

# OVERVOLTAGE IN THE ELECTRODEPOSITION AND SOLUTION OF METALS

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The systematization of metals according to the rate of reduction of their ions and ionization of the atoms is one of the fundamental problems of electrochemistry. The first attempts at the systematization of metals with respect to the overvoltage value were made by Frölich and Klark in 1925 [1]. According to Frölich and Klark there is a definite relation between the overvoltage of the liberation of hydrogen and the metal. The greater the overvoltage of hydrogen liberation on the given metal, the smaller is the overvoltage of the metal itself.

Increase in hydrogen overvoltage  
 Pd, Pt, Ni, Co, Fe, Zn, Cu, Au, Ag  
← Increase in metal overvoltage

In 1934, Fol'mer [2] suggested the division of metals into three groups according to the difficulty of their electrochemical reduction: Hg, Pb < Zn, Cd, Cu, Ag < Fe, Co, Ni. By comparing the interaction factor of Antropoff [4] with the liberation overvoltage, Ioffe [3] came to the conclusion that metals should be arranged in the following sequence with respect to overvoltage: Pb, Cd, Sn, Zn, Ag, Cu, Au, Co, Ni, Fe, Cr, Pt. Ioffe considered that the greater the hardness of the metal, the higher should be its overvoltage. Piontelli [5] showed that the order of metals with respect to their overvoltage will differ, depending on the nature of the salts used for the electrodeposition of the metals.

The most thorough work on the systematization of metals with respect to overvoltage is that of Antropov [6]. The author associated the reason for the different overvoltage of a series of metals with the electrocapillary zero points and considered that the magnitude of the observed overvoltage of metals during the reduction of their ions on an electrode and consequently the degree of hindrance to separation are caused by the change in the charge of the electrical double layer. The normal potential of a metal, expressed on the electrocapillary zero scale, is thus determined in the following way:

$$\varphi_0 = \epsilon^0 - \epsilon_{q=0},$$

where  $\epsilon^0$  is the normal potential of the system and  $\epsilon_{q=0}$  is the electrocapillary zero potential, expressed on the hydrogen scale. The values of  $\varphi_0$  for various metals are given in Table 1.

Antropov considered that if  $\varphi_0 > 0$ , the surface of the cathode is positively charged and attracts anions, as a result of which the metal is reduced readily. If  $\varphi_0 < 0$ , the cathode surface is negatively charged and cations are adsorbed on it so that the reduction of the metal is strongly hindered.

It should be noted that some experimental data are clearly contradictory to this point of view. Thus, the separation of metals of the iron group on mercury should be considerably facilitated as its surface is positively charged and, according to Antropov, negatively charged ions concentrate at the mercury surface on the solution

TABLE 1

|                              | Ni    | Fe    | Co    | Zn    | Cu    | Bi    | Sn    | Cd    | Pb    | Tl    | Ag    | Hg    |
|------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $\epsilon^0$                 | -0,23 | -0,44 | -0,27 | -0,76 | 0,34  | 0,20  | -0,14 | -0,40 | -0,13 | -0,34 | 0,799 | 0,798 |
| $\epsilon_{q \rightarrow 0}$ | 0,00  | -0,37 | —     | -0,63 | -0,12 | -0,40 | -0,34 | -0,74 | -0,69 | -0,76 | -0,05 | -0,21 |
| $\varphi_0$                  | 0,23  | -0,07 | —     | -0,13 | 0,22  | 0,60  | 0,2   | 0,34  | 0,56  | 0,42  | 0,8   | 1,00  |

side and facilitate the discharge of cations. However, as experiments in [7] showed, the reduction of metals of the iron group on a mercury cathode proceeds with much more difficulty than the separation of these metals on like electrodes. An analogous contradictory result is observed during the electrodeposition of silver. Thus, according to recent data [8], the electrocapillary zero of a silver surface is displaced in a negative direction by -0.6-0.7 v relative to a hydrogen electrode. According to Antropov's opinions, positively charged ions should be adsorbed at the electrode surface, strongly hindering the reduction of silver ions. However, as experimental investigations show, in the separation of silver from solutions of simple silver salts, hardly any overvoltage is observed.

From the data presented by various authors it follows that together with the general accuracy of the arrangement of metals with respect to overvoltage, there are also some substantial discrepancies. For an accurate assessment of the position of metals in the overvoltage series it is obviously necessary to have quantitative data obtained under comparable experimental conditions. A series of essential difficulties are encountered in obtaining such data. The most important of these are as follows: 1. Difficulties associated with the deposition of different metals from the same solutions in order to exclude the effect of anions on the electrolysis process. The electrodeposition of such metals as Ag, Cr, and Fe is carried out from solutions of different salts. It should be noted that to obtain high-grade deposits of a number of metals, even from the same salts, various additives are used and this makes it difficult to carry out investigations under comparable experimental conditions. 2. In the determination of the polarization of metals, the concentration polarization is eliminated to different extents (Sn, Cu, Ni, Cd, Tl, Ag.) 3. In the electrodeposition of a number of metals, the structures of the deposits and hence the true current densities are different, which also hampers the comparison of the results obtained. In the deposition of such metals as Cr, Mn, etc., high apparent current densities are used, while for others (Ag, Tl, and Sn,) low apparent current densities are used. 4. In the electrodeposition of some metals, hydrogen is liberated simultaneously and under the conditions where high-grade deposits are obtained, the current yields of metal are quite different. For example, in the electrodeposition of chromium, the current yield of metal is 8-12%, for iron, 70-80%, and for copper, 100%. 5. In the measurement of polarization by different methods, the potential drop between the cathode and the end of the capillary of the auxiliary electrode is allowed for, to different extents. In addition, the use of different designs of electrolytic cells and electrodes produces a nonuniform distribution of current on the electrode surface and consequently a different degree of error in the polarization measurement, depending on the section where the measurement is made.

#### EXPERIMENTAL

In connection with what has been stated, it is hardly possible to arrange metals in a series with respect to overvoltage on the basis of data presented in the literature by different authors. To obtain quantitative data on the overvoltage in the separation of metals under comparable experimental conditions, we studied the electrodeposition of nickel, cobalt, iron, copper, zinc, cadmium, thallium, and tin from 1 N sulfate solutions in an electrolytic cell of special design. All measurements were made by a rapid method to eliminate concentration polarization and to determine only the chemical component of polarization.

Fig. 1 shows an oscillogram of polarization curves plotted at different speeds during the electrodeposition of iron. The polarization of the cathode and anode are plotted on the ordinate axis and the current density on the abscissa. As the curves show, the polarization did not change substantially with plotting at different speeds. The latter indicates that in the given case the supply of substance to the electrode was not the limiting stage of the process. With an increase in the plotting rate of the polarization curve, there was some displacement to the right, which did not lead to an appreciable change in the polarization. Figure 2 shows polarization curves

TABLE 2

| Current density in ma/cm <sup>2</sup> | Overvoltage in mv | Ni  | Co  | Fe  | Cu  | Zn  | Cd | Tl   | Sn |
|---------------------------------------|-------------------|-----|-----|-----|-----|-----|----|------|----|
| 15                                    | — $\varphi_c$     | 613 | 238 | 161 | 58  | 50  | 18 | 11,5 | 11 |
|                                       | + $\varphi_a$     | 161 | 94  | 80  | 33  | 32  | 15 | 11   | 5  |
| 20                                    | — $\varphi_c$     | 662 | 255 | 202 | 86  | 64  | 23 | 17   | 16 |
|                                       | + $\varphi_a$     | 291 | 128 | 91  | 46  | 40  | 17 | 20   | 8  |
| 50                                    | — $\varphi_c$     | —   | —   | —   | 133 | 100 | 40 | 28   | 17 |
|                                       | + $\varphi_a$     | —   | —   | —   | 72  | 80  | 37 | 51   | 11 |

plotted at different rates for the electrodeposition of zinc. With a slow plotting rate (curve 1,) the polarization was considerably higher than with a high plotting rate (curves 2 and 3) and this was due to concentration polarization [9].

Experimental data on cathode and anode overvoltages of different metals, obtained from analogous oscillograms, are given in Table 2. The polarization was obtained from curves plotted at 8.3 cm/sec.

The experimental data obtained (Table 2) show, first of all, that cathode polarization is higher than anode polarization and the rate of reduction of metals from 1 N sulfate solutions at identical overvoltages increases in the following order: Ni, Co, Fe, Cu, Zn, Cd, Tl, Sn. The rate of anode solution of metals increases in the series: Ni, Co, Fe, Cu, Zn, Cd, Tl, Sn. These data show that if the cathode reduction of metal ions proceeds at a high rate, then the ionization of the metal atoms also proceeds at a high rate.

The rule given for the rate of reduction of metal ions may be explained on the basis of the crystallization theory developed by Frenkel' [10] and Burton, Cabrera, and Frank [11], in which it was shown that as a result of the thermal motion of atoms, at the actual face of a crystal there appears a different sort of crystallographically active zone, whose growth requires lower supersaturation than for the growth of an ideal planar crystal face. From this theory it follows that for metals with a high melting point, the probability of such active zones arising will be lower than for metals with a low melting point. On the basis of these concepts it may be considered that the rate of reduction of metal ions on active centers of a crystal will be much greater than on the other parts of its surface and therefore there should be a definite parallelism between the overvoltage of the separation of metals and their melting point.

TABLE 3

| Metal       | Ni   | Co   | Fe   | Cu   | Zn  | Cd  | Tl  | Sn  |
|-------------|------|------|------|------|-----|-----|-----|-----|
| M. p. in °C | 1455 | 1496 | 1535 | 1083 | 419 | 320 | 303 | 232 |

A comparison of the melting points of metals (Table 3) with the overvoltage shows that this parallelism is well fulfilled for metals with a low separation overvoltage. A certain discrepancy is observed in the positions of nickel, cobalt, and iron and this may be caused by the inaccuracy in the determination of the equilibrium potential, relative to which the overvoltage was measured.

In a number of studies [12] of the elementary act of metal ion discharge it was shown that on active zones of the electrode surface the process proceeds very rapidly without appreciable polarization, while on passive zones the reduction rate is much less. Since the separation of a metal on a passive surface is hindered, it may be considered that the considerable retardation of the discharge and ionization of metals with a high melting point is connected with their passivation.

Antropov [6] demonstrated the existence of a relation between the magnitude of exchange currents and the overvoltage of metal separation. The existence of this relation naturally may be explained by the tendency

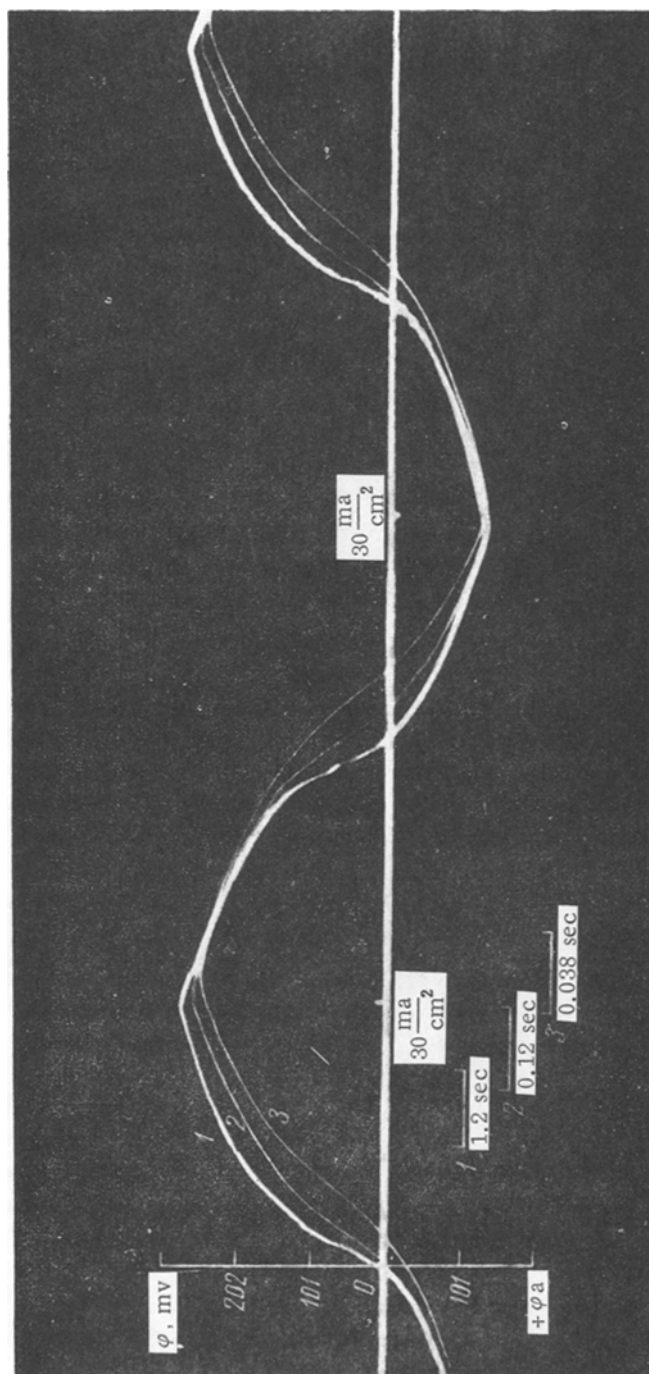


Fig. 1. Oscillogram of a polarization curve plotted during the electrodeposition and solution of iron: 1 N  $\text{FeSO}_4$ ; pH 2.5;  $i_{\text{max}} 30 \text{ ma/cm}^2$

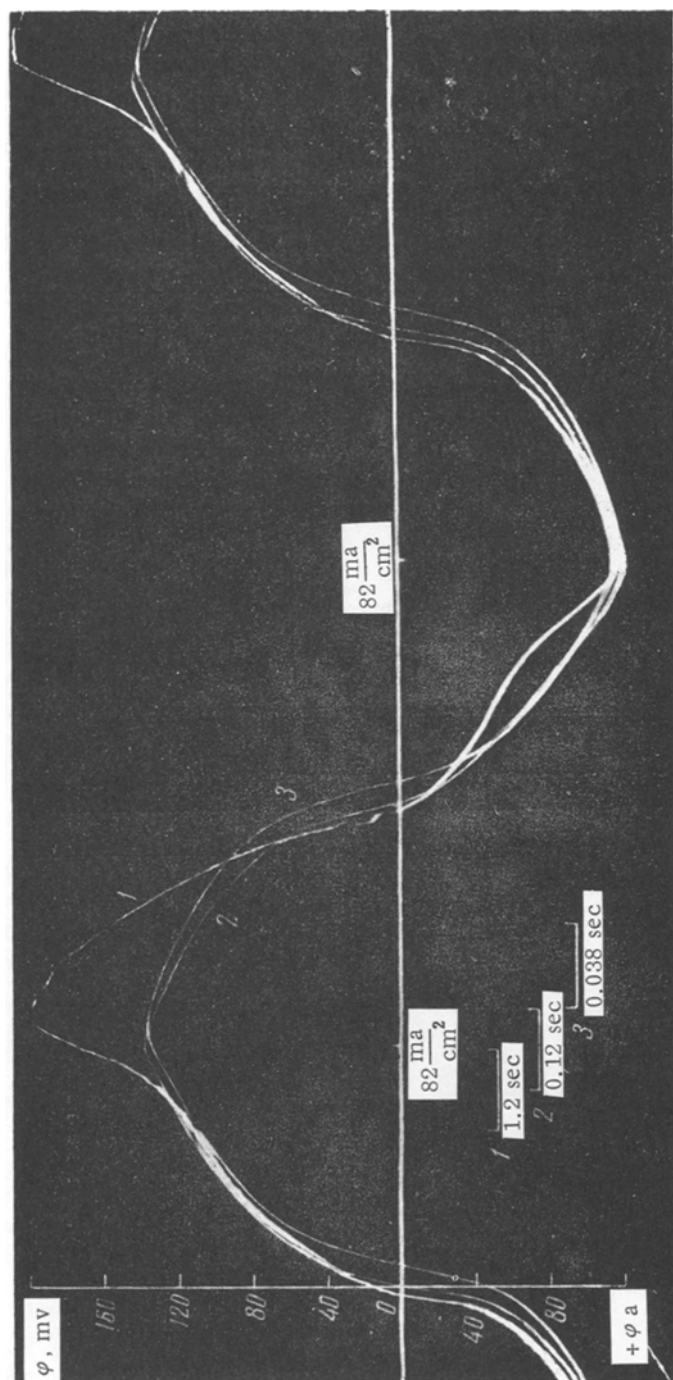


Fig. 2. Oscillogram of a polarization curve plotted during the electrodeposition and solution of zinc: 1 N  $\text{ZnSO}_4$ ; pH 3.8;  
 $I_{\text{max}} 82 \text{ ma}/\text{cm}^2$

of metals for passivation. Obviously, on a passive metal surface the exchange current will be less than on an active metal surface, which is in agreement with the point of view presented above.

In conclusion, it may be pointed out that the observed parallelism between the overvoltage, melting point, and tendency of metals for passivation in all probability is connected with the fact that the forces impeding the evaporation or movement of metal atoms and decreasing the number of active centers on the crystal surface also increase the adsorption of foreign particles and thus promote passivation of the metal surface.

#### SUMMARY

1. The rate of reduction of metal ions from 1 N sulfate solutions increases in the following order: nickel, cobalt, iron, zinc, copper, cadmium, thallium, and tin.
2. The rate of anode solution increases in the series: nickel, cobalt, iron, copper, zinc, cadmium, thallium, and tin.
3. The hypothesis is put forward that the different rates of electrochemical reduction of metal ions is connected with the different rates of passivation of the cathode surface during electrolysis.

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