

The current distribution in an electrochemical cell. Part IV. The relation to the Haring-Blum method

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It was shown that the current density-cell voltage curves recorded in a cell with parallel plate electrodes for different distances between the edges of the electrodes and side walls of the cell can be used to determine the current distribution in cells of the Haring-Blum type.

Key words: metal electrodeposition, electrochemical cell, current distribution.

It has been shown earlier¹ that the ohmic resistance of the electrolyte in a cell decreases as the distance between the edge of the electrode and the side wall of the cell increases, according to relation

$$R_{\text{eff}} = \frac{R_h}{2k} \ln(1 + 2k) \quad (1)$$

where R_{eff} is the electrolyte resistance in a cell in which the edges of the electrodes do not touch the side wall of the cell and R_h is the electrolyte resistance of the same cell but with the edges of the electrodes touching the side walls. The parameter k is given by

$$k = \frac{L}{A} \quad (2)$$

where L is the distance between the edge of the electrode and the side wall of the cell, and A is the electrode length.

It was found experimentally, using the bridge method, that Eq. (1) is valid up to $k \approx 1$, when $R_{\text{eff}} \approx 0.5 R_h$. The value of R_{eff} does not change as k increases further.

As a consequence of this, the current in a cell in which the edges of the electrodes do not touch the side wall will be considerably larger than in a cell in which the edges of the electrodes do touch the side walls²⁻⁴ (at the same cell voltage and inter-electrode distance and if the activation overpotential is not very large). It

is easy to show that, for a distance l_{eff} , the ohmic resistance of the electrolyte in a cell in which the edges of the electrodes touch the side walls is equal to the ohmic resistance of the electrolyte in a cell in which the edge of the electrode is at a distance L from the side wall of the cell and at the inter-electrode distance l , providing

$$l_{\text{eff}} = \frac{lA}{2L} \ln \left(1 + \frac{2L}{A} \right) \quad (3)$$

Hence, from the current density-cell voltage dependences for different distances between the edge of the electrode and the side wall of the cell, the current distribution between cathodes at different distances from the anode can be obtained and used for the calculation of the current distribution indexes according to Haring and Blum,⁵ Heatly,⁶ Pan,⁷ Field,⁸ and Popov *et al.*⁴ It is to note that the throwing power index, defined recently by Popov *et al.*, is very similar to that of Heatley⁶ and Pan.⁷ In all the above methods, the ratio of the primary current densities, P , and that of the actual metal distribution, M , are included in the corresponding formulas.

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

$$T = \frac{P-M}{P} \times 100\% \quad (4)$$

and according to Heatley⁶ and Pan⁷

$$T = \frac{P-M}{P-1} \times 100\% \quad (5)$$

and Field⁸

$$T(\text{BSI}) = \frac{P-M}{P+M-2} \times 100\% \quad (6)$$

where $P = \frac{l_{\text{far}}}{l_{\text{near}}}$ and $M = \frac{\Delta m_{\text{near}}}{\Delta m_{\text{far}}}$, l_{far} and l_{near} are the far and near cathode-anode distance, respectively, and Δm_{far} and Δm_{near} the weight of deposit on the far and near electrode, respectively. It is obvious that $l_{\text{far}} = l$ and $l_{\text{near}} = l_{\text{eff}}$ in the region where Eq. (3) is valid, and that it is possible to obtain the P values as the ratio of corresponding ohmic resistances calculated from the slopes of ohmic controlled current density-cell voltage curves. The values of M are obtained from mixed controlled current density-cell voltage curves for the same geometry of the system, because, in the case of copper deposition from acid sulphate solution, M can be substituted by current density ratios.

It can be seen from Eqs. (4) and (5) that for no deposit on the far cathode T must be minus infinity and according to Eq. (6) – 100%. According to a more suitable definition, the throwing power index S can be viewed as the degree to which the secondary current density distribution cancels the bad effects of the primary current density distribution from 0 – 100% or, for no deposit on the far cathode, from $\frac{-1/P}{1 - 1/P}$ up to 100%, as can be seen from Eq. (7).

$$S = \frac{\frac{1}{M} - \frac{1}{P}}{1 - \frac{1}{P}} \times 100 \% \quad (7)$$

Typical Haring-Blum throwing power cells have $P = 5$, *i.e.*, the far cathode is 5 times as far from the anode as the near cathode. Also, cells with $P = 2$ are used. These measured quantities depend on the scale of the experiment and so are not absolute values; but, in general, a solution exhibiting good throwing power in such a test will exhibit it in practise also.

RESULTS AND DISCUSSION

The different effects on the current distribution can be illustrated in a qualitative way by all the cited equations, however, Eq. (7) seems to be the best one.

The values of T calculated using Eqs. (4–6) and S using Eq. (7) for different situations as functions of the normalized deposition current density (to the limiting diffusion current for $L = 0$) are shown in Figs. 1–3. The primary current distributions for $l = 50$ mm and $l = 150$ mm were calculated from the slopes of the current density-cell voltage curves (complete ohmic control) for different electrode edgeside wall distances from Figs. 3 and 6 from Ref. 3, respectively, and the actual current density distribution from Figs. 5 and 7 from Ref. 2, and Figs. 1 and 2 from Ref. 3 (mixed controlled deposition).

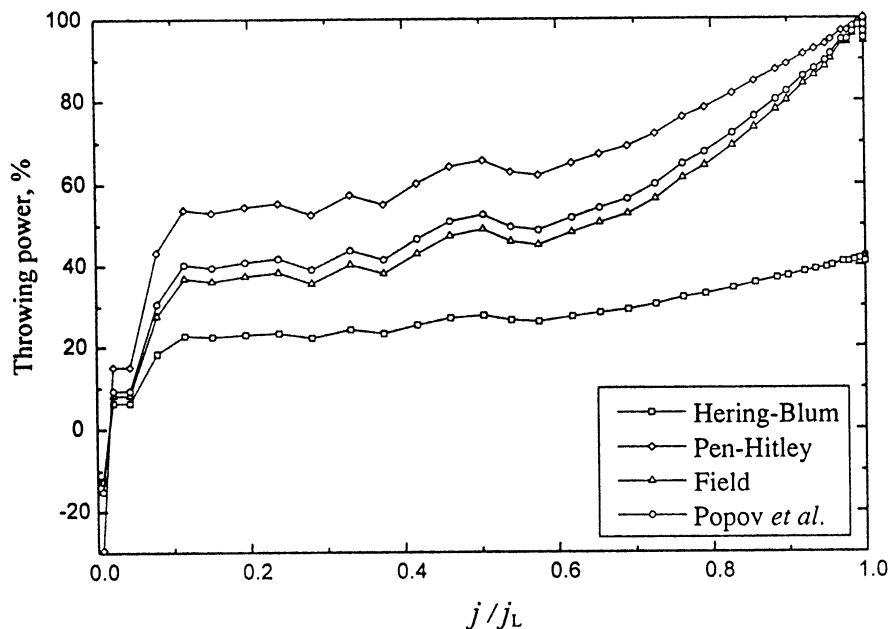


Fig. 1. The throwing power indexes for the system $\text{Cu}|\text{0.1 M CuSO}_4, \text{0.1 M H}_2\text{SO}_4|\text{Cu}$ with $l = 50$ mm and $L = 25$ mm as functions of the normalized current density. (Data from Fig. 5, Ref. 2 and Fig. 3, Ref. 3).

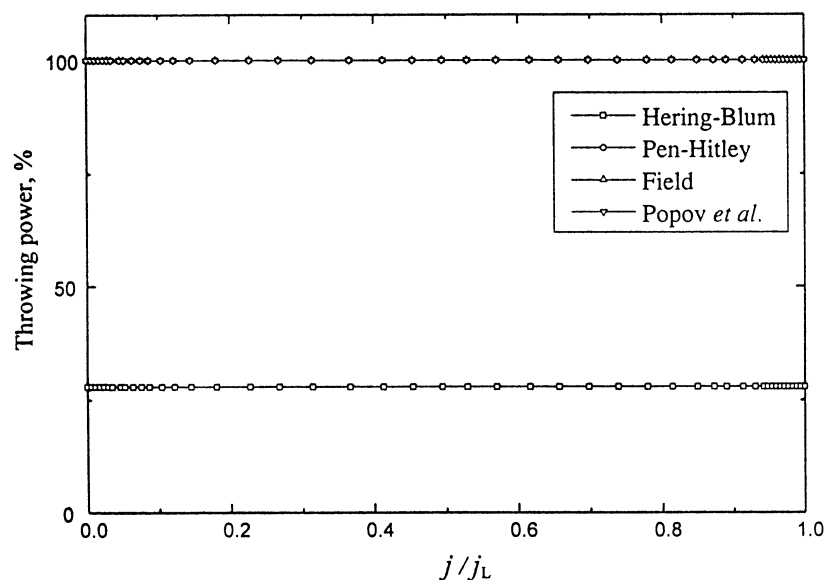


Fig. 2. The throwing power indexes for the system Cu|0.1 M CuSO₄, 0.5 M H₂SO₄|Cu with $l = 50$ mm and $L = 25$ mm as functions of the normalized current density. (Data from Fig. 1 and Fig. 3, Ref. 3).

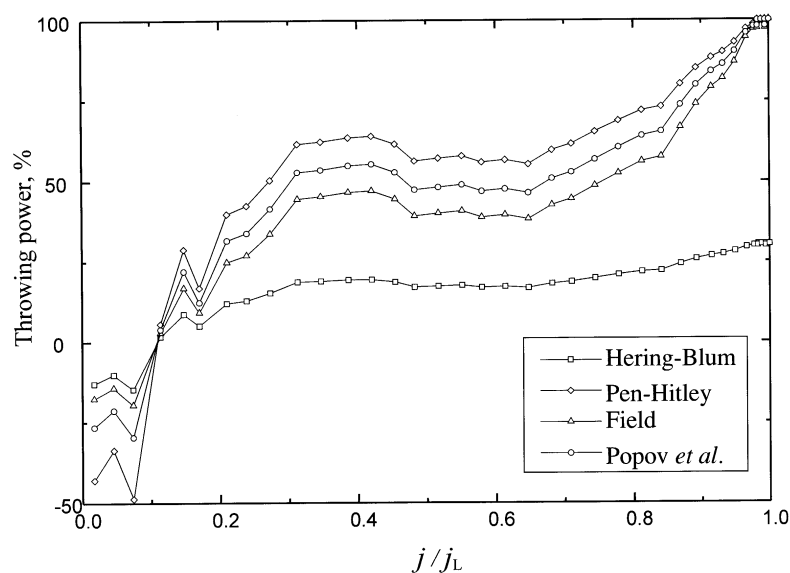


Fig. 3. The throwing power indexes for the system Cu|0.1 M CuSO₄, 0.5 M H₂SO₄|Cu with $l = 150$ mm and $L = 50$ mm as functions of the normalized current density. (Data from Fig. 2 and Fig. 6, Ref. 3).

The effects of the inter-electrode distance and resistivity of the electrolyte are illustrated by Figs. 3–6. It can be seen that the current distribution is better with smaller

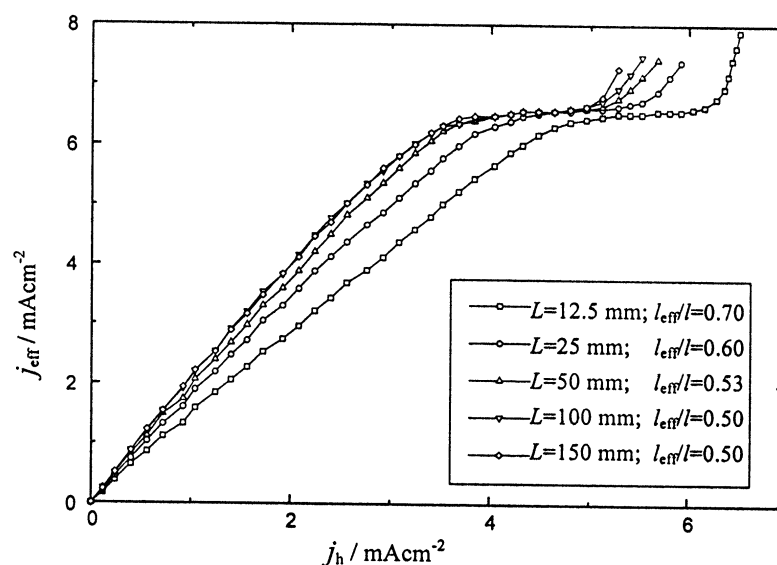


Fig. 4. Current density for different L and l_{eff} as a function of the current density in the cell with inter-electrode distance l and $L = 0$ for the system $\text{Cu}|0.1 \text{ M CuSO}_4, 0.1 \text{ M H}_2\text{SO}_4|\text{Cu}$. (Data from Fig. 7, Ref. 2).

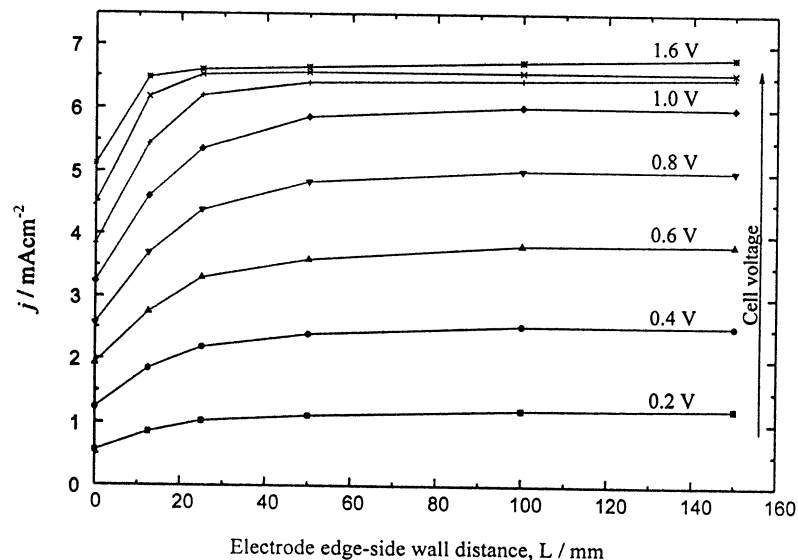


Fig. 5. Current density for different cell potentials as functions of L in a cell with an inter-electrode distance $l = 150 \text{ mm}$ for the system $\text{Cu}|0.1 \text{ M CuSO}_4, 0.1 \text{ M H}_2\text{SO}_4|\text{Cu}$. (Data from Fig. 7, Ref. 2).

inter-electrode distances and larger supporting electrolyte concentrations.³ The ideal current distribution for an inter-electrode distance of 50 mm is obtained at 0.5 M H_2SO_4 ; for an inter-electrode distance of 150 mm with the same concentration of supporting electrolyte, the current distribution is similar to that from Fig. 1.

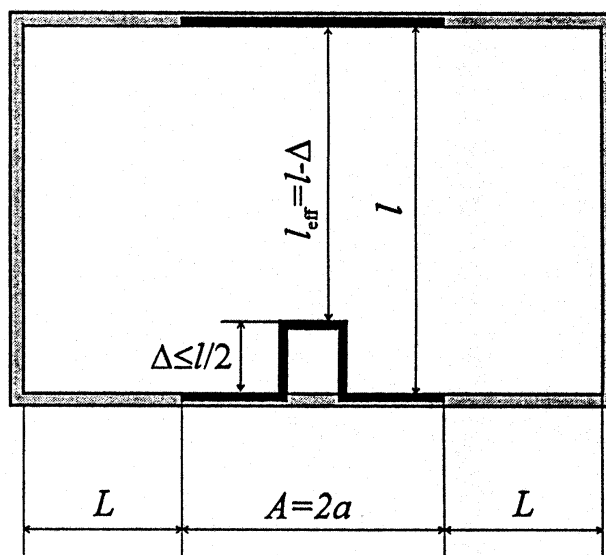


Fig. 6. The scheme of the electrochemical cell with plane-parallel electrodes and different inter-electrode distances.

On the other hand, the absolute values of current densities on the flat electrode surfaces at different distances from the anode can be obtained directly from the current density-cell voltage dependences from Ref. 2–4, making the calculation of the throwing power indexes unuseful. Besides, in this way, j_h/j_{eff} for different inter-electrode distances in the region $0 \leq l_{\text{eff}} \leq l/2$ can be easily determined from the polarization curves slopes up to $L = l/2$. The current density-cell voltage dependences from Ref. 2–4 can be replotted in the form permitting the correlation between the current in the cell for an inter-electrode distance l and $L = 0$ mm and the current in the same cell for $0 < L \leq l/2$, i.e., with different l_{eff} , as seen from Fig. 4. They can also be replotted in the form shown in Fig. 5, permitting the determination of current in cell with different L at different cell potentials. It is also seen from Fig. 5 that the change of current with increasing L is practically finished at $L = A$, and is completely finished at $L = l/2$. Hence, for the determination of the current density distribution in the cell, schematically shown in Fig. 6, a method for the estimation of the current densities at the very edges of the electrodes is required. Such a method will be proposed in a future paper.

ИЗВОД

РАСПОДЕЛА СТРУЈЕ У ЕЛЕКТРОХЕМИЈСКОЈ ЋЕЛИЈИ. ДЕО 4.
ВЕЗА СА МЕТОДОМ ХАРИНГ-БЛУМА

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Показано је да се криве густина струје-напон регистроване за ћелију са план-паралелним електродама различитих растојања између ивица електрода и бочних зидова ћелије могу искористити за одређивање расподеле струје у ћелијама типа Харинг-Блум.

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