JOURNAL OF APPLIED ELECTROCHEMISTRY 8 (1978) 75–79

SHORT COMMUNICATION

A computer simulation of copper depostion by pulsating overpotential

K. I. POPOV, M. D. MAKSIMOVIĆ, R. R. ADŽIĆ, G. R. OSTOJIĆ
Faculty of Technology and Metallurgy and Institute for Electrochemistry, University of Beograd, Beograd, Yugoslavia

V. B. MILOJKOVIĆ
Institute 'B. Kidrič', Beograd, Yugoslavia

Received 12 April 1977

1. Introduction

The application of pulsating potential electrolysis in the electrodeposition of metals has been treated in several recent papers. It was demonstrated that such electrolysis gives smooth metal deposits at the current densities which, in the constant overpotential electrolysis, give coarse deposits [1,2]. In addition, it was shown that the pulsating overpotential can produce a homogenous distribution of metal deposit inside the cylindrical pore [3, 4], and, in general, can give more compact deposits [5]. These effects, tested in various plating processes, showed that the porosity of layers was smaller for the layer obtained with pulsating overpotential [6, 7] than the porosity of layers of the same thickness obtained with constant potential electrolysis.

The fact that these conditions give smooth deposits at the limiting current density leads to the possible polarographic determination of the ions of positive metals; this has been explored in a series of papers [8–11]. Interesting effects were obtained in the winning of metal powders. It was shown that it is possible to control the dimensions and shapes of various metal powders [12, 13]. Most recently, the pulsating overpotential electrolysis was applied to the electrocatalytic reactions, namely the oxidation of formic acid on platinum [14].

A number of the interesting possibilities found in the application of pulsating potential electrolysis require, at this moment, a more rigorous analytical description of the electrochemical processes. This was initiated with a digital simulation of copper electrodeposition [2]. In that paper, on the basis of the polarization curves corresponding to the average values of current and overpotential, the idea of energy savings in such electrolysis was advanced. A recent work on hydrogen evolution on a silver electrode with pulsating overpotential in the activation overpotential range [15] has shown that this is quite a complex question. The purpose of this work is to investigate in detail the energetics of electrolysis with pulsating overpotential and to give precise definitions of all variables relevant to the process.

2. Basic definitions and mathematical model

In the case of electrolysis with pulsating overpotential, the overpotential η is given as a function of time, $\eta(t)$, while the current density is a function of η, and indirectly, through η, of time. Accordingly,

$$\eta = \eta(t) \tag{1}$$

$$i = i[\eta(t)] = i(t). \tag{2}$$

The average values of these functions, during a time period T, are given as,

$$\eta_{\text{av}} = \frac{1}{T}\int_0^T \eta(t)\,\mathrm{d}t \tag{3}$$

$$i_{\text{av}} = \frac{1}{T}\int_0^T i[\eta(t)]\,\mathrm{d}t. \tag{4}$$

In general, the average values of alternating current and voltage are defined in the same way. In other words, the effective values of alternating current and voltages are defined as equivalent values of d.c. current and voltage which produce the same heat in a pure ohmic resistor. The effective values in electrolysis should be defined on the basis of the main parameters of the electrochemical process. The effective current density, i_{eff}, in the pulsating potential electrolysis of a reversible reaction is equal to its average value, i_{av}. This fact is used in electrochemical coulometers, which are used as current integrators. In that case we can write,

$$i_{\mathrm{eff}} = i_{\mathrm{av}}. \tag{5}$$

The effective value of overpotential, η_{eff}, has to be defined as a constant overpotential which, when multiplied with a corresponding effective current density, gives the product, $\eta_{\mathrm{eff}} i_{\mathrm{eff}} T$, which is equal to the integral value of the corresponding time functions. Therefore, we can write,

$$\eta_{\mathrm{eff}} i_{\mathrm{eff}} T = \int_0^T \eta(t) i(t)\,\mathrm{d}t \tag{6}$$

or on the basis of Relations 3 and 5,

$$\eta_{\mathrm{eff}} = \frac{\int_0^T \eta(t) i(t)\,\mathrm{d}t}{\int_0^T i(t)\mathrm{d}t} \tag{7}$$

If a pulsating overpotential is a periodic function of time, then the corresponding average and effective values can be calculated on the basis of the above relations for the time interval equal to one period of the function when a stationary state is reached.

The specific energy consumption for the constant potential electrolysis, is defined by the following relation,

$$W_{\mathrm{sp}} = \frac{\eta i t}{\mu i t} = \frac{\eta}{\mu} \tag{8}$$

where μ is electrochemical equivalent. In the case of pulsating potential electrolysis, Equation 8 should be written as,

$$W_{\mathrm{sp,eff}} = \frac{\eta_{\mathrm{eff}}}{\mu}. \tag{9}$$

Therefore, for the same current density in the constant, η_i, and pulsating overpotential, $\eta(t)_i$ cases, only in the case when $\eta_i > \eta_{\mathrm{eff},i}$ is less energy required to carry out the electrolysis with pulsating overpotential.

The analysis of the possibilities of energy savings in metal deposition processes using pulsating overpotential electrolysis has been performed by digital simulation of copper deposition. The mathematical model used in this work is identical with the one published previously [2].

It is given by the following equations,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{10}$$

$$C(x,0) = C_0 \tag{11}$$

$$C(\delta,t) = C_0 \tag{12}$$

$$\frac{\partial C}{\partial x}(0,t) = \frac{i_0}{nFD}\left[\frac{C(0,t)}{C_0}\exp\left(\frac{\alpha_c F}{RT}\eta(t)\right) - \exp\left(-\frac{\alpha_a F}{RT}\eta(t)\right)\right] \tag{13}$$

$$i_{\mathrm{eff}} = i_{\mathrm{av}} = \frac{nFD}{T}\int_0^T \frac{\partial C}{\partial x}(0,t)\,\mathrm{d}t. \tag{14}$$

A digital simulation is performed for the square wave, sinusoidal, triangular and parabolic pulsating overpotential cases defined by Equations 15–18 respectively,

$$\eta(t) = \begin{cases} \eta_A, & kT \leqslant t \leqslant (2k+1)\dfrac{T}{2} \\ 0, & (2k+1)\dfrac{T}{2} \leqslant t \leqslant (k+1)T \end{cases} \tag{15}$$

$$k = 0, 1, 2 \ldots$$

$$\eta(t) = \frac{\eta_A}{2} + \frac{\eta_A}{2}\sin\frac{2\pi t}{T} \tag{16}$$

$$\eta(t) = \begin{cases} \dfrac{2\eta_A}{T}\left(t - kT + \dfrac{T}{4}\right), & \dfrac{4k-1}{4}T \leqslant t \leqslant \dfrac{4k+1}{4}T \\ -\dfrac{2\eta_A}{T}\left(t - kT - \dfrac{3T}{4}\right), & \dfrac{(4k+1)T}{4} \leqslant t \leqslant \dfrac{4k+3}{4}T \end{cases} \tag{17}$$

$$k = 0, 1, 2, \ldots$$

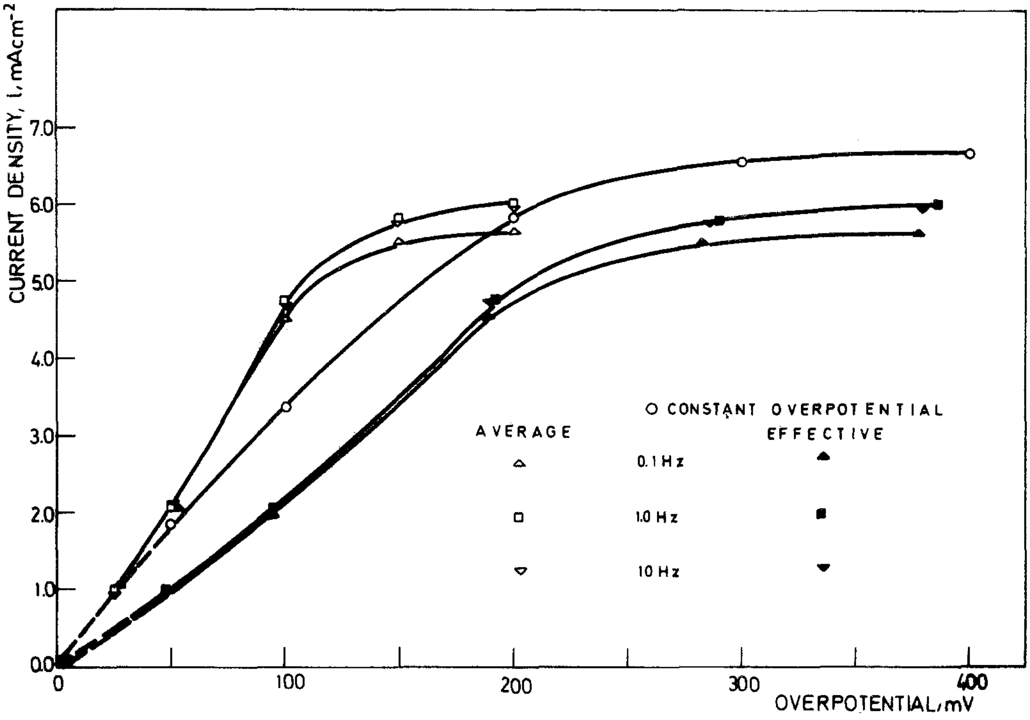

Fig. 1. Polarization curve for constant potential electrolysis and digital simulation of polarization curves for average and effective values of overpotential. Square-wave overpotential at three different frequencies.

$$\eta(t) = \begin{cases} \dfrac{\eta_A}{T^2}(t-kT)^2; \; kT \leqslant t \leqslant \dfrac{2k+1}{2}T \\[2ex] \dfrac{\eta_A}{T^2}(t-kT-T)^2; \; \dfrac{(2k+1)T}{2} \leqslant t \leqslant (k+1)T \end{cases} \qquad (18)$$
$$k = 0, 1, 2 \ldots.$$

The symbols have their usual meanings in electrochemistry. η_A is an amplitude value of pulsating overpotential, and T, a period of pulsation. The simulation was performed with the following set of physical constants: $C_0 = 1 \cdot 10^{-4}$ mol cm^{-3}; $n = 2$; $F = 10^5$ A s mol^{-1}; $(\alpha_c F)/2.3RT = 1/120$ mV^{-1}; $D = 10^{-5}$ cm^2 s^{-1}; $i_0 = 1 \times 10^{-3}$ A cm^{-2}; $\delta = 3 \times 10^{-2}$ cm; $(\alpha_a F)/2.3RT = 1/40$ mV^{-1}. The method of digital simulation is identical with that used previously [2].

3. Results and discussion

The results of the digital simulation of copper deposition with different shapes of pulsating overpotentials for the frequencies 0.1, 1.0 and 10 Hz are shown in Figs. 1–4. The curves represent the average and effective values of overpotentials. Also, for the purpose of comparison, the curves of constant overpotential electrolysis are given. It is seen that in each case, for all current densities, the effective overpotentials are higher than the constant overpotentials. This means that the pulsating overpotential electrolysis requires a somewhat larger energy consumption. This should not be considered as an important drawback of such electrolysis bearing in mind the other considerable improvements to the processes of metal deposition mentioned in the first part of the paper. It appears that in each particular case one should compare all the characteristics of constant and

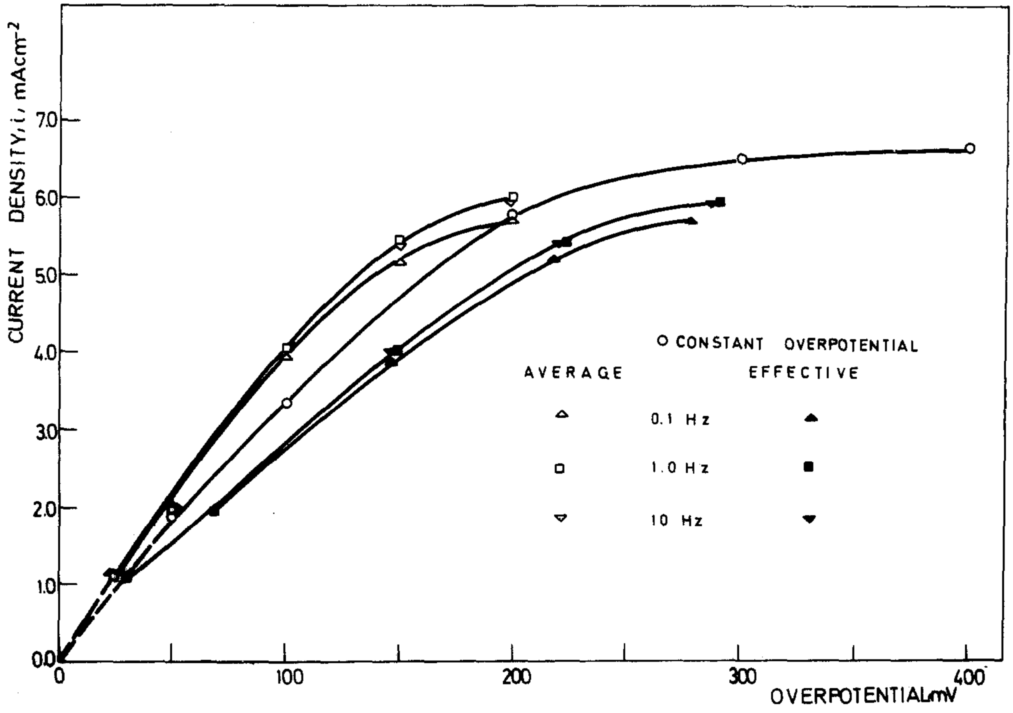

Fig. 2. The same as in Fig. 1. but for triangular overpotential.

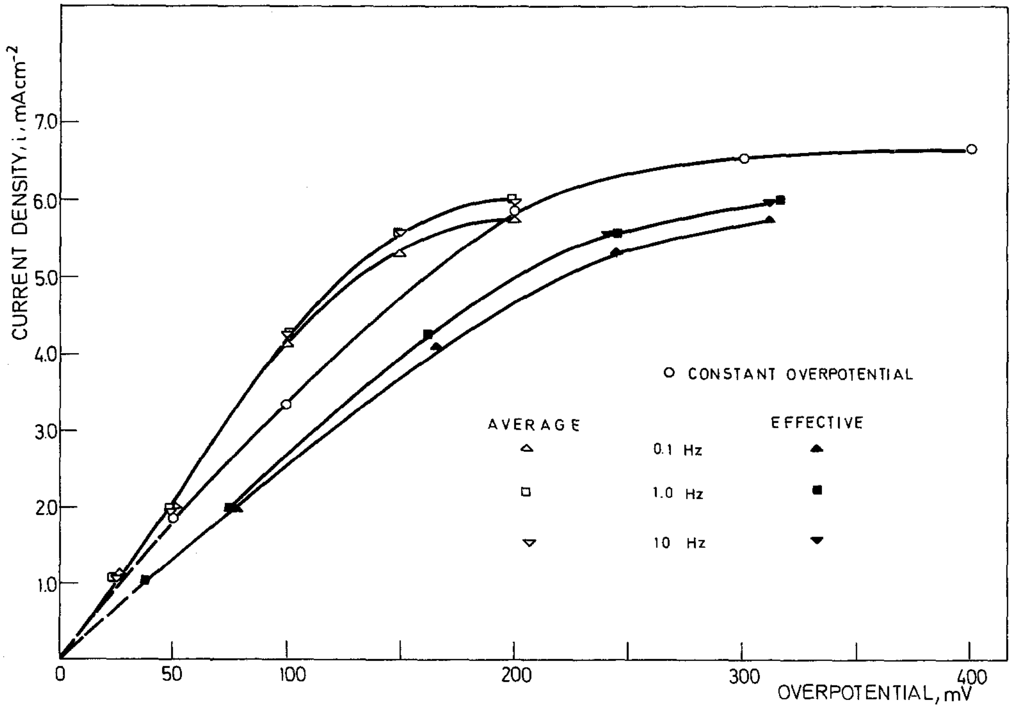

Fig. 3. The same as in Fig. 1. but for sinusoidal overpotential.

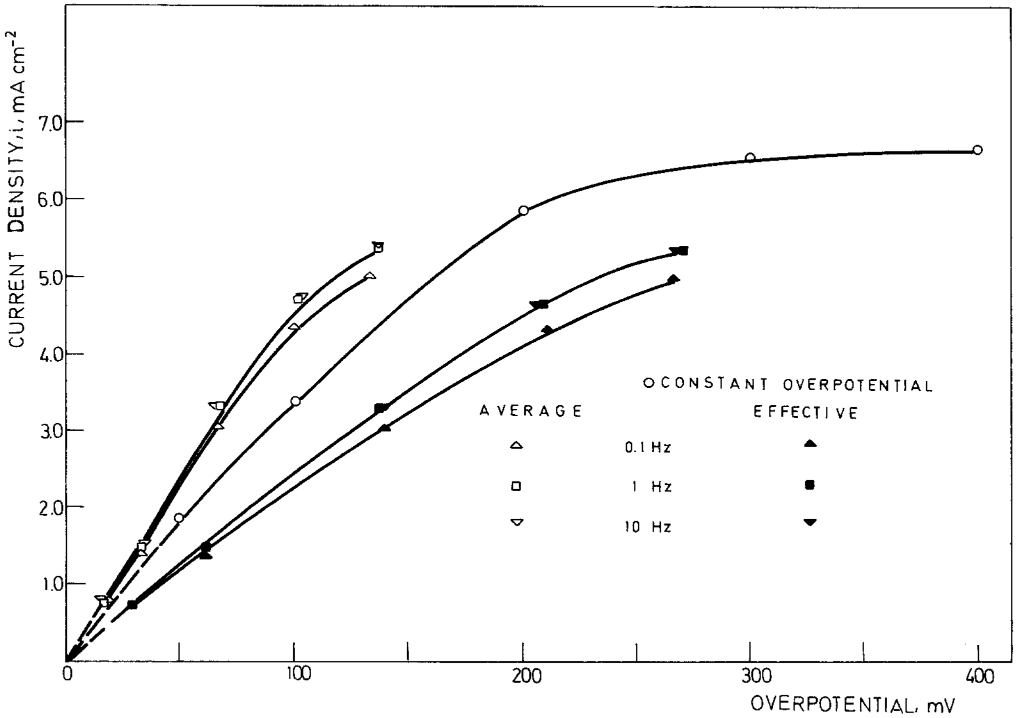

Fig. 4. The same as in Fig. 1. but for parabolic overpotential.

pulsating overpotential electrolysis respectively, and then decide which one to apply, considering all requirements in the quality of deposits, productivity of the electrolyser, and other parameters of electrolytic production.

Acknowledgements

The authors are indebted to the N.S.F. (USA) for its sponsorship under the PL-480 Programme and to the Fund for Research of the SR of Serbia, whose material support has made this work possible.

References

[1] A. R. Despić and K. I. Popov, *J. Appl. Electrochem.* 1 (1971) 275.
[2] K. I. Popov, D. N. Keča, S. I. Vidojković, B. J. Lazarević and V. B. Milojković, *ibid* 6 (1976) 365.
[3] K. I. Popov, B. J. Lazarević, D. N. Keča, M. V. Vojnović and D. S. Dojčinović, *Glasnik hem. društva, Beograd* 40 (1975) 379.
[4] K. I. Popov, B. J. Lazarević, V. B. Milojković, D. N. Keča, M. V. Vojnović and Dj. B. Damjanović, *ibid* 40 (1975) 385.
[5] K. I. Popov, D. N. Keča and G. R. Ostojić, *J. Appl. Electrochem.* 6 (1976) 425.
[6] K. I. Popov, D. N. Keča, D. A. Drašković and B. I. Vuksanović, *ibid* 6 (1976) 155.
[7] K. I. Popov, D. N. Keča and B. I. Vuksanović, *ibid*, 7 (1977) 185.
[8] K. I. Popov, D. N. Keča and M. D. Maksimović, *Glasnik hem. društva Beograd,* (in press).
[9] K. I. Popov, M. D. Maksimović and D. N. Keča, *ibid* (in press).
[10] M. D. Maksimović, N. S. Blagojević and K. I. Popov, *ibid* (in press).
[11] N. S. Blagojević, M. D. Maksimović and K. I. Popov, *Chem. Eng. J.* (in press).
[12] K. I. Popov, D. N. Keča and M. D. Maksimović, *J. Appl. Electrochem.* 7 (1977) 77.
[13] K. I. Popov, M. D. Maksimović, M. G. Pavlović and G. R. Ostojić, *ibid* 7 (1977) 331.
[14] R. R. Adžić, K. I. Popov and M. A. Pamić, *Electrochim. Acta* (submitted).
[15] K. I. Popov, R. R. Adžić, M. D. Maksimović and G. R. Ostojić, *Glasnik hem. drůstva Beograd* (in press).