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# PHYSICAL CHEMISTRY

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## Abstract

## Full Text

PHYSICAL CHEMISTRY

S. I. KRICHMAR

# NONSTATIONARY PROCESSES DURING THE ANODIC DISSOLUTION OF COPPER IN ORTHOPHOSPHORIC ACID

*(Presented by Academician A. N. Frumkin, 14 XII 1956)*

In studying electrochemical polishing, as well as other electrode processes accompanied by considerable concentration polarization, one encounters phenomena whose nature is directly connected with the formation of the near-electrode diffusion layer.

V. I. Lainer <sup>(1)</sup> points to the presence of a more or less sharply expressed voltage jump on potential–time curves during the electrochemical polishing of copper in solutions of orthophosphoric acid. When maintaining a constant voltage on the bath, we observed analogous phenomena on current–time curves.

During the anodic dissolution of copper in orthophosphoric acid, maxima are observed on the volt-ampere curves at the beginning of the limiting-current plateau. The shape of the curve in the limiting-current region depends on the procedure used to record the curve <sup>(2)</sup>. In the case considered in the present work, of the anodic dissolution of copper in phosphoric acid, nonstationary processes during the period of formation of the near-anode layer are associated mainly with diffusional transport of matter in the near-electrode region, since in strongly concentrated solutions of  $\text{H}_3\text{PO}_4$  (8–15 mole/l), owing to the considerable viscosity (10–60 centipoise), convective transport of matter in the electrolysis process probably plays a secondary role.

Fig. 1. Dependences of  $V$  on  $t$ . Concentration  $\text{H}_3\text{PO}_4$  15 mole/l

The mechanism of diffusion kinetics for the case of a nonstationary process at a cathode in a motionless electrolyte at a prescribed current strength was described by Sand and Levich <sup>(3)</sup>. For the case considered here, the problem can be solved in an analogous way.

The boundary and initial conditions for the equation of molecular diffusion

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

are the following:

$$1) C(0, y) = 0; \quad 2) \left( \frac{\partial C}{\partial y} \right)_{y=0} = \frac{I}{nFDS} = \text{const},$$

where  $C$  is the concentration of copper in the solution;  $I$  is the current strength;  $S$  is the surface of the electrode;  $D$  is the effective diffusion coefficient.

Let us introduce a new variable:

$$u = C_n - C, \quad (2)$$

where  $C_n$  is the saturation concentration. In the new variable the boundary-value problem has the form:

$$1) u(0, y) = C_n; \quad 2) \left( \frac{\partial u}{\partial y} \right)_{y=0} = \left( \frac{\partial C}{\partial y} \right)_{y=0} = \frac{I}{nFDS};$$

the form of the basic equation (1) does not change.

In this form the boundary and initial conditions of our problem coincide with the conditions for the cathode; therefore one may directly use the solution proposed by Sand and Levich for the cathode:

$$u = C_n - \frac{2I}{SnF} \sqrt{\frac{t}{\pi D}} e^{-y^2/4\pi D} + \frac{2Iy}{SnFD\sqrt{\pi}} \int_{y/2\sqrt{Dt}}^{\infty} e^{-z^2} dz. \quad (3)$$

Substituting the value of  $u$  in (3), we obtain

$$C = \frac{2I}{SnF} \sqrt{\frac{t}{\pi D}} e^{-y^2/4\pi D} + \frac{2Iy}{SnFD\sqrt{\pi}} \int_{y/2\sqrt{Dt}}^{\infty} e^{-z^2} dz. \quad (4)$$

The change in the concentration of the reaction products directly at the anode will be expressed by the formula

$$C = \frac{2I}{SnF\sqrt{\pi}} \sqrt{\frac{t}{D}}. \quad (5)$$

It was indicated above that in the case under consideration the concentration of the substance at the anode surface cannot increase without limit. After the

Figure 2

Figure 2: Figure 2

saturation concentration is reached, a potential jump occurs and a new process begins (gas evolution). Depending on the current imposed in the system, the potential jump occurs after different time intervals: the higher the current, the more rapidly the activity at the anode is exhausted and the potential jump occurs.

Fig. 2. Dependence of  $T$  on  $I$ . 1–8 mol/l; 2–10 mol/l; 3–15 mol/l

In Fig. 1 a series of typical potential–time curves is presented, obtained during anodic dissolution of copper in  $\text{H}_3\text{PO}_4$  under the condition  $I(t) = \text{const}$ .

Figure 2 presents curves of the dependence of the time of occurrence of the potential jump  $T$  on the current imposed in the system, constructed according to the equation

$$T_n = \left( \frac{SnFC_n}{2I} \right)^2 \pi D; \quad (5a)$$

the points are experimental data. In doing so it was assumed that the order of the diffusion coefficient of the reaction products is the same as that of the acid molecules. The diffusion coefficient was calculated from the Stokes–Einstein equation from data on the viscosity of  $\text{H}_3\text{PO}_4$  solutions.<sup>(4)</sup> The saturation concentration was found by extrapolating the dependence of the limiting-current magnitude on the concentration of reaction products in the solution from<sup>(5)\*</sup>

The values of the constants entering into equation (5a), for the electrolyte concentrations studied, are given in Table 1.

\* Since the limiting current for the case of electropolishing of copper in  $\text{H}_3\text{PO}_4$ , as was shown in<sup>(5)</sup>, obeys the relation:  $i = nFD(C - C_0)/\delta$ , where  $C$  is the concentration of products at the surface and  $C_0$  in the bulk; then, in the limit, when the concentration in the bulk has reached saturation, we have  $i = 0$  and  $C = C_n$ .

From the data presented it is evident that for high concentrations of  $\text{H}_3\text{PO}_4$ , where natural-convective transport of matter is hindered by the high viscosity of the solution, the Sand and Levich formula is quite acceptable for calculating the time at which the potential jump occurs. For  $\text{H}_3\text{PO}_4$  concentrations below 6 mol/l this equation is not applicable, since under these conditions natural-convective transport of matter increases considerably.

On the basis of the considerations discussed concerning the role of nonstationary processes in the anodic dissolution of a metal, the following explanation can be given for the appearance of maxima on current–voltage curves during the electropolishing of copper in phosphoric acid. The usual method of recording

current-voltage curves consists in successively changing, by a definite amount, the potential difference at the terminals of the bath, with simultaneous (or subsequent) recording of the current. With such a recording method, after each preceding measurement the electrode enters the new electrochemical state already partially polarized. The intensity of polarization each time is determined by the quantity of electricity that has passed through the electrolyzer, i.e., ultimately, by the duration of electrolysis. Thus, if the curve was recorded rather rapidly, the anode enters the electrochemical state corresponding to the limiting current with the near-electrode layer still unformed; therefore, with a further increase in potential the current continues to increase for some time. This leads to the appearance on the curve of a maximum at the beginning of the limiting-current region. Thus, the size of the maximum and its shape depend entirely on the duration of polarization of the anode.

**Table 1**

| Conc.<br>$\text{H}_3\text{PO}_4$ ,<br>mol/l | $C_H$ , mol/l | $S$ , $\text{cm}^2$ | $D$ , $\text{cm}^2/\text{sec}$ | $n$ |
|---|---------------|---------------------|--------------------------------|-----|
| 8   | 2.0           | 0.5                 | $10^{-5}$                      | 2   |
| 10  | 2.2           | 0.4                 | $6.6 \cdot 10^{-6}$            | 2   |
| 15  | 2.4           | 0.3                 | $1.1 \cdot 10^{-6}$            | 2   |

**Fig. 3.** Dependences of  $I$  on  $V$ . Polarization duration: 1–10 sec.; 2–20 sec.; 3–30 sec.; 4–4 min.

This dependence is clearly illustrated by the following experiment. In Fig. 3 a series of current-voltage curves is presented, obtained for a 5 M  $\text{H}_3\text{PO}_4$  solution. The points of these curves were obtained as follows: each time the anode was subjected to electrolysis at the corresponding potential for a strictly definite time, after which the current was interrupted, the electrode was depolarized, and the next measurement was made at a new potential value. It is seen from the figure that the height of the maximum decreases regularly with increasing polarization duration, and at a comparatively large value of  $T$  the maximum on the curve is absent.

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*Note: Figure translations are in progress. See original paper for figures.*

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