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The mechanism of formation of a surface film of silver on a platinum electrode

K. I. POPOV, D. N. KEČA, G. R. OSTOJIĆ

Faculty of Technology and Metallurgy, University of Beograd, Yugoslavia

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The mechanism of the growth of thin metal films on inert substrates in potentiostatic metal electrodeposition is given. A possible relation to the porosity of metal deposits is discussed. The effects of pulsating overpotential on the electrodepositon of the first monolayers are described.

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1. Introduction

It was recently shown that metal deposits produced by a pulsating overpotential are of lower porosity compared to those obtained by standard potentiostatic electrodeposition [1]. It was not possible to explain this solely in terms of mass transfer effects [2, 3]. Instead, the effects of pulsating overpotential on the electrodeposition of the first monolayers of metal must also be taken into account. No work dealing with this problem has been found in the literature so far, although galvanostatic studies of thin metal electrodeposition have been published. Thus, Oberbek [4] and Nichols [5] deposited copper on platinum and showed that an electrodeposit of copper of the order of a few atoms thick behaved as a copper electrode. More recently, Brainina *et al.* [6] reported similar results for silver electrodeposition on a graphite electrode.

In these experiments the potential of the inert electrode was recorded as a function of quantity of electrodeposited metal. The transformation of the electrode surface was taken to be complete when the film of metal gave the same potential as a massive metal.

We note, however, that the simple Nernst equation fails to consider variations in the activity of the solid phase [7] and no direct conclusions about the mechanism of first layer metal electrodeposition can be obtained from potential–charge transients. This mechanism can be delineated from potentiostatic experiments where the current density on the substrate as well as on the metal deposit is known for each value of overpotential [8]. It is the purpose of this paper to present some results on the mechanism of potentiostatic electrodeposition of the first monolayers on an inert substrate, and to try to relate it to porosity of metal deposits.

2. Experimental

The deposition of silver was carried out onto a platinum electrode from 0·05 M $AgCH_3COO$ in aqueous 0·1 M $NaCH_3COO$ in an open cell. The potentiostat and pulse generator were similar to those described previously [3]. The temperature of the cell was maintained at 25·0 ± 0·1°C.

The platinum electrode was cleaned by anodic treatment (2 h at 1·1 V versus standard hydrogen electrode) and by washing in concentrated nitric acid (20 min).

3. Results and discussion

Typical experimental results obtained in this work are shown in Figs. 1 and 2. The shape of current density–time relationships can be explained by the following discussion. Erdey-Grúz and Volmer [8] showed that in some cases of metal electrodeposition on an inert substrate two different kinds of polarization curves can be obtained.

If the current density–overpotential plot is obtained by step wise increase of overpotential, the current densities at each overpotential are smaller than those obtained at the same overpotential when going in reverse direction, i.e. an hysteresis in current is observed. The first polarization curve represents deposition at low coverage, (in the first approximation deposition on an inert substrate)

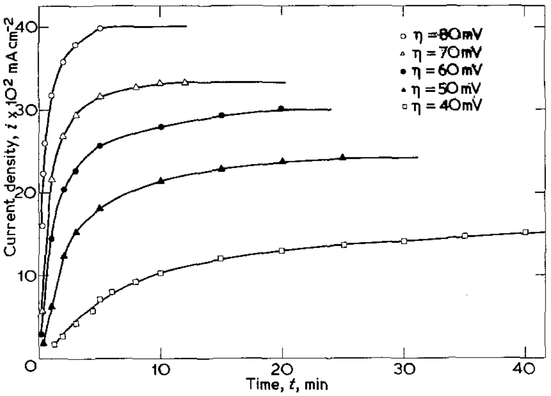

Fig. 1. Current density–time relationships during the deposition of silver on platinum for different values of constant overpotential. The current densities i_2 are extracted from the plateaux.

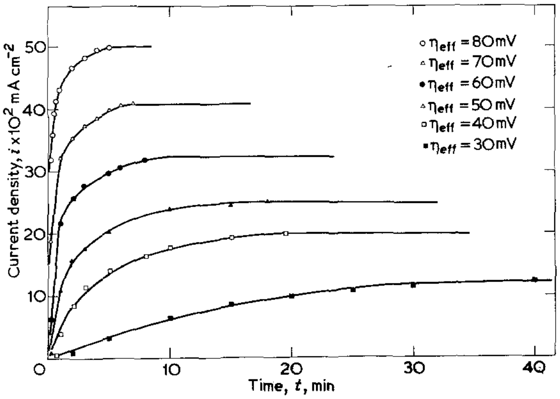

Fig. 2. Effective current density–time relationships during the deposition of silver on platinum for different values of effective overpotential at a frequency 10 cps. Effective current densities i'_2 are extracted from the plateaux.

and the second curve deposition at high coverage (in the first approximation deposition on a completely covered surface). On the basis of these polarization curves it can be concluded that metal electrodeposition on partially covered inert surface will take place with different current densities on the inert part of the electrode's surface and on the covered part. The mechanism of formation of the surface film of deposited metal at selected values of overpotential can therefore be discussed without consideration of the mechanism of nucleation on the uncovered and electrodeposition on the covered part of the electrode surface. If this is so, the increase of coverage with time can be given by

$$\frac{d\theta}{dt} = ki_1(1-\theta), \tag{1}$$

where: θ – coverage; t – time; k – constant; i_1 – current density of metal electrodeposition on an inert substrate at the given overpotential. The integral form of Equation 1 is

$$\theta = 1 - e^{-ki_1 t}. \tag{2}$$

Hence, the coverage is a function of i_1 and t. At the same time, the current density of deposition on the covered part of the electrode surface at the same overpotential will be i_2. The apparent current density i at a partially covered electrode will then be

$$i = i_1 e^{-ki_1 t} + i_2(1 - e^{-ki_1 t}). \tag{3}$$

This model of potentiostatic metal electrodeposition on an inert substrate is correct for each value of overpotential. With pulsating overpotential, the model can be applied if the mechanism of nucleation is the same at all overpotentials used. In this case, all effects related to nucleation are expressed by the current density of deposition on the inert substrate, i_1.

The reaction rates of first-order reactions can be compared in terms of their half-lives. Thus the rates of transformation of inert surfaces can be compared by comparing the quantities of electrodeposited metal $Q_{1/2}$, required to obtain $\theta = 0{\cdot}5$. It is easy to show that $Q_{1/2}$ is given by

$$Q_{1/2} = \frac{0{\cdot}5}{\mathrm{k}} + \frac{0{\cdot}2}{\mathrm{k}}\frac{i_2}{i_1} \tag{4}$$

if

$$t_{1/2} = \frac{\ln 2}{\mathrm{k}i_1} \simeq \frac{0.70}{\mathrm{k}i_1}.$$

If the mechanism of nucleation does not change with overpotential, k is constant for all overpotentials used. Then, the quantity $Q_{1/2}$ is a function of overpotential because the current densities i_1 and i_2 are functions of overpotential.

The current densities i_1 and i_2 extracted from the results of Figs. 1 and 3, and the effective current densities i'_1 and i'_2 extracted from these (Figs. 2 and 4) relating to pulsating overpotential of frequency of 10 cps are shown in Fig. 5 as functions of overpotential. Similar polarization curves for d.c. silver deposition on platinum from the same electrolyte were obtained by Erdey-Grúz and Volmer [8].

At all overpotentials used $i'_1 > i_1$ and $i'_2 > i_2$.

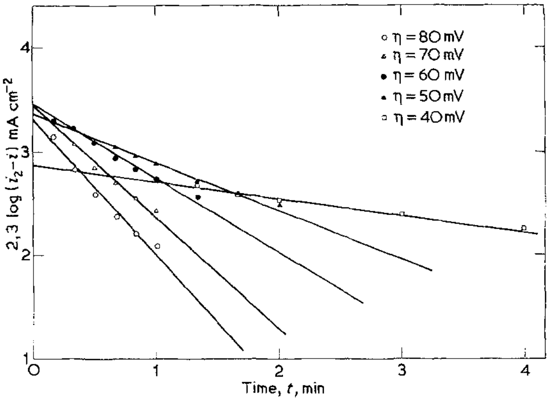

Fig. 3. 2·3 log ($i_2 - i$) as a function of time for different values of constant overpotential. Current densities i_1 are calculated from the intercepts. The slopes are proportional to i_1. The straight lines obtained confirm the mathematical model given by Equation 3.

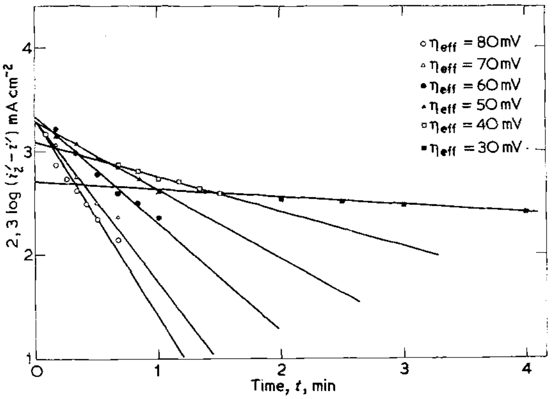

Fig. 4. 2·3 log ($i'_2 - i'$) as a function of time for different values of effective overpotential at a frequency of 10 cps. Current densities i'_1 are calculated from the intercepts. The slopes are proportional to i'_1.

This is in accordance with earlier reported results on the effective values of current density and overpotential in pulsating overpotential electrodeposition [9]. If the values of current densities in constant overpotential electrodeposition and effective current densities in pulsating overpotential electrodeposition, for the same values of constant and effective overpotentials, are related to each other by

$$i'_1 = C_1 i_1 \tag{5}$$

$$i'_2 = C_2 i_2 . \tag{6}$$

Where C_1 and C_2 are functions of overpotential, Equation 4 for pulsating overpotential electrodeposition becomes

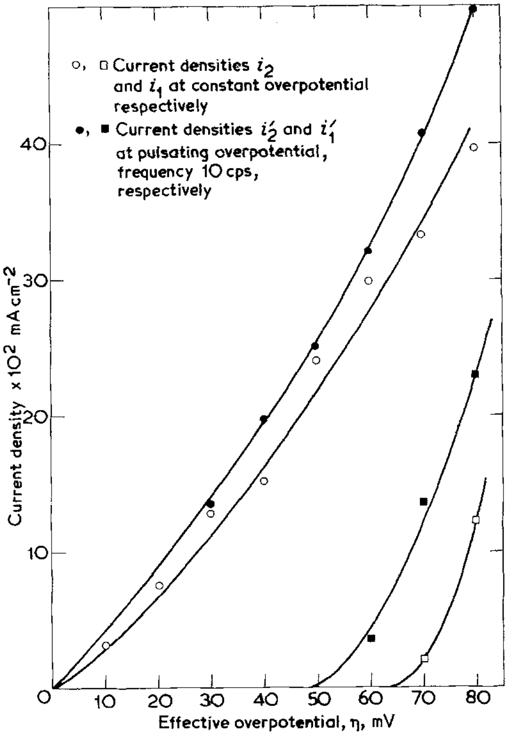

Fig. 5. Current density (i_1, i_2)–overpotential and effective current density (i'_1, i'_2)–effective overpotential relationships for constant and pulsating overpotential, respectively.

$$Q'_{1/2} = \frac{0{\cdot}5}{k} + \frac{0{\cdot}2}{k}\frac{i'_2}{i'_1} \tag{7a}$$

or

$$Q'_{1/2} = \frac{0{\cdot}5}{k} + \frac{0{\cdot}2}{k}\frac{C_2 i_2}{C_1 i_1} . \tag{7b}$$

$Q'_{1/2}$ can be related to $Q_{1/2}$ by combining Equations 4 and 7b. This relation is given by

$$Q'_{1/2} = Q_{1/2} + \frac{0{\cdot}2}{k}\left(\frac{C_2}{C_1} - 1\right)\frac{i_2}{i_1} . \tag{8}$$

The values of $C_2(\eta)$ can be obtained by digital stimulation of the process [3]. A similar procedure for calculating $C_1(\eta)$ does not yet exist. $C_1(\eta)$ and $C_2(\eta)$ can be extracted from experimental results similar to these, presented in Fig. 5, by using the relationships 5 and 6.

The comparison between $Q_{1/2}$ and $Q'_{1/2}$ can be performed by using Equations 4 and 7a and results from Fig. 5. The values of k$Q_{1/2}$ and k$Q'_{1/2}$ are presented in Fig. 6 as functions of overpotential. Increasing overpotential leads to a decrease of $Q_{1/2}$ and $Q'_{1/2}$. This is because deposition on

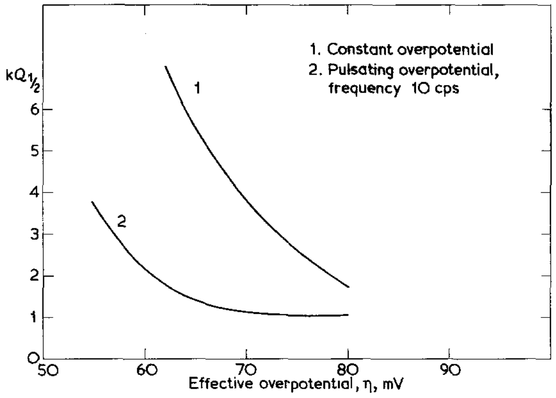

Fig. 6. $kQ_{1/2}$ and $kQ'_{1/2}$ as functions of overpotential and effective overpotential at a frequency 10 cps, respectively.

deposited film (i_2, i'_2) becomes activation-diffusion controlled. Deposition on inert substrate (i_1, i'_1) is not controlled by diffusion from the electrolyte and the increase of i_1 and i'_1 is relatively larger as compared to the increase of i_2 and i'_2. At all overpotentials $Q'_{1/2} < Q_{1/2}$ because $C_2 > C_1$.

From the results presented here, it can be concluded that the effect of pulsation on metal electrodeposition on an inert substrate is qualitatively the same as that earlier reported for pulsating overpotential copper deposition on copper electrodes [9]. Effective current densities in pulsating overpotential deposition are larger as compared to current densities in constant overpotential electrolysis for the same value of constant and effective overpotential. This is due to the non-linearity of the stationary polarization curve $i_1 - \eta$. The effect of pulsation on nucleation itself can be the object of further investigation.

In this work, experiments have been carried out at relatively low overpotentials. At higher values of overpotential, an increase of $Q_{1/2}$ and $Q'_{1/2}$ can be expected because of the non-uniform flux distribution on the rough surfaces of deposited films when electrodepostion becomes diffusion-controlled [2, 10].

The effect of frequency on the electrodeposition of metal on an inert substrate is shown in Figs. 7 and 8. The values of i'_1 and i'_2 (extracted from results similar to those presented in Figs. 2 and 4) for a pulsating overpotential of effective value 70 mV are shown as functions of frequency in Fig. 7. These results permit the calculation of the $Q'_{1/2}/Q_{1/2}$ ratios presented as a function of frequency in Fig. 8. This relationship is similar to the one reported earlier for porosity of nickel deposits on steel [1].

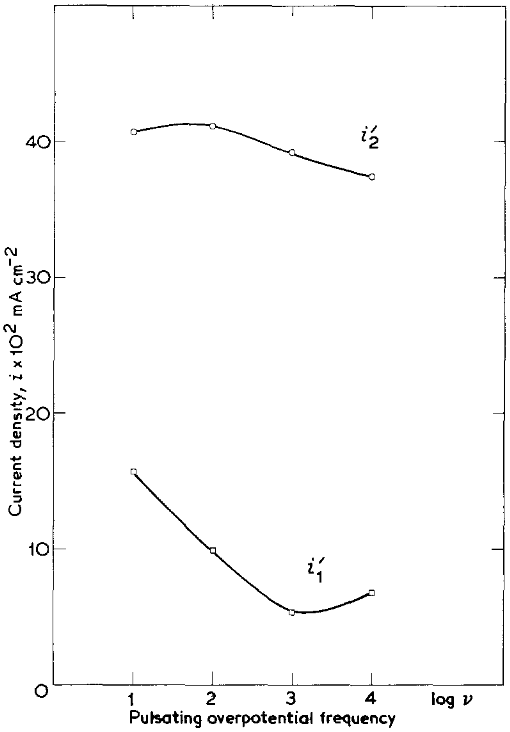

Fig. 7. Relationships between the effective current densities i'_1 and i'_2 and frequency of pulsating overpotential for $\eta_{\text{eff}} = 70$ mV.

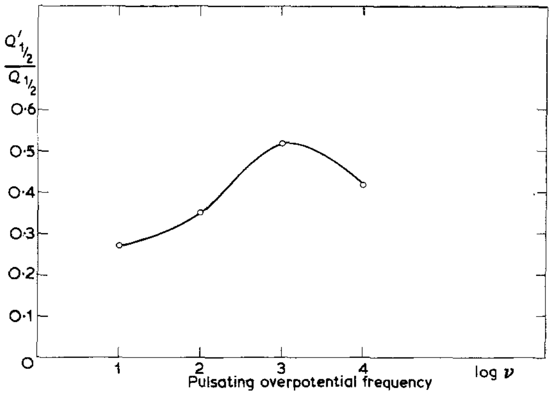

Fig. 8. The ratio $Q'_{1/2}/Q_{1/2}$ as a function of frequency of pulsating overpotential for $\eta_{\text{eff}} = 70$ mV.

On the basis of these results one can speculate that effects related to the electrodeposition of the first monolayers of metal on an inert substrate, cannot be neglected in considerations of the porosity of metal deposits.

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