

# THE ELECTROLYTIC REDUCTION OF COPPER ON A DISC-RING ELECTRODE

L. N. Nekrasov and N. P. Berezina

M. V. Lomonosov Moscow State University

(Presented by Academician A. N. Frumkin, September 27, 1961)

Translated from Doklady Akademii Nauk SSSR, Vol. 142, No. 4,  
pp. 855-858, February, 1962

Original article submitted September 22, 1961

An examination of the chemical literature reveals that the reduction of cupric ions to copper metal on a dropping mercury electrode may proceed by various routes depending on the composition of the solution [1]. The reduction of simple  $\text{Cu}^{++}$  ions in a solution of inert electrolytes which do not form copper complexes yields a single polarographic wave representing a two-electron transfer process,



If the solution contains ligands capable of forming stable complexes with  $\text{Cu}^{++}$  and  $\text{Cu}^+$  ions, or with  $\text{Cu}^+$  only, the polarization curve will exhibit two waves, each one representing the addition of a single electron



In this case the cuprous ion represents a reaction intermediate which is stable in the region of the first wave but unstable in the region of the second. It would seem reasonable that even in the absence of complexing agents the reduction should proceed in two stages and the fact that only one wave is observed might be due to the instability of  $\text{Cu}^+$  ions in such solutions within the investigated range of potentials. One piece of indirect evidence in favor of this explanation comes from the observation that as the concentration of  $\text{Cl}^-$  ions in a solution containing  $\text{Cu}^{++}$  ions is decreased the two reduction waves approach each other and merge into one when the chloride concentration drops to 0.02 N [2].

Consequently it seemed worthwhile to investigate the mechanism of electrolytic reduction of cupric ions in a sodium sulfate solution in order to find some direct evidence for the formation of cuprous copper as an unstable reaction intermediate. To solve this problem we used the previously described [3] revolving disc electrode surrounded by a ring; this apparatus constitutes a unified mechanical system consisting of two electrically independent electrodes, a disc and a concentric ring, lying in the same plane and separated by a thin insulating band. In addition to this, study of the reduction of cupric chloride enabled us to get additional experimental support for the theoretical relationships derived by Yu. B. Ivanov and V. G. Levich for a ring-disc electrode [4].

According to Ivanov and Levich if no reaction takes place in the bulk of the solution the current on a ring electrode  $I_K$  will be given by the equation

$$I_K = \frac{0.8 [1 - 0.75 (r_1/r_2)^3] I_A}{1 + k\delta_B/D_B} \frac{n_B}{n_A} \int_1^{r_3/r_2} \frac{x^2 dx}{(x^2 - 1)^{1/2} [x^3 - 0.75 (r_1/r_2)^3]}, \quad (4)$$

where  $I_A$  is the current on the disc electrode limited by the diffusion of the reactant to the disc;  $r_1$  is the radius of the disc;  $r_2$  and  $r_3$  are the inside and the outside radii of the ring;  $k$  is the rate constant for the conversion of the intermediate to the final product on the disc electrode;  $D_B$  is the diffusion coefficient of the reaction intermediate;  $\delta_B$  is the width of the phase boundary diffusion layer of the intermediate;  $n_A$  and  $n_B$  give the number of electrons

involved in reactions on the disc and the ring electrodes, respectively. Combining all the parameters dependent on the electrode geometry into a coefficient  $N$  we get

$$I_K = \frac{n_B}{n_A} \frac{NI_A}{1 + k\delta_B/D_B} \quad (5)$$

Equation (5) can also be converted into another form [3]:

$$I_K = Nn_B F \frac{D_B c_B^S}{\delta_B} = N \frac{n_B}{n_A} I_A \left( \frac{D_B}{D_A} \right)^{1/2} \frac{c_B^S}{c_A^0 - c_A^S}, \quad (6)$$

where  $c_B^S$  is the concentration of the reaction intermediate at the disc surface at the given potential;  $c_A^0$  and  $c_A^S$  are the bulk and surface concentration of the starting material;  $D_A$  is the diffusion coefficient of the same material;  $F$  is Faraday's number.

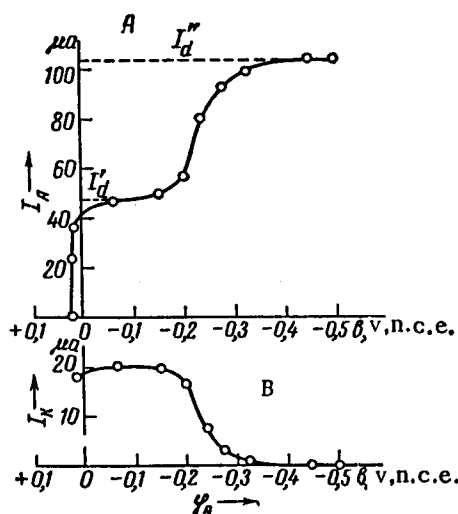


Fig. 1. A) The polarization curve for the reduction of  $\text{Cu}^{++}$  ions on a gold-amalgam disc cathode in a  $5 \cdot 10^{-4} \text{ N CuSO}_4 + 1 \text{ N KCl}$  solution ( $m = 5200 \text{ rpm}$ ); B) the corresponding limiting  $\text{Cu}^+$  oxidation current on the ring electrode plotted as a function of the disc electrode voltage.

On our experiments the limiting current for the oxidation of the cuprous ions formed in the reduction of  $\text{Cu}^{++}$  ions on the disc electrode was measured on a gold ring electrode. Measurements were done under nitrogen at  $21 \pm 1^\circ \text{C}$  on electrodes revolving at rates ranging from 900 to 9000 rpm.

Figure 1 shows the polarization curve for the reduction of  $\text{Cu}^{++}$  in a solution of  $5 \cdot 10^{-4} \text{ N CuSO}_4 + 1 \text{ N KCl}$  on a gold amalgam disc cathode (A) and the corresponding curve of the limiting current for the oxidation of cuprous ions on the ring as a function of the disc electrode voltage (B).

From data obtained through such measurements one can evaluate the coefficient  $N$  in Equation (5). A precise determination of  $N$  requires that the current recorded on the ring electrode be corrected for the background current, which is determined under conditions where no  $\text{Cu}^+$  ions are formed on the disc electrode—in general this means when  $I_A = 0$ . If however an amalgamated electrode is used cuprous ions may form at the surface of the disc even in the absence of a polarization current on account of a reaction involving the mercury which then dissolves,

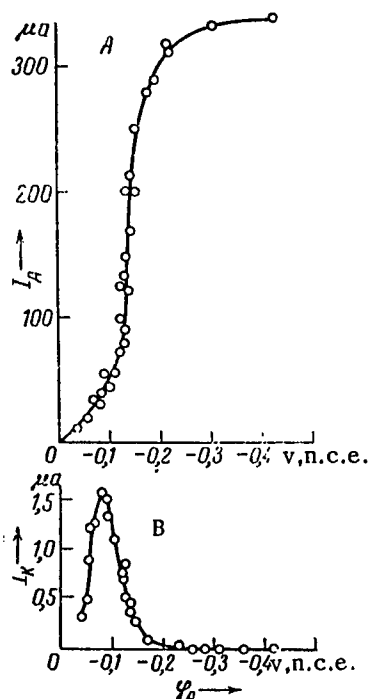
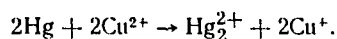


Fig. 2. A) The polarization curve for the reduction of  $\text{Cu}^{++}$  ions on a platinum disc cathode in a  $3 \cdot 10^{-2} \text{ N CuSO}_4 + 1 \text{ N Na}_2\text{SO}_4$  solution ( $m = 2150 \text{ rpm}$ ); B) the corresponding  $\text{Cu}^+$  oxidation current on the ring electrode plotted as a function of the disc electrode voltage.



(7)

As a result even when  $I_A = 0$  an appreciable current will be recorded on the ring electrode.

These complications can be eliminated either by the use of an unamalgamated gold disc or by measuring the background current on the ring under conditions where the current on the gold amalgam disc electrode is equal to the second limiting current on the cathode curve ( $I_A = I_d^*$ ) and the surface concentration  $[\text{Cu}^+]_s$  is essentially zero.

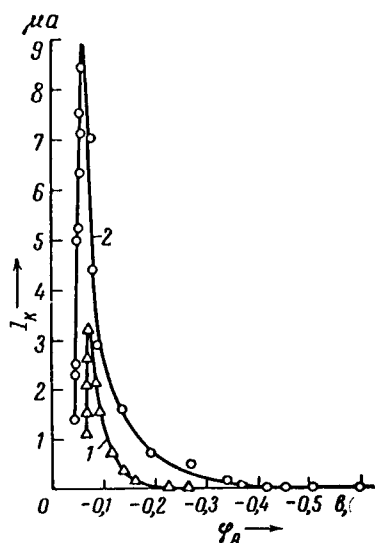


Fig. 3. The limiting current in the oxidation of  $\text{Cu}^+$  ions on a ring electrode (sulfate solutions) as a function of the disc electrode voltage;  $\text{CuSO}_4$  conc.: 1)  $3 \cdot 10^{-2}$  N; 2)  $3 \cdot 10^{-1}$  N (n.c.e.).

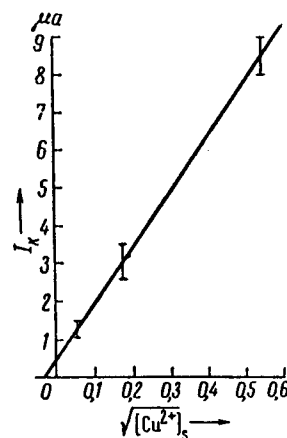


Fig. 4. The limiting current on the ring electrode as a function of the square root of the surface concentration of  $\text{Cu}^{2+}$  in sulfate solutions.

For an electrode with the dimensions:  $r_1 = 0.25$  cm,  $r_2 = 0.276$  cm, and  $r_3 = 0.359$ , and rotating at velocities below 5000 rpm, we got a coefficient  $N = 0.415 \pm 0.01$ , which is a slight improvement over the value obtained before (0.38 [3]) and is in good

agreement with the theoretical value of 0.41-0.42 calculated from Eq. (4); one has to allow for a probable uncertainty of 5% due to the approximate nature of Equation (4). At higher rotational velocities turbulent flow tends to reduce the value of  $N$  a little (at  $m = 7200$  rpm  $N = 0.36$ ).

In Fig. 2A we have plotted the polarization curve for the reduction of  $\text{Cu}^{2+}$  on a rotating platinum disc electrode in a  $3 \cdot 10^{-3}$  N  $\text{CuSO}_4 + 1$  N  $\text{Na}_2\text{SO}_4$  solution. As in the case of the dropping mercury electrode the curves exhibit only one wave. In Fig. 2B, where the current on a ring anode at a potential  $\phi_K = 0.4$  v (n.c.e.) is plotted against the disc voltage  $\phi_A$ , one can see that in a certain range of disc voltages a non-zero current is detected on the ring which at first increases with increasing  $\phi_A$ , attains a maximum, and drops to zero. The fact that a current does flow through the ring indicates that the reduction taking place on the disc electrode produces an intermediate product which can undergo oxidation and which could not under the circumstances be anything else but a cuprous ion. As additional evidence we might point out that the polarization curve for the oxidation of this intermediate on a gold ring electrode exhibits the same characteristics as the corresponding curve for the oxidation of  $\text{Cu}^+$  in a KCl solution. A tenfold increase in the concentration of cupric ion raises the peak on the ring curve by a factor of 2.5-3 (Fig. 3). In a sodium sulfate solution free of copper ions the ring current within the same range of potentials does not exceed the background current.

Thus it is possible to detect the cuprous ions formed during the reduction of cupric sulfate on a disc electrode.

The concentration of cuprous ions on the surface of the disc will depend on the reversibility of the reaction in which the second electron is taken up, Eq. (3). Should this reaction be irreversible the  $[\text{Cu}^+]_s$  will exceed the equilibrium concentrations. In such cases the rate constant  $k$  can be readily determined from Eq. (5). But if the reaction is reversible we will have a  $[\text{Cu}^+]_s$  equal to the equilibrium concentration, which can be determined from the Nernst equation.

The 58 mv region within which the ring curve descends sharply and the shape of the ring current vs.  $[\text{CuSO}_4]$  curve provide evidence for the reversibility of reaction (3). Equation (6) shows that the oxidation of  $\text{Cu}^+$  ions on the ring should yield a current proportional to the surface concentration  $[\text{Cu}^+]_s$ . The experimentally determined maximum ring currents were approximately proportional to  $[\text{Cu}^{2+}]_s^{0.5}$  (Fig. 4), which agrees with what one would expect from the law of mass action  $[\text{Cu}^+]_s = \sqrt{K [\text{Cu}^{2+}]_s}$ , (8), where  $K$  is the equilibrium constant.

When the surface concentration  $[\text{Cu}^+]_s$  measured on a disc-ring electrode at a voltage which would maintain a disc current of 0.1  $I_d([\text{Cu}^{2+}]_s = 0.27 \text{ N})$  is compared with the value determined under similar conditions from the limiting  $\text{Cu}^+$  oxidation current on a disc electrode in a solution in which a thermodynamic equilibrium has been established between  $\text{Cu}^{++}$ ,  $\text{Cu}^+$ , and  $\text{Cu}^0$  ( $[\text{Cu}^{++}]_0 = 0.27 \text{ N}$ ) one finds that the former is 2.8 times greater than the latter. The difference, though, is relatively small. Hence if all these factors are taken into consideration one has to conclude that the investigated reaction step is reversible but the copper deposited on the electrode surface is in a slightly activated state. That problems involved in the growth of the crystal lattice may have something to do with this effect [5] can be deduced from the fact that the surface concentration  $[\text{Cu}^+]_s$  on a copper-plated disc electrode declines with time after the polarization is terminated. Mattson and Bockris likewise concluded in their work [6] that the step discussed above is reversible.

The rise on the  $I_K = f(\varphi_A)$  plot (Fig. 2B and 3) is caused by the irreversible reduction of  $\text{Cu}^+$  on a platinum disc surface which has not as yet become plated with copper. The very sharpness of the rise can be explained as follows: at low current densities copper is deposited only on individual activated portions of the platinum electrode [7], and also the reaction initially proceeds at very high overvoltages. The formation and expansion of copper-plated sites greatly increase the rate of the  $\text{Cu}^+ \rightleftharpoons \text{Cu}^0$  process.

An electrode freshly plated with copper fails to yield a rise on the polarization curve thus providing additional evidence for the reversibility of the cuprous ion reduction reaction.

The authors wish to express their deep gratitude to Acad. A. N. Frumkin for his comments on the results.

#### LITERATURE CITED

1. I. M. Kolthoff and J. J. Lingane, Polarography [Russian translation], M., 1948, p. 182.
2. M. Stackelberg and H. Freyhold, Zs. Elektrochem., 46, 120 (1940).
3. A. N. Frumkin and L. N. Nekrasov, DAN 126, 115 (1959); A. Frumkin, L. Nekrasov, V. Levich, and Ju. Ivanov, J. Electroanalytical Chem., 1, 84 (1959).
4. Yu. B. Ivanov, and V. G. Levich, DAN 126, 1029 (1959).
5. M. Lorenz, Zs. phys. Chem., N. F., 19, 25 (1959); H. Gerischer, Electrochim. Acta, 2, 1 (1960); H. Seiter, H. Fischer, and L. Albert, Electrochim. Acta, 2, 97 (1960).
6. E. Mattson and J. O'M. Bockris, Trans. Farad. Soc. 55, 1586 (1959).
7. P. Y. Hillson, Trans. Farad. Soc. 50, 385 (1954).

---

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

---