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Short communication

SHORT COMMUNICATION

The current distribution in an electrochemical cell. Part V. The determination of the depth of the current line penetration between the edges of the electrodes and the side walls of the cell

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A method for the calculation of the depth of the current line penetration between the edges of the electrodes and the side walls of the cell in a cell with plane parallel electrode arrangement is proposed. The method is verified by the calculation of the polarization curves for the cells in which the electrode edges do not touch the side walls of the cell. The agreement between the calculated and the measured values was fair.

Keywords: metal electrodeposition, electrochemical cell, current distribution.

It was shown earlier[1] that the current density-cell voltage relationship for cells with plane parallel electrodes, in which the electrode edges do not touch the side walls of the cell, is given by

$$U = U_r + \eta_a - \eta_c + \frac{\rho l j A}{2L} \ln\left(1 + \frac{2L}{A}\right) \qquad (1)$$

where U is the cell voltage, U_r is the reversible cell voltage, η_a and η_c are the anodic and cathodic overpotentials, respectively, ρ is the resistivity of the electrolyte, A is the length of the electrode, l is the distance between the electrodes, L is the depth of current line penetration between the edges of electrodes and the side walls of the cell and j is the current density, assuming a homogeneous current distribution over all the electrode, except the very edge. On the other hand, η_a and η_c are given by

$$\eta_a = b_a \log (j/j_{0,a}) \qquad (2)$$

and

$$\eta_c = - b_c \log\left(\frac{j}{j_{0,c}} \frac{j_L}{j_L - j}\right) \qquad (3)$$

where b_a and b_c are the anodic and cathodic Tafel slopes, $j_{0,a}$ and $j_{0,c}$ are the exchange current densities for the anodic and cathodic processes and j_L is the limiting diffusion current for the cathodic process.

As was shown earlier,[2] Eq. (1) is valid when

$$0 < L \leq L_{max} \tag{4}$$

where

$$L_{max} = \frac{l}{2} \tag{5}$$

A method for the calculation of L was given recently,[2] but with the unrealistic assumption that the maximum length of the current line between the edges of the electrodes l' is ∞. Following the same procedure, but taking into account that the maximum value of l' is l 2, which is in accordance with Eq. (5), one obtaines

$$L = \frac{l}{2}\left[\left(\frac{\eta_a - \eta_c + \rho l j}{\eta_a - \eta_c + \frac{\sqrt{2}}{2}\rho l j}\right)^2 - 1\right]^{1/2} \tag{6}$$

It can easily be shown that $L = 0$ when

$$\eta_a - \eta_c >> \rho l j \tag{7}$$

and when

$$\eta_a - \eta_c << \rho l j \tag{8}$$

$L=l/2$, which is equal to Eq. (5).

This means that in the case of total ohmic control the current line penetration into the solution is maximum and that in the case of total electrochemical control it is not present.

Substitution of L from Eq. (6) into Eq. (1) permits the calculation of the polarization curve for $L > 0$, if the distance between the electrode edges and the side wall is equal to or larger than L_{max}.

Obviously, L from Eq. (6) will be substituted into Eq. (1) if

$$L' > L \tag{9}$$

where L' is the electrode edges-side wall distance. If

$$L' < L \tag{10}$$

the L' value should be substituted into Eq. (1). The equation of the polarization curve for $L = 0$ is obviously

$$U = U_r + \eta_a - \eta_c + \rho l j \tag{11}$$

RESULTS AND DISCUSSION

As was shown in the previous paper in this series, the system Cu|0.1 M $CuSO_4$, 0.1 M H_2SO_4|Cu can be described by b_a=40 mV dec^{-1}, b_c=120 mV dec^{-1}, j_0=1 mA cm^{-2} and r=17 W cm. Also the system Cu|0.1 M $CuSO_4$, 0.1M H_2SO_4|PbO_2 can be described by b_a=120 mV dec^{-1} and $j_0(O_2)=2\cdot 10^{-4}$ mA cm^{-2} and U_r=1.1 V if the kinetic parameters for copper deposition are the same as in the previous case.

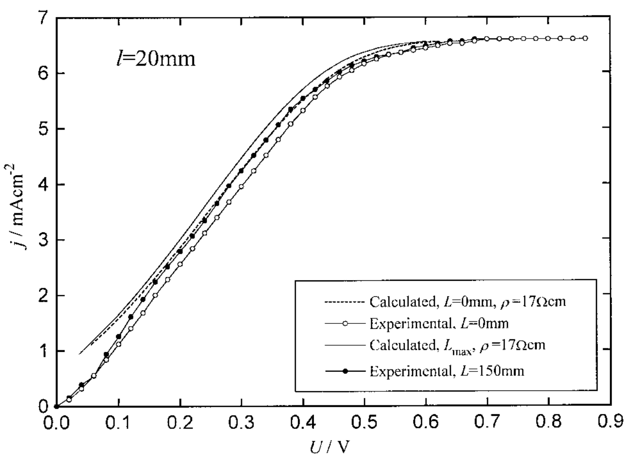

Fig. 1. The current density-cell voltage dependences of the system Cu|0.1 M $CuSO_4$, 0.1 M H_2SO_4|Cu with an interelectrode distance l = 20 mm for the distances between the edges of the electrodes and the side wall L=0 and L=150 mm. The calculation was done using Eqs. (1), (6) and (11).

The polarization curves for $0 < L < L'$ (normalized to the polarization curves for L = 0, obtained from Figs. 4–7 and Figs. 12 and 13, Ref. 2) and for $L' < L$ (normalized to the polarization curves for L = 0, obtained from Figs. 7 and 13, Ref. 2), calculated from Eqs. (1), (6) and (11), are presented in Figs. 1–6. The agreement

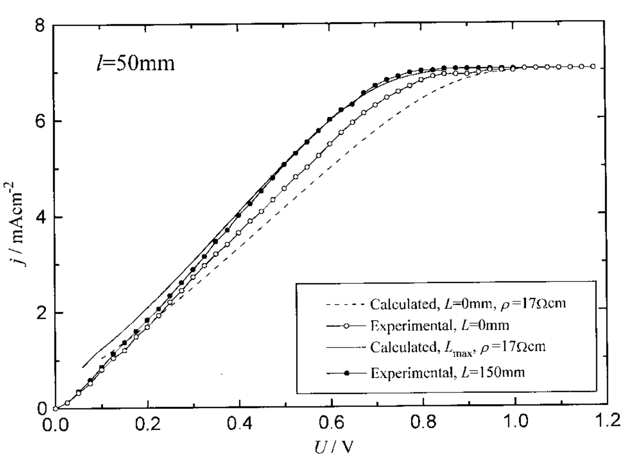

Fig. 2. The current density-cell voltage dependences of the system Cu|0.1 M $CuSO_4$, 0.1 M H_2SO_4|Cu with an interelectrode distance l = 50 mm for the distances between the edges of the electrodes and the side wall L=0 and L=150 mm. The calculation was done using Eqs. (1), (6) and (11).

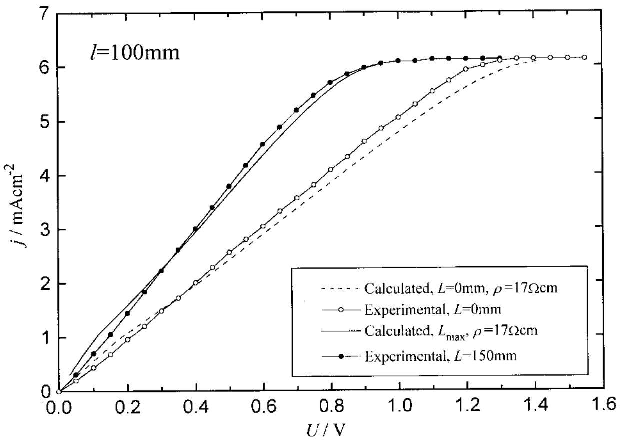

Fig. 3. The current density-cell voltage dependences of the system Cu|0.1 M $CuSO_4$, 0.1 M H_2SO_4|Cu with an interelectrode distance l = 100 mm for the distances between the edges of the electrodes and the side wall $L = 0$ and L=150 mm. The calculation was done using Eqs. (1), (6) and (11).

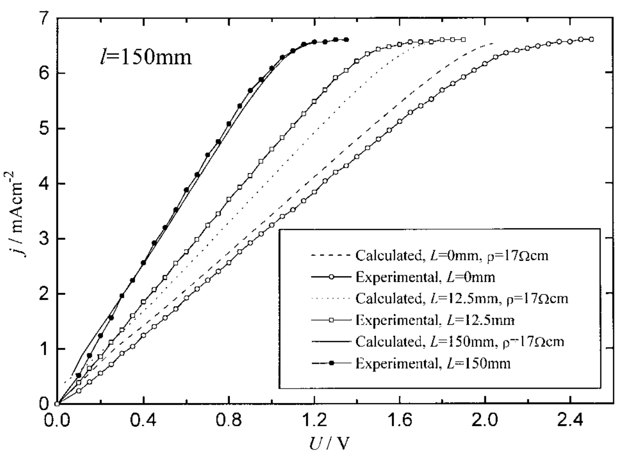

Fig. 4. The current density-cell voltage dependences of the system Cu|0.1 M $CuSO_4$, 0.1 M H_2SO_4|Cu with an interelectrode distance l = 150 mm for different distances between the edges of the electrodes and the side wall. The calculation was done using Eqs. (1), (6) and (11).

between the calculated and the experimentaly obtained values is very good. It is seen that polarization curves can be calculated for different interelectrode distances and copper anodes (Figs. 1–4), and lead anodes (Figs. 5 and 6). Comparisons of the experimental and calculated curves for different $L' < L$ for copper and lead anodes are shown in Figs. 4 and 6, respectively. In this way the calculation of L was verified, as well as the possibility of using L' directly in the calculation of polarization curves, if $L' < L$. Hence, the method of calculation of the very edge current density, proposed in an earlier paper,[2] has been verified in an indirect way. The direct proof of this method will be given in the next paper.

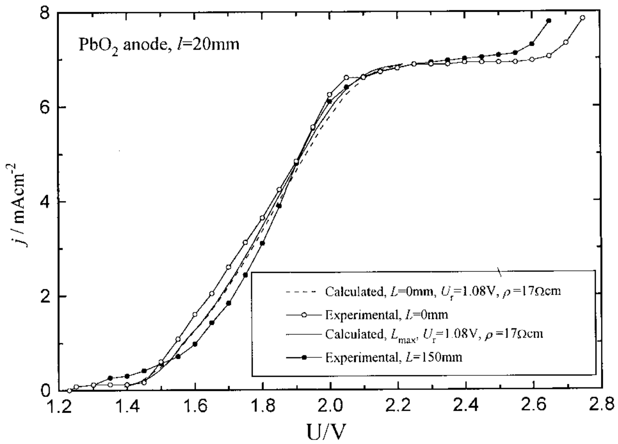

Fig. 5. The current density-cell voltage dependences of the system Cu|0.1 M $CuSO_4$, 0.1 M H_2SO_4|PbO_2 with an interelectrode distance l = 20 mm for the distances between the edges of the electrodes and the side wall L = 0 and L=150 mm. The calculation was done using Eqs. (1), (6) and (11).

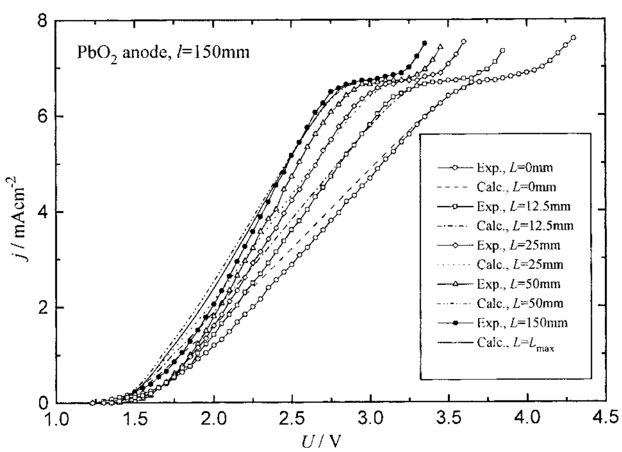

Fig. 6. The current density-cell voltage dependences of the system Cu|0.1 M $CuSO_4$, 0.1 M H_2SO_4|PbO_2 with an nterelectrode distance l =150 mm for different distances between the edges of the electrodes and the side wall. The calculation were done using Eqs. (1), (6) and (11).

И З В О Д

РАСПОДЕЛА СТРУЈЕ У ЕЛЕКРОХЕМИЈСКОЈ ЋЕЛИЈИ. ДЕО 5. ОДРЕЂИВАЊЕ ДУБИНЕ ПРОДИРАЊА СТРУЈНИХ ЛИНИЈА ИЗМЕЂУ ИВИЦА ЕЛЕКТРОДА И БОЧНИХ ЗИДОВА ЋЕЛИЈЕ

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Предложен је метод за израчунавање дубине продирања струјних линија у простор између ивица електрода и бочних зидова ћелије за случај планпаралелних електрода. Верификација метода је извршена израчунавањем поларизационих кривих за ћелије код

којих ивице електрода не належу на бочне зидове ћелије. Слагање између прорачуна и мерених вредности је добро.

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