

01 Jan 1987

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T. J. O'Keefe et al., "Calculation Of Mass Transfer Coefficients In Metal Deposition Using Electrochemical Tracer Techniques," *Journal of the Electrochemical Society*, vol. 134, no. 3, pp. 547 - 551, The Electrochemical Society, Jan 1987.

The definitive version is available at <https://doi.org/10.1149/1.2100507>

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To cite this article: Thomas J. O'Keefe *et al* 1987 *J. Electrochem. Soc.* **134** 547

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# Calculation of Mass Transfer Coefficients in Metal Deposition Using Electrochemical Tracer Techniques

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## ABSTRACT

A modification of the tracer technique of Ettel *et al.* has been developed for determining mass-transfer coefficients in electrolytes for both electrowinning and electrorefining systems. The method involves the direct measurement of the limiting current density of a more noble tracer ion at low concentration by cyclic voltammetry techniques in an electrolyte of choice. A  $\text{Ag}^+$  tracer in acid copper sulfate is used as the example. Additional tests were made by codepositing the tracer with copper to compare the results of the two methods. The effect of copper ion concentration and temperature on the electrochemical and transport properties of the solution were determined. The results obtained using cyclic voltammetry techniques were found to be in good agreement with those from the standard codeposition determinations. Additional refinement of the technique is needed to more clearly define the limitations of the technique when used for metal deposition evaluations.

A major limitation of many existing electrometallurgical operations is the relatively low production rate per unit volume of the reactor vessel. Any increase in the daily cathode tonnage usually is equatable to substantially improved economics. Thus, a primary thrust in the industry is directed toward increasing the operating current density without sacrificing metal quality. The latter is most often gauged in terms of deposit smoothness, since rough, irregular growth occurs when the current density becomes excessive.

Recent theoretical and applied studies (1, 2), ranging from bench scale to full sized pilot cells, have shown the importance of enhanced mass transfer in improving the performance of many electrolytic systems. Whether by means of optimized alternative cell design or improved forced convection in existing plants, the key feature involves minimizing the deleterious influence of the low diffusivities of the plating ions.

A rather simple and convenient, but useful, technique for obtaining quantitative data on mass-transfer coefficients in electrowinning cells was developed by Ettel *et al.* (3). The limiting current density of a tracer ion was determined in the electrolyte of interest and the mass-transfer coefficient ( $k$ ) was calculated. The mass-transfer coefficient of the main cation, for a forced laminar convection flow regime, could then be determined using the expression (3)

$$k_{\text{metal ion}} = k_{\text{tracer}} (D_{\text{metal ion}}/D_{\text{tracer}})^{2/3} \quad [1]$$

where  $D$  is the diffusion coefficient. For concentration driven natural convection (such as is likely to occur in electrorefining cells) the dependence is on the diffusivity ratio to the three-quarters power.

The tracer ion is more noble than the bulk metal cation, which allows plating at the tracer limiting current density, while normal deposition occurs for the major species. After a desired time of codepositing the two species, the deposit is chemically analyzed, allowing the limiting current of the tracer to be calculated.

The method to be described is a modification of the one described above and employs voltammetry in the determination of the limiting current. The ability to use the modified version directly in large scale operations would be limited. However, there do seem to be numerous possibilities of employing it over a broad range of applications from fundamental to applied evaluations involving mass transfer in metal deposition systems in laboratory and pilot scale operations.

The technique involves combining previously developed electrochemical methodologies and applying them to electrometallurgical systems involving cathode deposition and growth. Quite simply, the tracer is used in a system of interest, and its limiting current is measured

using cyclic voltammetry at potentials more noble than required for deposition of the major metal ion. Thus, the limiting current density,  $i_L$ , of the tracer is determined directly under quiescent conditions in the absence of any of the more extensive convective or area change effects which occur during plating at normal current density. The mass-transfer coefficient is calculated from the expression

$$k_{\text{tracer}} = i_{L,\text{tracer}}/(nFC_{\text{tracer}}) \quad [2]$$

$F$  is Faraday's constant,  $C$  is the concentration of the tracer (usually in the ppm range), and  $n$  is the valence change of the reacting ion. The mass-transfer properties of the major metal ion are then calculated using Eq. [1]. In this case, copper sulfate electrolytes were evaluated using  $\text{Ag}^+$  tracer in order to determine the feasibility of the technique.

## Experimental

A one liter cylindrical cell with a separate anolyte compartment for the Pt counterelectrode was used. A  $\text{Hg}/\text{Hg}_2\text{SO}_4$  in 200 g/l  $\text{H}_2\text{SO}_4$  ( $\approx 0.664\text{V}$  vs. SHE) served as the reference electrode. Usually the working electrode was a Pt rotating disk of  $0.476\text{ cm}^2$  area and was prepared by polishing with  $0.05\text{ }\mu\text{m}$  gamma alumina. Other electrode materials were also evaluated and included silver, stainless steel, and glassy carbon. A Petrolite Potentiodyne Model M-4100 analyzer and a Pine Rotator System were used for the voltammetry test. Deposits made potentiostatically and galvanostatically were chemically analyzed (Atomic Absorption Spectrophotometer) to verify and compare with results obtained using the polarization procedure. The viscosity measurements were made using a Cannon-Fenske viscometer.

Unless otherwise specified, 500  $\text{cm}^3$  of solution (25 g/l  $\text{Cu}^{2+}$ , 100 g/l  $\text{H}_2\text{SO}_4$  with desired amounts of  $\text{Ag}^+$  added as  $\text{Ag}_2\text{SO}_4$ ) sparged with  $\text{N}_2$  gas for 30 min were used for the tests. During all measurements a nitrogen atmosphere was maintained over the surface of the solution. The scan rate used was 5 mV/s and the scan range was  $-0.05$  to  $-0.30\text{V}$  vs.  $\text{Hg}/\text{Hg}_2\text{SO}_4/200\text{ g/l H}_2\text{SO}_4$  to generate the voltammetric curves.

## Results and Discussion

**Polarization curves.**—Typical polarization curves obtained for experiments at  $23^\circ\text{C}$  for 10 mg/l silver concentration in a sulfuric acid electrolyte of 100 g/l are shown in Fig. 1. Using the limiting currents from these curves the diffusion coefficient for silver ions can be calculated according to Levich's theory for mass transport by convective diffusion using the relationship (4)

$$i_L = 0.62 nFD_{\text{Ag}}^{2/3} \nu^{-1/6} \omega^{1/2} C_{\text{Ag,bulk}} \quad [3]$$

where  $i_L$  is the limiting current density,  $\omega$  the electrode

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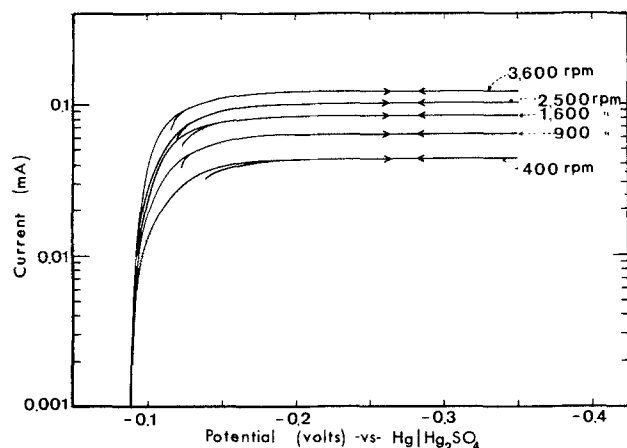


Fig. 1. Polarization curves for an electrolyte containing 100 g/l  $\text{H}_2\text{SO}_4$ , 10 mg/l  $\text{Ag}^+$ ; Pt electrode ( $0.476 \text{ cm}^2$  area) for various rotational velocities at  $23^\circ\text{C}$ .

rotational velocity, and  $\nu$  the kinematic viscosity of the solution.

Figure 2 shows the straight line plots of  $i_L/C_{\text{Ag}^+}$  vs.  $\omega^{1/2}$  resulting from similar experiments using various other supporting electrolytes. Extrapolations of the lines pass through the origin which indicates that the process is diffusion controlled. The diffusion coefficients calculated for silver from these straight lines are presented in Table I. The results are in fairly good agreement with values reported in the literature (3, 5-14), the variations probably resulting from differences in the supporting electrolyte and the ionic strength of the solution used. The results reported by Ettel (3) at room temperature were much lower than those obtained in this study. The low values are thought to be due to some inhibition to deposition. Also, only limited testing was conducted at the lower temperature since the elevated temperatures were of primary interest in his applications.

Tests were also made at different  $\text{Ag}^+$  contents (10, 15, 50, and 100 mg/l  $\text{Ag}^+$ ) in a supporting electrolyte of 100 g/l  $\text{H}_2\text{SO}_4$  and 25 g/l  $\text{Cu}^{2+}$ . The  $D_{\text{Ag}^+}$  values calculated ranged between  $11.4$  and  $12.2 \times 10^{-6} \text{ cm}^2/\text{s}$ . These tests showed that the  $\text{Ag}^+$  concentration did not appreciably affect the measured diffusion coefficient.

Figure 3 shows that at constant angular velocity the limiting current density is proportional to the  $\text{Ag}^+$  concentration. The diffusion coefficient for  $\text{Ag}^+$ , calculated from the slope, is  $12.7 \times 10^{-6} \text{ cm}^2/\text{s}$ , a value similar to the ones shown in Table I. The  $\text{Ag}^+$  diffusion coefficient is also calculated by finding the limiting current density using Faraday's law. An example of the results obtained when only silver is plated at constant voltage ( $-0.2 \text{ V vs. Hg/Hg}_2\text{SO}_4$ ), and when Ag and Cu are plated simultaneously at a fixed current density of  $35 \text{ mA/cm}^2$  or potentiostatically at  $-0.45 \text{ V vs. Hg/Hg}_2\text{SO}_4$ , are given in Fig. 4. The  $D_{\text{Ag}^+}$  found shows good agreement with the results obtained using the polarization technique. The codeposition of silver and copper did not affect the ex-

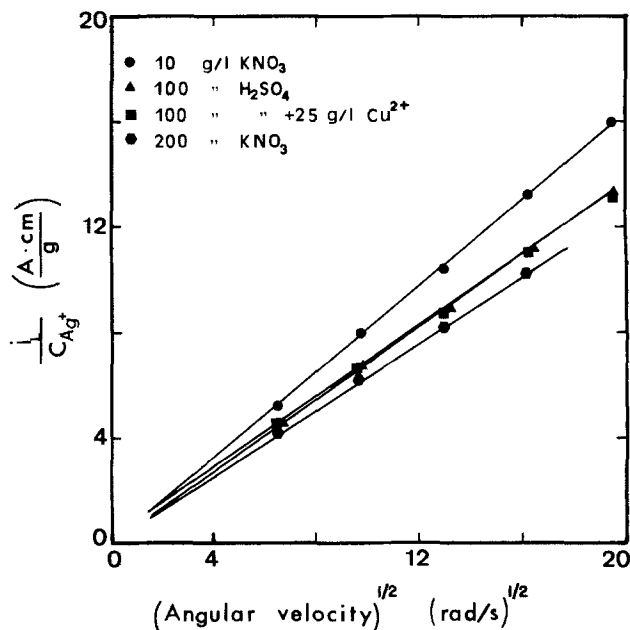


Fig. 2. Levich plot for various supporting electrolytes containing  $\text{Ag}^+$ ; Ag electrode at  $25^\circ\text{C}$ .

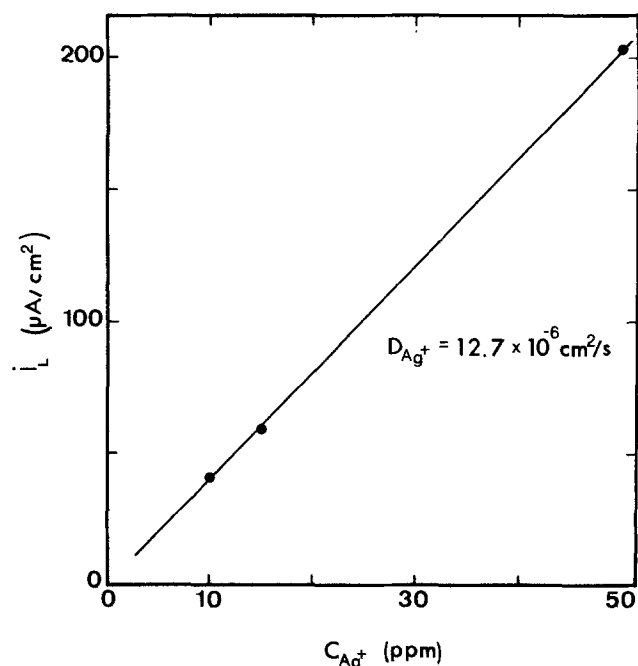


Fig. 3. Levich plot at a constant angular velocity of 400 rpm for 100 g/l  $\text{H}_2\text{SO}_4$ , 25 g/l  $\text{Cu}^{2+}$ ; Pt electrode at  $23^\circ\text{C}$ .

perimentally measured value of  $D_{\text{Ag}^+}$ ; this is not the case when the temperature was raised to  $55^\circ\text{C}$  as will be shown later.

Table I. Comparison of diffusion coefficients of  $\text{Ag}^+$  ions

Electrolyte	$\text{Ag}^+$ concentration	$D_{\text{Ag}^+} \times 10^6$ ( $\text{cm}^2/\text{s}$ )	Temperature ( $^\circ\text{C}$ )	Reference
0.1M $\text{KNO}_3$	25 ppm <sup>a</sup>	17.3	25	Present work
2.0M $\text{KNO}_3$	40 ppm	12.6	23	Present work
1.0M $\text{H}_2\text{SO}_4$	15 ppm	13.2	23	Present work
0.4M Cu, 1M $\text{H}_2\text{SO}_4$	25 ppm	12.2	23	Present work
0.4M Cu, 1M $\text{H}_2\text{SO}_4$	10 ppm	4.3	25	(3)
0.05M $\text{H}_2\text{SO}_4$	5 ppm	16.0	25	(5)
0.1M $\text{KNO}_3$	539 ppm <sup>b</sup>	16.9	25	(6)
Aqueous solution		16.6	25	(7)
0.2M $\text{KNO}_3$	2.2 to 80.6 ppm <sup>b</sup>	14.2	25	(8)

<sup>a</sup>  $\text{Ag}^+$  from  $\text{Ag}_2\text{SO}_4$ .

<sup>b</sup>  $\text{Ag}^+$  from  $\text{AgNO}_3$ .

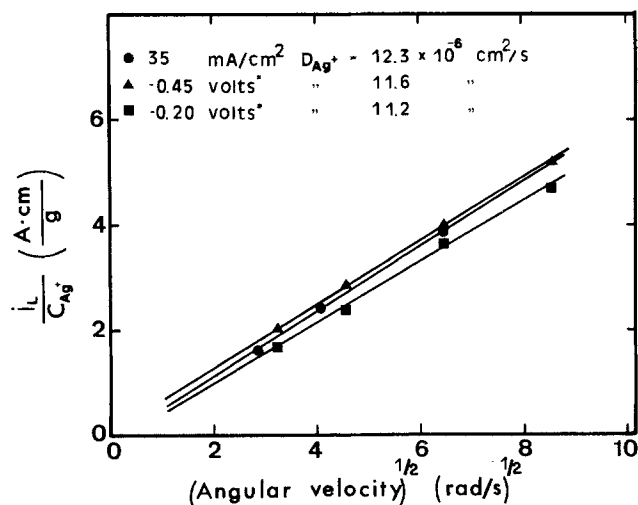


Fig. 4.  $D_{Ag^+}$  values from electrolyte containing 100 g/l  $H_2SO_4$ , 25 g/l  $Cu^{2+}$ , 10 mg/l  $Ag^+$ ; Pt electrode, at 23°C (vs.  $Hg/Hg_2SO_4/200$  g/l  $H_2SO_4$  reference electrode).

**Substrate effect.**—The substrate used in making the limiting current measurements for the tracer ion did influence the values. Since relatively small currents are involved, any residual current due to side reactions could cause substantial error and also problems with reproducibility.

Oxygen reduction currents are a problem on platinum and stainless steel, but these could be eliminated by sparging the electrolyte with nitrogen. Glassy carbon worked satisfactorily initially, but with time, deposit roughening occurred which caused variations in results. A silver electrode, or platinum or stainless steel electrodes plated with a thin layer of silver performed the best, as the oxygen reduction reaction is not observed.

**Effect of  $Cu^{2+}$  concentration on  $D_{Ag^+}$ .**—The presence of copper ions in the solution causes a shortening of the potential range in which the silver limiting current is observed, as indicated by the onset of a current increase at a more anodic potential. The specific potential at which the current increase occurs is a function of the copper concentration and the temperature; the latter will be explained later. Figure 5 shows the effect obtained when the  $Cu^{2+}$  concentration is increased.

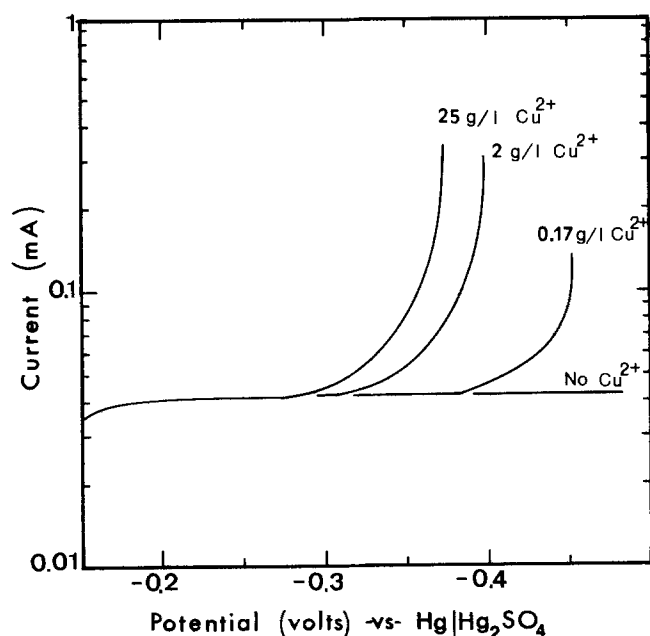


Fig. 5. Effect of  $Cu^{2+}$  concentration on the Ag limiting current plateau for a 100 g/l  $H_2SO_4$ , 20 mg/l  $Ag^+$  solution at 23°C.

Table II. Silver mass-transfer coefficient and diffusion layer thickness for a 100 g/l  $H_2SO_4$ , 25 g/l  $Cu^{2+}$ , and 15 mg/l  $Ag^+$  solution,  $D_{Ag^+} = 12.2 \times 10^{-6} \text{ cm}^2/\text{s}$ ,  $\nu = 0.0117 \text{ cm}^2/\text{s}$  at 23°C

rpm	$\omega^{1/2}$ (rad/s) <sup>1/2</sup>	$i_L/C_{Ag^+}$ (A cm/g)	$k_{Ag^+}$ (cm/s)	$\delta_{Ag^+}$ ( $\mu\text{m}$ )
400	6.4721	4.200	0.00470	26.1
900	9.7081	6.200	0.00693	17.7
1600	12.9442	8.200	0.00917	13.4
2500	16.1802	10.200	0.01140	10.7

Electrode radius = 0.564 cm.

According to Mattsson and Bockris (15), copper deposition from a purified acid sulfate solution is a two-step reaction with the cupric to cuprous step being rate-determining ( $Cu^{2+}/Cu^+$ ,  $E^\circ = -0.51 \text{ V vs. } Hg/Hg_2SO_4$ ). For a very low  $Cu^+$  concentration (assuming  $10^{-6} \text{ M}$ ), the take off point shown in Fig. 5 for 2 g/l  $Cu^{2+}$  concentration could be due to this surface reaction (metallic copper will deposit on the electrode at a more negative potential:  $-0.40 \text{ V vs. } Hg/Hg_2SO_4$  for 2 g/l  $Cu^{2+}$  at 23°C).

Levich plots for  $Ag^+$  in solution containing various  $Cu^{2+}$  concentrations at 23°C indicate that an increase in  $Cu^{2+}$  concentration produces a slight decrease in  $D_{Ag^+}$  from  $13.2 \times 10^{-6}$ , when no  $Cu^{2+}$  is present, to  $10.9 \times 10^{-6}$  for 40 g/l  $Cu^{2+}$  present. It has not been determined if the ionic strength of the solution or the  $Cu^{2+}$  ion is the most influential on the diffusion coefficient.

Using the experimentally determined  $Ag^+$  diffusion coefficient, the  $Ag^+$  mass-transfer coefficient and the diffusion layer thickness can be calculated from Eq. [2] and the relationship

$$\delta_{Ag^+} = D_{Ag^+}/k_{Ag^+} \quad [4]$$

Table II shows the results calculated for a 100 g/l  $H_2SO_4$  and 25 g/l  $Cu^{2+}$  solution at 23°C,  $D_{Ag^+} = 12.2 \times 10^{-6} \text{ cm}^2/\text{s}$ , and  $\nu = 0.0117 \text{ cm}^2/\text{s}$ . The highest Reynolds number estimated for 2500 rpm is 34,960, and it is below the limit for  $\omega$  governed by the onset of turbulent flow which, for a well-centered electrode, occurs at about  $(16) Re_{cr} = 2 \times 10^5$ . This indicates that Eq. [3] is applicable in the flow regime investigated.

The  $k_{Cu^{2+}}$  is calculated from the  $k_{Ag^+}$  tracer data using Eq. [1] with  $D_{Cu^{2+}}$  being determined from the expression (13, 17)

$$D_{Cu^{2+}, 18^\circ C} = 47 \times 10^{-6}/(5.0 + \Gamma) \quad [5]$$

$\Gamma$  is the ionic strength. For a 100 g/l  $H_2SO_4$ , 25 g/l  $Cu^{2+}$  solution,  $D_{Cu^{2+}}$  is  $4.88 \times 10^{-6} \text{ cm}^2/\text{s}$  and  $D_{Ag^+}$  is  $12.2 \times 10^{-6} \text{ cm}^2/\text{s}$ . At 400 rpm,  $k_{Ag^+} = 0.00470 \text{ cm/s}$  as given in Table II and using these values for solving Eq. [1] gives  $k_{Cu^{2+}} = 0.00254 \text{ cm/s}$ .

**Temperature effect.**—As the temperature is increased for solutions containing copper, the onset of a current increase is at more positive potentials and may reflect a possible temperature enhancement of the cupric to cuprous reaction. To measure the  $Ag^+$  limiting current above 30°C, it was necessary to increase the silver concentration in order to shift the initial deposition potential to a more positive value of the  $Ag/Ag^+$  couple and to facilitate the measurement of  $i_L$  by lengthening and stabilizing the limiting current plateau.

At 55°C, sets of voltammograms were obtained at different silver contents (from 25 to 100 mg/l) in supporting electrolytes of 100 g/l  $H_2SO_4$  and 25 g/l  $Cu^{2+}$ . The  $D_{Ag^+}$  values calculated from Fig. 6 ranged between  $19.1 \times 10^{-6}$  and  $21.4 \times 10^{-6} \text{ cm}^2/\text{s}$ . These results are in good agreement with the elevated temperature values reported previously by Ettel (3).

At constant angular velocity of the disk electrode, the direct proportionality between  $i_L$  and  $C_{Ag^+}$  was observed when the silver concentration was increased gradually in a 100 g/l  $H_2SO_4$ , 25 g/l  $Cu^{2+}$  electrolyte at 55°C. The  $D_{Ag^+}$  value obtained from the slope was similar to the above result.

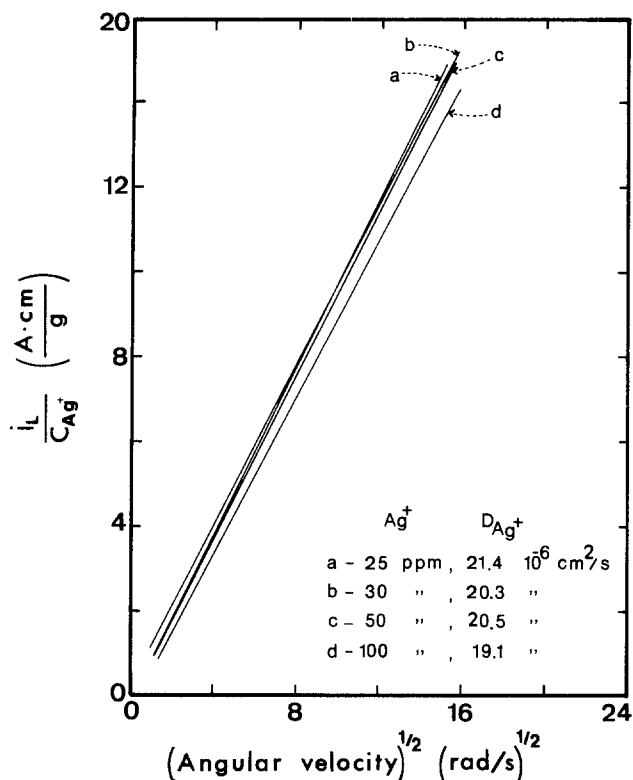
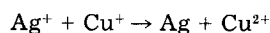


Fig. 6. Effect of  $\text{Ag}^+$  concentration on  $D_{\text{Ag}^+}$  for 100 g/l  $\text{H}_2\text{SO}_4$ , 25 g/l  $\text{Cu}^{2+}$ ; Pt electrode at  $55^\circ\text{C}$ .

Verification of the voltammetric results at  $55^\circ\text{C}$  were also made by chemically analyzing the silver deposit as mentioned previously. When only silver was plating at a constant potential but using different rotational speeds, the  $D_{\text{Ag}^+}$  value obtained was in good agreement with the ones calculated using the polarization technique. However, when the electrochemical conditions were shifted to a region in which silver and copper plated simultaneously at  $-0.37\text{V}$  and  $-0.45\text{V}$  vs.  $\text{Hg}/\text{Hg}_2\text{SO}_4$  or galvanostatically at  $35 \text{ mA}/\text{cm}^2$ , the  $D_{\text{Ag}^+}$  values were nearly two to three times greater than obtained when only silver was deposited. Initially, it was thought that the enhanced Ag removal could be due to an area effect resulting from a rough or dendritic copper surface. But, in other experiments, the electrode was potentiostated at values slightly more positive and negative than the copper deposition potential ( $-0.33\text{V}$  vs.  $\text{Hg}/\text{Hg}_2\text{SO}_4$  for 25 g/l  $\text{Cu}^{2+}$  at  $55^\circ\text{C}$ ); and the deposit was then chemically analyzed. The results showed a much higher silver extraction than expected in both cases, the calculated  $D_{\text{Ag}^+}$  being six times greater than that obtained from limiting current measurements. Ultimately, in seeking other explanations for the observation, an SEM-EDX analysis of the electrode surface was made and revealed that the silver had also deposited on the nonworking area (Fig. 7) whenever a larger than expected  $D_{\text{Ag}^+}$  was obtained. One possible cause for the silver deposit was thought to be the result of a redox reaction of the type



The reaction was apparently less prevalent at room temperature, and so the phenomenon was not observed until the higher temperature tests.

The explanation also seemed reasonable in light of previous studies (3) where it was noted that the codeposition technique gave reliable and reproducible results for electrowinning solutions, but the data were very inconsistent for electrorefining solutions. Particular difficulty was noted in maintaining a proper mass balance between bulk silver content and the deposited silver concentration in the electrorefining mode. The latter might be explained by the apparent influence of  $\text{Cu}^+$  on causing silver reduction by spontaneous reaction in solution.

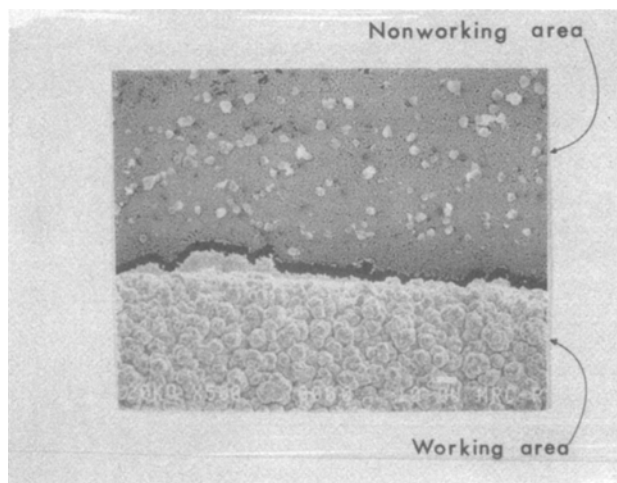


Fig. 7. Photomicrograph showing the Cu and Ag deposit in the working and nonworking area of a Pt electrode plated at a constant potential of  $-0.4\text{V}$  vs.  $\text{Hg}/\text{Hg}_2\text{SO}_4/200 \text{ g/l H}_2\text{SO}_4$  at  $55^\circ\text{C}$ .

The  $\text{Cu}^+$  would remain very low in an electrowinning electrolyte because of the  $\text{Fe}^{3+}$  and/or  $\text{O}_2$  present. However, in the absence of these oxidizers, as would occur in electrorefining, the  $\text{Cu}^+$  would increase and could spontaneously react with the  $\text{Ag}^+$ .

### Conclusions

The cyclic voltammetric technique for measuring the limiting current of a tracer ion more noble than the bulk metal cation, using a RDE system, is a convenient and rapid means for obtaining quantitative data on diffusivities. The utilization of a silver ion tracer for a laminar flow regime under forced convection allows us to calculate the mass-transfer coefficient for copper. Silver and platinum working electrodes give better results than stainless steel and glassy carbon; and increasing  $\text{Cu}^{2+}$  concentration produces a slight decrease in  $D_{\text{Ag}^+}$ .

The electrochemical method employing  $\text{Ag}^+$  is confirmed by chemically analyzing the tracer ion plated galvanostatically or potentiostatically. All give reproducible results which are in good agreement with other reported values in the literature. Care must be exercised when plating both ions at high temperature due to some possible redox reaction in the nonworking area of the electrode.

Additional refinement of the technique and in-depth research is needed to more clearly define the limitations of the technique when used for metal deposition evaluations where additives are present.

### Acknowledgments

The continued financial and technical assistance of AMAX Zinc Company, Sauget, Illinois, and the AMAX Foundation is gratefully acknowledged. Portions of the work were also supported under U.S. Bureau of Mines Contract no. H02220022.

Manuscript submitted, April 14, 1986; revised manuscript received Aug. 1, 1986.

The University of Missouri-Rolla assisted in meeting the publication costs of this article.

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## Three-Dimensional Modeling of the Potential and Current Distributions in an Electrolytic Cell

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### ABSTRACT

In this paper, the mathematical modeling in three dimensions of the local current density distribution on a planar cathode is analyzed by using potential theory and Green's theorem for a uniform Wagner polarization parameter,  $k_c$ , and a uniform exchange current density on the cathode surface. The resultant Fredholm integral equations of the second kind are solved numerically by computer. Both large and small  $k_c$  are considered. The ratio of the local current density to the average value is computer plotted in three dimensions for different  $k_c$  values and positions on the electrode. The results are in accord with the trends in current density established by Wagner based on a similar two-dimensional analysis. Corner effects and variations along the edge are predicted from the three-dimensional analysis.

Current density distribution is a major factor in the successful electrodeposition of metals and alloys as well as in other electrode processes such as cathodic protection and electropolishing. Wagner (1), using potential theory and Green's theorem, has previously presented a general two-dimensional model of current distribution in electrolytic cells based on a linear potential-current approach. In the present paper, which is a more complete description of earlier work (2), this approach is used in a three-dimensional analysis of the current distribution on a planar cathode.

Because the local current density is closely related to the polarization behavior of the electrode, Wagner's polarization parameter is used for obtaining the solution of the resultant integral equation of the local current density. Hence, the slope of the polarization curve, specific electrical conductivity, and certain linear dimensions determine the current distribution, as explained by numerous authors (1-6). Implicit in this statement are the assumptions that the electrode surface is homogeneous and is supporting only the reaction of interest. Otherwise, other considerations arise such as a variable slope of the polarization curve (7) or a variable exchange current density (8-10).

Although the model is based on a linear relation between current density and potential, it is applicable to nonlinear sections of the polarization curve, being more accurate the closer the approach to linearity. Some indication of the applicability of the model is available in the results of other researchers (11) who calculated the current distribution for the Tafel region using an integral equation based on Tafel polarization kinetics, and compared the resulting current distribution with that predicted by the Wagner integral equation. The two calculated distributions were essentially identical. A similar application of the linear model to a nonlinear region of the polarization curve has been shown by Newman

(12, 13), who also calculated similar current distributions for the Tafel region using the integral equation of Wagner (1) and the integral equation of Gnusin *et al.* (11).

Thus, the Wagner modeling approach has general utility, being applicable in the Tafel and other nonlinear regions of the polarization curve. Its generality also extends to nonplanar electrodes of various shapes (1), an important consideration in commercial electroplating and other processes. Its application is greatly facilitated by use of a computer to accomplish the numerical analysis for obtaining the solutions of the integral equations and for obtaining the current distribution plots. Solution of the three-dimensional analysis provides, for the first time, the current distribution at corners for planar cathodes and the trends in current density for nonplanar surfaces at other three-dimensional features.

### Mathematical Analysis

In this analysis of current distribution on a planar cathode, the Laplace equations are solved by means of potential theory (14-17), and using also Green's theorem (15-18) the resultant Fredholm integral equations of the second kind are solved numerically using a computer (18-21). Both large and small polarizations are considered. The ratio of local current density to the average value is computer plotted for different Wagner polarization parameters and positions on the electrode. Although the particular elementary solution of the Laplace equation used in this paper is different from that used by Wagner, the charging density solution for the two dimensional analysis is the same, and the results obtained by numerical integration using a computer give validity to Wagner's two-dimensional analysis. This analysis is presented in the Appendix. In what follows, the mathematical modeling of the three-dimensional problem using the approach developed for two dimensions, provides the current distribution on planar surfaces, including along the edges and at the corners.

Four assumptions are made in the analysis: (i) uniform specific electrical conductivity in the electrolytic cell, (ii) the slope of the polarization curve in a narrow range does

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