

# A Possible Mechanism For The Increase in Limiting Current of Copper Electrodeposition From Nitrate Solutions

A. V. Sokirko and Yu. I. Kharkats

UDC 541.138.3

The mutual influence of copper ion ( $\text{Cu}^{2+}$ ) deposition and  $\text{NO}_3^-$  ion reduction was analyzed theoretically while allowing for the possible formation of  $\text{Cu}(\text{OH})_2$ . The influence of  $\text{H}^+$  ion concentration on the rate of  $\text{Cu}(\text{OH})_2$  deposition was investigated.

Copper electrodeposition from acidified nitrate solutions was investigated experimentally in [1], and it was shown that the limiting current of copper deposition increases with increasing hydrogen ion concentration. In sulfate solutions the current of copper deposition is practically independent of solution pH. It was pointed out in [1, 2] as a possible explanation of the effect observed that it could be due to parallel  $\text{NO}_3^-$  ion reduction and interaction of the two processes through a mechanism of diffusion and migration coupling in reactant transport to and product transport away from the electrode.

In a series of papers [3-5] the mechanisms of the influence of  $\text{NO}_3^-$  ion reduction were theoretically analyzed for different possible reaction schemes in acidic solutions. It was shown in these papers that an influence of the concentration of  $\text{H}^+$  ions on copper deposition should be observed for different mechanisms of  $\text{NO}_3^-$  ion reduction. This influence could lead, both to an increase and to a decrease in the rate of copper deposition, but any acceleration of copper deposition should not be very important.

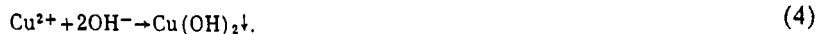
In the present work we consider the possibility that copper deposition and  $\text{NO}_3^-$  ion reduction occur in parallel according to the scheme of



At hydrogen ion concentrations in the solution which are not particularly high, the  $\text{H}^+$  ions which move from the bulk solution toward the electrode will undergo recombination with the  $\text{OH}^-$  ions which are produced in reaction (2) and move away from the electrode toward the bulk solution:



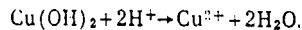
We shall assume that the  $\text{Cu}^{2+}$  ions, like the  $\text{H}^+$  ions, will react with the hydroxyl ions to form insoluble hydroxide:



At sufficiently high  $\text{H}^+$  and  $\text{Cu}^{2+}$  ion concentrations the regions where the homogeneous reactions take place will move right up to the electrode. We can say, therefore, that reactions (2) and (4) occur directly at the electrode surface, so that formally we can regard them as the consecutive steps [(2), (3) and (2), (4)] of the two parallel electrode reactions



It is necessary for reaction (6) to have a  $H^+$  concentration in the bulk solution which is high enough for reaction (3) to occur at the electrode surface. On the other hand, the  $H^+$  concentration should not be overly large, so that the reaction scheme of  $NO_3^-$  reduction would not change. The best experimental way of confirming the scheme of (1), (5), (8) would be the direct observation of  $Cu(OH)_2$ . We point out that in the experiments described in [1, 2] the substance  $Cu(OH)_2$  was not observed, since short galvanostatic pulses had been used. The current was made to flow in the system for a brief time interval which was sufficient for the formation of a certain quantity of  $Cu(OH)_2$ . During the pauses between current pulses the  $H^+$  ion concentration at the electrode goes up and the copper hydroxide dissolves:\*



As a result the three parallel reactions (1), (2), and (5) can occur at the electrode when current flows in the system. In the first reaction ordinary copper deposition occurs, while in the other two reactions [(2) and (5)] the  $NO_3^-$  ions are reduced, in one case in a process involving hydrogen ions, in the other case in a process involving the cations.

The system of electrodiffusion equations describing the reactions (1), (2), and (5) occurring in parallel at the electrode is given by the equations

$$\frac{dc_1}{dx} + 2c_1 \frac{d\Psi}{dx} = \frac{i_1 L}{2FD_1 c^0} + \frac{i_2 L}{2FD_1 c^0} = j_1, \quad (7)$$

$$\frac{dc_2}{dx} + c_2 \frac{d\Psi}{dx} = \frac{i_3 L}{FD_2 c^0} = j_2, \quad (8)$$

$$\frac{dc_3}{dx} - c_3 \frac{d\Psi}{dx} = \frac{i_2 L}{2FD_3 c''} + \frac{i_3 L}{2FD_3 c^0} = j_3, \quad (9)$$

$$\frac{dc_4}{dx} - c_4 \frac{d\Psi}{dx} = \frac{-i_2 L}{2FD_4 c^0} - \frac{i_3 L}{2FD_4 c^0}, \quad (10)$$

$$2c_1 + c_2 = c_3 + c_4, \quad (11)$$

Here the  $c_i$  are the dimensionless concentrations of the  $Cu^{2+}$ ,  $H^+$ ,  $NO_3^-$ , and  $NO_2^-$  ions (they have been made dimensionless through  $c^0$ , which is the  $Cu^{2+}$  concentration in the solution), the  $D_i$  are the corresponding diffusion coefficients,  $i_1$ ,  $i_2$ , and  $i_3$  are the current densities of reactions (1), (2), and (5), respectively,  $\Psi = FE/RT$  is the dimensionless potential,  $L$  is the thickness of the Nernst diffusion layer,  $F$  is the Faraday constant,  $x$  is the dimensionless coordinate ( $0 \leq x \leq 1$ ),  $j_1$ ,  $j_2$ , and  $j_3$  are the dimensionless fluxes of the corresponding components. Equation (11) describes the condition of local electroneutrality. We shall assume below for the sake of simplicity that the ions  $NO_2^-$  and  $NO_3^-$  have the same diffusion coefficient, i.e.,  $D_3 = D_4$ .

As boundary conditions in the system (7) to (11), we shall assume that the component concentrations at the diffusion-layer boundary ( $x = 1$ ) are given by the bulk concentrations, and that the potential is zero:

$$c_1(1) = 1, \quad c_2(1) = k, \quad c_3(1) = 2 + k, \quad c_4(1) = 0, \quad \Psi(1) = 0, \quad (12)$$

where  $k$  is the ratio of  $H^+$  and  $Cu^{2+}$  concentration in the stirred solution part.

We shall write the current densities  $i_{1,2,3}$  in terms of the  $j_{1,2,3}$  by using the definitions of the dimensionless fluxes (7) to (9):

$$i_1 = \frac{FD_2 c^0}{L} \left( 2 \frac{D_1}{D_2} j_1 + j_2 - 2 \frac{D_3}{D_2} j_3 \right), \quad (13)$$

$$i_2 = \frac{FD_2 c^0}{L} \left( 2 \frac{D_3}{D_2} j_3 - j_2 \right), \quad (14)$$

$$i_3 = \frac{FD_2 c^0}{L} j_2. \quad (15)$$

\*We point out that  $Cu(OH)_2$  has catalytic properties [6] toward the dissociation and recombination of water which may influence reactions (2), (3), and (5).

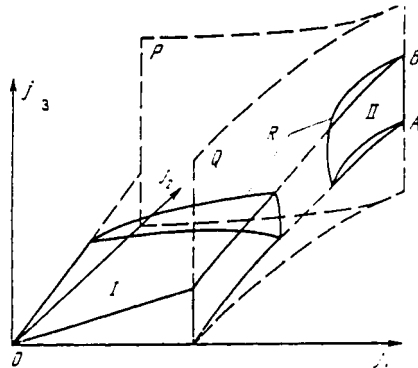


Fig. 1. Location of the regions admissible for a physical realization in the space of fluxes  $j_1, j_2, j_3$ . Line  $AB$  corresponds to the state of a totally limiting current;  $P$  is the surface corresponding to the condition of  $c_2(0) = 0$ ,  $Q$  is the surface corresponding to the condition of  $c_1(0) = 0$ , and  $R$  is the surface corresponding to the condition of  $c_3(0) = 0$ .

We notice that the ionic transport by diffusion and migration which is described by the system of Eqs. (7) to (11) allows, both for the mutual influence of the different component fluxes on account of migration and for the constraints imposed upon the component concentrations by the stoichiometries of reactions (1), (2), and (5).

We shall assume in order to more distinctly recognize the importance of the stoichiometric limitations that an excess of base electrolyte is present in the system, so that migration can be neglected ( $d\Psi/dx \approx 0$ ). In this case the concentration profiles of all components are linear, while the dimensionless fluxes observed in the limiting-current modes with respect to the corresponding components coincide with the values of the dimensionless concentrations of the same components in the bulk solution.

In the limiting case where the hydrogen ion concentration in the bulk solution is negligibly small the current of reaction (2),  $i_2$ , tends toward zero. The current of reaction (1),  $i_1$ , then becomes negative, formally, according to relation (13) and allowing for the fact that concentrations  $c_1(1)$  and  $c_3(1)$  are related through (11) and (12). Physically this is due to the fact that the  $\text{Cu}^{2+}$  ions cannot reach the electrode but instead enter reaction (3) before reaching the electrode. Reactions of this kind occurring within the diffusion layer have been analyzed in [5, 7]. The region where reaction (4) occurs moves closer to the electrode surface as the  $\text{H}^+$  ion concentration in the solution increases; starting from a certain  $\text{H}^+$  concentration the current  $i_1$  becomes positive (i.e., reaction (5) starts to occur at the electrode) and then increases linearly with increasing  $k$ , i.e., with increasing  $\text{H}^+$  concentration.

Thus, the increase in copper deposition current which occurs with increasing hydrogen ion concentration can lucidly be explained, in this specific case where an excess of base electrolyte is present, by noting that as the  $\text{H}^+$  ion concentration is raised, the rate of reaction (2) which consumes increasing amounts of  $\text{NO}_3^-$  ions goes up, and as a result reaction (5) becomes slower. Then the consumption of copper in reaction (5) decreases, and hence a higher rate of copper deposition in reaction (1) becomes possible.

Under conditions where excess base electrolyte is present, relations (13) to (15) can be used for a theoretical calculation of the limiting currents of reactions (1), (5), and (6), the rates of which can be measured experimentally. The system of electrodiffusion Eqs. (7) to (11) with boundary conditions (12) was solved in [4], where functions  $c_l(x)$  were obtained in a parametric form, while function  $\Psi(x)$  was obtained in an implicit form.

In the system of three electrode reactions (1), (2), and (5) considered here, limiting currents can basically be attained for each of the components  $c_1, c_2$ , and  $c_3$ . Each of the conditions

$$c_l(0) = 0, \quad l = 1, 2, 3 \quad (16)$$

imposes a certain constraint on the admissible dimensionless reaction currents  $I_l = i_l L / F D_2 c^0$  and dimensionless fluxes  $j_l$ .

Each of the conditions (16) corresponds to a certain surface in the three-dimensional space of  $j_1 \geq 0, j_2 \geq 0, j_3 \geq 0$ , while the region bounded by these surfaces corresponds to all reaction modes below the limit, where  $c_1(0) > 0$ . The curve of intersection of two surfaces corresponding to the conditions of  $c_m(0) = 0$  and  $c_n(0) = 0$  corresponds to the conditions of limiting currents with respect to two components simultaneously. We point out that when the conditions for limiting currents with respect to components 1 and 2 are fulfilled simultaneously, i.e., when  $c_1(0) = 0$  and  $c_2(0) = 0$ ,

we also have  $c_3(0) = 0$  and  $c_4(0) = 0$  owing to the electroneutrality condition; this corresponds to the mode of "totally limiting current". Additional limitations as to the region where the process will occur in a steady manner follow from the conditions of  $I_1 \geq 0$ , which as we can readily see yield the inequalities of  $j_1 \geq 0$ .

Using solutions of the system of (7) to (11) of [4] we can write the conditions  $c_1(0) = 0$  and  $c_2(0) = 0$  parametrically as

$$j_1 = \left\{ 3 + 2k - 2(2+k) \left[ \frac{2k-3J}{4+2k} \right]^{\frac{2+J}{4+3J}} \right\} / (1+J) \quad (17)$$

and

$$j_2 = \left\{ 3 + 2k - 1.5(2+k) \left[ \frac{3J-2k}{1.5J(2+k)} \right]^{\frac{2+J}{4+3J}} \right\} / (1+J), \quad (18)$$

respectively, where  $j_2 = Jj_1$ . The surfaces defined by Eqs. (17) and (18) in the space of  $j_1, j_2, j_3$  are cylindrical (they are independent of the value of  $j_3$ ), and intersect along a vertical straight line of  $j_1 = 3, j_2 = 2k$  (Fig. 1).

The region beneath the plane the equation of which follows from (13):

$$j_3 = j_1/\eta + j_2/\nu, \quad (19)$$

corresponds to the condition of  $I_1 \geq 0$ , in the space of  $j_1, j_2, j_3$ ; here  $\eta = D_3/D_1$  and  $\nu = 2D_3/D_2$ . The region beneath the plane the equation of which follows from (14):

$$j_3 = j_2/\nu, \quad (20)$$

corresponds to the condition of  $I_2 \geq 0$ , in the space of  $j_1, j_2, j_3$ . Finally,  $j_2 \geq 0$  corresponds to the condition of  $I_3 \geq 0$ . The conditions reported define a wedge-shaped region with two curved walls (Fig. 1).

The surface defined by the condition of  $c_3(0) = 0$  is that which has the most complicated shape. It can be described parametrically in terms of the relations

$$j_1 = A(1 - e^{\Psi_0}) + B(1 - e^{\lambda\Psi_0}), \quad (21)$$

$$j_2 = Jj_1, \quad (22)$$

$$j_3 = \frac{(2+k)j_1}{B \frac{\lambda}{\lambda-1} (1 - e^{(\lambda-1)\Psi_0}) - A\Psi_0}, \quad (23)$$

where

$$A = \frac{6(2+k)}{4+3J}, \quad B = \frac{2k-3J}{(4+3J)(1+J)}, \quad \lambda = -\frac{2(1+J)}{2+J}, \quad (24)$$

and where  $J$  and  $\Psi_0$  serve as the variable parameters ( $0 < J < \infty$  and  $-\infty < \Psi_0 < 0$ ).

An investigation shows that the surface of  $c_3(0) = 0$  intersects the wedge-shaped region in a complicated way, so that the resulting region of admissible fluxes  $j_1, j_2$ , and  $j_3$  which will satisfy all of the six conditions of  $c_l(0) \geq 0$  and  $I_l \geq 0$  ( $l = 1, 2, 3$ ) listed above generally is doubly connected (Fig. 1). We point out that the existence of doubly connected regions of admissible fluxes (or currents) had been demonstrated for the case of two parallel electrode reactions in [4]. The region where a steady state of reactions (1), (2), and (5) can physically be realized with monotonically rising currents  $I_1, I_2$  and  $I_3$  or fluxes  $j_1, j_2$  and  $j_3$  corresponds to the region  $I$  abutting the coordinate origin in Fig. 1.

The admissible regions undergo deformation when the hydrogen ion concentration in the bulk solution is raised, i.e., when parameter  $k$  increases. It follows from relations (17) and (18) that this deformation first of all consists in an extension of the wedge-shaped region along the axis of  $j$ , and increasing distance between the sections of surfaces  $c_2(0) = 0$  and  $c_3(0) = 0$  which are within the wedge-shaped region and constitute the boundaries of region  $I$ . This should lead to an increase in limiting reduction current  $i_1$  with increasing  $H^+$  ion concentration.

In the particular case of a totally limiting current with respect to all three sorts of ions, of  $c_1(0) = c_2(0) = c_3(0)$ , which corresponds to segment AB in Fig. 1, the dependence of  $I_1$  on  $k$  is given by the relation

$$I_1 = 3/\eta + 2k - j_3/\nu.$$

where  $2k \leq j_3/\nu \leq 3/\eta + 2k$ .

Thus, the above analysis has shown that effects which in their nature are similar to a migration current exaltation should be realized in the system being discussed. It is a special feature of the processes discussed that a "competitive exaltation" of the currents takes place here: the current of copper deposition increases with increasing concentration (or flux) of the hydrogen ions involved in  $\text{NO}_3^-$  ion reduction, and in this way the rate of reaction (5) is reduced.

The increase in limiting current of copper deposition which in [1, 2] was found to occur with increasing  $\text{H}^+$  concentration can be explained qualitatively on the basis of above analysis. It would be desirable for a quantitative verification of the theory developed, to set up an experiment in excess base electrolyte where all reaction products are monitored.

#### LITERATURE CITED

1. Yu. Ya. Gurevich, M. I. Donchenko, T. I. Motronyuk, A. V. Sokirko, and Yu. I. Kharkats, *Elektrokhimiya*, **25**, 784 (1989).
2. L. I. Antropov, M. I. Donchenko, and T. I. Motronyuk, in: Abstracts of Papers, Seventh All-Union Conference on Electrochemistry [in Russian], VINITI, Moscow (1988), Vol. 1, p. 246.
3. A. V. Sokirko and Yu. I. Kharkats, *Elektrokhimiya*, **25**, 1299 (1989).
4. A. V. Sokirko and Yu. I. Kharkats, *Elektrokhimiya*, **25**, 1306 (1989).
5. A. V. Sokirko and Yu. I. Kharkats, *Elektrokhimiya*, **26**, 36 (1990).
6. V. I. Zabolotskii, N. V. Shel'deshov, and N. P. Gnusin, *Usp. Khim.*, **57**, 1403 (1988).
7. A. V. Sokirko and Yu. I. Kharkats, *Elektrokhimiya*, **25**, 34 (1989).