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Some Problems of Electrocrystallisation of Metals

A. R. Despić

Faculty of Technology, University of Belgrade, Belgrade, Yugoslavia

Problems associated with electrodeposition of metals are treated with special interest devoted to (1) location of discharge of metal ions onto a solid, and (2) the effect of diffusion on the morphology of metal deposits. Experimental results indicate that discharge on edges is preferred due to much lower energies of activation. Other results confirm the theory of Despić, Diggle, and Bockris, according to which in diffusion controlled processes exponential increase in surface roughness is to be expected.

The problem of electrodeposition of metals is of course a very complex and multisided one. In this lecture two specific aspects only are to be touched upon, namely those which have been lately the subjects of author's occupation but may be considered of somewhat more general interest.

Location of Discharge of Metal Ions onto a Solid Metal Surface

The first is the rather old and controversial question of the detailed mechanism of transfer of an ion from the solution to a position in the metal lattice, or specifically, the question of the position at the surface at which the electron exchange between the electrode and the hydrated ion in solution takes place.

The problem arises as to whether discharge occurs at the very position at which the crystal lattice is being extended, or does it represent an independent act occurring somewhere at the plane surface inbetween the centers of growth, thus resulting in a freely moving and only partially discharged and partially dehydrated adion. The question has interesting and not unimportant repercussions in as much as it decides whether the electric current of deposition is smeared out evenly over the surface or is concentrated at certain points and hence dependent on the number of those points at unit surface.

This problem was considered at length by Conway and Bockris in their well known paper of 1957[1]. They have analyzed the energetics of the two possible deposition path shown in Fig. 1: *(a)* the path 1, 1′, 4, consisting of diffusion of the hydrated ion at the outer Helmholtz plane parallel to the electrode surface, to the position of discharge followed by a simultaneous disharge and incorporation into the crystal lattice, and *(b)* the path 1, 2, 3, 4 consisting of discharge, surface diffusion at the plane surface to a step and diffusion along the step to a kink, *i. e.* the point of incorporation. They have made approximate enough calculations of the zero energy levels of various states along each path and also of the approximate shapes of potential energy curves as to obtain the picture of energy barriers along the reaction co-

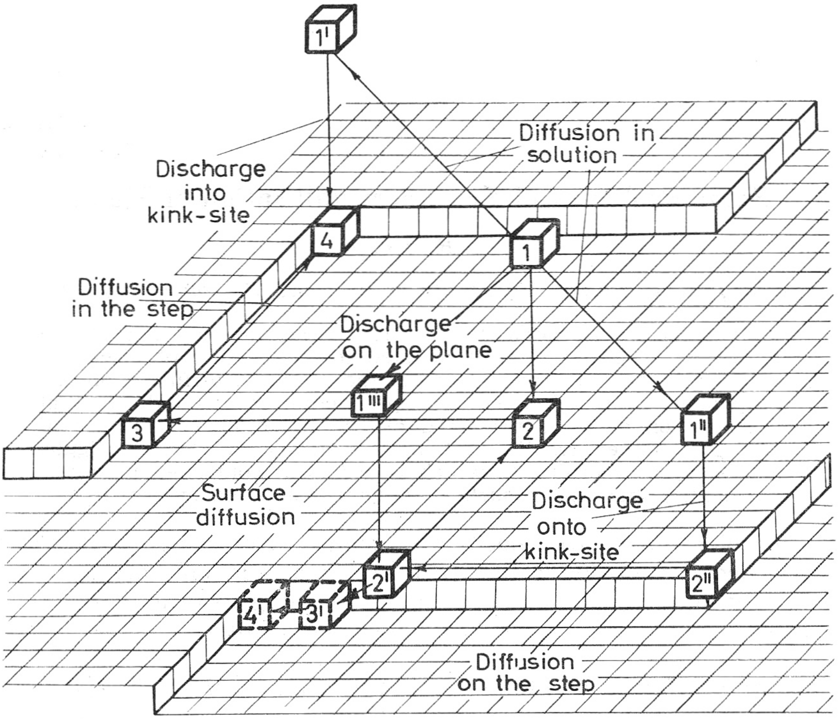

Fig. 1. Possible path in the discharge and deposition of an ion from solution.

ordinates. The calculations have shown simultaneous discharge and incorporation into a kink to be connected with prohibitively high activation energy. It is significant to note that this was due primarily to the very unfavourable geometry, *i. e.* to a large distance between the center of the ion in its equilibrium position, placed in the best possible way against the kink, and that of the atom built in into kink. Hence, although the zero energy level of the atom in the kink is very favourable, at the large distance to which the ion-solvent bonds have to be streched for the transition to take place, the potential energy takes very large values before the peak of the barrier is reached. This is much less so at the plane surface. The distance for bond stretching is much less and hence so is the climb in potential energy. However, the difference between the obtained activation energies is somewhat less than expected from this single factor, because the zero energy level of the adion at the surface is higher than that of the atom in the kink. Hence, the potential energy curve of the final state is shifted to higher energy values, with a corresponding shift in the point of intersection. Nevertheless, the obtained difference in activation energies is such that it leaves no doubt that the second path should be by far the dominant one. One should note also that, of course, the frequency factor should be larger in the second case than in the first, because there are more ions facing plane surface than kinks and this should be an additional reason for the preference of the second path.

The whole of the Conway-Bockris argument is of course based on a Horiuti--Polanyi, *i. e.* transition state theory model of the process, with possible extention to the electron tunneling concept of Bockris-Mattews based on Gurney's considerations of a fixed energy barrier tunneling. It would be interesting to analyze in detail how the conclusions stand in view of the more modern concepts like the Levich theory of discharge which separates the discharge process into two steps: that of the solvent reorganization and that of charge transfer by quantum mechanical tunneling through the Landau-type oscillating barrier. Indeed this would represent a major theoretical task and it is to be hoped that this shall be done in the near future. So far it does appear that similar results should be expected since in the new theory the same distance between the initial and the final position of the particle undergoing discharge is relevant for the probability of tunneling calculation.

In spite of the conclusion that discharge should take place on a plane surface, there seems to be some evidence that the current density of deposition depends on the concentration of steps or dislocations at which crystal growth takes place. This could be particularly well demonstrated in the experiments with controlled concentration of points of growth, carried out by the Bulgarian metal deposition school[2]. This could, of course, be due to a strongly inhibited surface diffusion when, as shown by us long time ago[3], only ions depositing at the plane surface quite near to the growing step, could reach the points of incorporation and be built-in there, thus maintaining a steady current. At the rest of the surface, further from steps no net discharge should take place. Yet this phenomenon can influence the current only at low overpotentials, close to the reversible electrode potential. At higher overpotentials the effect vanishes. Finding this effect in a wider range of conditions points out to some other cause.

Indeed a closer consideration of the system along the same line of reasoning as that used by Conway and Bockris has lead us to the conclusion that their model should be extended to encompas some additional situations *i. e.* possible paths which have not been taken into account so far. On the same Fig. 1. one can see that the third possibility is in that the ion may be discharged on a step edge or on a corner, rather than in the step or in the kink. (Paths $1, 1'', 2' 2, 3, 4$ or $1, 1''', 2'', 2', 2, 3, 4$). Calculations of zero point energies for an adion on the corner and on the edge were carried out in the same way as those done by Conway and Bockris. They were found to be considerably higher than this for discharge onto a plane. Consider the case of silver. If the heat content of an atom built into the bulk of the metal is taken as reference, the relative heat content of an adion at a plane appears to be about 20 kcal mole^{-1}, at the edge about 24 kcal mole^{-1}, while that of an adion at the corner should be about 36 kcal mole^{-1}. Thus, because of that single factor, the shift in potential energy curves to higher values would result in an increase in the activation energy barriers. Yet, Fig. 2. shows that in such cases there is also considerable reduction of the distance between the center of the ion and the center of the atom in the lattice.

For the case of silver it is seen that instead of 0.97 Å, to discharge an ion onto an edge the ion should move only 0.29 Å inside its hydration shell and little motion of the solvent is required. When such a situation, the potential energy distance diagrams change in the sense shown in Fig. 3. The first line shows the energy profile for the deposition onto the plane, and $(\Delta H^*)_p$ is the activation energy obtained by Conway and Bockris.

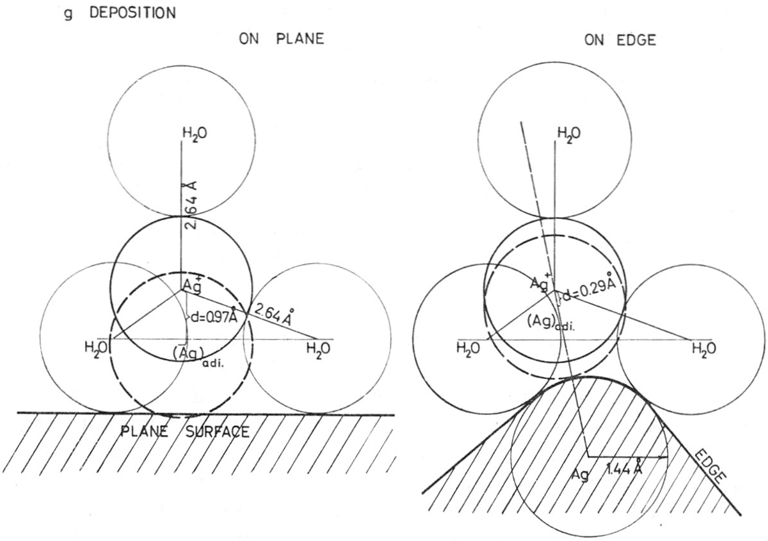

Fig. 2. Model representation of a silver ion being discharged on a plane and on an edge.

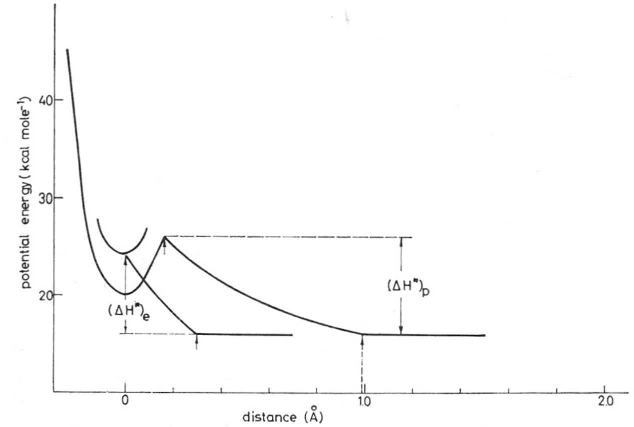

Fig. 3. Potential energy profiles for the discharge of silver ions on a plane surface and on an edge.

The second line shows the potential energy profile for the deposition onto the edge. It is seen that the shift of the minimum of the potential energy curve for the initial state to shorter distance produces the reduction of the activation energy barrier practically to zero, and it is only the difference in the heat contents of the initial state and the intermediate state of the adion which determines the exponential factor of the rate constant. In fact this is the case of the activationless discharge of Krishtalik[4]. Nevertheless this acts as the activation energy of the process and is seen to be less for that case than for discharge onto the plane. As for the deposition onto the corner the adion obtained has such a high heat content, *i. e.* represents such

A similar situation exists for the deposition of copper from cupric ions. Fig. 4 shows the estimate of the distances of the centers of the species depositing at the edge, at various states. Thus, the center of a hydrated cupric ion is 1.1 Å further away than the center of the cuprous adion (which represents the final state of the discharge) while that of the hydrated cuprous ion is 0.6 Å away. Hence, taking the same potential energy curves as those used by Conway and Bockris for the discharge onto the plane (Fig. 5) *(a)* and shifting the curve for cupric ion and that for cuprous ion to the positions of the minima at 1.1 and 0.6 Å respectively, *(b)* is seen to reduce considerably the energy barriers both for the first and the second step of discharge.

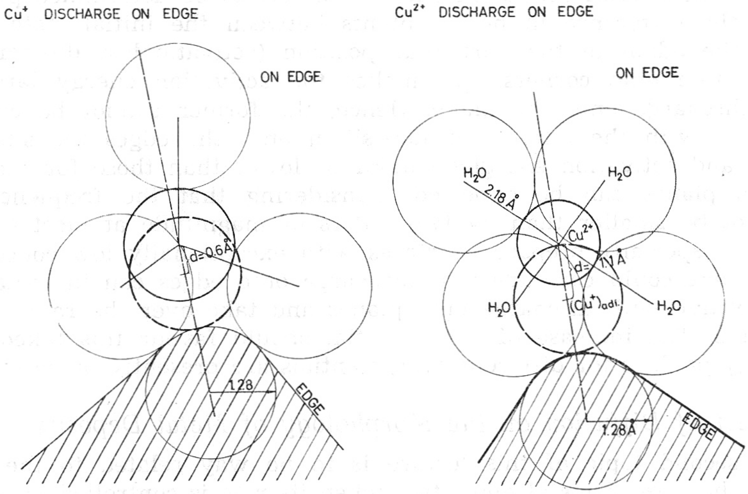

Fig. 4. Model representation of cupric and cuprous ions being discharged on edge.

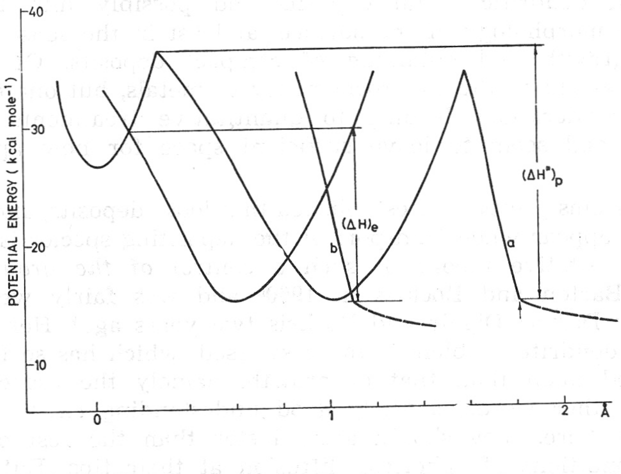

Fig. 5. Potential energy profiles for the discharge of cupric ions to copper at a plane surface *(a)* and at an edge *(b)*.

In conclusion one can say first that this analysis shows the discharge on the corners and edges to be favoured in the case of *redox processes* (like the cupric to cuprous ion reduction), for much less solvent reorganization is needed and much narrower is the activation energy barrier for electron tunneling.

In this consideration the work function for the electron is taken as independent of position of discharge. Needless to say that, if anything, this should be smaller at corners and edges than at planes, and this should bring a further reduction of the barrier.

As for discharge into adions, those species exhibit considerable heat contents. Hence, the high zero energy level of their potential energy curves makes for the overall activation energy barriers to be determined practically only by the difference in heat contents between the initial state and the state of the adion in the particular position (activationless discharge). For the deposition onto corners, this makes the activation energy larger than for the discharge onto the plane. Hence, the former cannot be considered competitive with the latter. For deposition onto the edges the situation is different and activation energies similar or lower than those for the deposition onto planes can be expected. Considering that the frequency factor should not be smaller than by two orders of magnitude at most (except in the case of specially prepared surfaces with exceptionally low concentration of steps), one could conclude that discharge onto edges can in certain cases be competitive with discharge onto planes and take over the rate control of the process. The increase of overpotential should favour this takeover, and the energy profiles for different overpotentials are presently being calculated.

The Effect of Diffusion on the Morphology of Metal Deposits

The second topic of this lecture is in no way related to the first. It concerns the case of metal deposition when its rate is controlled by transport of the discharging ions from the bulk of solution to the surface. This research was started in an attempt to get a deeper insight into the reasons of the appearance of dendritic metal deposits and possibly into the modes of control of the morphology of the surface, at least in the sense of prevention of loose outgrowth and obtaining of compact deposits. Of course, these questions are as old as the electrochemistry of metals, but one could say that theoretical considerations leading to quantitative treatments are of more recent origin and seem to leave sufficient space for new approaches and results.

So far it seems pretty well established that loose deposits, and in particular the dendrites, appear when transport of the depositing species is insufficiently fast. The quantitative theory of such a control *of the growth itself* was initiated by Barton and Bockris in 1960[5] and was fairly well brought to completion by Despić, Diggle and Bockris two years ago[6]. Here, a particular aspect of the dendrite problem is to be stressed, which has so far been much less elaborated upon than that of growth, namely the aspect of dendrite initiation. In other words, a fairly good undestanding exists that once the dendrites are there, they should grow faster than the rest of the surface because of conditions of spherical diffusion at their tips. But, what makes the dendrites appear in the first place?

i) Qualitative model

There, a rather simple model is developed, which shows that the dendrite initiation, as well as the growth, could be a non-specific phenomenon, dependent, not on the properties of the depositing metal, but solely on the initial micro-roughness of the surface and the conditions of diffusion.

Consider any metal surface immersed into the electrolyte, out of which metal ions are to be discharged and deposited. The surface always contains certain roughness, meaning that its profile is irregular (Fig. 6). This can be described by some unknown function $y_0 = F(x)$. Suppose that, by application of appropriate overpotential, discharge is made so fast that transport of ions from the bulk cannot provide sufficient supply of material. The concentration change will occur at the electrode and a diffusion layer will be formed. Three effects will appear.

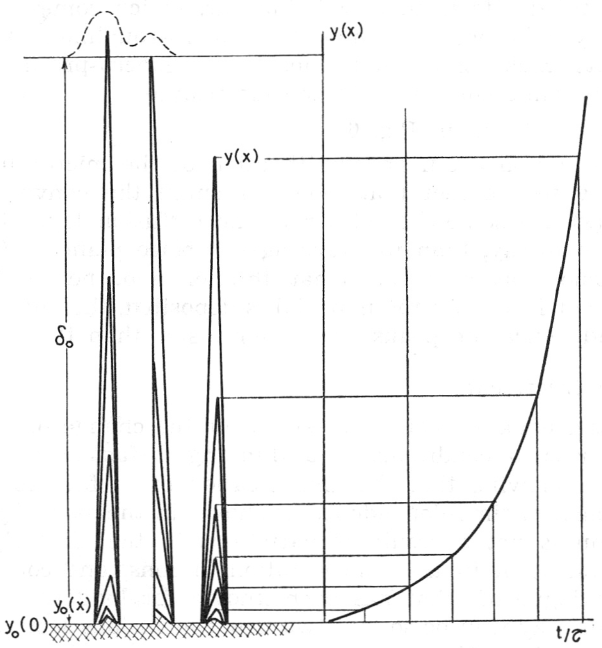

Fig. 6. Schematic representation of the amplification of surface roughness at a normally rough metal surface.

In the initial period in which this layer is still thin enough to follow closely the surface irregularities, the supply of ions will be faster to convex parts than to concave ones. Hence, more material shall be deposited at the former than at the latter and there should be some amplification of the original surface roughness. One may call this the reverse Wagner effect, for Wagner has shown[7] that, in electropolishing, smoothening occurrs as a result of faster dissolution of convex parts than of the concave ones. The second effect is the limiting case of the first effect and this arises when a convex irregularity has amplified to that extent that it may be called a protrusion and when spherical diffusion conditions are established at its tip, which provide for a much faster supply of material than the linear diffusion at the rest of the surface. One may call this the Barton-Bockris effect, since this was shown by them to be the essential condition for the propagation of needlelike and thread-like formations.

While the reverse Wagner effect can be considered as the possible cause for the initiation of such outgrowth, the Barton-Bockris effect is already outside this scope, for it concerns the process of growth itself. Now, the reverse Wagner effect has limited amplifying capacity and doubts arose as to whether it can be taken as a base of dendrite initiation. It was then found that there is a third effect, neglected thus far, which comes into play when the diffusion layer becomes so thick that micro-roughness is burried deep in it and that its thickness is determined by the macro-profile of the surface and the hydrodynamic conditions in the electrolyte.

Such a case is shown in Fig. 6.

In such a situation again an amplification of the microroughness occurs. This is due now to the fact that, however small the convex irregularities, their peaks $y_0(x)$ are somewhat closer to the diffusion layer boundary than their base, or, so to say, than the »average« surface plane, $y_0(O)$. Hence, for them the diffusion layer is somewhat thinner and, hence, the supply of material somewhat faster. As the material is deposited, this difference becomes even larger, and hence the peaks grow ever faster than the average surface.

ii) Quantitative treatment

A differential equation could be set up for the change of the height $y(x)$ with time under such conditions of a thinning diffusion layer. Its solution was an equation showing that the amplification of surface roughness should follow an exponential time-dependence as shown in the same figure. Although this phenomenon is not a result of variations in the electrolyte resistance, but rather of variation in the concentration of ions, one could say that all this is some analogue of what has been known for long as primary current distribution. This may well be so, but two new conclusions seem to be indicated by this model: (*a*) that effect is not necessarily connected with macroprofiles but appears equally well when micro-roughness is concerned and (*b*) that differences in the thickness of the deposit increase exponentially with time.

The time constant of this process was shown to be a very simple function of the diffusion parameters, *i. e.*

$$\tau = \frac{\delta^2}{(M/\varrho)\,DC_0}$$

where M and ϱ are the atomic weight and density of the metal, respectively, D is the diffusion coefficient of the ions and C_0 their bulk concentration.

The so-called initiation time, or induction period for dendrite formation, which is always observed in this type of deposition, seems to be, in view of this initiation theory, merely the time necessary for the exponential *i. e.* avalanche-like nature of this amplification process to make for a sudden appearance of a needle-like protrusion outside the diffusion layer boundary. Further on, laws of different nature take care of the growth, making usually its rate almost constant.

One should note here a matter which has already caused some misunderstanding of the concept: While the time constant is determined only by the given diffusional parameters and *does not* depend on the initial elevation of the irregularity, the initiation time does so. The larger y_0 (x) *i. e.* the rougher the surface, the sooner will the value of y (x), which is simply y_0(x) multiplied by the exponential of time, become such, as for the protrusion to be observable.

The question arises now how this theory could be investigated experimentally. Two directions of research were assummed. First, it was realized that the exponential rise of any point at the surface can occur only if the supply of material, *i. e.* the current also rises exponentially. If this is so for any point irrespective of the surface profile, this is so then for all points, and, hence, the current, observed at potentials sufficiently negative to cause complete concentration polarization, should also exhibit an exponential rise with the same time constant dependent on diffusional parameters, *i. e.* on concentration of the depositing ions and on the diffusion layer thickness.

Indeed, an exponential-like rise in current is observed when conditions of concentration polarisation are achieved equally well in the deposition of *e. g.* zinc from alkaline zincate solution and copper from the copper sulphate bath. This is contrary to the usual experience with diffusion polarisations, where limiting currents are either constant (in steady-state diffusion), or decreasing with time. It may well be the cause why diffusion limiting currents of metal deposition at solid electrodes were always considered as poorly reproducible.

In Fig. 7. several current time relations are shown for deposition of zinc from zincate solutions of different concentrations. Those were obtained by John Diggle at the Electrochemistry Laboratory of the University of Pennsylvania. Now, it is the excess current over the linear diffusion limiting

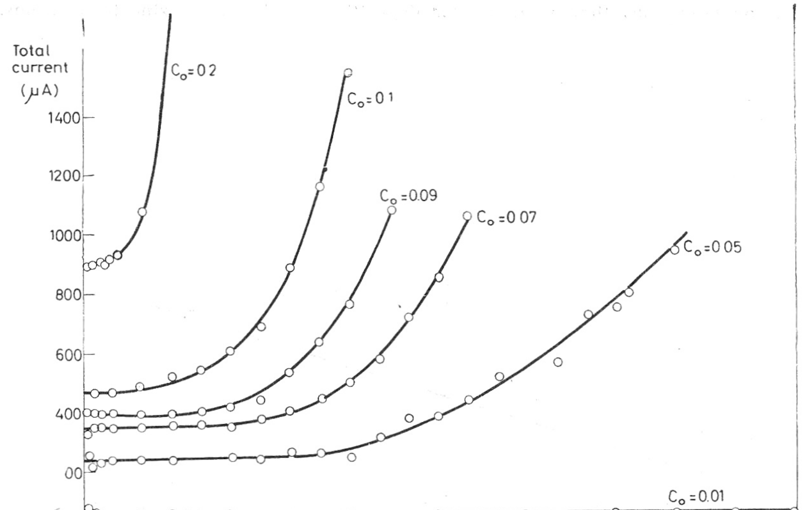

Fig. 7. Current-time relations in zincate solutions of different concentrations.

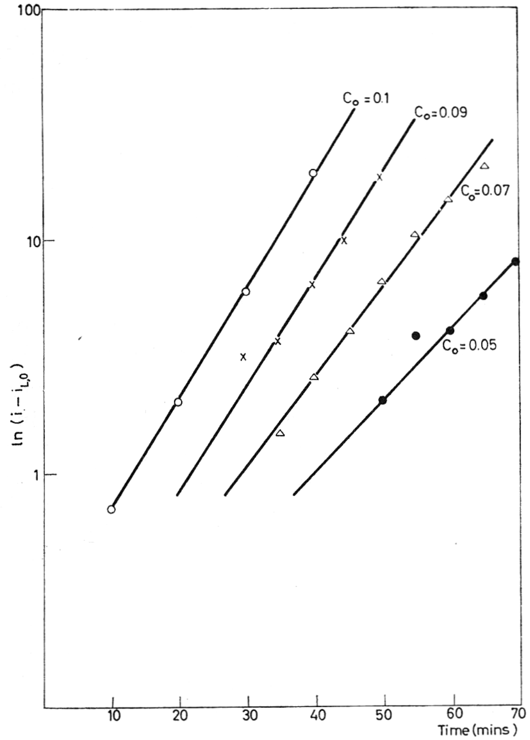

Fig. 8. log $(i - i_L)$ *vs.* time relations for deposition of zinc from zincate solutions.

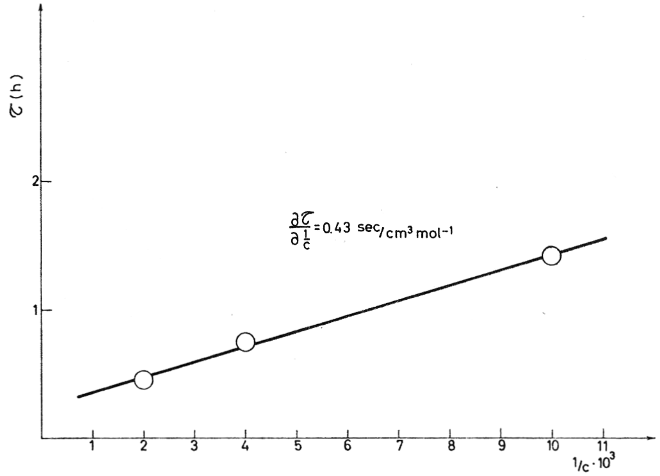

Fig. 9. The plot of time constants as function of reciprocal concentrations.

current which undergoes the exponential rise. Hence, the log of $(i - i_L)$ should be linearly dependent on time. This is shown in Fig. 8. The slopes of these lines give the value of the time constant. This is shown in Fig. 9. as a function of reciprocal concentration. The dependence is shown to be linear as expected from the equation for τ.

iii) Some new experiments

An attempt was made also to investigate τ as a function of the diffusion layer thickness. This was done by Konstantin Popov in our laboratory in Beograd. Well defined system was obtained in the following way: A gramophone record negative was taken as an example of a surface with very regular surface profile, consisting of flat portions and of elevations about 20μ high, of triangular cross-section. A warm solution, 0.1 *M* in copper sulphate, containing agar, was placed upon such a surface in layers of varying thickness (0.5, 1 and 1.5 mm) and was left to solidify. Such an electrode was then placed in a well stirred copper sulphate bath of the same concentration. Fig. 10. shows the change in current with time. The first portion represents the decrease in current as the hydrodynamic boundary layer, fixed by agar, is emptied of cupric ions. The minimum in current represents the linear diffusion limiting current for the corresponding steady-state diffusion through a diffusion layer equal to the hydrodynamic boundary layer. Further exponential rise is interpreted in the same manner as before, as seen in Fig. 11, for the three different diffusion layer thicknesses. The values of the time constants were extracted from the slopes and plotted as a function of δ_0^2. A rather good straight line is obtained as seen in Fig. 12. as expected from the equation for τ.

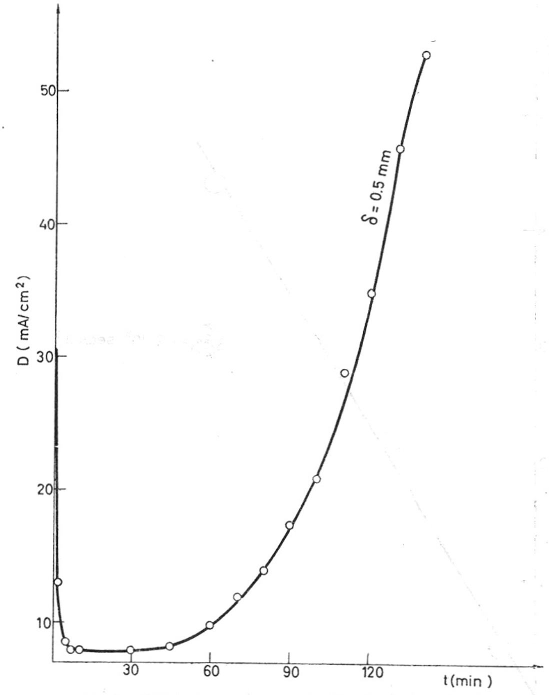

Fig. 10. Change in current of copper deposition from a solution with a fixed hydrodynamic boundary layer at the electrode.

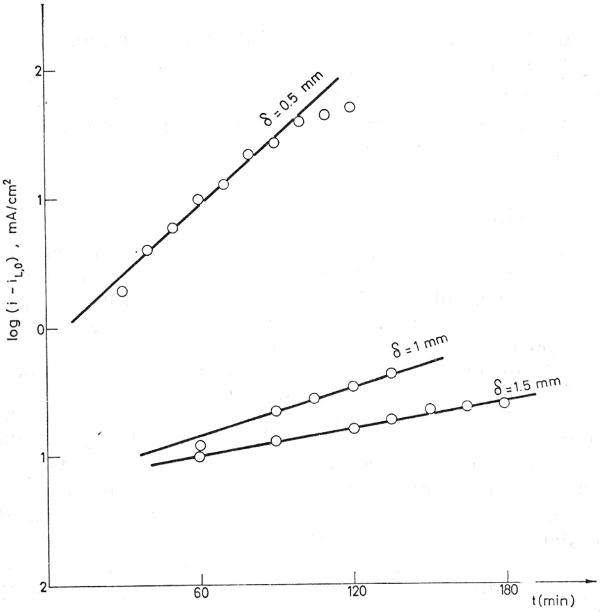

Fig. 11. log $(i - i_I)$ *vs.* t dependence for deposition of copper through a defined hydrodynamic boundary layer.

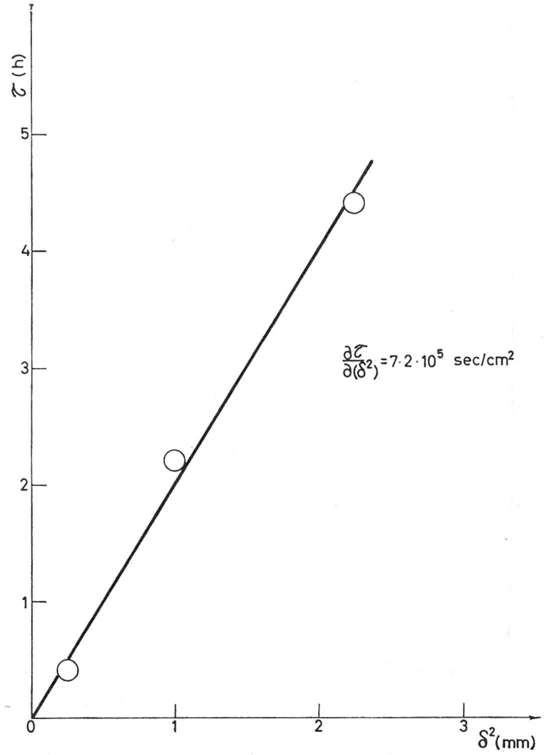

Fig. 12. Plot of time constants as functions of δ_0^2.

However, there is a puzzle here in the slope of that dependence. Theoretically it is a fairly straightforward quantity, *i. e.* and for the given case it should be about

$$\frac{\partial \tau}{\partial (\delta_0^2)} = \frac{\varrho}{MDC_0}$$

3×10^8. Yet, it is found to be about 2 orders of magnitude lower, and this has remained a mystery still unsolved. In fact, in the previous experiments of concentration dependence, the slope indicated smaller δ than could be expected under the given conditions which represents deviation in the same direction.

The very dependence of τ on C_0 and δ_0 leaves no doubt that the exponential increase in current is a diffusion controlled phenomenon, and the obtained linearities on $1/C_0$ and δ_0^2, indicate that the model used is correct.

To check the theory more directly the deposits obtained under various conditions were observed under microscope as metallographic samples were made in wax and cut and polished perpendicular to the direction of elevations. The result of one such experiment is seen in Fig. 13a. The deposit is obtained under conditions of prevailing, but not total, concentration polarisation (at 0.3 V cathodic overpotential). The uneven deposition is evident. In Fig. 13b the same is shown for the case of total concentration polarisation (0.6 V cathodic overpotential). Here, deposition is seen to occur practically only at the elevation peaks, and exhibits clearly the dendritic character.

At 0.3 V, for fixed other conditions, deposition was done for different times, the samples were then treated as described, and the difference in the height of the deposit at the flat portion and at the peak was measured. Since the exponential time-dependence of growth is expected here, the logarithm of this difference divided by the original difference should be linear with time. This is seen indeed to be the case in Fig. 14. Moreover, the time constant of this growth should be the same as that found in the current-time relations. Indeed, the value of τ obtained from this graph is the same as that for the increase in current for $\delta_0 = 1$ mm, within the limits of error of the experiment.

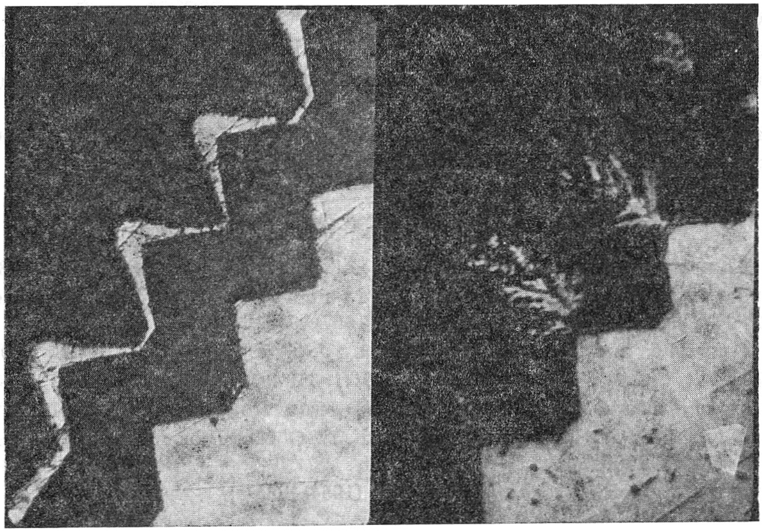

Fig. 13. Deposition of copper through a fixed hydrodynamic boundary layer onto a surface of well defined surface roughness, at cathodic overpotential of 0.3 (a) and 0.6 V (b).

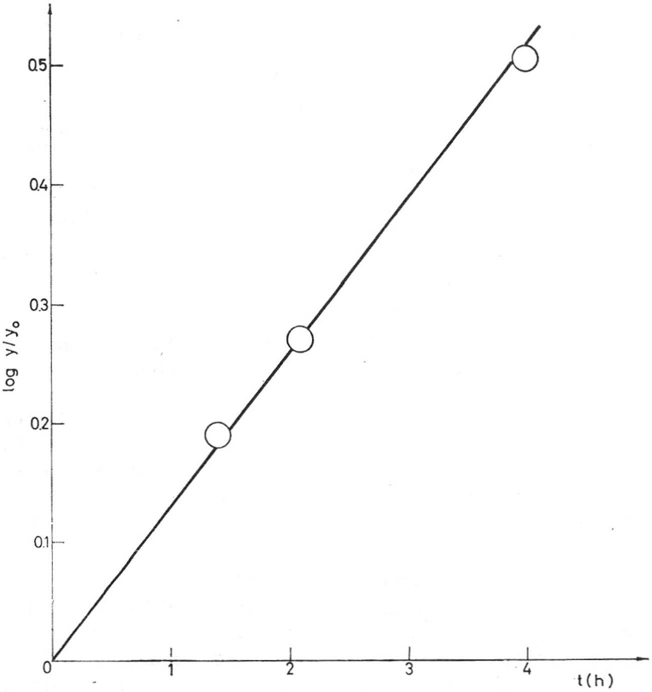

Fig. 14. log y/y_0 *vs.* t dependence for the growth of copper deposit.

Hence, it seems justified to maintain that sufficient proof is obtained of the validity of the model used and theory derived for the initiation of dendritic growth. At the present time one is preocupied with a reverse problem, namely that of preventing dendrite initiation and growth. One hopes to be able to report some findings in that direction at a later instance.

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IZVOD

Neki problemi elektrokristalizacije metala

A. R. Despić

U ovom izlaganju razmatrana su dva specifična aspekta elektrodepozicije: problem lokacije razelektrisanja metalnih jona i problem uticaja sporosti transporta mase na morfološke osobine metalnog depozita.

Po prvom problemu izložena je teorija Bockrisa i Conwaya, i pokazano je da dosledna primena te teorije mora da obuhvati i mogućnosti koje do sada nisu razmatrane, tj. razelektrisavanje **na** ivicama i **na** rogljevima kristala metala na površini. Približni proračun aktivacionih energija za te reakcione puteve pokazao je da je u slučaju jednovalentnih jona razelektrisanje na rogljevima malo verovatno.

Nasuprot tome, razelektrisanje na ivicama povezano je sa znatno manjim iznosima aktivacione energije nego na ravnoj površini, te je sasvim verovatno da se reakcija može odigravati prevashodno tim putem. U slučaju dvovalentnih jona, prvi stupanj redukcije verovatniji je i na rogljevima i na ivicama nego na ravnoj površini.

U okviru razmatranja drugog problema pokazani su eksperimentalni rezultati koji potvrđuju teoriju Despića, Digglea i Bockrisa, po kojoj u uslovima difuzione kontrole procesa depozicije dolazi do eksponencijalnog povećanja rapavosti sa vremenom.

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