THE NATURE OF POLARIZATION DURING ANODIC DISSOLUTION OF COPPER IN CONCENTRATED SOLUTIONS OF $\mathrm{H_3PO_4}$

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Abstract

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THE NATURE OF POLARIZATION DURING ANODIC DISSOLUTION OF COPPER IN CONCENTRATED SOLUTIONS OF H_3PO_4

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Despite the fact that a large number of studies have been devoted to the behavior of a copper anode in concentrated solutions of orthophosphoric acid, up to the present time the character of the polarization curve and the reason for the appearance of the limiting current have remained essentially unexplained. The hypotheses of the formation of a saturated layer of reaction products directly at the metal surface ([1]) or of a decrease in the concentration of acceptor ions to zero ([2]), which attempt to explain this phenomenon, contain a number of contradictions and are not sufficiently substantiated experimentally.

Our experiments to determine the influence of the content of dissolved copper on the viscosity of H_3PO_4 showed that, even without this, the high viscosity of concentrated solutions increases considerably with the amount of metal ions, so that when considering questions of diffusion kinetics it is no longer possible to neglect this dependence. Figure 1 gives the dependences of the logarithm of the ratio of the viscosity of acid solutions containing copper on the concentration of the latter. As can be seen from the data presented, to a first approximation these slightly concave curves may be replaced by straight lines passing through the origin. If one takes into account that in concentrated solutions the reaction products and acid molecules are associated and the diffusing particles are therefore sufficiently large, then the diffusion coefficient D may be calculated rather accurately from the equation $D = \text{const}/\eta$. Taking this into account, we shall have

$$D = D_0 \exp(-zc), \tag{1}$$

where c is the concentration of metal in the solution, z is a constant, and D_0 is the diffusion coefficient of the pure acid. Since the solution of problems of convective diffusion with a variable diffusion coefficient is extremely complicated, we shall restrict ourselves to considering purely diffusional transport of matter through a certain effective layer. The equation of linear diffusion with a variable diffusion coefficient has the form:

$$D\left(\frac{\partial^2 c}{\partial y^2}\right)+\left(\frac{\partial D}{\partial y}\right)\left(\frac{\partial c}{\partial y}\right)=0 \tag{2}$$

where y is the distance from the boundary with the bulk of the solution of the diffusion zone, which, after substitution of (1) into it, gives:

$$\frac{\partial^2 c}{\partial y^2}-z\left(\frac{\partial c}{\partial y}\right)^2=0. \tag{3}$$

Let us introduce the auxiliary function $u=e^{-zc_p}-e^{-zc}$ (where c_p is the concentration of metal in the bulk of the solution). This substitution transforms (3) into the simple expression:

$$\partial^2 u/\partial y^2=0 \tag{4}$$

or

$$u=Ay+B, \tag{5}$$

whose solution, under the condition that at the metal surface at $y=\delta$, $c=c_0$, and at the outer boundary at $y=0$, $c=c_p$, will be

$$c=c_p-\frac{1}{z}\ln\left[1-\frac{y}{\delta}\left(1-e^{-z(c_0-c_p)}\right)\right], \tag{6}$$

whence the current density to the anode (i) will be equal to:

$$i=nFD\left(\partial c/\partial y\right)_{y=\delta}=nFD_0e^{-zc_0}\left(\partial c/\partial y\right)_{y=\delta}=nFD_0\left(e^{-zc_p}-e^{-zc_0}\right)/z\delta \tag{7}$$

(n is the valence of the metal, F is the Faraday number). The last expression only at low concentrations passes into the Nernst equation for the flow through an immobile near-electrode diffusion layer. On the other hand, at metal concentrations at the electrode surface of the order of several moles and z of the order of 1 l/mol, the second term in (7) may be neglected as small. Then the expression for the limiting current (i) will be:

$$i\ =nFD_0\exp(-zc_p)/\delta z=i^*\exp(-zc_p), \tag{8}$$

where

$$i^*=nFD_0/\delta z \tag{9}$$

Fig. 1. Dependence of lg(η/η_0) (dashed line) and lg(i^*/i) (solid line) on the concentration of copper in H_3PO_4 (c_p) at 20°. 1—2.5; 2—5.0; 3—7.5; 4—10.0 mol/l H_3PO_4.

Figure 1: Fig. 1. Dependence of lg(η/η_0) (dashed line) and lg(i^*/i) (solid line) on the concentration of copper in H_3PO_4 (c_p) at 20°. 1—2.5; 2—5.0; 3—7.5; 4—10.0 mol/l H_3PO_4.

is the limiting current in pure acid. Here i no longer depends on the concentration of metal at the surface. What is essential is that, as experiment shows, solutions of H_3PO_4 containing copper possess a very high viscosity* and are prone to strong supersaturation; therefore, near the electrode surface at high current densities, owing to a number of uncontrolled factors, regions of different concentration may arise even under identical conditions. If one starts from the usual expression for the limiting current

$$i = nFD_0(c_0 - c_p)/\delta, \tag{10}$$

then extremely poor reproducibility should have been observed experimentally. The considerations given here remove these difficulties, since the only condition for the appearance of a limiting-current region becomes a high concentration of metal at the electrode surface, because the reason for its formation now lies in the compensating effect of the decrease in the diffusion coefficient with concentration on the growth of its gradient at the electrode surface.

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It follows from equation (7) that in one and the same acid solution there should be observed a linear dependence between ln(i^*/i) and the magnitude c_p. This dependence was checked experimentally (see Fig. 1). The measurements were carried out by a potentiostatic method at a temperature of 20° and a potential of 1.0 V versus the n.c.e., with a horizontal copper electrode enclosed in a viniplast capillary$^{(3)}$ (inner diameter 1 mm and depth $\delta = 0.5$ mm)**. Before each experiment the capillary parameters were restored with a special milling cutter. The systematic error in determining the depth capillary, introduced by spherical diffusion at the capillary outlet, is, according to our estimate, no more than 20%. As is seen from the figure presented, the

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* Thus, 7.5 M H_3PO_4 containing 2 moles of copper has a viscosity of 32.6 centipoise at 20°, while for 10 M acid at $c_p = 1.9$ mol/l, $\eta = 55.5$.

** The use of a deeper capillary was limited by the long time interval required to establish the stationary state. In our experiments it amounted to from 1.5 to 2.5 hours.

expected linear dependence is well confirmed. In agreement with the predictions of the theory, the values of z obtained for the same acid concentrations from the slopes of the curves $\lg(\eta/\eta_0) = f(c_p)$ and $\lg(i_\mathrm{n}^*/i_\mathrm{n}) = \psi(c_p)$ also coincide (see Table 1). On the basis of equations (7), (8) and the dependence of D on η, it follows that at high concentrations of H_3PO_4 the product should be constant

Table 1

$c_{H_3PO_4}$, mol/l	i_n^*, A/cm^2	z, l/mol at $c_p = 1$ mol/l, z_η	z, l/mol at $c_p = 1$ mol/l, z_i	η, centipoise	$i_\mathrm{n}^* z_\eta \eta$
2.5	$2.98 \cdot 10^{-2}$	0.32	–	2.32	$2.2 \cdot 10^{-2}$
5.0	$2.50 \cdot 10^{-2}$	0.57	0.55	4.35	$6.2 \cdot 10^{-2}$
7.5	$1.25 \cdot 10^{-2}$	0.62	0.64	7.93	$6.1 \cdot 10^{-2}$
10.0	$0.63 \cdot 10^{-2}$	0.64	0.67	15.08	$6.1 \cdot 10^{-2}$
12.5	$0.27 \cdot 10^{-2}$	1.74	–	31.21	$6.2 \cdot 10^{-2}$

$$i_\mathrm{n}^* z \eta = \mathrm{const.} \tag{11}$$

The last column of Table 1 gives the experimental values of these products. At acid concentrations above 5 mol/l the product remains constant.

Since at high concentrations the dependence of the equilibrium electrode potential on the concentration of the potential-determining ions cannot be established theoretically, for the case under consideration it was found experimentally. Potential measurements were carried out relative to a saturated calomel electrode at $t\,20°$ in H_3PO_4 solutions containing a definite amount of dissolved copper. Before the measurements began, the end electrode of an electrolytic copper rod 5 mm in diameter was subjected to 5-minute polishing at a potential of 1 V in the solution under study. In order to eliminate the effect of copper accumulation in the electrolyte as a result of electrode preparation, its final concentration* was determined after the potential measurement. The measurements were carried out in an air atmosphere, since special experiments performed in a nitrogen atmosphere established the absence of any effect of oxygen on the magnitude of the potential. The results of the determination are presented in Fig. 2. As is seen from the data given, in the range of H_3PO_4 concentrations of interest in electropolishing (2.5-10 mol/l), and of copper concentrations in solution from hundredths of a mole to 1.5-2 moles per liter, this dependence is rectilinear. The slope of the straight lines is 27-33 mV per tenfold change in concentration, which makes it possible to write for this case the concentra-

Fig. 2. Dependence of $\Delta\varphi_1$ on c_p (reference electrode—saturated calomel, $t\,20°$). 1—2.5; 2—5.0; 3—7.5; 4—10 mol/l H_3PO_4.

[*] Determination of Cu^{2+} was carried out by the iodometric method.

Fig. 2. Dependence of $\Delta\varphi_1$ on c_p (reference electrode—saturated calomel, $t\,20°$). 1—2.5; 2—5.0; 3—7.5; 4—10 mol/l H_3PO_4.

Figure 2: Fig. 2. Dependence of $\Delta\varphi_1$ on c_p (reference electrode—saturated calomel, $t\,20°$). 1—2.5; 2—5.0; 3—7.5; 4—10 mol/l H_3PO_4.

Fig. 3. Experimental and theoretical polarization curves for 7.5 mol/l H_3PO_4 (t $20.0 \pm 0.2°$). 1 —theoretical curve, 2 —experimental curve

Figure 3: Fig. 3. Experimental and theoretical polarization curves for 7.5 mol/l H_3PO_4 (t $20.0 \pm 0.2°$). 1 —theoretical curve, 2 —experimental curve

···of the concentration shift of the potential in the usual form, taking the valence of the metal in it to be 2:

$$\varphi = \varphi_0 + (RT/2F)\ln c. \tag{12}$$

Substitution of (7) and (8) into (12) gives a relation between the concentration polarization and the current density:

$$\Delta\varphi = \frac{RT}{2F}\ln\left[1 - \frac{1}{zc_\mathrm{p}}\ln\left(1 - \frac{i}{i_\mathrm{p}}\right)\right]. \tag{13}$$

For experimental verification of this expression it is convenient to take the half-wave potential as the origin. At small c_p, in the new reference system we finally obtain:

$$\Delta\varphi_{1/2} \simeq (RT/2F)\{\ln[-\ln(1 - i/i_\mathrm{p})] + 0.37\}. \tag{14}$$

Experimental verification of this equation was carried out with a potentiostat with linear automatic change of potential in time and simultaneous recording of the polarization curve (^{3}) in an electrolyzer of the design described.

Fig. 3. Experimental and theoretical polarization curves for 7.5 mol/l H_3PO_4 (t $20.0 \pm 0.2°$). 1 —theoretical curve, 2 —experimental curve

The rate of change of the potential was 0.41 mV/min, which ensured practically the establishment of a steady state at any point of the curve. Figure 3 shows an example of experimental and calculated polarization curves in 7.5 mol/l H_3PO_4. For comparison, the dashed line shows the curve obtained on the basis of the usual concentration concepts, corresponding to the expression:

$$\Delta\varphi_{1/2} = (RT/2F)[\ln(1 - i/i_\mathrm{p}) + 0.3].$$

Thus, experiments on the influence of the metal concentration on the magnitude of the limiting current and the good agreement between the theoretical and experimental polarization characteristics quite convincingly, in our opinion, confirm the proposed mechanism of concentration polarization with a variable diffusion coefficient for the behavior of copper in concentrated H_3PO_4 solutions.

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1. W. S. Elmore, *J. Appl. Phys.*, **10**, 724 (1939).
2. J. Edwards, *J. Electrochem. Soc.*, No. 7, 100, 189 (1953).
3. S. I. Krichmar, *ZhFKh*, **38**, No. 1, 239 (1964).

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