On the Question of Determining Current Density at the Cathode in Connection with the Structure of Electrolytic Metal Deposits

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An exact determination of current density at the cathode in the course of an electrolytic metal deposition is of great moment in the study of the phenomena of overvoltage and passivity in the process of electrocrystallization of metals.

However, the task of determining current density is more complicated than it seems at the first glance.

The common determination of current density by means of dividing the current strength by the total surface of the cathode (denoted by d_1) gives us a roughly approximate value considerably differing from the true one.

The discrepancy between the current density estimated in such way and the true value often leads us to wrong conclusions in the study of other dependent factors.

As an example we may cite our experiment of simultaneous deposition of silver from two different electrolytes (0,2 mol AgCN, 0,4 mol KCN in one litre and $3N$ $AgNO_3$), a current of 0,001 A/cm² being passed through series cells.

The cathodes of both cells had an identical surface and had undergone identical cleaning. In case of depositing silver from the cyanide solution a uniformly distributed deposit was formed on the whole surface of the cathode, while the deposition from the solution of $AgNO_3$ occurred only on a small part of the cathode surface. The greater part of the cathode behaved in the latter case as an isolated (passive) surface.

The methods of the above-mentioned experiments have been described in the previous work [1]. If we calculate the current density for the part of the cathode surface on which a deposit has been formed, it is in the second case about 400 times as great as in the first [2].

If we assume an identical current density for both cases (which follows from its common determination) the estimated value of current density for the second case will be 400 times less than its true value, and, obviously, all the deductions made on this basis concerning the relationship between current density and other factors will be wrong.

Thus, while determining current density, only that part of the cathode should be taken into account which participates in electrolysis, i. e. the sum of surfaces of growing crystals denoted by us d_2.

Kohlschütter and Torricelli [3] as well as the writer himself, while investigating the normal growth of a silver monocrystal at strictly constant voltage on the electrodes, found that after the formation of crystal nucleus the current strength grows linearly with time ($\frac{I}{\text{time}} = \text{const}$).

In the course of electrolysis, the increase of the current strength is accompanied by the growth of monocrystals. Hence, we may assume that the current density on the surface of growing crystals remains constant [4].

Samarcev [2] while studying cathode passivity of silver has obtained results corroborative of this deduction. For keeping up a constant current density, Samarcev placed the electrolytic cell into the anode circuit of an electron valve which worked on a saturation current [5]. The cathode surface was then observed with a microscope.

[1] Wahramian, J. phys. Chem. (Russ.), **9**, 511 (1937).

[2] It is necessary to point out, as has been shown by Samarcev, (C. R. Acad. Sci. URSS, **2**, 478, 1935), that the electrolytes prepared during various periods of time, as well as from different $AgNO_3$-preparations, give different values of current density.

[3] Kohlschütter u. Torricelli, Z. Electrochem., **38**, 213 (1932).

[4] The assumption that the increase of the current strength may be accompanied by a simultaneous increase of current density (d_2) seems unlikely and ungrounded. On the contrary, a decrease of current density may be expected within a certain range on active surfaces owing to the impoverishment of metal ions around the growing crystals (see below).

[5] Samarcev a. Jewstropiev, J. phys. Chem. (Russ.), **5**, 854 (1934).

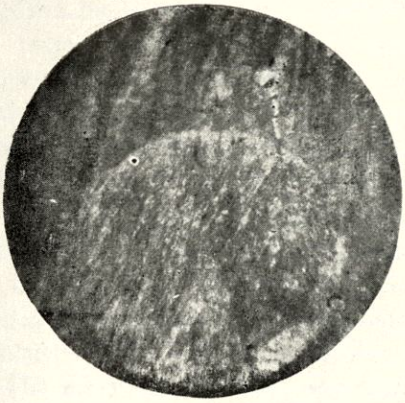

Fig. 1.

Ag-deposit obtained from 3 *N* $AgNO_3$; the metal is deposited (at 10^{-6} A) only at the end of the filament. With the increase of the current strength (4.10^{-6} A) the filament of a large cross-section continues to develop further.

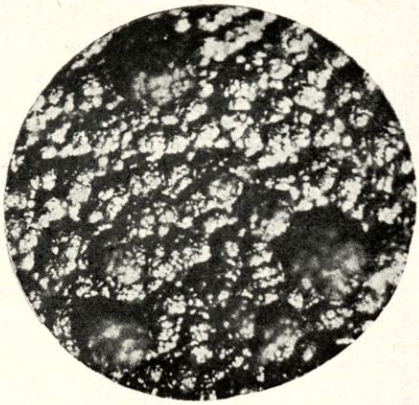

Fig. 2.

Cu-deposit obtained from 1 *N* $CuSO_4$, 0,5 *N*. H_2SO_4 at 19°C and 0,1 A/cm².

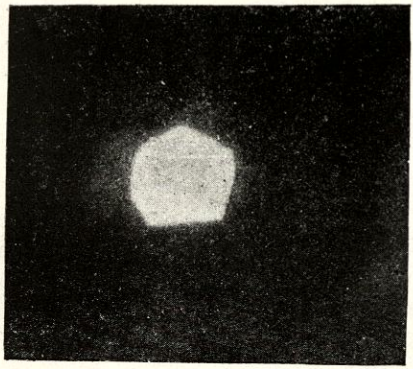

Fig. 5.

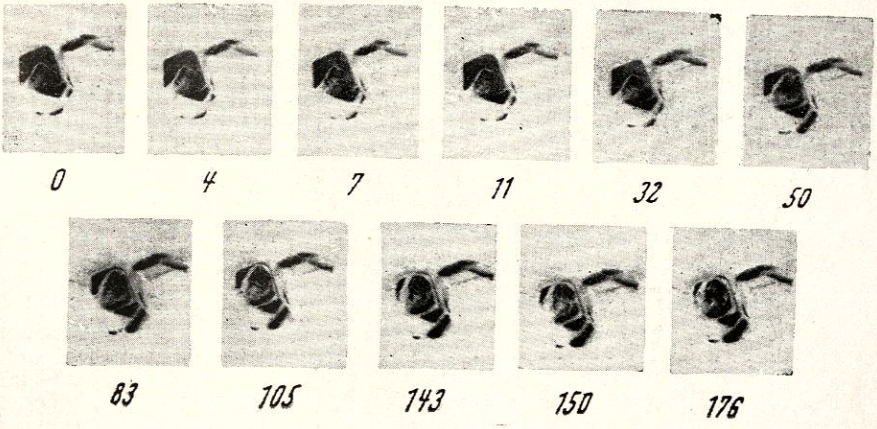

Fig. 6

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After the formation of a crystal on the cathode its active surface was increased because of its further growth and as the current strength was kept constant, a gradual decrease of current density could be observed. In this case the current density varied within a small range and in a very short period of time because after reaching a certain minimum value of current density we may note that separate crystal faces are gradually becoming passive, and after a certain period of time metal deposition occurs on one face only. The value of the active surface remains afterwards unchanged, and growing crystals are transformed into a needle or a filament of constant section (see Fig. 1, Plate 2).

The metal is deposited only at the end of the filament because of its side surface being passive. While measuring the rate of growth of a similar crystalline silver filament, Samarcev determined the current density on the active surface (in his experiments the current density reached 0,6 A/cm^2).

In Samarcev's experiments the active surface increases with the increase of the current strength in the circuit, and the filament of a large cross-section continues to develop further. In this case the linear rate of growth of the filament remains unchanged (see Fig. 3 in the above-mentioned work of Samarcev) which evidently shows that the current density (d_2) does not vary.

In this way, not only with a spontaneous increase of the current strength as in the case with Kohlschütter's and Torricelli's experiments, but also with an artificial increase, the current density (d_2) as shown in Samarcev's work, is kept constant.

Samarcev further noted that the linear rate of crystallization of silver changes according to the freshness of the electrolyte and to the quality of the preparation which has served for this purpose.

Hence it follows that the current density (d_2) is very sensitive to the conditions of electrolysis.

The experiments which we carried out[1] (with a constant current strength in the circuit $6 \cdot 10^{-6}$ A) with silver mono- and polycrystals, and also our preliminary experiments with lead have confirmed the results of Samarcev's investigations that the value of active surface adapts itself to the current strength.

The constancy of the current density (d_2) for the given electrolyte gives the possibility of determining the value of ac-

tive surface of the cathode corresponding to the given current strength [6].

In the previous papers [1] we also studied the effect of concentration of the electrolyte upon the rate of change of the current strength with a constant voltage on the electrodes. In these experiments such conditions were chosen as to ensure in all cases the growth of only one regular silver crystal on the cathode. It was checked by means of a microscope. The investigation of $AgNO_3$-solutions of various concentrations proved that the rate of growth of the current strength at high concentrations is greater than at low ones. Hence it follows, as might be expected, that with the increase of electrolyte concentration the current density (d_2) on the active surface grows too.

The fact that the density (d_2) for the given electrolyte is not changed with the increase of the current strength, easily accounts for the effect of the current strength upon the structure of the electrodeposit. With the increase of the current strength its density can hardly be increased, as the concentration polarization formed near the given crystal face hinders a further increase of the current density. Therefore, with increase of the potential or the current strength, the formation of new crystal nuclei is made possible as well as the increase of the active surface of the cathode. Hence the change of the structure of the metal electrodeposit. With a very large current strength the constancy of its density may be kept only with a great increase of the active surface of the cathode (see Fig. 2, Plate 2) i. e. with formation of a spongy or porous deposit which takes place in reality.

It is known that the possibility of formation of a metal deposit is avoided by the use of high concentrations of the electrolyte and stirring. It may be followed by an increase of the current density (d_2) without any increase of the active surface of the cathode, i. e. without forming any spongy deposit.

We shall not consider here the cases when the formation of a spongy deposit is accounted for by the liberation of hydrogen

[6] In connection with the fact that the current density on the cathode remains constant with the change of the current strength, the relationship between the current strength and polarization may, from this point of view, be accounted for in a new way. This question will be discussed in the next paper.

and by the formation of a metal hydrate. A more detailed investigation of the process of crystallization by various authors[7] has shown that the growth of separate crystals observed with a microscope is regular not on all the surface of the growing crystal face, but only on strictly definite active spots of the face, while the remaining part of the surface of the crystal face does not participate in electrolysis.

The tops and edges of crystals are original active spots in electrolysis from water solutions. On these very spots begins the formation of the metal which is the beginning of a new layer on the crystal face. The angles and faces of the steps formed by this layer become new active spots, along which there occurs further deposition leading to an expansion of the layer on all the surface of the crystal face.

In examining a growing crystal with a microscope one can see that about its top or its edges steps of new layers are being formed which continue their further growth along the edges of the crystal. The growth of the crystal occurs only by superposition of such layers.

This picture of the deposit-formation is analogous to Stranski's[8] ideas about the growth of homopolar crystals (see Fig. 3).

A further investigation showed that, with the electrolytic formation of metals, the newly-formed layer has different degrees of thickness.

In this case the rate of growth of the given layer is the greater the less is its thickness. The change of the current strength involves a temporary change in the rate of layer growth, as well as in their number on the given face. These temporary changes disappear as soon as the current density (d_2) on the face reaches its former value with the change of the crystal surface.

The rate of expansion of layers varies on different crystal faces. On the faces with high indices the layers expand at lesser

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[7] Volmer, Z. physik. Chem., **102**, 267 (1922); Erdey-Gruz u. Volmer, Z. physik. Chem., **157**, 167 (1931); Hockstras, Recueil des travaux chimiques des Pays-Bas, No **3**, 1931; Gorbunova a. Wahramian, C. R. Akad. Sci., **4**, 448 (1934); Volmer, Das Elektrolitische Kristallwachstum, Paris, 1934; Volmer, J. phys. chem., (Russ.), **5**, 319 (1934); Erdey-Gruz, Z. physik. Chem., **172**, 157 (1935). Kohlschütter a. Torricelli, l. c.

[8] Stranski, Z. physik. Chem., B **11**, 342 (1931).

rates. With the switching off of the current the expansion of layers is immediately stopped, but with a subsequent switching on, the layers continue their growth in case the period of time between the switching off and on is not great.

Evidently, the electrolysis occurs on the steps formed by these layers, these steps being real active spots.

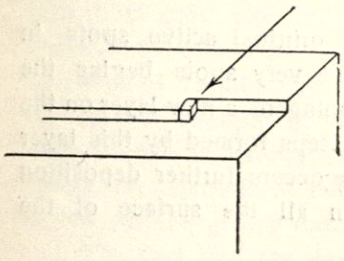

Fig. 3.

Consequently, the ratio of the current strength to the sum of the surfaces of these steps is the most accurate and real expression of the current density, d_s.

However, the thickness of these newly-formed layers is various according to different factors. It depends to a great extent on the change of the concentration of the electrolyte as well as on the amount of impurities — foreign salts, colloids etc.[9] The thickness of the layers, on its part, determines, as we shall see below, the form of crystals.

Therefore the thickness of the layers formed should be determined in each separate case. The thickness of layers can be determined by means of the following formula:

$$d = k \frac{I}{N_s},$$

where d is the thickness of the layer measured by the number of atoms. I is the current density (A/cm²). Here the active surface of a growing crystal is taken into account, i. e. the summary surface of growing faces. $\frac{1}{k}$ is a constant equal to the value of the current necessary for forming a monatomic net with the surface of 1 cm² in one second. Finally N_s is the number of layers formed in one second on given surface.

The determination of the thickness d of the layers formed can be carried out with ease and a great degree of precision if electrolysis proceeds on one crystal face only, as was the case in S a-

[9] Influence of surface active substances on the growth of monocrystals and on the thickness of the layer is being studied by us.

marcev's experiments. However, in a number of cases of electrolysis this condition is hard to be realized.

Let us calculate the thickness of thin layers observed by Kohlschütter and Torricelli, using these investigators' data.

Kohlschütter and Torricelli, while studying the growth of silver monocrystals, found that at the current strength equal to $5 \cdot 10^{-5}$ A 100—120 layers are formed per minute on a crystal with a diameter of 0,2 mm.

The layers moving at the rate of 0,4 mm per second, the authors, unfortunately, did not mention the shape of the crystals, wherefore we find it expedient to make calculations for a minimum and maximum value of crystal surface.

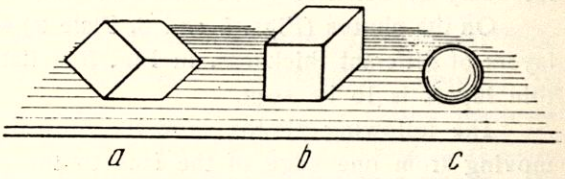

Fig. 4.

In case *A* (see Fig. 4) the crystal surface will be equal to 0,0024 cm², in case *B* to 0,002 cm². If the crystals represent a complicated combination with the surface which is close to that of a sphere, its surface will be equal to 0,0013 cm². As the linear growth rate of crystal faces is identical in all directions, we can determine the current density of all the crystal surface which represents the current strength divided by the sum of surfaces of its regularly growing faces. Further, as one square cm of silver crystal lattice contains $1{,}2 \cdot 10^{15}$ atoms, and as the current strength equivalent to this number of atoms is equal to $2 \cdot 10^{-4}$ A per sec., it is not difficult to calculate the thickness of the layer.

In case of 120 layers being formed per minute

$$d_a = \frac{5 \cdot 10^{-5} \cdot 60}{0{,}0024 \cdot 2 \cdot 10^{-4} \cdot 120} = 52 \text{ atoms}$$

$$d_c = \frac{5 \cdot 10^{-5} \cdot 60}{0{,}0013 \cdot 2 \cdot 10^{-4} \cdot 120} = 96 \text{ atoms.}$$

In case of 100 layers being formed per minute

$$d_a = \frac{5 \cdot 10^{-5} \cdot 60}{0{,}0024 \cdot 2 \cdot 10^{-4} \cdot 100} = 62 \text{ atoms}$$

$$d_c = \frac{5 \cdot 10^{-5} \cdot 60}{0{,}0013 \cdot 2 \cdot 10^{-4} \cdot 100} = 115 \text{ atoms.}$$

The layers in question are very thin (some hundreths of micron) and quickly moving. The thickness of slowly moving layers sometimes reaches some thousand atoms. The shape of the crystals changes according to the thickness of the layers formed. During the generation of thin layers, the crystals usually grow with flat faces, and the simple crystallographic shape of crystals is preserved.

During the formation of thick layers the crystals adopt a more complex shape, so that new faces with higher indices appear.

By way of illustration we shall give a few photos from the microcinema film „The Growth of a Silver Crystal During Electrolysis" obtained in the Colloid-Electrochemical Laboratory of the U.S.S.R. Academy of Sciences (Garbunova and Wahramian, 1933).

On the photos (Figs. 5 and 6, Plate 2) we see a crystal face with layers of different thickness. In Fig. 5 a flat crystal face with three thin layers is to be seen.

The following photos show the growth of a curved thick layer moving from one edge of the face to the other. The figures under the photos represent the duration of the electrolysis in seconds.

As can be seen from the photos the thick layer does not continue its normal growth up to the end of the crystal face, because, owing to its slow movement in the course of a long period of time, the deposition of metal on the other part of the crystal face does not occur. The face becomes passive and the onward movement of the thick layer stops half-way.

The step of this layer, on expansion, turns into a new face. Thus, in case of a formation of thick layers on the original smooth crystal surface, new faces with higher indices are formed.

From the above-mentioned it follows that an accurate calculation of the active cathode surface (i. e. participating in the electrolysis) enables us to understand the effect of the change of current strength in the cells on the structure of the cathode deposit.

Besides, the calculation of the thickness of newly-formed layers (from which crystals have grown) in connection with the theory of cathode passivity enables us to understand the shape of crystals and their deformation.

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