Rotating Ring-Disk Studies of Cu Anodes: Effect of Chloride Ions and Organic Additives

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The effects of Cl⁻, organic additives and hydrodynamics on copper electrodissolution in acid $CuSO_4$ solutions were investigated, using rotating ring-disk electrodes. Additions of approximately 100 mg/L (2.8 mM) Cl⁻ to additive-free solutions significantly decreased electrodissolution in the transition and limiting current regions as a result of formation of surface CuCl films; Cu(I) ring currents were reduced in the entire potential region examined. Cu electrodissolution was not affected significantly by the presence of thiourea or a proprietary brightener in Cl⁻free solutions; however, benzotriazole significantly inhibited Cu electrodissolution, and the additional presence of Cl⁻ further increased inhibition.

Oxygen-free copper or phosphorized Cu anodes are commonly chosen for Cu plating processes from acid copper sulfate solutions.¹⁻³ Cu electrodissolution occurs at the anode, while Cu is electrodeposited at the cathode. To obtain bright Cu deposits, about 10 to 100 mg/L (0.28 to 2.8 mM) chloride ions are usually required with proprietary commercial brighteners.³⁻⁵

Electrodeposition and electrodissolution kinetics of copper in acid $CuSO_4$ have been studied by a number of inves-



Fig. 1—Effect of rotation rate on Cu electrodissolution in acid $CuSO_4$: (a) anodic polarization; (b) ring current.

tigators.^{6,7} Mattsson and Bockris proposed a two-step electron transfer mechanism for electrodeposition and electrodissolution with Cu⁺ as an intermediate.⁶ Their model, which assumed that the Cu⁺²/Cu⁺ reaction step was ratedetermining, showed good agreement with experiment.

Chloride ions, at relatively high concentrations (> 0.1 M), were found to increase Cu electrodissolution in acidic solutions with the formation of cuprous chloride complex species.⁸ At low chloride ion concentrations (< 0.05 M), Cu is primarily oxidized to Cu⁺² in the limiting current region.⁹ Little information is available, however, on Cu electrodissolution in acid CuSO₄ solutions containing very low concentrations of chloride ions and/or organic additives.

The present study is directed to the investigation of the effects of Cl⁻, thiourea (TU), a proprietary brightener (PB),^a benzotriazole (BTA) and hydrodynamics on Cu electrodissolution in acid CuSO₄ solutions with a rotating ring-disk electrode (RRDE). Hydrodynamic conditions in the RRDE system are well-defined, so that mass transport processes can be precisely controlled, and intermediate and product species can be detected at the ring electrode.

Experimental Procedure

A detailed description of the rotating ring-disk electrode assembly and the electrochemical cell has been given elsewhere.^{10,11} Oxygen-free pure copper (99.99%) and pure gold (99.99%) were used as the disk and ring electrodes, respectively. The diameter of the disk was 0.597 cm, of which the cross sectional area was 0.280 cm². The inner and outer ring diameters were 0.704 cm and 1.23 cm, respectively. The collection efficiency for this RRDE was experimentally obtained as 0.552.

^a Composite three-component additive containing a polyethylene glycol, a dye derivative and a surfactant.



Fig. 2—Limiting diffusion current of Cu⁺² in acid CuSO₄ vs. $\omega^{1/2}$.

Electrolytes were prepared from doubly distilled, deionized water and analytical reagent grade chemicals. Unless otherwise noted, the acid copper sulfate solution consisted of 0.3 M CuSO₄ and 2 M H₂SO₄, which is representative of plating solutions used for printed wiring board manufacturing because of its high throwing power. The electrolyte was maintained at room temperature (23 ± 1 °C) and deoxygenated with prepurified nitrogen gas for at least 12 hr prior to an experiment. Nitrogen gas was passed over the electrolyte during an experimental run.

The experimental procedure has been described previously.¹¹ Ring potentials were set at +0.6 V vs. SCE (saturated calomel electrode) to detect cuprous species, which oxidize to cupric species. Anodic polarization behavior of Cu was obtained with a sweep rate of 2 mV/sec from the rest potential, three min after the electrode was immersed in the electrolyte, unless otherwise noted. The surface appearance of the Cu deposit was visually checked during the anodic potential sweep by illuminating the disk surface with a lamp. All potentials are reported relative to the SCE.

Results and Discussion

Anodic Polarization Behavior of Cu in Acid CuSO₄ Typical anodic polarization behavior of Cu in acid CuSO₄ at various rotation rates is shown in Fig. 1a. In the potential range examined (rest potential to +1.3 V), there were three distinct regions: (I) Tafel, (II) transition, and (III) current plateau. The disk current represents the net rate of electrode reactions; the ring current corresponds to the flux of intermediate species, Cu(I), transported to the ring during electrodissolution of the Cu disk. In the Tafel region, the disk current was independent of rotation rate, and the anodic Tafel slope was approximately 45 mV/dec. In the transition region, the disk current increased with increasing disk potential and rotation rate. A current peak, which increased with increasing rotation rate, was followed by a current minimum. The peak potential (the potential at the peak current) increased to more positive potentials with increase in rotation rate; at higher rotation rates the current minimum was less distinct. In the current plateau region, the limiting current increased with increasing rotation rate.

Typical ring current behavior during Cu electrodissolution in acid $CuSO_4$ at various rotation rates is shown in Fig. 1b. As the Cu disk potential increased from the rest potential, ring current increased and a brown film began to develop on the disk surface at the end of the Tafel region (~0.14 V).

In the transition region, the ring current fluctuations appeared to be related to the instability of the surface film; the peak ring current occurred after the Cu disk was completely covered by a brown film. As the potential increased, the ring current dropped, then increased again when the brown film spalled; it spalled from the edge to the center of the disk.

For stationary electrodes (0 rpm), the ring current remained nearly zero over the entire potential range examined. On the other hand, for rotating electrodes, ring currents relative to the background ring current were significant from the rest potential through the current plateau region (Fig. 1b). Background ring currents, measured using only the rotating gold ring electrode (no Cu disk), were about $2 \ge 10^{-7}$ A and independent of rotation rate.



Fig. 3—Effect of Cl⁻ (1, 10, 100 mg/L) on Cu electrodissolution in acid $CuSO_{a'}$ 1000 rpm: (a) anodic polarization; (b) ring current.



Fig. 4—Effect of Cl[.] (50, 500, 5000 mg/L) on Cu electrodissolution in acid CuSO₄; 1000 rpm: (a) anodic polarization; (b) ring current.

Copper electrodissolution in acid CuSO_4 proceeds in two consecutive electron transfer steps, with Cu^+ as an intermediate. If the second step is rate determining, an anodic Tafel slope of 40 mV/dec is obtained,⁶

 $Cu \to Cu^+ + e^- \text{ (fast)} \tag{1}$

$$Cu^{2} \rightarrow Cu^{2} + e^{-} (slow)$$
 (2)

Cu⁺ may also be formed by the disproportionation reaction,

$$Cu^{+2} + Cu \rightarrow 2Cu^{+}$$

The equilibrium constant for this reaction is 5.6 x 10⁻⁷ at 25 °C.¹²

The anodic Tafel slope in the present work was approximately 45 mV/dec, which is in reasonable agreement with the above work.⁶ The ring current, which measured the flux of Cu⁺ from the disk, was much smaller than the disk current, indicating that Cu⁺² was the dominant product species of Cu electrodissolution in acid CuSO₄.

The plots of limiting anodic current density vs. $\omega^{1/2}$ are shown in Fig. 2. The straight lines, which pass through the origin, indicate that electrodissolution of Cu was controlled by mass transport of Cu⁺² from the disk to the bulk electrolyte. At a specific rotation rate, limiting diffusion currents were larger at lower Cu⁺² and H₂SO₄ concentrations. The surface concentrations of Cu⁺² ([Cu⁺²]_s) in 1 M and 2 M H₂SO₄ were calculated to be 1.014 M and 0.799 M, respectively, using the Levich equation, $i_a = 0.62nFD^{2/3}v^{-1/6}\omega^{-1/2}[Cu^{+2}]_s$ and the diffusion coefficients of Cu⁺² determined in our previous study.¹¹ The calculated [Cu⁺²]_s of 1.014 M in 1 M H₂SO₄ and 0.799 M in 2 M H₂SO₄ are in satisfactory agreement with saturated CuSO₄ concentrations in H₂SO₄ (1.07 M in 1 M H₂SO₄ and 0.770 M in 2 M H₂SO₄).¹³ Clerc and Alkire reported the

precipitation of a CuSO₄ salt film on a rotating Cu disk in 0.5 M H₂SO₄ at the limiting current.¹⁴ They proposed a duplex salt film based on impedance data. Similar corrosion film models have been proposed for Cu corrosion in acidic media¹⁵ and in H₂SO₄ solutions containing benzotriazole,^{14,16} Fe corrosion in FeCl₂ solutions,¹⁷ Ni corrosion in LiCl/HCl solutions,¹⁸ and Al corrosion in AlCl₃ solutions.^{19,20} In general, a dual structure with a thin, compact inner layer and a thick, hydrated, porous outer layer has been ascribed to the salt films formed at the limiting current.

The abrupt decrease in disk current at the end of the transition region (Fig. 1a) is probably a result of precipitation of the $CuSO_4$ film. In the current plateau region, there is a balance between the build-up and dissolution of the $CuSO_4$ salt film. Good agreement between calculated surface concentrations of the salt film and its saturated concentration in H_2SO_4 at the limiting diffusion current region, indicated that the Cu surface was covered by a $CuSO_4$ salt film, and its dissolution was controlled by mass transport of Cu^{+2} from the disk to the bulk electrolyte.

Effect of Cl^- on Cu Electrodissolution in Acid $CuSO_4$ The electrodissolution kinetics and mechanisms of Cu in acidic chloride media at relatively high Cl⁻ concentrations (>0.1 M) have been well established.^{8,21}Cu electrodissolution increases with increasing Cl⁻ concentrations from the rest potential to the post-limiting-current region.⁸ Previous results indicate mixed mass transfer and kinetic control with cuprous chloride complex as the diffusion species in the apparent Tafel region.^{8,9} In the limiting current region, Cu dissolution is mass-transfer-controlled. In the post-limiting-



Fig. 5—Effect of organic additives on Cu electrodissolution in acid CuSO₄; 1000 rpm: (a) anodic polarization; (b) ring current.



Fig. 6—Effect of BTA on Cu electrodissolution in acid $CuSO_4$; 1000 rpm: (a) anodic polarization; (b) ring current.

current region, there is mass transfer control of the cuprous chloride complex and kinetic control of Cu^{+2} formation via the reaction, $CuCl_2^- \rightarrow Cu^{+2} + 2Cl^- + e^-$. Much less is known, however, of Cu electrodissolution at very low Cl⁻ concentrations.

The effect of Cl⁻ on the anodic polarization of Cu in acid $CuSO_4$ is shown in Figs. 3a and 4a. No appreciable change in the anodic polarization behavior was observed with Cl⁻ additions up to 50 mg/L. At [Cl⁻] \geq 100 mg/L, the rest potential decreased with increasing Cl⁻ concentrations, with significant disk current inhibition observed in the transition and current plateau regions.

The ring current behavior during anodic polarization of Cu in acid CuSO, at various Cl⁻ concentrations is shown in Figs. 3b and 4b. Surges in ring currents were observed in the transition region with addition of 10 and 50 mg/L Cl⁻; in the range of 50 mg/L \leq [Cl⁻] \leq 500 mg/L, the ring current decreased with increasing Cl⁻ concentration. At 5000 mg/L Cl, ring currents significantly increased at all potentials examined. A brown film (probably redeposited copper) was observed around the ring current peak in the transition region at $[Cl^{-}] \leq 50 \text{ mg/L}$; the ring current surges at 10 and 50 mg/ L for lower potentials indicate the unstable nature of the film. A loosely adhering surface film (hydrated CuSO, layer) remained on the Cu disk at the end of anodic potential sweeps for $[Cl^{-}] \leq 50 \text{ mg/L}$. The essentially unchanged anodic polarization behavior by addition of as much as 50 mg/L Cl indicates that Cu electrodissolution is not significantly affected at very low Cl⁻ concentrations. For [Cl⁻] < 100 mg/L, a white film (CuCl) on the Cu surface was observed at the end of potential sweeps.

The inhibited disk currents in the transition and current plateau regions, and decreased rest potentials at $[Cl^-] \ge 100$

mg/L are attributed to precipitation of CuCl on the Cu surface. This significant change in the anodic polarization behavior indicates that Cu electrodissolution is affected by addition of [Cl⁻] \geq 100 mg/L. The "critical Cl⁻ concentration" to precipitate CuCl in acid CuSO₄ was experimentally determined as about 30 mg/L (0.85 mM).¹¹ The film observed on Cu at [Cl⁻] \geq 100 mg/L was indicative of precipitated CuCl. The decreased ring current in the transition region with increasing Cl⁻ concentration between 50 mg/L \leq Cl⁻ \leq 500 mg/L was attributed to increased surface coverage of CuCl.

Effect of Organic Additives

On Cu Electrodissolution in Acid CuSO

The organic additives, thiourea, benzotriazole and the proprietary commercial brightener, selected for the previous Cu electrodeposition study¹¹ have been investigated in this study. Bright Cu deposits were obtained from acid CuSO₄ solutions containing 5 mg/L (0.07 mM) TU and 50 mg/L (1.4 mM) Cl. Although there have been previous studies investigating the effect of TU on the appearance of Cu deposits from acid CuSO₄ solutions (*e.g.*, refs. 22–25), the effect of TU on Cu dissolution from acid CuSO₄ solutions apparently has not been examined.

The effects of TU on anodic polarization of Cu and the corresponding ring currents in acid $CuSO_4$ are shown in Figs. 5a and 5b, respectively. No appreciable change in disk and ring currents was observed by addition of 5 mg/L TU, except that the jog in the current plateau, where spalling of the surface film was observed, appeared at a lower potential.

Bright Cu deposits were obtained from acid $CuSO_4$ containing 119 mg/L (1 mM) BTA. Copper deposits were not brightened by addition of Cl⁻ to acid $CuSO_4$ -BTA solutions. The effect of BTA on Cu electrodissolution and its corre-



Fig. 7—Effect of BTA on Cu electrodissolution in acid $CuSO_4$ (1 hr immersion); 1000 rpm: (a) anodic polarization; (b) ring current.



Fig. 8—Effect of Cl-(1, 10, 100, 500 mg/L) on Cu electrodissolution in acid CuSO₄ and 5 mg/L TU; 1000 rpm: (a) anodic polarization; (b) ring current.

sponding ring current in acid CuSO₄ are also shown in Fig. 5. In the Tafel region, the addition of 1 mM BTA decreased the disk current; this inhibition of Cu electrodissolution was enhanced at the end of the Tafel region between 0.15 and 0.20 V, with the formation of a visible surface film, Cu(I)BTA, and a corresponding decrease in the Cu(I) flux from the disk. Protective films formed on Cu in acidic solutions containing BTA have been identified as Cu(I)BTA, using infrared spectroscopy.^{26,27} At approximately 0.2 V, breakdown of the film began; the instability of the film in this potential region was indicated by surges in the ring current. A limiting diffusion current was observed at potentials > 0.85 V.

The effects of BTA concentration (1 and 5 mM) on Cu electrodissolution in acid $CuSO_4$ and the corresponding ring current are shown in Figs. 6a and 6b, respectively. In the Tafel region, inhibition of the disk current increased when the BTA concentration increased from 1 to 5 mM. The disk current in the transition and current plateau regions was essentially the same in the presence of 1 and 5 mM BTA. A smaller ring current was observed, however, at all potentials for 5 mmol than for 1 mM BTA; in the latter case, the instability of the film is shown by the ring current surges. The increased inhibition and smaller ring currents in the Tafel region for 5 mM BTA are attributed to increased stability, surface coverage, and/or thickness of the Cu(I)BTA surface film.

The effectiveness of BTA on the inhibition of Cu electrodissolution during anodic potential sweeps of Cu in acid $CuSO_4$ for short (3 min) and longer term (1 hr) immersion was investigated. The results of the latter in acid $CuSO_4$ containing 1 and 5 mmol BTA and the corresponding ring current are shown in Figs. 7a and 7b, respectively. Comparison of Figs. 6 and 7 shows that the longer immersion time of

1 hr had little effect on disk and ring currents in 1 mM BTA. The longer immersion time had a significant effect, however, on the disk and ring currents in 5 mM BTA solutions. This increased inhibition at 1 hr immersion and 5 mM BTA on both disk and ring currents is the result of increased coverage and a thicker, more adherent Cu(I)BTA surface film on Cu. Previously, it was found that in acidic solutions (pH = 3)thicknesses of Cu(I)BTA films (20 mmol BTA) increased with increasing immersion time.27 Alkire and Cangellari surmised that the Cu(I)BTA film in 0.5 M H₂SO₄ was less protective at lower BTA concentrations (< 16 mM) than at higher concentrations (≥ 30 mM).¹⁶ They proposed a dual structure model of the film, consisting of a thin, compact, inner layer, which increased linearly in thickness with increasing applied potential, and a more porous outer layer. The inner layer consisted of hydrated copper sulfate containing BTA, with a porous copper benzotriazolate outer layer.^{14,16}

The effects of the proprietary commercial brightener (PB) on Cu electrodissolution in acid CuSO_4 and the corresponding ring current are also shown in Figs. 5a and 5b, respectively. In the presence of 1 vol percent PB in acid CuSO_4 , disk currents were slightly inhibited in the Tafel and transition regions, but ring currents significantly increased in the transition region. A step increase of both disk and ring currents occurred at potentials around 0.8 V, at which point the surface film spalled. Limiting diffusion currents were observed at potentials > 0.85 V.

The slight inhibition of the disk current in the Tafel and transition regions by addition of PB is thought to be the result of either adsorbed PB or a Cu(I) PB surface film on the Cu disk. As mentioned previously for organic-free acid CuSO₄ solutions, a brown film formed near the end of the Tafel



Fig. 9—Effect of Cl (1, 10, 100, 500 mg/L) on Cu electrodissolution in acid CuSO₄ and 1 mMBTA; 1000 rpm: (a) anodic polarization; (b) ring current.



Fig. 10—Effect of CI on Cu electrodissolution in acid $CuSO_4$ and 1 vol percent PB; 1000 rpm: (a) anodic polarization: (b) ring current.

region; the film spalled near 0.18 V. As soon as the brown film was removed, the ring current increased substantially, reaching a maximum at about 0.3 V. Between 0.15 and 0.40 V, both BTA and PB had an inhibiting effect on the second electron transfer step in Cu electrodissolution (Eq 2), resulting in increased flux of Cu(I) from the disk to the ring in this potential region.

Effect of Cl⁻ in Acid CuSO₄

Containing Organic Additives

In the previous study, the presence of Cl in the TU- and PBcontaining acid $CuSO_4$ was required to produce bright Cu deposits. For the BTA-containing acid $CuSO_4$, however, bright Cu deposits were only obtained in the absence of Cl.

The effect of Cl⁻ on Cu electrodissolution in acid CuSO₄ containing 5 mg/L (0.07 mM) TU and the corresponding ring current are shown in Fig. 8. Comparison with Figs. 3 and 4 shows that there was little change in the disk and ring currents by the addition of TU to acid CuSO₄ containing Cl⁻ up to 100 mg/L; therefore, the presence of small amounts of TU did not affect Cu electrodissolution in acid CuSO₄ containing low Cl⁻ concentrations.

The effect of Cl⁻ on Cu electrodissolution in acid CuSO₄ containing 1 mM BTA and the corresponding ring currents are shown in Fig. 9. In the presence of 10 to 100 mg/L Cl⁻, disk currents were reduced substantially; ring currents were negligible (*i.e.*, essentially no Cu[I] flux from the Cu disk). The enhanced inhibition of Cu electrodissolution in acid CuSO₄ by the presence of both Cl⁻ and BTA resulted in a Cu(I)Cl-BTA film that had a significantly reduced porosity compared to the Cu(I)BTA film; at Cl⁻ ≥50 mg/L, precipitated CuCl was included in the film. At 500 mg/L Cl⁻ both disk and ring currents increased substantially, indicating increased formation of CuCl₂⁻.

The effect of Cl⁻ on Cu electrodissolution in acid CuSO₄ containing 1 vol percent PB and the corresponding ring current are shown in Figs. 10a and 10b, respectively. The presence of 10 to 100 mg/L Cl⁻ in the PB-containing acid CuSO₄ inhibited the disk current in the Tafel and transition regions, possibly because of formation and adsorption of either Pb-Cl or Cu(I)PB...Cl complexes. The presence of this surface film resulted in substantially increased ring currents (increased flux of Cu[I] from the disk) as a result of a reduced rate of step (2) in the electrodissolution of Cu.

Summary and Conclusions

Potentiodynamic electrodissolution of Cu in acid $CuSO_4$ solutions with and without Cl ions and selected organic additives was investigated with RRDE. Three distinct regions were observed: Tafel, transition and limiting current (or current plateau). The two-step mechanism with Cu(I) as intermediate is supported by the anodic Tafel slopes and ring current behavior. The much smaller ring current, compared to the disk current, indicates that Cu⁺² is the dominant product species.

In the transition region, the formation of a brown film on the disk (a result of the disproportionation reaction) limited or decreased the ring current. Observed ring current surges are attributed to instability and/or spalling of the film. In the limiting-current region, the disk surface is covered with a $CuSO_4$ salt film. Dissolution of this film is controlled by mass transfer of Cu^{+2} to the bulk electrolyte.

Low concentrations of Cl⁻ ($\leq 10 \text{ mg/L}$) in additive-free acid CuSO₄ solutions increase the ring currents, while disk currents are unaffected. Increased Cl⁻ concentrations ($\geq 100 \text{ mg/}$ L) decreased both disk and ring currents because of formation of CuCl films on the Cu disk. Higher Cl⁻ concentration (*e.g.*, 5000 mg/L) resulted in increased ring currents over the entire potential range because of formation of CuCl₂⁻ complexes.

The addition of TU (5 mg/L) to acid CuSO₄ solutions did not affect the electrodissolution of Cu. Disk currents were only slightly inhibited in the Tafel and transition regions by addition of PB to acid CuSO₄ solutions.

The addition of BTA to Cl⁻free solutions decreased disk currents in the Tafel and transition regions because of formation of inhibiting Cu(I)BTA films. Lower BTA concentrations (1 mM) exhibited larger ring currents than 5 mM BTA concentration, and prolonged immersion (1 hr) prior to polarization sweeps, substantially decreased the disk current in the current plateau region for the 5 mM BTA-containing solution, but had little effect at the lower BTA concentration. The ring currents at the higher concentration were completely inhibited, indicating the absence of a Cu(I) flux. Addition of 10 to 100 mg/L Cl⁻ to 1 mM BTA-containing solutions significantly inhibited Cu electrodissolution.

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