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Letter to the editor: on optimization of electrolysis

In a recent paper on 'Time optimal electrodeposition of metals with a pulsating current' [1] the authors specify the final state to be reached over a minimum time period as

$$C(T,x) = C_s + (C_0 - C_s)\frac{x}{\delta} \qquad (6)$$

where C_s is a critical surface concentration. The diffusion problem defined in Equations 1–4 has been shown [2] to possess an analytical solution, according to which one can write that

$$C(T,x) = C_0 - \frac{2\lambda D^{1/2}\,T^{1/2}}{\pi^{1/2}} \exp\left(-\frac{x^2}{4DT}\right) + \lambda x \operatorname{erfc}\frac{x}{2D^{1/2}\,T^{1/2}}; \lambda \equiv \frac{\partial C}{\partial x}\bigg|_{x=0}$$

and

$$C_s(T) = C_0 - \frac{2\lambda D^{1/2}\,T^{1/2}}{\pi^{1/2}}.$$

It then follows, that

$$C(T,x) = C_s(T) + \frac{2\lambda D^{1/2}\,T^{1/2}}{\pi^{1/2}}\left(1 - \exp\left(-\frac{x^2}{4DT}\right) + \lambda x \operatorname{erfc}\frac{x}{2D^{1/2}\,T^{1/2}}\right).$$

If one now stipulates small x, then in the neighbourhood of the electrode, we have

$$C(T,x) = C_s(T) + \frac{C_0}{\delta}x - \frac{C_0 x^2}{D^{1/2}\,T^{1/2}\delta}\left(\frac{1}{\pi^{1/2}} - \frac{1}{2\pi^2}\right)$$

Equation 6 appears to be questionable, although its linear form is rather enticing for mathematical analysis.

Secondly, the authors state on p. 164 in the footnote that an effective value is given as 66% of the pulse plateau. Since the pulse form in Fig. 1 is aperiodic, an associated effective value is at best, a fictitious quantity. One can, however, force periodicity on it, for the sake of calculation, by writing a Fourier series, using an appropriately chosen period. Then, the effective value can be defined as

$$I_e^2 = 2\sum_{n=1}^{\infty} |a_n^2| + a_0^2$$

where a_n are the coefficients of the Fourier expansion. In a rigorous calculation, I_e^2 is rather involved in the given case; its lower bound can be quickly estimated by considering the first pulse only and taking the overall pulse-form period as the period of expansion. The one-sided even-function expansion yields

$$\text{lower bound of } I_e^2 = \frac{4I_{\max}^2}{\pi^2}\sum_n \frac{\sin^2(n\pi 200)/557}{n^2} + \frac{4I_{\max}^2 200^2}{557^2}$$

whose first term ($n = 1$) yields the crude estimate of the lower bound of

$$\frac{I_e^2}{I_{\max}^2} = 0{\cdot}857;$$

this is significantly higher than 0·66.

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T. Z. FAHIDY,

University of Waterloo,

Waterloo, Ontario, Canada.

Rererences

[1] K. I. Popov *et al.*, *J. Appl. Electrochem.* 3 (1973) 161.
[2] P. Delahay, 'New Instrumental Methods in Electrochemistry', Interscience (1954).

Author's reply

The solution quoted in [1] is the solution of the semi-infinite linear diffusion problem at *constant* current at the electrode surface. However, the problem stated in [2] is quite different. First of all, the stirred solution (finite diffusion layer thickness) was considered. Secondly, it was desired to find the *time variable* current at the electrode surface which will transfer the system, for minimal time T, to the specified final state

$$C(T, X) = C_s + (C_0 - C_s)\frac{X}{\delta}.$$

It can be seen from the derivation in the Appendix A of [2] that this state is the reachable state.

Concerning the second remark, the word 'effective' has been used in the sense 'that produces the same effect' i.e. the effective current is the d.c. current which produces the same amount of metal deposit. Consequently the effective current in our paper is the average d.c. current ($0{\cdot}66\, I_{\mathrm{max}}$).

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K. I. POPOV
Institute for Chemistry,
Technology and Metallurgy
Beograd, Yugoslavia
B. J. LAZAREVIĆ
Institute for Nuclear Sciences
"Boris Kidrič", Beograd
Yugoslavia

References

[1] T. Z. Fahidy *J. Appl. Electrochem.* 4 (1974) 275.
[2] K. I. Popov *et al.*, *J. Appl. Electrochem.* 3 (1973) 161.