

# Isolation of the Diffusion Layer at an Electrode and the Determination of Concentration Polarization

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## ABSTRACT

A method has been developed for sampling the electrolyte (concentration  $C_i$ ) that exists during electrolysis at the interface of electrode electrolyte. Copper was electrodeposited from sulfate baths (concentration  $C_b$ ) on to the outside surface of a hollow, microporous metal cylinder, and electrolyte was slowly drawn into the interior which contained an organic liquid immiscible with water. The electrolyte being less dense rose to the surface of the organic liquid and was collected.

The difference,  $C_b - C_i = \Delta C_u$ , was somewhat greater than theoretical. Also,  $\Delta C_u$  was larger for baths of higher copper content.

From the values of  $C_i$ , the Nernst concentration polarization was calculated and shown to be about 10 mv in ordinary plating operations and hence is not significant.

A knowledge of the concentrations of ions in the vicinity of an electrode is necessary for a clear understanding of the mechanism of electrochemical processes. The concentrations of metal-containing ions affect various phenomena, such as polarization, the structure of electrodeposits, and the composition of electrodeposited alloys. The authors were particularly interested in the relation between polarization and the concentrations existing at the interface of cathode and electrolyte. There has been a considerable amount of speculation about the magnitude of concentration polarization. It has not been measured with certainty, because the methods that have been used were indirect and involved unproved assumptions.

The most direct method for determining concentration polarization would be to measure the metal ion concentration existing at the interface of the electrode and the solution and apply Nernst's formula to the data. Although several methods have been proposed for measuring concentrations at the interface, each one has certain disadvantages. A new method for isolating the interfacial solution has been developed and was applied to the study of the concentration polarization that occurs during electrolysis of copper sulfate solutions.

## Methods of Measuring the Concentrations at the Electrode-Solution Interface

Two general methods have been used for determining the concentrations that exist at the electrode-solution interface: optical and sampling techniques. The optical method was first applied to the measurement of the composition of the cathode diffusion layer by Samarcev (1) who used schlieren interferometry to determine the concentration profile of copper ion in a diffusion layer formed during electrolysis of a copper sulfate solution streaming between horizontal electrodes. The same general

method was later used by Ibl and co-workers (2) and by Lin and co-workers (3). Ibl determined the concentration profile and the thickness of the diffusion layer on vertical cathodes under conditions of natural convection.

The optical method has the advantages over sampling techniques of being very sensitive and of not disturbing the diffusion layer. It has the disadvantage of being nonspecific, since it depends on a shift in the index of refraction. Hence, the optical method cannot be used to determine the concentrations of several different solutes present in one solution. Another difficulty with the method is that at high current densities large differences in the density of the diffusion layer occur and cause the diffraction bands to become diffuse. Also, the optical method cannot be used readily with deeply colored solutions such as a chromium plating bath.

Sampling techniques include the drainage, pinhole, and freezing methods. The drainage method consists of the quick removal of the electrode from the bath while the current is still flowing. The solution is allowed to drain from the vertical electrode for several seconds, and the remaining solution is removed with a squeegee and collected. It is a crude method, but gives a fair indication of the concentrations existing at the electrode solution interface. This method has been used by Brenner (4) for determining the concentrations at the cathode in several solutions and by Brenner and Wranglen (5) for measuring the pH at the cathode-solution interface of nickel baths.

In the pinhole method developed by Graham, Heiman, and Read (6) the diffusion layer is sampled by withdrawing it through a capillary tube cemented on the back-side of the cathode over a hole. The sampling rate was about 7 ml/hr through a capillary having an inside diameter of 1 mm. This corresponds to a rate of flow of about 12 cm/min

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normal to the electrode. Since the diffusion layer in a conventional plating bath is only about 0.3 mm thick and requires about 1 min to reach equilibrium with respect to concentration, it is evident that this rate of sampling is too great. The concentration changes observed by Graham, Heiman, and Read were only about one-tenth of those observed by Brenner (4). This indicates that a large proportion of the sample of Graham, Heiman, and Read probably came from the body of the bath.

The freezing method developed by Brenner (4) involves deposition on the outer surface of a hollow cylindrical electrode. At the moment that the current is cut off, a slurry of partially frozen isopentane is poured into the cylinder causing the diffusion layer to be frozen on the cylinder. This layer is turned off in increments on a lathe and each one analyzed. The freezing method permits the measurement of both the concentration profile and the thickness of the diffusion layer. Difficulties with the method are the collection of frost during the turning operation, the occasional poor adhesion of the frozen layer to the cylinder, and the low eutectic temperature of some solutions.

### Experimental

A new method of sampling the diffusion layer has been developed which involves the use of a sheet of microporous metal to form part or the entire wall of a hollow electrode. The method will be referred to as the porous-electrode method. The electrochemical reaction takes place on the outer surface of the microporous metal, and the solution existing at the interface of the electrode and the bath is slowly withdrawn into the interior of the hollow electrode and collected. The pores of the microporous metal were about  $5\mu$  in diameter and the voids amounted to about one-half the volume of the metal.

The use of a hollow, porous electrode for separating the reaction product of an electrolysis from the bulk of the solution is not new. It was mentioned by Knobel (7). Also some patents (8, 9) have been issued on the subject. The most important work was that carried out for the National Carbon Company by Heise (10), Janes (11), and Winslow (12). All of these prior studies of porous electrodes have dealt with the use of porous graphite. In the studies of the National Carbon Company, the aim was to obtain a high yield of product, and therefore the solution at the interface was withdrawn into the interior of the cell rapidly enough to accomplish this purpose.

The technique described in this paper is an improvement over the use of graphite electrodes for the study of diffusion layers in that microporous metal has a much finer porosity than graphite and, because of its greater strength, permits it to be fashioned into vessels with much thinner walls. Some further improvements in the technique are described in a later paragraph. The rate of sampling used in our experiments was about one-tenth of that used in the experiments of the National Carbon Company. A low rate of flow was necessary to prevent inclusion of solution from the body of the bath.

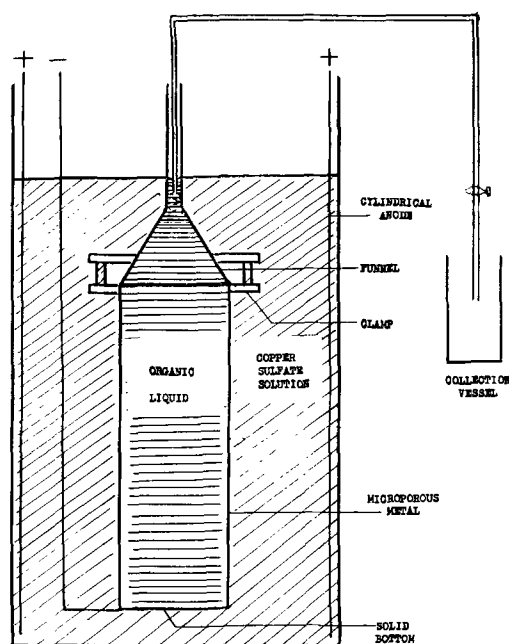


Fig. 1. Schematic diagram of hollow cylindrical cathode of microporous stainless steel and auxiliary equipment used for sampling the diffusion layer formed in the electrolysis of copper sulfate solution.

The hollow electrode vessel may take several shapes. For example, it may consist of a plane sheet of microporous metal attached to the mouth of a funnel. In the experiments described here, the electrode consisted of a vertical cylinder of microporous stainless steel, with a solid bottom, shown schematically in Fig. 1. The cylinder was 15 cm in length and 5 cm in diameter. The wall thickness was 0.07 cm. An inverted glass funnel was clamped to the top of the cylinder by two rings, the lower one of which was rigidly attached to the cylinder by a resin cement. The purpose of the funnel was to facilitate the collection of the sample which was drawn into the interior of the vessel at the rate of about 0.25 ml/min.

Two problems were encountered in the use of the vertical cylinder: (a) attaining a uniform hydrostatic pressure along the height of the cylinder, and (b) holding the solution inside the cylinder to a small volume so that a sample would not be mixed with part of a preceding one.

Since the hydrostatic pressure varied along the length of the vertical, cylindrical electrode and was greatest at the bottom, the tendency was for solution from the bath to be withdrawn into the cylinder more rapidly through the bottom walls. Various means were tried for obtaining a uniform hydrostatic pressure along the vertical length of the wall. The problem was solved by filling the interior of the cell with an organic liquid, immiscible with water, which had the same density as the body of the bath. In this manner the hydrostatic pressure was made equal on the inside and outside of the cylinder along its entire length, and a uniform flow of solution through the walls of the cylinder was obtained by reducing the pressure on the interior.

The use of the immiscible liquid had a further advantage in that it caused the less dense solution

collected at the cathode-solution interface to rise rapidly to the surface where it could be collected. Since the interior of the electrode was completely filled with the organic solvent at the start of the electrolysis, it also solved the problem of lessening the dilution of the sample with extraneous solution.

#### Porosity and Wall Thickness of the Electrode

In preliminary experiments, electrodes of different porosity were tried. The electrode with the smallest pores was the easiest to manipulate and seemed to give a more accurate sampling of the diffusion layer.

The porosity of the electrode was not uniform along its length. However, the uniformity of flow through the wall was considerably improved by pumping a suspension of alumina through the cylinder. Resistance to flow was increased about tenfold. This was desirable, since the effect of small differences in the hydrostatic pressure between the inside and outside of the electrode was diminished.

A thin electrode wall was desirable. The interstices of the wall were filled with plating bath at the beginning of the experiment, and the plating solution in the wall mixed with the sample of the diffusion layer as it passed through the wall. Consequently, the sampling had to be continued until all the bath initially in the wall had been drawn through. The thicker the wall, the longer was the time required for obtaining a representative sample of the diffusion layer. The thinnest wall commercially available was slightly less than 1 mm in thickness. Still thinner walls would be desirable.

#### Procedure

The first step in an experiment consisted in filling the pores of the cylinder with a suspension of alumina as mentioned previously. The excess was removed from the surface of the electrode by washing with a stream of water. The electrode was then immersed in a vessel of the plating solution in order to fill the pores. The interior of the electrode was next filled with a mixture of chloroform and paraffin oil having the same density as that of the bath. The organic liquid was slowly poured into the cylinder while the latter was slowly lowered into the bath at such a rate that the height of the liquids on the inside and outside of the cylinder were about the same. The siphon, also filled with organic liquid, was next attached to the inverted funnel.

After the electrolysis was started, the flow through the siphon was regulated with a stopcock to the desired rate, usually about 0.25 ml/min. At first a few milliliters of organic liquid was delivered, but soon the siphon which was of small diameter became filled with the aqueous solution and delivery of the latter began. A sampling rate of 0.25 ml/min was equivalent to a displacement of the interface layer of about  $4 \times 10^{-5}$  cm/sec. This calculation is based on an area of pores of about 1 dm<sup>2</sup>. It is believed that this rate of movement is too low to affect significantly the steady-state concentrations in the diffusion layer.

The electrolysis usually lasted about 1.5 to 2 hr, during which time 15 to 30 ml of solution was obtained, depending on the sampling rate. The first

solution delivered contained some of the solution which was initially in the porous walls of the electrode. Consequently, the concentration of each succeeding sample of solution diminished and approached either a constant value or a flat minimum which was taken as the concentration of the solute existing at the cathode-solution interface.

Copper sulfate solutions ranging in concentration from 0.25 to 0.94M were used. No additions, such as sulfuric acid, were made to the solution, as it was desired to keep the composition of the bath simple so that the data could be more easily compared with diffusion theory. The plating was done at about 25°C without stirring. The samples were analyzed for copper by the iodide method.

#### Results

##### Variation of copper content of successive samples.

—The decrease in the copper content of successive samples mentioned in the previous section is illustrated in Fig. 2. This datum was taken before the technique of plugging the pores of the cylinder walls with alumina was developed. With the latter technique the upturn of the curve at the right was not pronounced. The cause of the increase in the copper content of successive samples with period of plating is not definitely known, but it is believed to be caused by the covering over of the small pores on the outer surface of the cylinder with the copper deposit. This caused a larger proportion of the sample to be drawn into the cylinder through a relatively small number of larger pores, with the result that the velocity of flow of the diffusion layer at these points was greatly increased. The upturn was less pronounced with a plugged cylinder wall probably because the large pores were eliminated.

We believe that the copper content of the sample approximates the composition of the solution at the cathode-solution interface. The latter actually has no thickness and, strictly speaking, cannot be sampled. The decrease in copper content below that of the body of the bath is not caused, as has been suggested, by deposition of copper in the interstices of

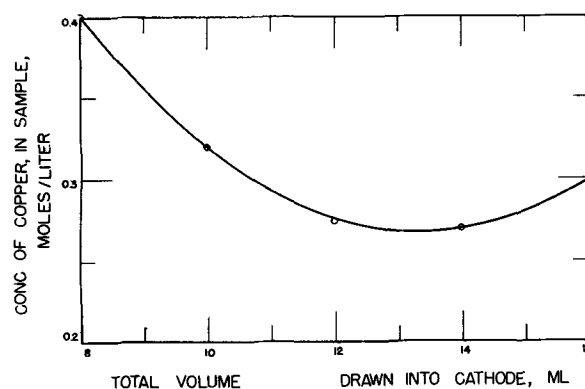


Fig. 2. Relation between the copper content of a sample drawn into the cylinder and the total volume of solution passing through the cylinder. The abscissa is the total volume of solution collected up to and including the volume of the sample used for analysis. The ordinate is the concentration of copper in a 1-ml sample individually collected. Rate of flow of liquid into cylinder, 0.25 ml/min; copper concentration in the body of bath, 0.94M; current density, 2.86 amp/dm<sup>2</sup>; room temperature; apparatus as shown in Fig. 1.

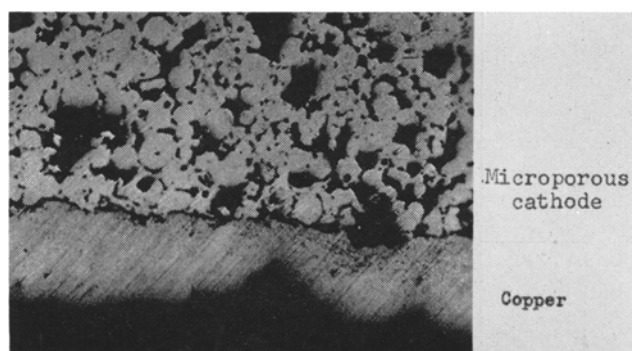


Fig. 3. Photomicrograph of a cross section of copper deposited on microporous stainless steel.

the cell wall. Deposition of copper within the interstices is improbable because of the minute current that flows into deep recesses having a cross section of the order of  $5\mu$ . Definite evidence that deposition does not occur in the pores of the cylinder is given in Fig. 3, which shows that the copper coating lies only on the outside surface of the microporous cathode.

Since the internal surface of the electrode walls is very large, the possibility exists that an appreciable amount of copper would deposit within the walls without attaining a thickness sufficient to be observed microscopically. This possibility was explored by determining the amount of copper leached out of the cell walls with nitric acid. The walls of this cell were twice the thickness of those of the cell used for obtaining the values of  $\Delta Cu$  reported in this paper. In a blank experiment, the thick-walled cell was immersed in copper sulfate solution for 2 hr to determine if copper deposited by immersion. The copper extracted from the cell walls with nitric acid amounted to only a few milligrams and hence was negligible. In another experiment, copper was deposited at  $4 \text{ amp/dm}^2$  from a 1M bath over the cylinder as in an ordinary experiment. The copper coating was then peeled from the exterior of the cylinder and any residual copper nodules were removed with a polishing wheel. The copper obtained

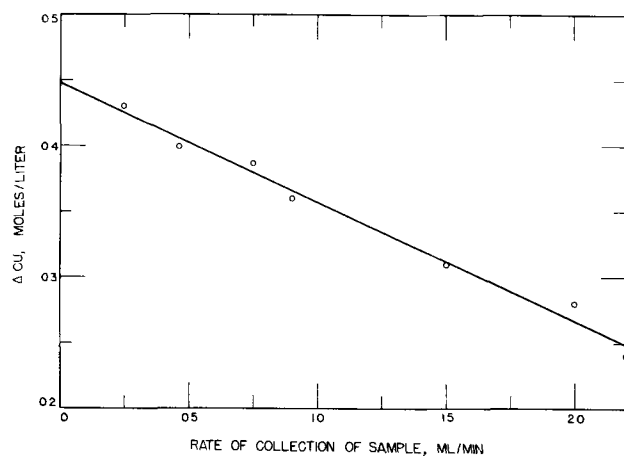


Fig. 4. Variation of  $\Delta Cu$  with rate of sampling.  $\Delta Cu = C_b - C_1$  where  $C_b$  is the concentration of copper in the body of the bath and  $C_1$  is the concentration of copper in the sample of the diffusion layer.  $C_b = 1M$ ; current density,  $1.5 \text{ amp/dm}^2$ ; temperature,  $28^\circ C$ ; microporous cathode,  $0.15 \text{ cm}$  thick; apparatus as in Fig. 1.

by a nitric acid extraction amounted to only 12 mg. This copper was probably not deposited on the interior of the wall but probably existed in surface cracks too deep to be reached by the polishing wheel. This amount of copper would affect the value of  $\Delta Cu$  only about 1%, which is less than the experimental reproducibility.

*Rate of withdrawing samples.*—The rate of withdrawing samples was an important variable. At a high sampling rate, some of the bulk solution was drawn into the cell along with the diffusion layer. Figure 4 shows the relation between the decrease in the copper content in the collected sample and the rate of collection of the sample. At a rate of  $0.25 \text{ ml/min}$  the decrease in the copper concentration,  $\Delta Cu$ , differed by only 3% from the value of  $\Delta Cu$  obtained by extrapolating the straight line of the figure to zero rate of sampling. Each point of Fig. 4 was obtained by the method illustrated in Fig. 1.

#### Relation between Current Density and $\Delta Cu$

The relation between  $\Delta Cu$  and current density is shown in Fig. 5 for copper sulfate solutions of three different concentrations. The current densities are based on the apparent area of the cylinder, considered as a continuous surface. Some observations were made at higher current densities than those recorded in Fig. 5. At the highest current density, which was above the limiting current density of metal deposition, the samples withdrawn from the electrode were virtually colorless indicating almost complete removal of copper.

One interesting aspect of Fig. 5 is that  $\Delta Cu$  at a given current density is larger the more concentrated the plating bath. A similar trend of metal depletion in the cathode diffusion layer was observed by Brenner (4) with nickel solutions and by Samarcev (1) with copper sulfate solutions. The explanation given by Samarcev, as well as by Brenner, was that in the dilute solution, and particularly in the still more dilute diffusion layer, the rate of diffusion of the metallic ions was greater than in

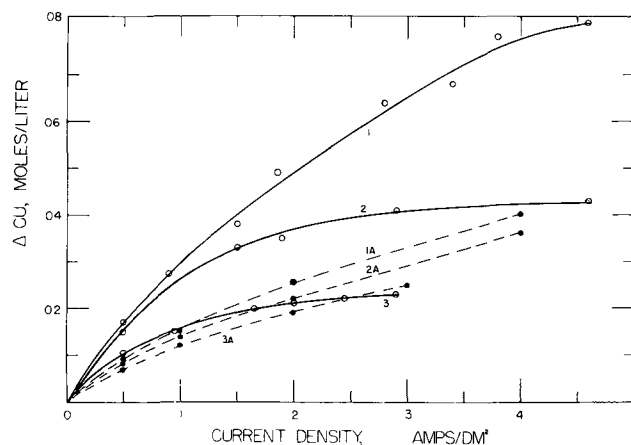


Fig. 5. Relation between  $\Delta Cu$  and current density in the electrolysis of copper sulfate solutions of three different concentrations. Rate of collection of sample,  $0.25 \text{ ml/min}$ . Curve 1.  $0.94M$  copper sulfate; Curve 2.  $0.49M$  copper sulfate; Curve 3.  $0.24M$  copper sulfate; Curves 1A, 2A, and 3A are calculated curves based on diffusion theory (see Table I) according to Keulegan (13), for the same bath concentrations as curves 1, 2, and 3.

the concentrated solutions. This would result in a smaller value of  $\Delta\text{Cu}$  for the more dilute baths. However, the variation of the diffusion constant of copper sulfate with concentration seems inadequate to explain the differences of more than twofold in the values of  $\Delta\text{Cu}$  obtained at a given current density for the different baths.

#### Comparison of Data with Theory

Within recent years a considerable amount of theoretical and experimental investigation has been made of the hydrodynamics of electrode diffusion layers by Ibl and co-workers (2, 21, 22), Wagner (17, 18), and Tobias, Eisenberg, and Wilke (19, 20). The various approaches lead to similar numerical results for  $\Delta\text{Cu}$  (23) even though they involve some different assumptions.

The values of  $\Delta\text{Cu}$  obtained with the porous electrode were compared with those theoretically expected. The theory of the diffusion layer developed by Keulegan (13) was used in making the calculations. This theory was used because the authors were more familiar with it, and its use does not imply that it is more correct than the other theories. Actually it involves two assumptions that did not obtain in our experiments, namely, that the depletion of metal ion was uniform over the cathode and that the hydrodynamic boundary layer coincided with the diffusion layer.

Theory based on hydrodynamics and diffusion does not predict widely separated curves, as shown in Fig. 5, for solutions of different initial concentrations. Keulegan's theory leads to the following equation for  $\Delta\text{C}$ . This  $\Delta\text{C}$ , like the  $\Delta\text{Cu}$  obtained with the porous electrode, is the value of the reduction in metal ion concentration *averaged* over the cathode surface.

$$\Delta\text{C} = \left( \frac{It_a}{0.63F} \right)^{4/5} \cdot \frac{(\rho_1\nu xm)^{1/5}}{g^{1/5} D^{3/5}}$$

where  $I$  = current density, amp/dm<sup>2</sup>;  $t_a$  = transference number of anion;  $F$  = 96,500 coulombs;  $\rho_1$  = density of the bulk of the bath;  $\nu$  = kinematic viscosity, poises;  $x$  = length of cylinder, (13.2 cm);

$$m = \frac{dc}{d\rho} = 0.0132 \text{ g equiv/g, } c \text{ is the concentration}$$

of the copper sulfate solution in gram equiv/ml, and  $\rho$  is the density of the copper sulfate solution;  $g$  = 981 cm/sec<sup>2</sup>;  $D$  = diffusion constant of copper sulfate, cm<sup>2</sup>/sec. This equation is based on equations 89 and 118 of Keulegan's paper. For the present experiments, the above equation simplifies to the following:

$$\Delta\text{C} = 2.5 \times 10^{-5} (It_a)^{4/5} \cdot \frac{(\rho_1\nu)^{1/5}}{D^{3/5}}$$

In using this equation, the values of the variables are those of the solution at the interface of the cathode and the solution, except for  $\rho_1$  which refers to the density of the bulk of the bath.

Calculations were made using the above equation. The values of the different variables are given in Table I. The results are represented in Fig. 5 as

dotted curves. The three curves based on Keulegan's equation lie close together, indicating that the effects of the variations of transference number, viscosity, and diffusion constant with concentration were not sufficient to explain the large difference in  $\Delta\text{Cu}$  experimentally obtained with the three different solutions at a given current density. The agreement of experiment with diffusion theory was best for the 0.24M copper sulfate solution.

We do not have a satisfactory explanation for the large difference between the three curves of Fig. 5 and the difference between curve 1 and the theoretical curve. It is possible that the roughness of the cathode surface or some other experimental detail may be responsible. Also, electrical migration may directly affect the thickness of the diffusion layer.

This latter suggestion is based on the behavior of liquid junctions in the moving boundary method of determining transference numbers. With suitably chosen solutions, the junctions remain sharp while current is passing. However, it is also possible for the current to dissipate a junction, depending on the relative mobilities of the ions involved. A similar phenomenon occurs at the junction of two solutions of different concentration. Thus, the electrical migration may have an effect on the establishment, the thickness, and the sharpness of the diffusion layer in addition to the factors of hydrodynamics.

#### Concentration Polarization

The polarization that occurs during an electrochemical reaction has been considered by electrochemists to be of two types: activation polarization and concentration polarization. The division is somewhat arbitrary since there are no direct experimental measurements for distinguishing between them. Very roughly, concentration polarization is considered to be caused by the change in concentration of the reactive ions at the electrode surface (24). The remainder of the polarization is considered to be of the other type. Various means for discriminating between them have involved different assumptions. It is assumed that stirring eliminates concentration polarization but does not affect activation polarization. Also, it is assumed that the latter type disappears more rapidly than the former when the circuit is broken. However, since nothing is known definitely about the activation type of polarization, one cannot, a priori, assume that concentration polarization is affected by a certain variable, such as stirring and the other one is not.

Concentration polarization,  $P_c$ , at a cathode is usually defined by the Nernst expression:

$$P_c = \frac{RT}{nF} \log \frac{A_b}{A_i}$$

where  $A_b$  is the activity of the metal ion in the body of the bath and  $A_i$  is the activity of the metal ion at the cathode-solution interface. That is, the concentration polarization is equivalent to the potential of a concentration cell with negligible liquid junction. In actual measurements of polarization with a capillary, a variable liquid junction potential exists between the solution of the reference electrode and

Table I

Calculations of  $\Delta\text{Cu}$  from the formula,

$$\Delta\text{Cu} = 2.5 \times 10^{-5} \cdot (It_a)^{4/5} \cdot \frac{(\rho_1\nu)^{1/5}}{D^{3/5}}$$

$\Delta\text{Cu}$  is given by the formula in units of  $\frac{\text{g-equiv}}{\text{cm}^3}$

$I$ , current density, amp/cm<sup>2</sup>;  $t_c$ , transference number of cation;  $t_a$ , transference number of anion;  $\rho_1$  density of body of bath;  $\nu$ , kinematic viscosity, poises;  $D$ , diffusion constant, cm<sup>2</sup>/sec;  $C_b$ , concentration of copper in the body of the bath, g-equiv/cm<sup>3</sup>;  $C_i$ , concentration of copper at the cathode-solution interface, g-equiv/cm<sup>3</sup>.

$C_i$ g-equiv/cm <sup>3</sup> $\times 10^4$	$t_c$	$t_a$	$I$ amp/cm <sup>2</sup>	$(It_a)^{4/5}$ $\times 10^4$	$\nu$ $\times 10^2$	$(\rho_1\nu)^{1/5}$	$D$ $\times 10^6$	$D^{3/5}$ $\times 10^4$	$\Delta\text{Cu}$ g-equiv/cm <sup>3</sup> Calc. $\times 10^4$	$\Delta\text{Cu}$ g-equiv/cm <sup>3</sup> Exp. $\times 10^4$
		$C_b = 0.94M$		$\rho_1 = 1.130$						
15.4	0.275	0.725	0.005	111	1.27	0.428	5.05	6.6	1.8	3.4
12.8	0.285	0.715	0.01	192	1.22	0.425	5.1	6.68	3.0	6.0
8.6	0.300	0.700	0.02	329	1.10	0.416	5.2	6.76	5.1	10.2
3.8	0.34	0.66	0.04	546	0.98	0.406	5.4	6.9	8.0	15.0
		$C_b = 0.490$ moles		$\rho_1 = 1.075$						
6.4	0.307	0.693	0.005	108	1.05	0.408	5.25	6.80	1.6	3.4
4.6	0.325	0.675	0.01	183	1.00	0.404	5.30	6.84	2.7	5.2
2.6	0.370	0.630	0.02	302	0.96	0.400	5.56	6.98	4.3	7.2
1.2	0.390	0.610	0.04	512	0.93	0.398	5.6	7.06	7.2	8.6
		$C_b = 0.240M$		$\rho_1 = 1.035$						
2.7	0.370	0.630	0.005	99.7	0.96	0.397	5.5	6.98	1.4	2.1
1.8	0.390	0.610	0.01	169	0.94	0.396	5.65	7.10	2.4	3.0
0.6	0.395	0.605	0.02	293	0.91	0.393	6.2	7.51	3.8	4.2
0.2	0.395	0.605	0.03	405	0.90	0.392	6.9	8.00	5.0	4.6

Data for  $D$  taken from Eversole, Kindsvater, and Peterson (15) for concentration of copper sulfate up to 0.35M. Other values of  $D$  were obtained by extrapolation.

Data for  $t_c$  is that for  $\text{Zn}^{++}$  in zinc sulfate, as given by Conway (14B), as the transference number of  $\text{Cu}^{++}$  should be about the same.

that of the bath, because with no current flowing the capillary is immersed in a solution having an ion activity  $A_b$ , and with the current flowing the activity of the ion is  $A_i$ . However, this junction potential is too small to be of consequence.

Concentration polarization as defined by the Nernst equation will be referred to in the following discussion as Nernst concentration polarization. It has a definite meaning, because it depends only on the activities of a particular species of ion. From a knowledge of the concentrations of solute,  $C_i$ , at the interface of the electrode and solution, and  $C_b$ , the concentration in the body of the bath the Nernst concentration polarization can be calculated; or it can be measured by setting up a concentration cell, with metal concentrations  $C_i$  and  $C_b$ , provided the metal has a reversible static potential.

At a given current density, Nernst concentration polarization is a more definite and reproducible quantity than activation polarization. For example, the latter may increase greatly in the presence of a small amount of an addition agent in a solution although the basic electrode reaction has not changed. In contrast, the concentration of metal ions which determine concentration polarization is largely a function of current density and is fairly reproducible from one experiment to another.

Only one prior study has been made to calculate Nernst concentration polarization from measurements of concentration. This work was done by Samarcev (1) with a copper sulfate solution. He showed that the polarization was greater than that which could be accounted for on the basis of Nernst concentration polarization. Prior to his work many electrochemists had considered the polarization involved in the deposition of copper from a sulfate bath to be entirely concentration polarization. This work of Samarcev stands out as being the first determination of concentration polarization based on measurements of concentration.

Concentration polarization corresponding to curves 1, 2, and 3 of Fig. 5 were calculated by means of the Nernst equation using the activities for copper ion given by Conway (14A). The results of these calculations are shown in Fig. 6. To compare the magnitude of concentration polarization with the total polarization of copper deposition, curve 4 is included. This is for the deposition of copper from a 1M solution containing 0.05M sulfuric acid. A comparison of curve 1 with 4 shows that the contribution of concentration polarization to the total polarization is rather small.

Shreir and Smith (16) attempted to measure the concentration polarization of copper sulfate solu-

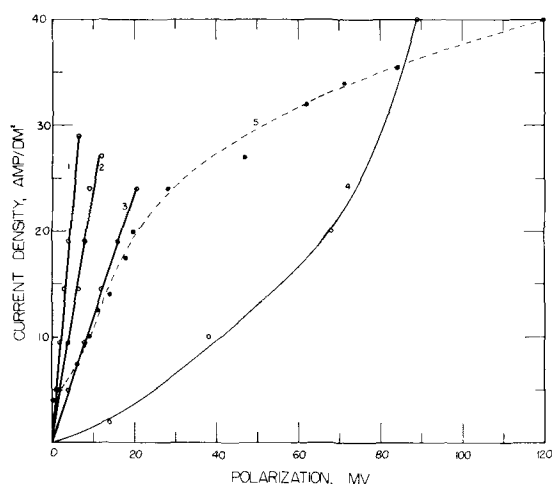


Fig. 6. Nernst concentration polarization calculated from the copper concentration,  $C_1$ , at the electrode interface. Curves 1, 2, and 3 refer to the like-numbered curves of Fig. 5. Curve 4 is the total polarization for a solution 1.0M in copper sulfate and 0.05M in sulfuric acid measured with a Luggin capillary. Curve 5 is the concentration polarization of a solution 0.5M in copper and 0.5M in sulfuric acid obtained by the stirring method. Data of Shreir and Smith (16). [Calculations for curves 1, 2, and 3 are based on the activities of copper ions given by Conway (14)].

tions by measuring the difference in potential of the electrode in a still and in a stirred bath. Their data for a bath 0.5M in copper sulfate and 0.5M in sulfuric acid is reproduced in Fig. 6 as a broken line. Their data indicates a considerably larger concentration polarization than was obtained by the present method. A comparison between our data and theirs is valid even though their bath contained sulfuric acid. The maximum effect of the acid would be to decrease the transport number of copper ions. If the transport number were reduced to zero, this would result in only about a 30% increase over our values of concentration polarization given in Fig. 6.

The probable reason that our values are smaller than those of Shreir and Smith is that the latter's values include some contributions due to activation polarization. Activation polarization is a function of concentration, as well as of current density, as is shown by the data of Shreir and Smith (16). Since the concentration of metal ion at the electrode surface in the still solution must have differed from that in a stirred solution, the activation polarization must also have varied under these two conditions. Thus the procedure of measuring the Nernst concentration polarization by the difference in potential between a stirred and unstirred bath is not accurate because it also includes the effect of concentration on activation polarization.

The relation between activation polarization and concentration of the solution could be determined in the following way. A series of solutions of different concentrations could be electrolyzed at the same current density and the concentration of metal at the electrode-solution interface and the total electrode polarization determined. The Nernst concentration polarization can be calculated and subtracted from the total polarization to yield the activation polarization. The latter could be related to either the metal concentration of the body of the

bath or to the concentration at the interface of the electrode and the solution.

### Discussion

The porous electrode method of sampling the diffusion layer has the advantage over the freezing method of being simpler to set up and operate. Also the diffusion layer can be continuously sampled. However, it does not yield the concentration profile of the diffusion layer as does the freezing method and cannot be used to study the rate of attainment of the steady state in the diffusion layer. The drainage method is simpler than the porous electrode method but is a less precise way of isolating the solution at the electrode interface. In carrying out the drainage method, some mixing of the bulk of the bath with the diffusion layer probably occurs.

The porous electrode method yielded larger values for  $\Delta Cu$  than either the freezing method or the optical method. The value of  $\Delta Cu$  given in Fig. 5 for the 0.94M solution at 4 amp/dm<sup>2</sup> was twice as large as that obtained by Brenner (4) with the freezing method. The value of  $\Delta Cu$  for the 0.49M solution at 0.5 amp/dm<sup>2</sup> was about three times larger than that obtained by Ibl and co-workers (2) with the interferometric method. The comparison of our results with those of the latter workers may not be strictly valid, because they measured a local  $\Delta Cu$ , not an average value, and the length of their electrode was only about one-fourth the length of ours.

The fact that the porous electrode method yielded larger values of  $\Delta Cu$  than other methods may be evidence that it comes closer than the other methods to giving the true concentration of metal ion at the electrode interface. Experimental difficulties, such as mixing of the cathode diffusion layer with the bulk of the bath, would have led to smaller values of  $\Delta Cu$ . The fact that the values of  $\Delta Cu$  in Fig. 5 were larger for the more concentrated solutions is further evidence that no large amount of mixing took place between the diffusion layer and the bulk of the bath.

The concentration polarizations shown in Fig. 6 are rather small compared with the total polarization. These results can be applied to electrodeposition in general, since the experiments with the copper sulfate solutions covered the usual range of concentration of metallic salts and of current density employed in conventional electroplating. The current densities used in electroplating are usually not over half of the limiting current density for metal deposition, that is, the concentration of metal ions at the cathode interface usually would not be reduced below about half that in the body of the bath. Consequently, on the basis of the results given in Fig. 6, it may be concluded that in ordinary electrodeposition the Nernst concentration polarization is small. In particular, Fig. 6 shows that the concentration polarization in the 0.49M and 0.94M solutions was less than 10 mv at a current density of 2 amp/dm<sup>2</sup>, which is a current density commonly employed in plating. Since the precision of measuring electrode polarization is usually of the order of 5 mv to 10 mv, the concentration polarization

should be barely detectable at the current densities used in conventional electroplating. The directly observed polarizations, such as curve 4 in Fig. 6, must be attributed to other causes than the Nernst explanation.

### Summary

1. A method for isolating the solution at the interface of an electrode and the bath has been developed.

2. The Nernst concentration polarization has been calculated for copper sulfate solutions.

3. It is concluded that the Nernst concentration polarization probably is not significant in plating baths operated at conventional current densities.

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## Phase Equilibria and Fluorescence in a Portion of the System ZnO-MnO-P<sub>2</sub>O<sub>5</sub>

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### ABSTRACT

Phase equilibrium data have been obtained for compositions in the ternary system lying near the Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> compound, particularly those on the orthophosphate join. It was found that "gamma zinc orthophosphate" is a ternary solid solution which has a region of stability on the orthophosphate join ranging from about 5 to about 25 mole % Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. A definitive x-ray pattern characteristic of the ternary solid solution series is given.

$\beta$ -Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> forms an extended series of solid solutions with Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> at temperatures above 940°C. The melting behavior of the  $\beta$ -Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> solid solution is difficult to determine in air due to the usual change in oxidation state of manganese at temperatures above 1000°C.

Emission curves for cathode ray excitation are presented for  $\alpha$  and  $\beta$  zinc orthophosphate, the so-called "gamma-zinc phosphate," Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, and the two forms of Zn(PO<sub>3</sub>)<sub>2</sub>.

In a recent paper by Katnack and Hummel (1), the equilibrium relationships for the system ZnO-P<sub>2</sub>O<sub>5</sub> were established, and it was shown that low- and high-temperature forms of ortho-, pyro-, and metaphosphate compounds existed.

The primary purpose of this paper was to establish the equilibrium relationships in the ternary system ZnO-MnO-P<sub>2</sub>O<sub>5</sub> in the neighborhood of

Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and to relate these data to the fluorescence of the  $\alpha$ ,  $\beta$ , and "gamma" forms of the orthophosphate. A second purpose was to obtain luminescence data on Zn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and the two forms of the metaphosphate.

### Compositions and Procedure

*General.*—The raw materials and experimental techniques were the same as those described in the