Lawrence Berkeley National Laboratory
Recent Work

Title
STOICHIOMETRY OF ANODIC COPPER DISSOLUTION AT HIGH CURRENT DENSITIES

Permalink
https://escholarship.org/uc/item/5ns4c54g

Authors
Kinoshita, K.J.
Landolt, D.
Muller, R.H.
et al.

Publication Date
1970-05-01
STOICHIOMETRY OF ANODIC COPPER DISSOLUTION
AT HIGH CURRENT DENSITIES

K. Kinoshita, D. Landolt, R. H. Muller, and C. W. Tobias

May 1970

AEC Contract No. W-7405-eng-48
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
STOICHIOMETRY OF ANODIC COPPER DISSOLUTION
AT HIGH CURRENT DENSITIES

by
K. Kinoshita,†
D. Landolt,††
R. H. Muller,
C. W. Tobias

Inorganic Materials Research Division, Lawrence Radiation Laboratory and
Department of Chemical Engineering, University of California
Berkeley, California

ABSTRACT

The influence of current density, flow rate and electrolyte composition on the stoichiometry of anodic copper dissolution was investigated under conditions comparable to those of electrochemical machining. Weight loss measurements, x-ray diffraction and chemical analysis were used for the characterization of the dissolution reaction. A sharp change in dissolution mechanism coincided with the transition from active to transpassive dissolution. For active dissolution, an apparent valence of the dissolution process of two was found in sulfate and nitrate electrolytes, and of one in chloride electrolytes. For transpassive dissolution, mixed valences lying between 1 and 2 were found in all electrolytes. The mixed valences are interpreted to result from the simultaneous production of monovalent and divalent reaction products, some of which are in solid form.

†Present Address: Pratt & Whitney Aircraft Corp.
Middletown, Connecticut 06457

††
University of California
School of Engineering & Applied Science
Los Angeles, California 90024
INTRODUCTION

Anodic dissolution of metals at current densities of up to several hundred amperes per square centimeter, and with electrolyte flow velocities of many meters per second is being carried out on a technical scale in the process of electrochemical machining (ECM). In an attempt to provide quantitative information on the electrochemical processes under high current densities, the anodic dissolution of copper is being investigated.\textsuperscript{1,2,3} Copper was chosen because its electrochemical properties are reasonably well understood.\textsuperscript{4-8} In a previous paper,\textsuperscript{1} the role of mass transfer in determining the occurrence of passivation phenomena during copper dissolution in K\textsubscript{2}SO\textsubscript{4} and KNO\textsubscript{3} solutions has been reported. It was found that apparent anode potentials and surface textures resulting from dissolution changed drastically while going from a low voltage (active) to a high voltage (transpassive) mode of dissolution.*

In the present study, the valence of the electrode reaction and the composition of reaction products of copper have been investigated in nitrate, sulfate and chloride electrolytes. Weight loss measurements of the anode, x-ray diffraction analysis of solids and chemical analysis of the solution were used for the characterization of the dissolution reaction. Current densities employed ranged from 0.1 to 80 A/cm\textsuperscript{2}. Experiments were performed under forced convection conditions in a flow channel at flow rates from 30-700 cm/sec, as well as in unstirred solutions under free convection conditions.

*Different definitions for the phenomenon of passivation can be found in the literature. The term is used here to describe an abrupt increase in measured anode potential with time for certain combinations of flow rate and current density (see e.g. Fig. 3).
EXPERIMENTAL

Most experiments were carried out under forced convection conditions in an experimental flow system similar to that described in a previous study, and schematically shown in Fig. 1. The electrolyte was pumped by a positive displacement pump and the flow rate was measured with a rotameter.** 1/2 inch stainless steel pipes were used throughout the system.

A 30 cm long rectangular flow channel of 1 x 3 mm cross section, constructed of laminated polyvinyl chloride, was positioned upstream of the experimental cell to establish fully developed velocity profiles at the electrodes.\(^1\) The electrolysis cell is shown schematically in Fig. 2. The cell body (B) was made of epoxy resin with the two glass side walls (H) held together by plates (C). The cell was connected to the inlet and outlet channel by end flanges (G). Optical observation of the inter-electrode gap could be performed through the glass walls. Back-side capillaries (K) which enter the channel walls next to the electrodes were used for electrode potential measurements and, in some experiments, for the sampling of solution on the downstream side of the electrodes. The copper electrodes (D) (purity \(\geq 99.9\%\)) had a geometrical surface area of 3 x 3 mm. The electrodes could be advanced manually by turning micrometer head (M). The electrode assembly was pushed back against insert (F) by sprint (O). Silicone rubber gaskets*** cast between glass wall and epoxy cell body were used for sealing the cell.

---


**Type 18410, Schutte and Koerting Co., Cornwall Heights, Pa.

Measurements of cell voltage, electrode potentials and current were made simultaneously on a multi channel light beam oscillograph.*

Electrical power connections to the cell were made by threaded connections screwed into aluminum cap (E). The current was recorded by measuring the voltage drop across a shunt. Anode and cathode potentials were measured with respect to saturated calomel reference electrodes, which were placed in small glass containers connected to the capillaries by tygon tubing. The electrolysis current was provided by an electronically controlled constant current supply.**

Prior to each run, the electrodes were ground on 600 grit emery paper, and washed with aqueous detergent. Following a dip in concentrated HCl, they were rinsed with distilled water and reagent grade acetone, and stored in vacuum until use. The electrodes were aligned with the channel wall by using a microscope with 20x magnification. During electrolysis, the 1 mm electrode gap was approximately maintained by manual adjustment of the micrometer.

* Series 2300, Brush Instrument Division, Cleveland, Ohio.
During a typical experiment, 25 mg of copper were dissolved, which corresponded to an average depth of dissolution of about 0.3 mm. After each run, the anode was removed from the cell, rinsed with water, dried with acetone and weighed on an analytical balance. The accuracy of the weight loss determination is estimated at ±1-2%. The amount of charge passed during the experiment was determined from the oscillographically recorded current trace. The accuracy of the charge measurement is estimated at ±2-3%.

From the measurement of charge and weight loss, an apparent valence n of the dissolution process was calculated according to eq. (1)

\[ n = \frac{ItM}{\Delta W F} \]  

(1)

where I is the current passed during time t, M is the atomic weight of copper, \( \Delta W \) is the anode weight-loss and F is the Faraday constant.

Solid reaction products formed during the anodic dissolution of copper were analyzed by x-ray diffraction. Initial analyses were made using a 11.46 mm Debye-Scherrer powder camera mounted on an x-ray diffraction unit.* Ni filtered Cu radiation (40 kV, 20 Ma) was used.

A sample of the anodic reaction product from the flow cell was collected by rubbing a glass fiber through the precipitate adhering to the wet surface. Diffraction patterns obtained were, however, difficult to analyze because of the faintness of the diffraction lines. Also, because of the small samples, exposure times to the x-ray beam from 6-12 hours were necessary.

---

*Norelco X-Ray Diffraction Unit, Type 12045 with Debye-Scherrer Camera Type 52056-0, North American Philips Co., Inc., New York, N.Y.
To provide a larger specimen, a continuous sampling technique was developed. An x-ray diffractometer* using a Ni filtered Cu radiation (40 kV, 14 mA) could then be used. Solution escaping through the (0.014 inch diameter) capillary on the downstream side of the anode was collected on a Whatman No. 41 paper by continuous vacuum filtration. Without washing, the filter paper with adhering precipitate was dried under vacuum, mounted onto a lucite sample holder using double-sided adhesive tape, and placed into the diffractometer. A preliminary x-ray pattern of the blank showed strong diffraction peaks at low θ values which did, however, not interfere with the diffraction peaks of possible compounds present in the precipitate.

In order to substantiate the apparent valence determination carried out under forced convection conditions, some experiments were performed in a stagnant electrolyte which allowed quantitative determination of dissolved Cu$^+$ and Cu$^{2+}$ ions. Since Cu$^+$ is unstable in aqueous solution unless complexing agents are present, only chloride electrolytes were analyzed this way. The electrolysis was carried out in an H cell with

*Picker X-Ray Corporation, Waite Manufacturing Division, Inc., Cleveland, Ohio 44112.
a glass frit separating anode and cathode compartments. In contrast to the highly diluted dissolution products obtained in the flow channel, concentrations which can be determined by simple analytical techniques could be obtained in this system. The analytical determination of Cu$^{2+}$ and Cu$^+$ was based on that given by Vogel. Cuprous ion was oxidized with ferric ammonium sulfate and the resulting ferrous ion was titrated with ceric sulfate. The cupric ion concentration was obtained as the difference between total copper concentration and cuprous ion concentration. The total copper concentration was determined iodometrically after oxidation of cuprous ion to cupric ion by sodium peroxide.

RESULTS

Current-voltage behavior: Figure 3 illustrates the transient cell voltage behavior during galvanostatic copper dissolution in 2 N KNO$_3$ under a given flow rate (30 cm/sec.). At low current density (3.4 A/cm$^2$), the dissolution proceeds indefinitely in a low voltage (active) mode. Above a critical current density, which is shifted to higher values by increased flow rates, the dissolution process switches to a high voltage (transpassive) mode, after a transition time with active dissolution. The length of the transition period decreases with increasing current density and decreasing flow rate (not shown). Figures 4 and 5 are examples of transient cell voltage behavior with K$_2$SO$_4$ and KCl solutions. In all cases, dissolution in the transpassive mode occurs at a cell voltage which is 10-20 volts higher than in the active mode. Voltage fluctuations are observed in the transpassive region and, at the higher current densities, a voltage maximum occurs before steady state is reached.
Apparent valence: Average steady state values of the cell voltage and apparent valence values are plotted versus current density in figures 6 to 8. The behavior in 2N KNO₃ and 1N K₂SO₄ solutions is very similar. With the transition from active to transpassive dissolution, a sharp drop in apparent valence occurs. The apparent valence value of n = 2 observed in the active region, indicates that copper is dissolved almost exclusively to divalent cupric ions. This is consistent with expectations based on thermodynamic considerations of the reversible potential of a copper electrode in contact with dissolved mono and divalent copper ions. In the transpassive region, on the other hand, the apparent valence depends on the value of the applied current density with respect to the current density at which passivation occurs. A limiting value of n ≈ 1.5-1.6 is reached at high current densities. In order to account for this value of n, it either has to be assumed that part of the copper is dissolved to a monovalent form, or that part of the metal disintegrates during the dissolution process. Since pH might have an influence in determining the reaction path, additional experiments were performed in a 2N KNO₃ solution adjusted to pH 1 by the addition of concentrated nitric acid, and also in a 1N H₂SO₄ solution. Voltage readings and apparent valences obtained in both of these electrolytes corresponded within experimental accuracy to those of the nitrate and sulfate solutions, respectively. This indicates that, within the range studied, pH has a negligible influence on apparent valence of the dissolution process. As illustrated by Fig. 8, the behavior in KCl solutions was quite different from that in KNO₃ and K₂SO₄ solutions. A sharp transition between active
and transpassive dissolution was absent. Instead, periodic fluctuations occurred (indicated by dotted lines in figure 8) in the transition region. Such oscillations in the copper/chloride system have also been reported in the literature for low current density conditions.\textsuperscript{6,10} Periodic oscillations have also been observed during high rate copper dissolution in sulfate and chlorate electrolytes, under certain conditions.\textsuperscript{1,2,3} The apparent valence, in the case of chloride solution, is $n = 1$ at low current densities. A maximum of $n = 1.4$ is observed at intermediate current densities and the apparent valence drops to $n = 1.2$ in the range of high current densities. While it appears that the observed changes in apparent valence are related to the occurrence of passivation, the relationships are not as clear cut as in nitrate and sulfate solutions. For example, at the highest flow rate (606 cm/sec), the maximum value of $n$ was attained at much higher current density than that corresponding to the active-passive transition derived from cell voltage measurements.

**Analysis of solid reaction products:** Anode precipitates were found during transpassive dissolution only. X-ray analysis of precipitates collected from experiments performed in $\text{KNO}_3$ and $\text{K}_2\text{SO}_4$ solutions showed $\text{Cu}_2\text{O}$ to be the principal copper compound. Diffraction peaks for metallic copper were also present, in some experiments. The metallic copper contents of precipitates from acidified solutions was increased at the expense of the cuprous oxide contents (Table I). No analysis of anodic precipitates in chloride solution was possible, because precipitates could not be collected in sufficient amounts. A typical diffraction
pattern of anode precipitate is given in Figure 9 together with patterns of known samples of Cu₂O and Cu. Precipitates collected in the drain tank showed a different composition from those collected close to the anode. They contained basic oxides of complex composition, owing to contact with the alkaline solution produced at the cathode.

**Analysis of dissolved reaction products:** Apparent valence determinations in chloride solution were also carried out in a separate cell under absence of forced convection. In these experiments, values of apparent valence obtained from weight loss measurements could be compared with those obtained by chemical analysis of dissolved reaction products. Calculation of the chemically determined apparent valence $n^*$ was based on eq. (2)

$$
Cu \rightarrow xCu^+ + yCu^{2+} + n^*e
$$

(2)

where $x$ and $y$ are the fractional amounts of $Cu^+$ or $Cu^{2+}$ respectively. Since, from the mass balance $x + y = 1$ and from the charge balance $x + 2y = n^*$, one gets eq. (3)

$$
n^* = 2 - x = 1 + y
$$

(3)

The results given in Table II illustrate the good agreement between the valence determined by chemical analysis with that derived from weight loss measurements for a wide range of current densities. In all cases a mass balance could be established within 1-2%. Changes in apparent valence with current density in chloride solutions are therefore indeed due to different ratios of $Cu^+$ and $Cu^{2+}$ produced. No oxygen evolution was observed during the experiments. The experiments also confirmed that the anodic behavior, i.e. the occurrence of active and transpassive dissolution, was essentially the same in stagnant as in flowing solutions, with the exception that passivation sets in at much lower current densities in the absence of external convection.
DISCUSSION

Nitrate and Sulfate Solutions: Two dissolution modes active and transpassive, were found differing in overvoltage and apparent valence of dissolution. The transition between active and transpassive dissolution depends on mass transfer conditions. Using the mass transfer correlations for channel flow discussed earlier, the interfacial concentration of ionic dissolution product at the onset of transpassive dissolution was estimated from the passivation current density for different flow rates and electrolytes. (A diffusion coefficient of $5 \times 10^{-6}$ cm$^2$/sec was assumed for this calculation.) A comparison of the results shown in Table III with solubility data given in Table IV indicates that the onset of transpassive dissolution coincides, at least qualitatively, with the limiting transport of dissolved reaction products by convective diffusion. This substantiates the validity of previous results which were obtained in a different flow system, mostly at higher current densities and flow rates. In addition, it was found here that passivation current densities in 1 N $\text{H}_2\text{SO}_4$ were essentially the same as in 1 N $\text{K}_2\text{SO}_4$. This suggests that limitations in the transport of cupric salt, rather than the formation of oxide or hydroxide, initiates the change to transpassive dissolution.

The present study also demonstrates that the transition between active and transpassive dissolution is associated with a drastic change in current efficiency for the metal removal process, with more copper being dissolved for a given amount of charge in the transpassive region. A mechanism involving the formation of monovalent copper species at the anode, especially cuprous oxide, rather than anodic disintegration by grain boundary attack$^{11,12}$, seems to be the cause for the apparent increase in current efficiency. The above conclusion, although it can
not be rigidly proven on the grounds of our results, is supported by the following experimental observations: (1) Cuprous oxide has been found to be the main constituent of anodic films. (2) Substantial amounts of metallic copper were observed in the x-ray patterns in acidic solutions only, consistent with the fact that Cu$_2$O disproportionates in these solutions into Cu$^{2+}$ and Cu. (3) No grain boundary attack was observed microscopically in the transpassive region. Instead, the surfaces after transpassive dissolution had a shiny appearance and were almost randomly pitted.\(^1,\(^2\)\(^4\) At least in the case of chloride solutions, the presence of cuprous ion could be quantitatively verified. All these factors indicate that a disintegration mechanism, which has been proposed primarily for more reactive metals (beryllium, magnesium, cadmium, zinc) at low current densities\(^13-16\), is not likely to be of importance in the present anodic dissolution process.

Measured apparent valences tended to reach a constant limiting value at high current densities. No satisfactory explanation for this phenomenon can be given at the present time. From a purely kinetic point of view we would expect a continuous variation of $n$ with current density. A possible explanation of the observed constancy of $n$ may, perhaps, be sought in a model viewing the surface as an ensemble of small surface area elements randomly fluctuating between active and passive states. Such active-passive fluctuations, which are most pronounced in chlorate electrolytes\(^2,\(^3\), are presently being studied in this laboratory.

**Chloride Solutions:** The dissolution behavior in chloride electrolytes is different because the monovalent ionic state becomes thermodynamically more favorable than the divalent state due to the formation of cuprous ion complexes\(^17,\(^18\). Thus, disproportionation of Cu$^+$, which
usually occurs in aqueous solutions is avoided. Since a variety of different complexes may be formed, depending on the local chloride concentration, the dissolution process in chloride solutions is expected to be much more complicated than in nitrate and sulfate solutions. For example, due to the effect of chloride concentration on the solubility of cuprous ion, the formation of precipitate layers depends not only on the rate of departure of cations from the interface, but also on the rate of arrival of anions. In addition to the mass transport of the dissolution product, the mass transport of chloride ion may therefore become a limiting factor, since chloride ions are consumed at the anode by complex formation. Such a mechanism has, for example, been reported by Landsberg et al.\textsuperscript{19} for the dissolution of gold in HCl. During the course of stoichiometric determinations in stagnant solution, a number of transient measurements were performed in 3N KCl solutions at constant current density. Table V summarizes the transition times determined for the onset of transpassive behavior. In spite of that the geometrical arrangement was not ideal to completely exclude free convection, the application of Sand's equation is justified because of the short times involved. From the average measured quantity \( \sqrt{t} \), a value for \( \Delta C \), the rate limiting concentration difference, was calculated according to eq. (4)

\[
\Delta C = \frac{2 \sqrt{t}}{n F V \pi D}
\]

assuming \( D = 5 \times 10^{-6} \text{ cm}^2/\text{sec} \) and \( n = 1 \). The resulting value of \( \Delta C = 3.6 \text{ mole/liter} \) is similar in magnitude to the solubility of CuCl in 3N KCl, (1.9 mole/liter\textsuperscript{17}). This indicates that, under the conditions of
these experiments, passivation may have been caused by a similar precipitation mechanism as in nitrate and sulfate solutions.

The increase in apparent valence $n$ upon passivation (Figure 8) is consistent with the fact that at higher anode potentials, the reaction $\text{Cu} \rightarrow \text{Cu}^{2+}$ becomes thermodynamically possible. No true anode potential measurements were possible under the conditions of this study; therefore, a discussion has to remain qualitative. The subsequent decrease in $n$ at still higher current densities may then be explained by assuming formation of $\text{Cu}_2\text{O}$, as observed in the case of nitrate and sulfate solutions. The oozing of a reddish brown, finely dispersed dissolution product from localized anode areas which changed their positions during electrolysis was observed visually in stagnant KCl solutions in the transpassive region. This solid might have been $\text{Cu}_2\text{O}$ but it was not possible to collect the precipitate due to its chemical instability in the chloride electrolyte. The formation of cuprous oxide during copper dissolution in chloride media has also been reported in the literature. The formation of a thin cuprous chloride film during transpassive dissolution in chloride solution was indicated by the white appearance of the surface.

**SUMMARY AND CONCLUSIONS**

1. The present study has confirmed earlier findings obtained under different experimental conditions that in nitrate and sulfate electrolytes, the transition from active to transpassive dissolution of copper is controlled by the mass transfer of dissolved dissolution products.

2. Although the details of copper dissolution in chloride solution are probably different from those in nitrate and sulfate, the gross current-voltage behavior is similar. Ionic mass transfer limitations
seem, therefore, to be the dominating factor determining the onset of passivation in chloride solutions, too.

3. The apparent valence of the dissolution process undergoes a noticeable change with the transition from active to transpassive dissolution. In nitrate and sulfate solutions, active dissolution proceeds with an apparent valence of 2. Transpassive dissolution leads to a lower apparent valence, which reaches a limiting value of 1.6 at high current densities. This drop in apparent valence is interpreted to be caused by the anodic production of monovalent copper species, rather than by anodic disintegration.

4. Active dissolution in chloride solution occurs with an apparent valence of one. This is due to the stabilization of cuprous ion by complex formation. Upon passivation the apparent valence increases, going through a maximum of 1.4 with increasing current density before reaching a limiting value of 1.2. This increase in apparent valence upon passivation is due to part of the copper being dissolved in divalent form.

5. No significant oxygen evolution occurred during copper dissolution under all the experimental conditions employed.

6. The formation of solid anodic dissolution products during transpassive dissolution has been demonstrated in agreement with earlier optical observations. Analysis of the precipitates by x-ray diffraction has shown Cu$_2$O to be the main constituent produced in potassium nitrate and sulfate solutions. Metallic copper, resulting from disproportionation of Cu$_2$O, is found in acidified solutions. In chloride solutions optical observation indicated the formation of cuprous chloride films.

This work was done under the auspices of the U. S. Atomic Energy Commission.
REFERENCES

14. M. E. Straumanis, J. L. Reed and W. J. James, this journal, 114, 885 (1967).
Table I. X-ray analysis of anode solid reaction products.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Compounds Identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>2N KNO$_3$</td>
<td>Cu$_2$O, Cu</td>
</tr>
<tr>
<td>2N KNO$_3$ + HNO$_3$(pH 1)</td>
<td>Cu</td>
</tr>
<tr>
<td>1N K$_2$SO$_4$</td>
<td>Cu$_2$O, Cu</td>
</tr>
<tr>
<td>1N H$_2$SO$_4$</td>
<td>Cu</td>
</tr>
</tbody>
</table>
Table II. Chemical Analysis of Dissolved Reaction Products in 3N KCl Solution After Passage of 60 coul, anode area 1 cm$^2$.

<table>
<thead>
<tr>
<th>Current Density (amp/cm$^2$)</th>
<th>Valence from dissolved Cu$^+$ and Cu$^{++}$</th>
<th>Valence from weight loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.10</td>
<td>1.19</td>
<td>1.15</td>
</tr>
<tr>
<td>0.13</td>
<td>1.21</td>
<td>1.28</td>
</tr>
<tr>
<td>0.16</td>
<td>1.27</td>
<td>1.31</td>
</tr>
<tr>
<td>0.21</td>
<td>1.28</td>
<td>1.30</td>
</tr>
<tr>
<td>0.26</td>
<td>1.26</td>
<td>1.28</td>
</tr>
<tr>
<td>0.51</td>
<td>1.22</td>
<td>1.20</td>
</tr>
<tr>
<td>0.82</td>
<td>1.19</td>
<td>1.20</td>
</tr>
<tr>
<td>1.00</td>
<td>1.13</td>
<td>1.10</td>
</tr>
<tr>
<td>1.31</td>
<td>1.14</td>
<td>1.16</td>
</tr>
<tr>
<td>1.58</td>
<td>1.10</td>
<td>1.08</td>
</tr>
<tr>
<td>1.87</td>
<td>1.08</td>
<td>1.06</td>
</tr>
<tr>
<td>1.98</td>
<td>1.07</td>
<td>1.07</td>
</tr>
</tbody>
</table>
Table III. Calculated interfacial concentration of copper salts at onset of transpassive dissolution.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Flow Velocity (cm/sec)</th>
<th>Reynolds number</th>
<th>Passivation Current density (amp/cm²)</th>
<th>Interfac. Conc. (moles/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2N KNO₃</td>
<td>30</td>
<td>510</td>
<td>3.8</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3390</td>
<td>8.5</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>627</td>
<td>10600</td>
<td>31.0</td>
<td>8.5</td>
</tr>
<tr>
<td>1N K₂SO₄</td>
<td>50</td>
<td>730</td>
<td>1.5</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>2920</td>
<td>4.1</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>686</td>
<td>10000</td>
<td>8.5</td>
<td>2.2</td>
</tr>
<tr>
<td>1N H₂SO₄</td>
<td>50</td>
<td>770</td>
<td>3.6</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3090</td>
<td>4.7</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>686</td>
<td>10600</td>
<td>11.8</td>
<td>3.0</td>
</tr>
<tr>
<td>2N KCl</td>
<td>50</td>
<td>820</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3270</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>606</td>
<td>10000</td>
<td>2.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Table IV. Solubilities of copper salts at room temperature.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Solvent</th>
<th>Solubility (moles/l)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cupric nitrate</td>
<td>H₂O</td>
<td>7.0</td>
<td>24</td>
</tr>
<tr>
<td>Cupric sulfate</td>
<td>H₂O</td>
<td>1.4</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>1N H₂SO₄</td>
<td>1.1</td>
<td>25</td>
</tr>
<tr>
<td>Cuprous chloride</td>
<td>2N KCl</td>
<td>1.0</td>
<td>17, 18</td>
</tr>
<tr>
<td></td>
<td>3N KCl</td>
<td>1.9</td>
<td>17, 18</td>
</tr>
</tbody>
</table>
Table V. Transition Times $\tau$ for Copper Dissolution at different Current Densities $i$ in 3N KCl without External Convection.

<table>
<thead>
<tr>
<th>$i$ (amp/cm$^2$)</th>
<th>$\tau$ (seconds)</th>
<th>$i\sqrt{\tau}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>38.90</td>
<td>0.62</td>
</tr>
<tr>
<td>0.16</td>
<td>11.60</td>
<td>0.56</td>
</tr>
<tr>
<td>0.21</td>
<td>9.20</td>
<td>0.69</td>
</tr>
<tr>
<td>0.26</td>
<td>5.63</td>
<td>0.62</td>
</tr>
<tr>
<td>0.51</td>
<td>1.85</td>
<td>0.70</td>
</tr>
<tr>
<td>0.82</td>
<td>0.65</td>
<td>0.68</td>
</tr>
<tr>
<td>1.00</td>
<td>0.48</td>
<td>0.69</td>
</tr>
<tr>
<td>1.31</td>
<td>0.28</td>
<td>0.69</td>
</tr>
<tr>
<td>1.58</td>
<td>0.20</td>
<td>0.70</td>
</tr>
<tr>
<td>1.87</td>
<td>0.16</td>
<td>0.75</td>
</tr>
<tr>
<td>1.98</td>
<td>0.15</td>
<td>0.77</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. Schematic of flow system. A - supply tank, B - dual piston pump, C - accumulator, D - bypass line, E - Rotameter, F - entrance length of flow channel, G - reference electrodes, H - cathode, I - anode, J - capillary for precipitate collection, K - drain tank.

Fig. 2. Side view of experimental cell with partial cross-sectioning. A - rectangular flow channel, B - epoxy cell body, C - stainless steel side plate, D - copper electrode, E - aluminum cap, F - nylon screw, G - stainless steel end flange, H - glass side window, I - bolt and nut assembly, J - O-ring seal, K - liquid junction connection to backside capillaries, L - aluminum micrometer holder, M - micrometer head, N - aluminum base plate, O - coil spring.

Fig. 3. Cell voltage transients measured in 2N KNO₃ at different current densities, flow rate 30 cm/sec.

Fig. 4. Cell voltage transients measured in 1N K₂SO₄ at different current densities, flow rate 50 cm/sec.

Fig. 5. Cell voltage transients measured in 2N KCl at different current densities, flow rate 50 cm/sec.

Fig. 6. Variation of apparent valence and cell voltage with current density in 2N KNO₃ for different flow rates: 0 = 30 cm/sec, Δ = 200 cm/sec, □ = 627 cm/sec.

Fig. 7. Variation of apparent valence and cell voltage with current density in 1N K₂SO₄ for different flow rates: 0 = 50 cm/sec, Δ = 200 cm/sec, □ = 686 cm/sec.
Fig. 8. Variation of apparent valence and cell voltage with current density in 2N KCl for different flow rates: $\dot{0} = 50$ cm/sec, $\Delta = 200$ cm/sec, $\Box = 606$ cm/sec.

Fig. 9. X-Ray diffractometer trace of anode precipitate (b) compared to known samples of Cu$_2$O (a) and Cu (c). Anode precipitate obtained at 11.1 amp/cm$^2$ and 50 cm/sec in 1N K$_2$SO$_4$. 
Fig. 3
Fig. 6
Fig. 7
Fig. 8

Cell voltage (V) vs. Current density (amp/cm²)

Apparent valence vs. Current density (amp/cm²)
LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.