

NOTE

**The current distribution in an electrochemical cell. Part VI.
The quantitative treatment for cells with three plane parallel
electrode arrangements**

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(Received 9 March, revised 9 April 2001)

A method for the quantitative determination of the current density distribution in cells with a three plane parallel electrode arrangement is proposed. It is shown that the current density distribution can be determined using the data obtained by simple polarization measurements. The relation to the Haring-Blum cell with $P = 2$ is discussed.

Keywords: metal electrodeposition, electrochemical cell, current distribution.

INTRODUCTION

In an electrochemical cell with plane parallel electrodes, the current density is higher at the edge than at the center of the electrode. This phenomenon is considered in this series of papers in order to promote a new method of the determination of the current density distribution. In parts I¹ and II² of this series the results of widely performed experimental investigations are presented since other papers deal with the interpretation of them. The purpose of this note is to show the possibility of the quantitative determination of the current density distribution using the results of the polarization measurements, as well as the possibility of calculation of it using the kinetic parameters data. The analysis of current density distribution is given for a cell with a three plane parallel electrodes arrangement, using the results obtained in cells with two plane parallel electrodes from Ref. 1.

The cell with a three plane parallel electrode arrangement is presented in Fig. 1.

The current density distribution in the cell shown in Fig. 1 can be easily determined by polarization measurements in cells with two plane parallel electrodes. For example, the diagrams from Figs. 4–7, Ref. 1, permit the determination of the values of

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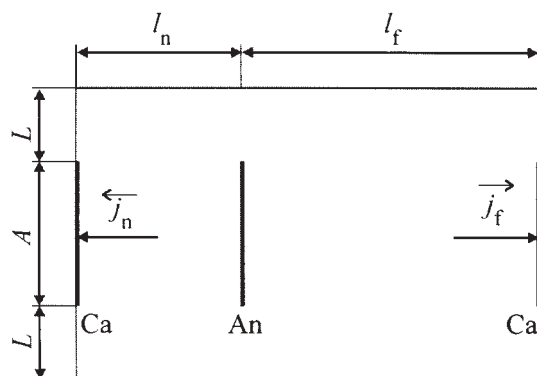


Fig. 1. The cell with a three plane parallel electrodes arrangement. An is the anode and Ca are the cathodes, L is the electrode edge – cell side wall distance, A is the electrode width, and l_n and l_f are the anode – near cathode and anode – far cathode distances, respectively, j_n and j_f are the corresponding current densities.

the current densities on the cathodes at four different distances from the anode and different electrode edges – cell side walls distance at different cell voltages.

The current density – cell voltage dependencies can also be calculated² using the equation

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

where U is the cell voltage, η_a and η_c are the anodic and cathodic overpotentials, ρ is the resistivity of the solution, j is the current density in the homogenous field and l is the interelectrode distance. L' in Eq. (1) represents the maximum depth of the penetration of the current lines in the space between the electrode edges and the cell side walls given by Eq. (2)³

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

It is equal to the half interelectrode distance only in the case of total Ohmic control. Obviously, Eq. (2) is valid if

$$L > L' \quad (3)$$

On the contrary, if

$$L < L' \quad (4)$$

L instead L' should be substituted into Eq. (1). Hence, the calculations of the current density – cell voltage dependencies must begin with the determination of the relation between L and L' . If Eq. (3) is valid, L' is substituted into Eq. (1), and *vice-versa*.

Using data from Figs. 4 – 7, Ref. 1, for $L = 0$ and different l , the cell voltage – interelectrode distance dependencies for different current densities can be obtained, which are shown in Fig. 2.

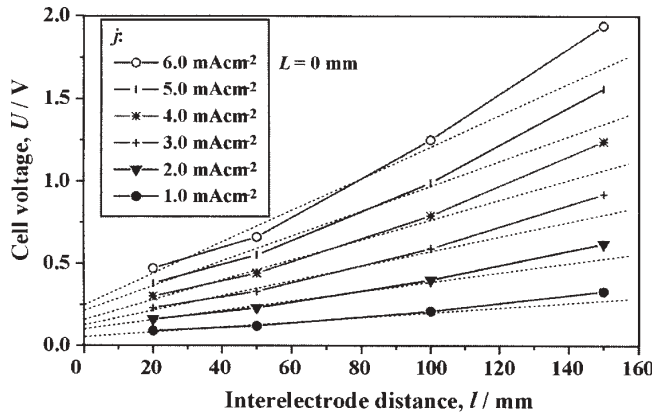


Fig. 2. The cell voltage – interelectrode distance dependencies for $L = 0$ in $\text{Cu}|0.1 \text{ M CuSO}_4, 0.1 \text{ M H}_2\text{SO}_4|\text{Cu}$, data from Fig. 4–7, Ref. 1.

Obviously, the intercepts represent the difference of anodic and cathodic overpotentials for selected values of current density, and the resistivity of the electrolyte can be determined from corresponding slopes, which are given in Table I.

TABLE I. The difference of the anodic and cathodic overpotentials and resistivity of the electrolyte for selected values of current density, obtained from Fig. 2

$j/\text{mA cm}^{-2}$	$\eta_a - \eta_c/\text{V}$	$\rho/\Omega \text{ cm}$
1.0	0.06	14.0
2.0	0.09	14.5
3.0	0.13	14.7
4.0	0.17	14.8
5.0	0.20	15.2
6.0	0.23	16.2

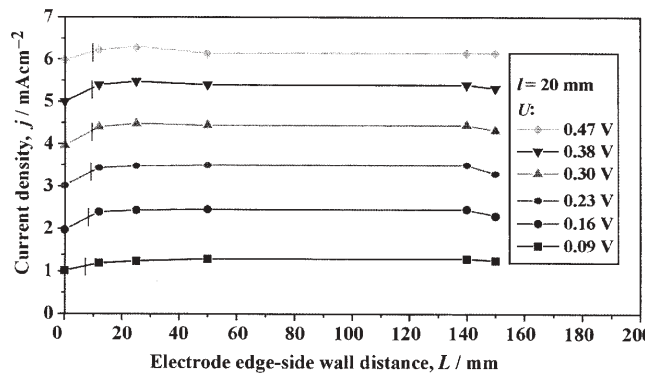


Fig. 3. Current densities for different cell voltages as a function of electrode edge – cell side wall distance in a cell with interelectrode distance $l = 20 \text{ mm}$ for the system $\text{Cu}|0.1 \text{ M CuSO}_4, 0.1 \text{ M H}_2\text{SO}_4|\text{Cu}$. Data from Figs. 4–7, Ref. 1.

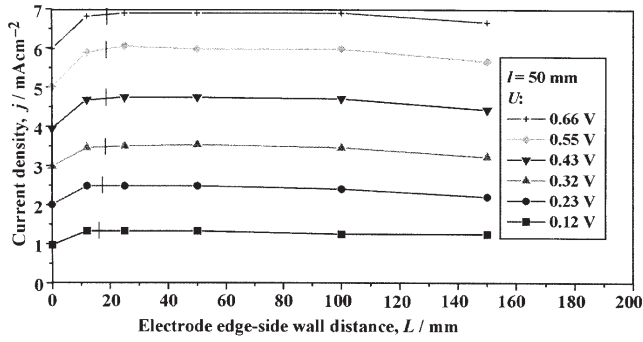


Fig. 4. The same as in Fig. 3 but for $l = 50 \text{ mm}$.

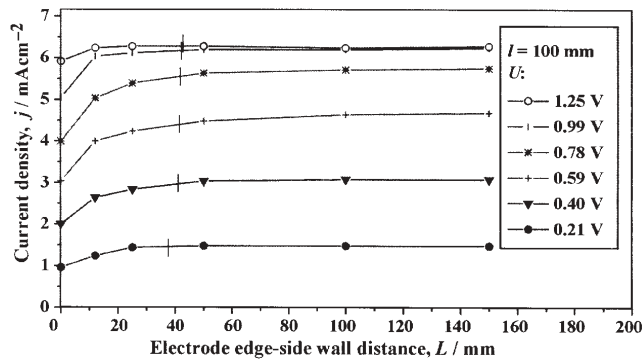


Fig. 5. The same as in Fig. 3 but for $l = 100 \text{ mm}$.

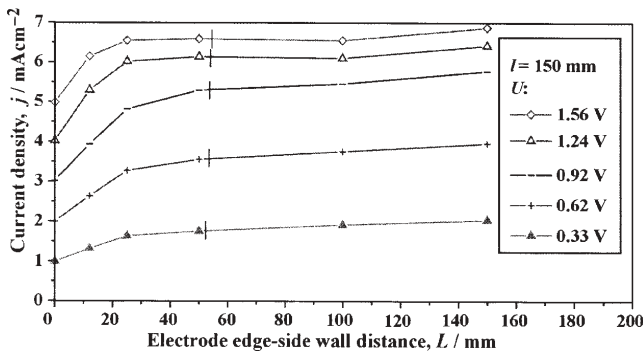


Fig. 6. The same as in Fig. 3 but for $l = 150 \text{ mm}$.

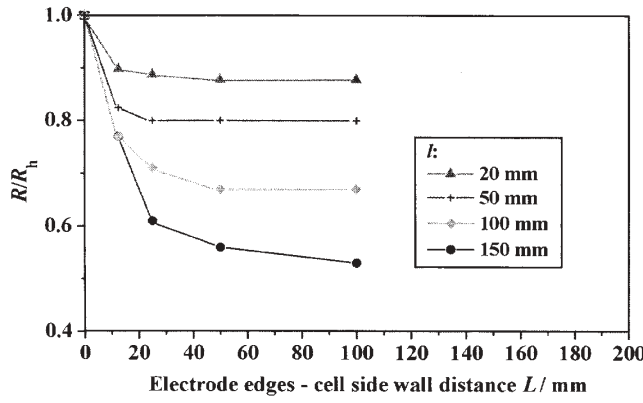


Fig. 7. R/R_h ratios calculated from polarization measurements (data from Figs. 3–6) using Eq. (5) as a function of L .

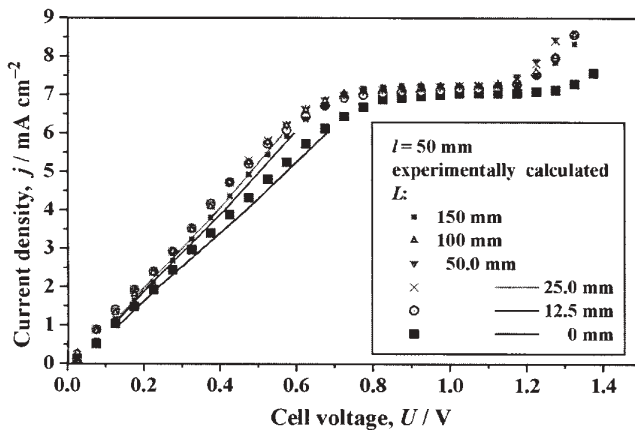


Fig. 8. The cell voltage – current density dependencies (lines) for $l = 50$ mm, calculated using Eqs. (1) and (2) and data from Fig. 2. Points are taken from Figs. 5, 6, Ref. 1.

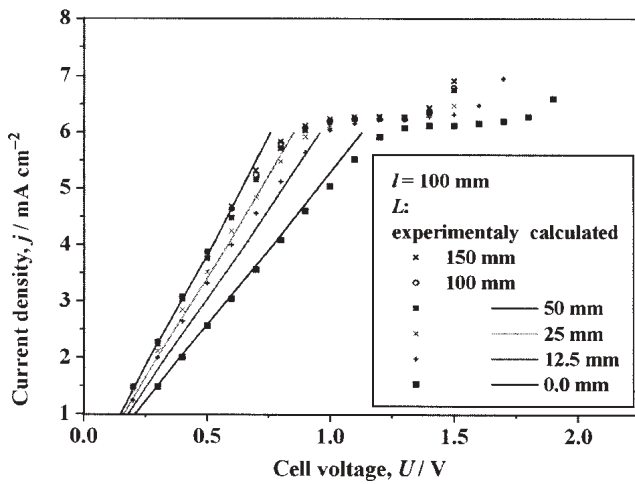


Fig. 9. The same as in Fig. 8. but for $l = 100$ mm.

The diagrams from Figs. 4 – 7, Ref 1, can also be presented in the form given in Figs. 3 – 6, respectively, in order to directly determine the depth of the penetration of the current lines in the space between the electrode edges and the cell side walls.

It can be seen from Figs. 3–6 that the change of current with increasing L virtually ceases at $L = l/2$ for $l < 2A$, at $L = A$ for $l > 2A$ and that L' can be successfully calculated using Eq. (2) and the values from Table I. The calculated L' is marked by a thin vertical line on the current density/electrode edge – side wall distance dependencies in Figs. 3 – 6.

In a previous paper the validity of Eqs. (1) and (2) was tested in the following way: using Eq. (2) and literature kinetic parameters data L' was calculated for different electrochemical cells and the polarization curves were calculated using Eq. (1). The agreement between calculated and measured polarization curves was fair, but this procedure permits the more direct proof of validity of Eq. (2).

Hence, Eq. (2) is valid for $l \leq 2A$ and $L > L'$. At larger interelectrode distances for $l > 2A$, L' remains constant and equal to A .

Besides, the Ohmic voltage drop for each case can be determined as the difference between cell voltage and the intercept values. It follows from

$$U_{\Omega} = RI \quad (5)$$

that

$$\frac{U_{\Omega}}{U_{\Omega,h}} = \frac{R}{R_h} \quad (6)$$

where U_{Ω} and $U_{\Omega,h}$ are the Ohmic voltage drops at fixed l and j or I values, for $L > 0$ and $L = 0$ and R and R_h are the corresponding values of the Ohmic resistance. Using the data from Figs. 3 – 6, the R/R_h ratios were calculated as a function of L for different l values and plotted in Fig. 7.

The good agreement with the result of Ohmic resistance measurements⁴ is obvious, for deposition in conditions close to complete Ohmic control. ($l = 100$ mm and $l = 150$ mm).

Using Eqs. (1) and (2) and the $\eta_a - \eta_c$ and ρ values from Table I, dependencies like those from Figs. 4 – 7, Ref. 1, were calculated and are presented in Figs. 8 and 9.

The experimental points in diagrams shown in Figs. 8 and 9 were taken from corresponding plots shown in Figs. 4 and 5, and the lines were calculated.

It can be seen from Figs. 8 and 9 that the agreement between the calculated and measured values is very good. In this way a method for the calculation of L' , and, hence, the edge current density is verified, as well as the possibility of the calculation of cell voltage – current density dependencies.

The current density distribution in the cell shown in Fig. 1 is determined by the j_n/j_f ratio. It is obvious that

$$1 \leq j_n/j_f \leq 2 \quad (7)$$

because 1 corresponds to a completely even distribution and 2 to a primary distribution.

For selected U and L values the j_n/j_f ratios can be calculated using measured values of current densities $(j_n/j_f)_m = v_m$ from Figs. 4 and 5 and calculated ones $(j_n/j_f)_c = v_c$ from Figs. 8 and 9. It can be seen from Table II that the agreement between the ratios j_n/j_f obtained using measured and calculated values of current densities is very good, meaning that the current density distribution in cells like that in Fig. 1 can be precisely determined using Eqs. (1) and (2) and data obtained by simple polarization measurements, or even literature kinetic parameters data.

TABLE II. Ratios j_n/j_f obtained from measured and calculated values; $l_n = 50$ mm, $l_f = 100$ mm

L/mm	U/V	Measured			Calculated			$(v_c - v_m)/v_m$ %
		$j_n/\text{mA cm}^{-2}$	$j_f/\text{mA cm}^{-2}$	$v_m=(j_n/j_f)_m$	$j_n/\text{mA cm}^{-2}$	$j_f/\text{mA cm}^{-2}$	$v_c=(j_n/j_f)_c$	
0		2.0	1.20	1.83	2.05	1.20	1.71	6.6
12.5	0.25	2.65	1.60	1.65	2.35	1.45	1.62	1.8
25		2.64	1.76	1.50	2.45	1.55	1.58	5.3
0		4.56	2.56	1.78	4.30	2.55	1.69	5.1
12.5	0.50	5.44	3.32	1.64	4.95	3.00	1.65	0.6
25		5.60	3.52	1.59	5.20	3.35	1.55	2.5

According to Haring and Blum,⁵ the throwing power T is given by

$$T = (P - M) / P \times 100 \% \quad (8)$$

where

$$P = l_{\text{far}} / l_{\text{near}} \text{ and } M = (\Delta m_{\text{near}}) / (\Delta m_{\text{far}}) \quad (9)$$

where l_{far} and l_{near} are cathode–anode distance, respectively, and Δm_{far} and Δm_{near} are the weight of deposit on the far and the near cathode, respectively. Assuming that the current efficiency is approximately the same, j instead Δm can be used in Eq. (9). The analysis given in this paper is performed for the cell in which the electrode edges do not touch the cell side walls. Obviously, the Haring–Blum cell is described if $L = 0$ in Eq. (1).

Typical Haring–Blum throwing power cells have $P = 5$, *i.e.*, the far cathode is 5 times further from the anode than near cathode, or $P = 2$. It should be noted that the electrode edges in Haring–Blum cells touch the cell side walls, and that current densities required in Eqs. (8) and (9) for $L = 0$ can be taken from Figs. 8 and 9.

ИЗВОД

РАСПОДЕЛА СТРУЈЕ У ЕЛЕКТРОХЕМИЈСКОЈ ЋЕЛИЈИ. ДЕО VI. КВАНТИТАТИВНА АНАЛИЗА ЋЕЛИЈА СА ТРИ ЕЛЕКТРОДЕ У ПЛАНПАРАЛЕЛНОМ РАСПОРЕДУ

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Описан је метод квантитативног одређивања расподеле густине струје у ћелијама са три планпаралелне електроде. Показано је да се расподела густине струје може одредити на основу једноставних поларизационих мерења. Разматрана је и веза са ћелијом Харинга и Блума за $P = 2$.

(Примљено 9. марта, ревидирано 9. априла 2001)

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