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ANODE POTENTIALS IN HIGH RATE DISSOLUTION OF COPPER

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ABSTRACT

A constant current interrupter technique was employed in the experimental determination of anode potentials during high rate anodic dissolution of copper. The influence of ohmic voltage drops in the solution on measured overvoltage have been compensated by electronic means. For short electrolysis times, dissolution proceeds in the active mode; in sulfuric acid, Tafel behavior was observed up to the highest current densities employed (100 A/cm^2). Passivation effects may lead to significantly higher anodic potentials.

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INTRODUCTION

In electrochemical machining (ECM), metals are dissolved anodically at current densities of many amperes per square centimeter. In order to get a better understanding of electrochemical factors governing metal dissolution proceeding at such high rates, meaningful anode potential measurements are needed. Potential measurements performed at high current densities with rapidly dissolving anodes pose many problems,¹ and anode potential data reported for technical ECM conditions appear to be of questionable value.^{2,3} The anodic dissolution of copper has been chosen in this laboratory for the study of some fundamental aspects of ECM.^{1,6,7,8} For high rate anodic dissolution of copper, abrupt potential changes of many volts have been found, coinciding with a change from an active to a transpassive dissolution mode.¹ However, the experimental techniques employed did not allow for the subtraction of ohmic voltage drops from the potential values measured. Electrode potential data obtained at low current densities have been extrapolated by Hoare et al. to predict high current density behavior of ECM electrolytes.^{4,5} In view of many unknowns inherent in ECM it appeared desirable, however, to develop experimental procedures which allow direct potential measurements over a wide range of current densities. In the present paper, a galvanostatic interrupter technique is described which was applied to the determination of anode potentials prevailing under conditions of high rate dissolution of copper in sulfate electrolytes. Experiments were performed under free as well as under forced convection conditions.

Experimental

Two cell types were employed, each assuring fast electrical response through low capacitance, and careful exclusion of ground loops. Cell I

(Fig. 1) was of cylindrical geometry, thus providing for even current distribution. No external convection was employed. A 10 mil dia 6.3 mm long 99999 copper wire served as anode, providing a surface area of 5 mm^2 . Since, due to dissolution, considerable loss of diameter resulted during experiments, it was necessary to replace the anode frequently. This was accomplished by simply advancing the continuous wire (A) by approximately 1/2 inch. During experiments, the anode was sealed by two Teflon compressible inserts (E) which were held tight by means of nylon screws (G). The anode was surrounded by a circular counter electrode made of copper. The whole interelectrode space was filled with liquid. Holes drilled in the cell cover (H) near the cathode provided for escape of cathodically evolved gas. The reference electrode (C), made of copper, was connected to the cell compartment by capillary D, positioned at a distance of 24 mm from the center. The cylindrical geometry of the cell allowed one to calculate the ohmic voltage drop between capillary and anode. No provision for excluding oxygen was made, since at the high current densities employed here, its effect on the dissolution kinetics was considered negligible. On the other hand, the presence of oxygen might influence the potential of the reference electrode by establishing a mixed potential. Numerical estimation showed, however, that this effect was always much smaller than 10 mV and, hence, could be neglected within the accuracy of the present study. Before insertion in the cell, the copper electrodes were cleaned in nitric acid and rinsed with distilled water. Several short anodic current pulses were applied before the start of measurements.

Cell II (Fig. 2) was a rectangular flow channel (D) through which the electrolyte was moved by means of a piston pump (C). A Teflon

piston was advanced at constant, preset rate in a PVC cylinder, sweeping out a volume of 400 cc. At the end of each stroke, the motion of the piston was stopped by means of microswitches. The direction of rotation of the motor was then reversed to refill the cylinder with electrolyte. An electrolyte reservoir of 2 liter was employed. Except for the electrodes, no metal parts were in contact with the solution.

The 0.5 x 3 mm copper anode was cast into epoxy, and its short length was positioned parallel to the flow direction. A copper counter electrode of the same surface area was used. The distance between anode and cathode was 0.5 mm, fixed by the thickness of a Teflon spacer into which a 3 mm wide slot, the flow channel, was cut. The cell was sealed by pressing the flat anode epoxy cast against the Teflon spacer by means of 4 knurled screws.

Linear flow velocities at the electrodes up to 10 meters per second were used, corresponding to a minimum discharge time of the pump of 25 sec. In order to reach such high velocities without requiring excessive inlet pressures, the distance between cell inlet and anode was kept short (1.5 cm). Thus, the hydrodynamic conditions in the present cell were not as well defined as those in previous experiments.^{1,6} In the present study, using transient techniques, it was considered more important, however, to achieve a compact design which allowed one to keep electrical connections to the cell short, and which made it possible to avoid any metallic contact, other than the electrodes, with the electrolyte solution. In addition, the present design permitted the achievement of high flow velocities at the electrodes without requiring large electrolyte volumes. A copper reference electrode was located in the cell wall upstream from the cathode.

All experiments were carried out at room temperature.

A galvanostatic pulse method was chosen for this study because it offers the most convenient technique for the elimination of large ohmic voltage drops inherent in high current density potential measurements. The electrical circuit is given schematically in Fig. 3. Current was drawn from a pulse generator* capable of providing square-pulses of up to 100 volts and 2 amperes with rise time < 15 nanoseconds. Pulse duration was varied between 10 μ sec and 10 milliseconds. Constant current through the cell was established by means of a series resistance (P). The current was measured in each experiment over a 5 Ω resistance (M), and displayed on a dual beam oscilloscope.**

Two types of potential measurements were performed. On one hand, the overall behavior of potential transients was determined on a millisecond time scale. These experiments yielded information on relative potential changes associated with passivation phenomena. On the other hand, potential decay upon switching off the current was measured on a microsecond time scale. These experiments allowed for estimates of the non-ohmic part of anode potentials in both the active and transpassive dissolution mode. Electronic compensation of ohmic voltage drops between capillary and anode surface was necessary in these experiments. This was achieved by means of variable gain preamplifier (E), the output signal of which was subtracted from the output signal of amplifier (F) connected to the reference electrode (R). A commercial amplifier unit*** was used in

* Model 214A Hewlett Packard

** Model 555 Dual Beam Tectronix

*** Model 1A1 Tectronix

this procedure. The difference signal was displayed on the dual beam oscilloscope together with the current signal and recorded on Polaroid film. Among several compensation procedures investigated, the following was found to give most satisfactory results. Low current density pulses, typically in the order of 20 mA/cm^2 , were applied to the cell in order to determine the ohmic resistance between capillary and anode. Double layer charging was sufficiently slow under these conditions to allow for easy separation of the ohmic and the non-ohmic part of the charging transient. The cell was then disconnected and replaced by an ohmic resistance of accurately known value, usually lower than the measured resistance between capillary and anode. The gain of amplifier (E) was adjusted to provide compensation equal to the value of the inserted resistance. The cell was then reconnected for the experiment while keeping the gain of (E) to the adjusted value. The use of a fixed compensating resistance of well known value, together with variable amplifier gain, allowed for frequent and easy recheck of the accuracy of compensation. Partial, rather than full, compensation of the ohmic electrolyte resistance was used in order to avoid saturation of the differential amplifier. The uncompensated part of the ohmic electrolyte resistance was subtracted from the decay transient in a conventional way.

ACTIVE DISSOLUTION

At high flow rates or very short experimental times, copper dissolves anodically in sulfate solutions in the active dissolution mode.¹ Experiments were performed here to investigate the validity of extrapolating Tafel behavior found at low current densities⁹ to high currents. For

this purpose, anode potentials as a function of current density were determined from decay transients. The length of the applied current pulse was kept short enough to avoid any significant influence of concentration polarization effects on the anode potentials measured. On the other hand, pulse lengths were long enough to completely charge the electrical double layer. Depending on current density, pulse duration was between 10 μsec and several milliseconds.

Results obtained in cell I with a 1 molar sulfuric acid solution containing 0.1 mole per liter copper sulfate are given in Fig. 4. Within the accuracy of the measurements, Tafel behavior is observed up to the highest current density studied (39 A/cm^2). The accuracy of the data at high current densities is limited mainly by two factors: the IR drop in the solution, and the rate of double layer discharge. The influence of the latter may be estimated by setting for the rate of change of overvoltage η after current switch off.

$$\frac{d\eta}{dt} = \frac{i_F}{C} \quad (1)$$

with i_F = Faradaic current density (negative quantity), C = double layer capacitance. For constant C the solution of equation (1) becomes¹⁰

$$\eta_{t=0} - \eta = b \log \left(1 + \frac{2.3 it}{bC} \right) \quad (2)$$

where i = applied current density (negative quantity).

Due to limitations in the frequency response of the amplifiers, η , cannot be determined experimentally exactly at $t=0$. One expects, therefore, that measured η values are lower than the true overvoltage prevailing at current switch off. The possible magnitude of this error

was estimated by inserting typical numerical values into equation (2). From oscilloscope traces, it was estimated that in present experiments, potential readings were possible within at least 0.5 μsec after switch off. Decay traces suggested that a reasonable value for C was $50 \mu\text{F}/\text{cm}^2$ *. The value of b was determined from Fig. 4 to be 40 mV. With these numerical values, one calculates $\eta_{t=0} - \eta_{t=0.5\mu\text{sec}} = 21 \text{ mV}$ at $4 \text{ A}/\text{cm}^2$ or 55 mV at $40 \text{ A}/\text{cm}^2$. The resulting uncertainty in potential measurements is indicated in Fig. 4 by the dotted line.

Large ohmic voltage drops exist between capillary and anode as illustrated by Fig. 5 in which measured IR drops and anode potentials for the experiments of Fig. 4 are plotted on a linear scale. At the highest current density of $39 \text{ A}/\text{cm}^2$, the ohmic voltage drop is approximately 28 times larger than the actual anode potential. From the measured slope, one calculates a conductivity of $0.364 \Omega^{-1}\text{cm}^{-1}$ at 24°C , in good agreement with the value one obtains at 25°C by using the estimation formula given by Hsue¹¹ $0.379 \Omega^{-1}\text{cm}^{-1}$ for 25°C . By employing optimum compensation conditions as described above, it was estimated that the value of the non-ohmic decay potential could be measured to $\pm 1\%$ of the IR drop corresponding to the current density of the measurements. The resulting uncertainty in measured anode potentials is indicated by the dashed line in Fig. 4. A least square fit of the measured points in Fig. 4 yielded a Tafel slope of 40 mV, coinciding with the value reported by Mattson and Bockris⁹ for copper dissolution in highly purified sulfuric acid electrolytes at low current densities under exclusion of oxygen.

* Experimentally determined C values showed large scattering and the value given has to be regarded as an order of magnitude estimate only.

Tafel parameters for anodic copper dissolution in sulfuric acid as well as values from the literature are summarized in Table I. Present results extend the previously reported Tafel region to higher current densities by two orders of magnitude.

At high current densities, uncertainties associated with fast double layer discharge and ohmic compensation become increasingly more important. The indicated Tafel behavior up to 40 A/cm^2 has, therefore, to be considered as an approximation rather than an exact representation of real behavior. Indeed, a deviation from the given Tafel slope of 40 mV at high enough current density is to be expected if the two step charge transfer mechanism suggested by Mattson and Bockris prevails:

The species Cu^+ is considered adsorbed on the surface; its surface concentration depending on potential. Assuming no loss of Cu^+ due to diffusion, the current for such a two step charge transfer process can be expressed¹² by

$$i = 2 \frac{\exp[-(\alpha_1 + \alpha_2)f\eta] - \exp[(2 - \alpha_1 - \alpha_2)f\eta]}{\frac{1}{i_{01}} \exp[(1 - \alpha_2)f\eta] + \frac{1}{i_{02}} \exp(-\alpha_1 f\eta)} \quad (3)$$

α_1 and α_2 are the charge transfer coefficients for steps I and II, i_{01} and i_{02} are the respective exchange current densities. Following the assumption usually made, one may set $\alpha_1 = \alpha_2 = \alpha = 0.5$. For the case of $i_{01} \gg i_{02}$ and intermediate overvoltage η , the first terms in the numerator and denominator can be neglected and equation (3) reduces to

$$i = -2 i_{02} \exp(2 - \alpha) \quad (1 \ll f\eta_\eta \gg \ln \frac{i_{01}}{i_{02}}) \quad (4)$$

This equation predicts a Tafel slope of 39 mV. At high values of η , the limiting value of equation (3) is

$$i = -2 i_{01} \exp (1 - \alpha) f\eta \quad (f\eta \rightarrow \infty) \quad (5)$$

corresponding to a Tafel slope of 118 mV. Since we do not know the value of i_{01} , no quantitative test of the above relationships is possible. A slight deviation from the slope of 40 mV consistent with the prediction of equation (4), cannot be excluded at the highest current density but the measured results seem to fit equation (4) much better than equation (5). No further mechanistic interpretation of results is justifiable here.

Flow channel cells have been used previously for studying high rate metal dissolution under forced convection conditions.^{1,6,7,8} Their advantage lies in the control of mass transfer and temperature effects. On the other hand, current distribution is inhomogeneous in such cells. To investigate experimentally the error that might be introduced in potential measurements performed under non-ideal current distribution conditions, the same experiments described above were performed with Cell II, the geometry of which resembled that of previously used flow channel cells.* Results comparable to those given in Fig. 4 are indicated in Fig. 8. The least square fit yielded a slope of 50 mV which is somewhat higher than the 40 mV obtained with cell I having cylindrical geometry. The scattering of data did not allow a quantitative analysis of this difference. Some qualitative comments may be appropriate, however. Upon current switch-off, two discharge processes may proceed now. Aside

* Since experimental times were kept short in the present experiments, convection did not influence these results.

from the Faradaic current, a current may flow in the solution between differently charged regions of the double layer. The second effect will be larger when the current distribution is more non-uniform. In the case of Tafel kinetics and in the absence of concentration polarization, the uniformity of current distribution is characterized by the magnitude of the parameter $K = \frac{\kappa b}{\ell i}$, where ℓ is a characteristic length, i the current density, κ the electrolyte conductivity and b the Tafel slope. Primary current distribution prevails for $K \ll 1$, secondary current distribution for $K \gg 1$. In our case $\kappa = 0.38 \Omega^{-1} \text{cm}^{-1}$, $\ell = 0.5 \text{ mm}$, $b = 40 \text{ mV}$. One may, therefore, assume primary current distribution for $K \leq 0.1$ or $i \geq 3 \text{ A/cm}^2$ and secondary current distribution for $K \geq 10$ or $i < 30 \text{ mA/cm}^2$. In the intermediate region, a gradual change from secondary to primary current distribution occurs with increasing current, i.e. the current density at the edge of the electrode will increase more than the average current density. The ohmic part of the measured decay transient, on the other hand, is independent of current distribution.¹⁴ Therefore, in the intermediate region $0.1 < K < 10$, one would expect that the measured non-ohmic part of the anode potential increases faster with current density than corresponding to the true Tafel slope. This is qualitatively consistent with the observed behavior of Fig. 6. It appears that, in the case of active copper dissolution in acid sulfate solutions, the anodic behavior at high current densities can be described adequately by extrapolating Tafel kinetics valid for low current density. For many electrochemical machining purposes, possible inaccuracies in anodic overvoltage measurements resulting from a non-uniform current distribution can be neglected.

TRANSPASSIVE DISSOLUTION

At sufficiently high current densities and longer experimental times, solid anodic layers may be formed which lead to a sharp rise in measured anode potentials. The behavior is illustrated by Fig. 7, trace a. The measurement was performed in cell II at a flow velocity of 140 cm/sec and a current density of 77 A/cm^2 . The electrolyte was $1 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M CuSO}_4$; no IR compensation was employed. An increase in overall measured anode potential by 25 volts takes place 1 msec after start of the galvanostatic run.* It has been shown previously that dissolution in the high voltage mode proceeds with different stoichiometry⁷ and leads to a different surface texture.¹ The transition between the two dissolution mechanisms, active and transpassive, is mass transfer controlled.¹ In the present study, experiments were performed aimed at further characterizing the current voltage behavior of copper anodes dissolving in the transpassive mode. This included the study of the influence of flow rate and of current density on the measured voltage rise and the measurement of decay potentials in the transpassive region.

Optical observation of anodically dissolving copper electrodes in acidic sulfate solutions suggested that relatively thick loosely adherent oxide layers are formed upon passivation.⁸ One would expect that their thickness and, hence, their effect on measured overall anode potential would strongly depend on the prevailing hydrodynamic conditions; at high

* Potential time transients of the type given exhibit a maximum before steady state is reached. This does not show here because of the short pulse length employed. The indicated voltage increase upon layer formation is therefore larger than the steady state voltage difference across the layer.

flow velocities, the loosely adherent deposits would be washed away from the anodes much more easily, and the extent of the voltage rise upon passivation ought to be reduced. Figure 8 gives five superimposed transients measured at 89 A/cm^2 with flow rates ranging from 65 to 1000 cm/sec. Qualitatively, the expected decrease in measured voltage with increasing flow rate is indeed observed, but the effect is small; for example, the difference between initial voltage (which represents mostly the IR drop in the solution) and maximum voltage is $\Delta E = 26$ volts at 65 cm/sec and $\Delta E = 23$ volts at 1000 cm/sec. This indicates that the observed voltage increase is caused by a tightly adherent layer rather than by the loosely adherent solids observed visually. A simple numerical estimation supports this argument. Figure 8 shows a 25 volt potential increase taking place within a time interval of approximately 2 msec during which a charge of $154 \text{ m coulomb/cm}^2$ is passed. The maximum possible volume of solid material formed during this time period, is obtained by assuming cuprous oxide formation at 100% current efficiency. For a bulk density of Cu_2O of 6.0 g/cm^3 , the maximum possible thickness of a non-porous layer is $d_n = 3.8 \times 10^{-5} \text{ cm}$. For the thickness d_p of a porous layer one may write $d_p = d_n / (1 - \theta)$, where the porosity θ is defined by the ratio of the pore volume to the total volume. In the simplest model, one may assume that all ionic conduction occurs through the electrolyte within the pores and the conductivity is given by $\mathcal{K} = \mathcal{K}_0 \theta$, where $\mathcal{K}_0$ is the electrolyte conductivity. The ohmic voltage difference across the layer then becomes

$$\Delta E = \frac{i d_n}{\mathcal{K}_0 \theta (1 - \theta)} \quad (6)$$

Using $\kappa_0 = 0.38 \Omega^{-1} \text{cm}^{-1}$ for the electrolyte of bulk temperature and concentration and the measured ΔE of 25 volts, one obtains a porosity θ of 3×10^{-4} for the example of Fig. 8. For such a small porosity $d_p \approx d_n$. The observed voltage increase, therefore, is due to a layer at most a few tenths of a micron thick. In order for the dissolution to proceed through pores, involving a direct contact between bare metal surface and electrolyte, the low porosity derived above would require unreasonably high local current densities. It is, therefore, highly unlikely that the observed high potentials in the transpassive dissolution mode are caused only by a partial blocking of the surface by an insulating layer.

Other experimental observations lead to a similar conclusion. A change in specific electrolyte conductivity by approximately a factor of two had no measurable effect on the voltage rise ΔE . Furthermore, a large fraction of ΔE was found to be non-ohmic as indicated by trace (b) in Fig. 7, which represents the potential decay after current interruption (time resolution $5 \mu \text{ sec/div}$) for the same electrolysis conditions under which charging trace (a) was observed.

The above discussion suggests that, during transpassive dissolution, the anode potential is determined by the presence of a thin compact layer. It can be speculated that dissolution occurs through this layer by solid state conduction, although no experimental proof for this view exists, at present. Extremely large heating effects are to be expected within the anodic layer (for example, 25 volts at 89 A/cm^2 within a $3.8 \times 10^{-5} \text{ cm}$ thick layer correspond to $1.4 \times 10^7 \text{ cal/cm}^3 \text{ sec}$). The associated temperature rise increases its ionic conductivity. This view is qualitatively consistent with the results shown in Fig. 9, which show that the voltage

rise ΔE is almost independent of current density, i.e. the effective resistance of the layer decreases strongly with increasing current density (and hence increasing power dissipation). It is possible that, as a result of the heating effect, stresses are generated within the layer, which lead to its periodic rupture during the anodic dissolution process.

A more detailed understanding of the nature of the anodic layers present is necessary to determine the sequence of events in transpassive dissolution. Kinoshita et al.^{7,8} analyzed solid reaction products during copper dissolution in sulfate media by X-ray diffraction. The products were sampled continuously downstream from the anode. Cuprous oxide which may disproportionate into copper ion and metallic copper was found to be a major constituent. The direct analytical study of anodic layers is complicated, however, by the fact that upon current switch-off their nature may be changed within a matter of milliseconds. This is evidenced by the experiments illustrated in Figs. 10 and 11. Two identical current pulses were applied to the anode in time intervals ranging from a fraction of a millisecond to several milliseconds. The shape of the second pulse then depended strongly on the elapsed time between the two pulses (Fig. 10). The time interval necessary for the second pulse to become identical with the first pulse was considered equivalent to the time necessary for removal of the anodic layer after current switch-off. In Fig. 10, this corresponds to approximately 6 msec. The time for removal depended on the flow rate as well as on the current density at which the layer had been formed. This is evidenced by Fig. 11 in which the difference between the initial voltage of the second pulse and that of the first pulse, as determined from transients similar to those given

in Fig. 10, are plotted as a function of the elapsed time between two consecutive pulses. The layers formed at high current density appeared to be removed faster than those formed at lower current density.

Increasing flow rate also accelerated removal. The latter effect is not unexpected; it may be related to an enhancement of either mechanical removal of solid products or of an increase in rate of mass transport of dissolved products. It is to be noted, however, that layer removal took somewhat longer than layer formation (Fig. 10). Since layer formation is initiated by a mass transport limited process,¹ it appears that removal is not entirely governed by a simple mass transport process.

Accelerated layer removal with higher formation current density may be due to higher local temperatures of the surface which speed up chemical dissolution, or to larger concentrations of hydrogen ions accumulated at the surface under conditions of high formation current density.

SUMMARY AND CONCLUSIONS

Galvanostatic transient techniques have been used for the study of current voltage relationships characterizing anodic copper dissolution at current densities of up to more than 100 A/cm^2 . With the possible accuracy of high current density potential measurements, results for active dissolution obtained in the present study were consistent with the Mattson-Bockris mechanism. Presence of oxygen and preelectrolysis of the solution apparently have little influence on measured anodic Tafel slopes at high dissolution rates.

Potential current relationships for active dissolution obtained in a flow channel cell were little different from those measured in a cylindrical cell. This indicates that the error introduced into transient

measurements by the non ideal geometry of the flow channel was small, and it appears that such cells are well suited for the study of active as well as transpassive metal dissolution under controlled flow conditions.

Dissolution in the transpassive mode proceeds by a different mechanism at much higher anode potential. Experimental results and numerical estimations show that the observed high values of the anode potential in the transpassive mode are due to a thin, well adhering layer. Since earlier studies showed that loose solid reaction products are generated during transpassive dissolution, it has to be assumed that the anodic layer has a dual structure, consisting of a thin compact layer in contact with the metal and loose material (mostly cuprous oxide) sitting on top of it. The loose material has little influence on observed transient behavior at constant current which is governed by the properties of the adherent layer. The effective resistance of this layer was shown to decrease with increasing current density; an effect which is attributed to local heating. Quantitative models for the description of the dynamics of transpassive dissolution have not been developed so far.

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References

1. D. Landolt, R. H. Muller and C. W. Tobias, J. Electrochem. Soc. 116, 1384 (1969).
2. R. R. Cole, Y. Hopenfield, Trans. ASME B 85, 395 (1963).
3. J. Bayer, M. A. Cummings and M. U. Jollis, Technical Documentary Report No. ML-TDR-64-313, General Electric Co. (1964).
4. J. P. Hoare, J. Electrochem. Soc. 117, (1970).
5. J. P. Hoare, M. A. LaBoda, M. L. McMillan and A. J. Wallace, J. Electrochem. Soc. 116, 199 (1969).
6. D. Landolt, R. Acosta, R. H. Muller and C. W. Tobias, J. Electrochem. Soc. 117, 839 (1970).
7. K. Kinoshita, D. Landolt, R. H. Muller and C. W. Tobias, J. Electrochem. Soc. 117, 1246 (1970).
8. K. Kinoshita, (Ph. D. thesis), University of California, Berkeley, UCRL-19051, Sept. 1969.
9. E. Mattson and J. O'M. Bockyis, Trans. Faraday Soc. 55, 1586 (1959).
10. K. Vetter, Electrochemical Kinetics, Academic Press (1967).
11. L. Hsueh, (Ph. D. thesis), University of California, Berkeley, UCRL-18597, Dec. 1968.
12. P. Delahay, Double Layer and Electrode Kinetics, Interscience Publ. (1965).
13. H. S. Mickley, T. K. Sherwood and C. E. Reed, Applied Mathematics in Chemical Engineering, 2nd Ed., McGraw Hill, (1957), p. 97.
14. J. Newman, J. Electrochem. Soc. 117, 507 (1970).

TABLE I

Tafel parameters for anodic copper dissolution in sulfuric acid

H_2SO_4 (M)	Electrolyte $Cu SO_4$ (M)	Current Density (A/cm ²)	Cell	Ref.	a (mV)	b (mV)
1	0.1	5×10^{-3} to 39	I	present	171 $\pm$ 16	40 $\pm$ 15
1	0.1	8×10^{-3} to 140	II	present	184 $\pm$ 21	51 $\pm$ 16
0.5	0.5	---		(9)	81, [†] 82	40 $\pm$ 6, [†] 36 $\pm$ 10
0.5	0.075	5×10^{-3} to 0.2*		(9)	93, [†] 113	44 $\pm$ 4, [†] 45 $\pm$ 4
0.5	0.011	---		(9)	100	41 $\pm$ 4

*The range of current density in which Tafel behavior was observed was estimated from two figures given in Ref. 9.

[†]First value for H_e annealed copper, second for electrodeposited copper. The standard deviation of the results given in Ref. 9 was multiplied by two to get a 95% confidence limit. The values of a were calculated from i_0 values given in Ref. 9.

Figure Captions

Fig. 1. Cross section of cell I for studies under free convection conditions.

A = copper wire anode

B = cylindrical copper cathode

C = reference electrode,

D = capillary

E = teflon inserts

F = set screw

G = nylon screws

H = lucite cell cover

I = lucite cell body

Fig. 2. Flow channel apparatus for studies under forced convection conditions.

A = motor drive

B = dial indicator for setting flow rate

C = piston pump

D = electrolyte reservoir

E = flow channel cell (cell II)

Fig. 3. Electrical circuit with IR compensation.

A = anode

B = cathode

C = pulse generator

D = current measuring preamplifier

E = preamplifier with variable gain

F = preamplifier for reference electrode signal

Fig. 3 continued

G = reference electrode.

H = series resistor

I = 5 Ω resistor.

Fig. 4. Anode potential vs current density for active dissolution of copper in sulfuric acid solution.

O data obtained in cell I in 1 M H_2SO_4 , 0.1 M $Cu SO_4$

.... uncertainty calculated from equation (2)

---- uncertainty due to IR subtraction

● data from Ref. 9 for 0.5 M H_2SO_4 0.075 $Cu SO_4$

Fig. 5. Measured ohmic drop (IR) and anode overvoltage (η) in cell I,
1 M H_2SO_4 0.1 M $Cu SO_4$.

Fig. 6. Anode potential vs current density for active copper dissolution
in 1 M H_2SO_4 0.1 M $Cu SO_4$ in flow channel cell (cell II).
Flow rate 140 cm/sec

.... uncertainty according to Eq. (2)

---- uncertainty due to IR subtraction

Fig. 7. Transpassive behavior of copper in 1 M H_2SO_4 + 0.1 M $Cu SO_4$,
Cell II. Current density 77 A/cm, flow velocity 140 cm/sec,
no IR compensation.

Trace a: overall potential transient, anode potential = 10 V/div,
time = 1 msec/div,

Trace b = decay transient after current switch-off
anode potential = 10 V/div, time = 5 μ sec/div

Trace c: current transients, 5 V/div

Fig. 8. Effect of flow rate on anodic transients in transpassive region.

Current density (b) 89 A/cm^2 . Time = 1 msec/div,

anode potential (a) = 10 V/div.

Flow rate for transients from top to bottom: 65 cm/sec,

140 cm/sec, 370 cm/sec, 610 cm/sec, and 1000 cm/sec.

Fig. 9. Voltage increase upon anodic layer formation in function of current density.

ΔE = peak voltage minus initial voltage.

Fig. 10. Double pulses applied at different time intervals. Current density

77 A/cm^2 , flow rate 1000 cm/sec. Anode potential traces =

10 V/div, time scale = 1 msec/div.

Fig. 11. Difference in initial voltage between first and second pulse as a function of time interval between pulses.

● 93 A/cm^2 at 1000 cm/sec

○ 46 A/cm^2 at 1000 cm/sec

▲ 93 A/cm^2 at 140 cm/sec

⊙ 50 A/cm^2 at 140 cm/sec

Fig. 1.

CBB681-213A

Fig. 2.

XBL 709-3819

Fig. 3.

XBL 709-3824

Fig. 4.

XBL709-3818

Fig. 5.

XBL 709-3821

Fig. 6.

XBB709-3984

Fig. 7.

XBB709-3985

Fig. 8.

Fig. 9.

XBL709-3823

XBB709-3986

Fig. 10.

XBL709-3822

Fig. 11.

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