions with and without Cl⁻, films with widely varying chemical and physical characteristics. Such similarity suggests that Δm_{Rev} results from the dissolution process. During dissolution, a diffusion layer containing electrolyte more concentrated and denser than the bulk solution exists at the sample surface. Like Δm_{Rev} , the diffusion layer increases and decreases in concentration with the anodic current for all cases. This diffusion layer adds to the mass of the sample. The gravimetric analysis presented above can be modified to account for a third contribution, the concentrated solution within the diffusion layer, to result in an equation similar to Equation 5:

$$\Delta m_{\text{D}} - \Delta m_{\text{E}} = \left(\frac{\rho_{\text{m}}}{\rho_{\text{m}} - \rho_{\text{s}}} \right) [\Delta x_{\text{f}}(\rho_{\text{f}} - \rho_{\text{s}}) + \Delta x_{\text{dl}}(\rho_{\text{dl}} - \rho_{\text{s}})] \quad [6]$$

where Δx_{dl} is the diffusion layer thickness ($\approx 120 \mu\text{m}$) and ρ_{dl} is an average diffusion layer solution density. When the current is turned on or off, the anodic film does not change in thickness, and the change in $(\Delta m_{\text{D}} - \Delta m_{\text{E}})$ or Δm_{Rev} is a result of a change in the diffusion layer as the concentrated solution forms or diffuses away. Conversely, while the current is on, the diffusion layer reaches a steady-state, Equation 6 becomes Equation 5, and Δm_{Irr} increases because of an increase in anodic film thickness, Δx_{f} . The magnitude of Δm_{Rev} ca. be calculated from Equation 6 if several assumptions are made. The

density of the plating bath saturated with CuSO_4 was measured to be 1.22 g/cm^3 , which is 0.09 g/cm^3 larger than the density of the standard plating bath. A current density of 15 mA/cm^2 is 13% of the limiting current density shown in Figure 3. If the surface concentration scales with the current density, the solution directly next to the electrode may be assumed to be denser than the bulk solution by 0.012 g/cm^3 . Assuming a linear density gradient in the diffusion layer, the average difference between the diffusion layer and bulk densities is 0.006 g/cm^3 . For these conditions, Equation 6 predicts $\Delta m_{\text{Rev}} \approx 0.1 \text{ mg/cm}^2$, which is on the order of the observed value of 0.2 mg/cm^2 .

After accounting for the weight loss from dissolution, the irreversible mass change reflects the thickness of the anodic film. Since the density of the black film is known, Δm_{irr} can be converted into thickness or volume change using the constant described above. The black film is thus $45.5 \mu\text{m}$ thick after a charge of 485 C/cm^2 has passed. The rate of mass increase of $2.72 \times 10^{-3} \text{ mg/C}$ is equivalent to a volume increase of $8.8 \times 10^{-6} \text{ cm}^3/\text{C}$. This is about 25% of the rate of metal loss. In other words, for every $1 \mu\text{m}$ of metal dissolved from the anode, $0.25 \mu\text{m}$ of black film will form. The densities for the anodic films other than the black film are not known. As a result, it is not possible to know the relationship of the mass changes to volume or thickness changes. The presence of metallic Cu in the brown film formed on Cu in Cl-containing solutions likely increases the density of the anodic film substantially. Thus, although the brown film is 10X heavier than the black film for a given charge density, it may even be thinner. In Cl-free solutions, the anodic films are noticeably thinner on both Cu and CuP. The densities of these films are probably also higher than that of the black film, since the film masses increase at only a slightly slower rate than the black film mass.

CONCLUSIONS

The films formed on anodes of OFHC Cu and Cu - 0.05 wt% P in $\text{CuSO}_4 + \text{H}_2\text{SO}_4$ solutions with and without Cl were studied under conditions typical of anodes in Cu electrodeposition. The following conclusions can be made:

1. The black film formed on CuP in Cl-containing solutions contains Cu^{+1} , Cl, and P. It is envisioned to be a porous CuCl-like structure that is laden with aqueous CuSO_4 solution. The brown film formed on Cu contains CuO and metallic Cu as a result of Cu^{+1} disproportionation.
2. The difference between the buoyancy-corrected measured mass change and the charge-equivalent mass change was found to have two components: a reversible part that comes and goes as the current is turned on and off, and

an irreversible part that remains on the surface and increases in mass with time.

3. The reversible mass change is caused by the weight of the dense diffusion layer, and the irreversible mass change results from the anodic film. The reversible mass change increases linearly with current density and is independent of charge density, whereas the irreversible mass change increases linearly with charge density and is independent of current density.
4. Less Cu^{+1} is detected at the ring of an RRDE than is predicted from the measured n value of slightly less than 2.
5. The Cu^{+1} that does not further oxidize to Cu^{+2} is bound into the anodic film in the case of CuP and largely disproportionates in the case of Cu.

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		With Cl ⁻		Without Cl ⁻	
		Cu	CuP	Cu	CuP
$d(\Delta m_{irr})/dq$	mg/C	0.0203	0.00272	0.00170	0.00216
n	cq/mole	1.890	1.997	1.998	2.004

Table 1. Slopes of irreversible mass change vs. charge density and values of n calculated after the gravimetric experiments.

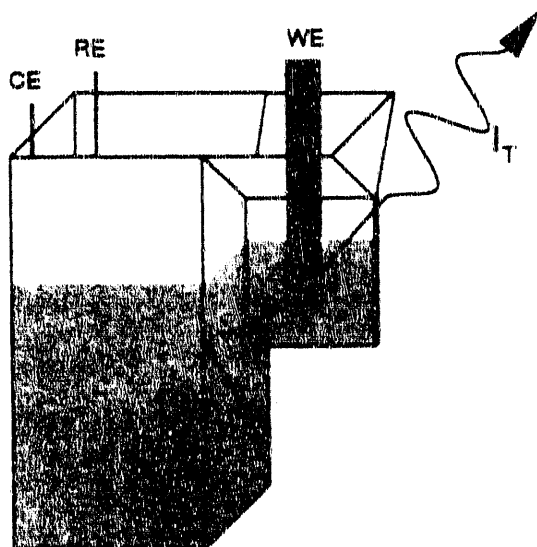


Figure 1. Schematic representation of cell used for *in situ* XAS experiments.

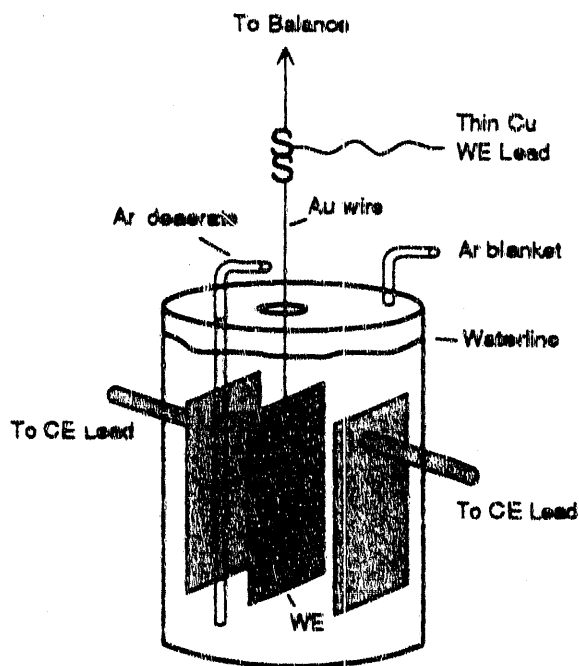


Figure 2. Schematic representation of cell used in gravimetric experiments.

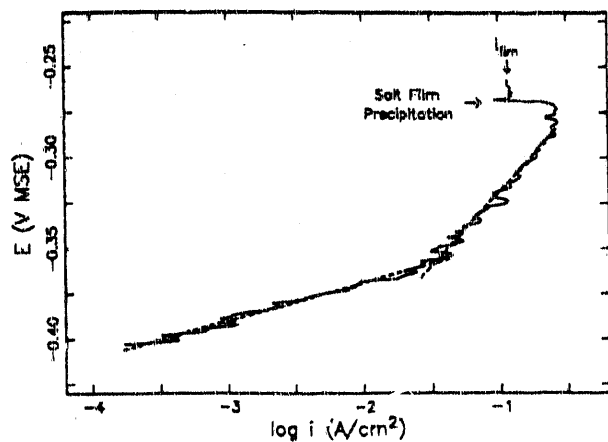


Figure 3. Potentiodynamic polarization curve for CuP rotating disk in full electrolyte. Fitted Tafel slopes are shown as dashed lines.

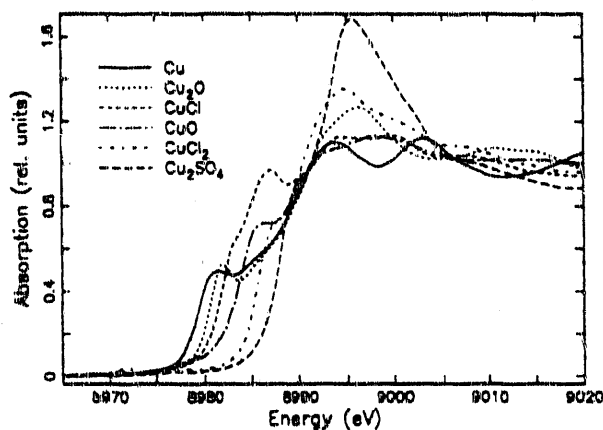


Figure 4. Absorption edges of Cu and Cu-containing compounds.

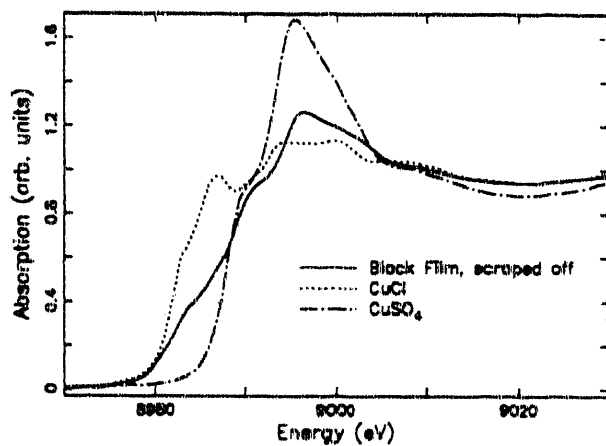


Figure 5. Absorption edge of black film scraped off of an anode and encapsulated in tape along with selected standards.

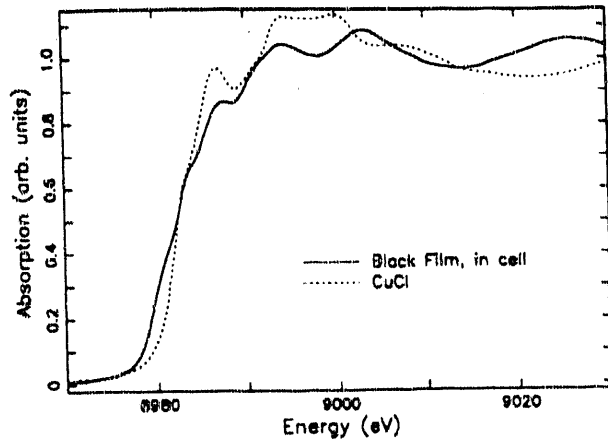


Figure 6. Absorption edges of CuCl and *in situ* black film formed by total conversion of CuP foil.

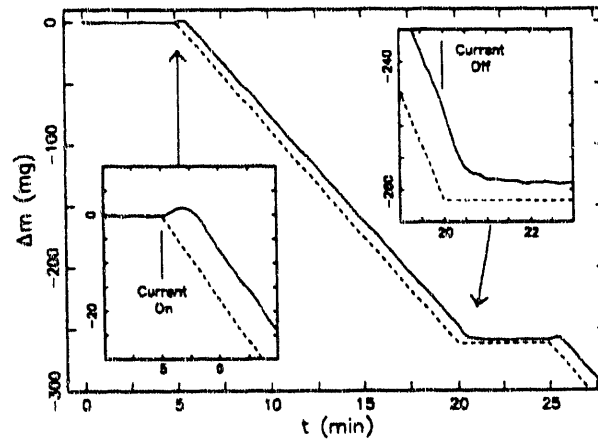


Figure 7. Buoyancy-corrected measured mass change, Δm_D (solid line), and charge-equivalent mass change, Δm_E (dashed line), for the initial part of an experiment with CuP in agitated Cl⁻-containing solution at 30 mA/cm².

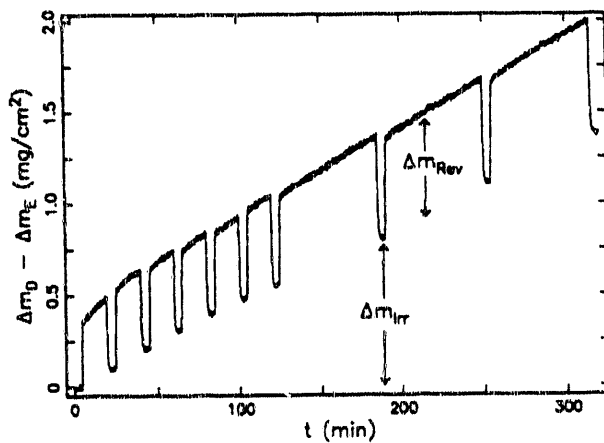


Figure 8. Difference between Δm_D and Δm_E for the same experiment as Fig. 7. The current was turned on for periods of 15 and 60 min. separated by periods of 5 min. with current off.

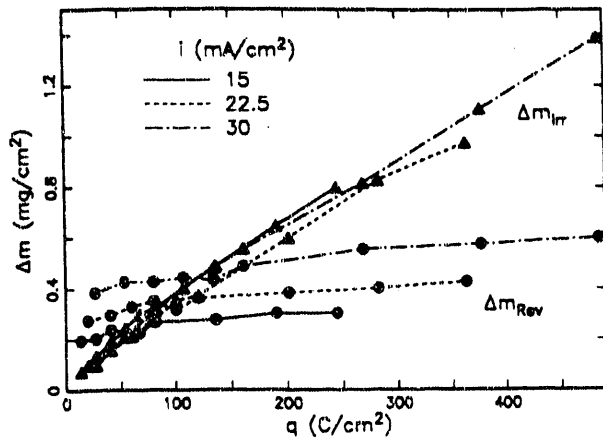


Figure 9. Influence of current density and charge density on reversible and irreversible mass changes for CuP in agitated Cl-containing solutions.

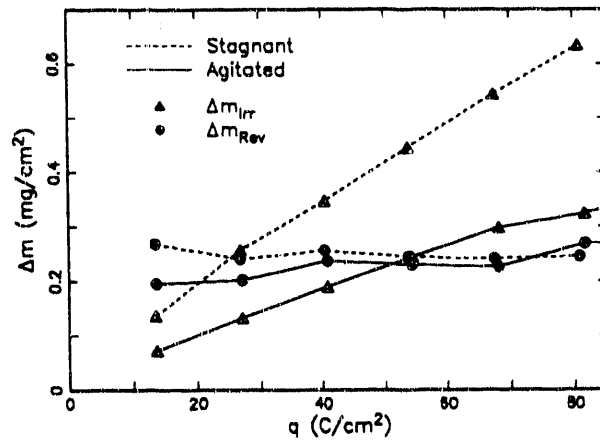


Figure 10. Influence of agitation on mass changes for CuP at 15 mA/cm² in Cl-containing solutions

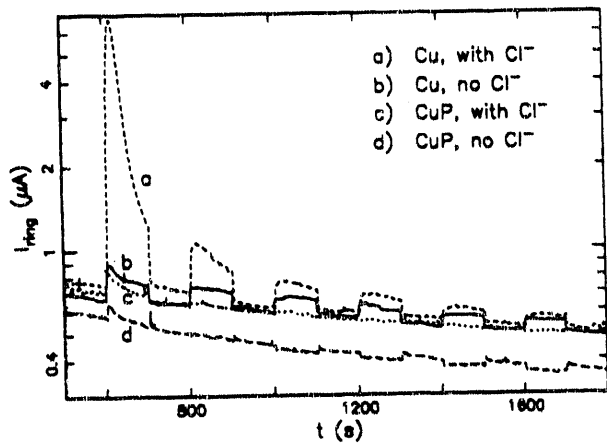


Figure 11. Ring current measured for disk current density of 15 mA/cm² = 2.85 mA. Disk current was turned on and off for periods of 100 s starting at 600 s.

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