The current distribution in an electrochemical cell. Part VII. Concluding remarks

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A new method for the determination of the ability of an electrolyte to distribute uniformly current density in an electrochemical cell is proposed. It is based on the comparison of the current in cells in which the electrode edges touch the cell side walls with the current in cells with different electrode edge–cell side wall distances. The effects of cell geometry, process parameters and current density are discussed and illustrated using the results presented in the previous papers from this series.

Keywords: metal electrodeposition, electrochemical cell, current distribution.

INTRODUCTION

The ability of an electrolyte to provide a uniform current density distribution over a cathode surface has been the subject of numerous investigations, resulting in a large number of different criteria to determine it as the throwing power indexes of an electroplating bath.\textsuperscript{1–7}

Two of these attempts were presented in this series.\textsuperscript{6–7} In both cases, however, the obtained results were expressed by relations without clear physical meaning and generally included a comparison of the actual current density distribution to the current density distribution in the case of total Ohmic control, \textit{i.e.}, under conditions of primary current distribution.

On the other hand, a method of current density distribution analysis based on the current density–cell voltage curves, desccribed in our previous papers,\textsuperscript{8,9} permits a more direct estimation of the ability of an electrolyte to distribute the current density uniformly in cells with non-uniform geometry. This can be done by direct comparison of the current density in cells with different interelectrode and different electrode edges–side wall distances under different deposition conditions, as illustrated below, on the basis of results from Refs. 8 and 9.

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EXPERIMENTAL

The cell with parallel plate electrodes used in this work was made of perspex and is shown in Fig. 1. Side screens enabled the distance $L$ between the edges of the electrodes and the side walls to be varied. In addition, one of the front walls was also movable in order to enable different interelectrode distances to be obtained. The electrodes were made of copper and had working dimensions 50 mm $\times$ 50 mm. The back sides of the electrodes were insulated. The electrolyte was made from p.a. chemicals and distilled water.

![Fig. 1. The cell with parallel plate electrodes used in this investigation.](image)

The measurements were done using a steady-state technique. The influence of the following variables on the $j$–$U$ polarization curves was investigated:
- electrode edge-side wall distance (0 mm, 12 mm, 25 mm, 50 mm, 100 mm, 150 mm),
- interelectrode distance (20 mm, 50 mm, 100 mm, 150 mm),
- anode material (Cu or Pb),
- concentration of $\text{H}_2\text{SO}_4$ ($0.01 \text{ M}, 0.1 \text{ M}$ and $0.5 \text{ M}$ $\text{H}_2\text{SO}_4$ containing $0.1 \text{ M} \text{CuSO}_4$),
- concentration of $\text{CuSO}_4$ ($0.03 \text{ M}, 0.1 \text{ M}$ and $0.3 \text{ M}$ $\text{CuSO}_4$ containing $0.1 \text{ M} \text{H}_2\text{SO}_4$),
- temperature ($20 ^\circ \text{C}$ and $40 ^\circ \text{C}$) and
- stirring.

Typical obtained current density–cell voltage dependencies are schematically presented in Fig. 2.

![Fig. 2. A typical current density–cell voltage dependence for $L = 0$ and $L > 0$.](image)

The dimensionless variables used in this work were extracted from them as the ratios $j_{L>0}/j_{L=0}$ and $j_{L=0}/j_{L}$, which permit a comparison of the current density distribution in different cells under different conditions.

RESULTS AND DISCUSSION

The effect of the interelectrode distance on the ability of the electrolyte to uniformly distribute the current density can be illustrated by plotting the ratios of the cur-
rent density in cells with different interelectrode distance $l$ (20, 50, 100 and 150 mm)
and electrode edge – cell side wall distance $L = 150$ mm to the current density in cells
with the same $l$ values and $L = 0$ as a function of the current density in a cell with $L = 0$,
normalized relative to the limiting diffusion current density. Data from Figs. 4–7, Ref. 8.

Fig. 3. The $j_{L=150}/j_{L=0}$ ratio in the cell Cu|0.1 M CuSO$_4$, 0.1 M H$_2$SO$_4$|Cu with electrode edges –
cell side wall distance $L = 150$ mm for different interelectrode distances a) $l = 20$ mm, b) $l = 50$
mm, c) $l = 100$ mm and d) $l = 150$ mm, as a function of the current density in a cell with $L = 0$, nornalized relative to the limiting diffusion current density. Data from Figs. 4–7, Ref. 8.

Fig. 4. The $j_{L}/j_{L=0}$ ratio in the cell Cu|0.1 M CuSO$_4$, 0.1 M H$_2$SO$_4$|Cu with electrode distance $l$ =
150 mm for different electrode edge – cell side wall distances a) $L = 12.5$ mm, b) $L = 25$ mm, c) $L$
= 50 mm and d) $L = 100$ mm, e) $L = 150$ mm, as a function of the current density in a cell with $L = 0$,
normalized relative to the limiting diffusion current density. Data from Fig. 7, Ref. 8.
The same plots, but for \( l = 150 \) mm and different \( L \) values is shown in Fig. 4.

Obviously, the larger the current density ratio, the lower is the ability of an electrolyte to distribute homogeneously the current in the cell.

Hence, an increase of the interelectrode distance leads to a worsening of the current density distribution, as does an increase of the electrode edges – cell side wall distance.

The effects of the supporting electrolyte concentration, depositing ion concentration, lead anode and the temperature on the ability of an electrolyte to homogeneously distribute the current density are illustrated by Fig. 5.

Increasing the reaction ion concentration, the stirring rate and decreasing the supporting ion concentration lead to complete Ohmic control and the polarization curves lose their "S" shape and become straight lines, meaning full Ohmic control, as can be seen from Figs. 3, 5 and 6 in Ref. 9. In all other cases, diffusion control becomes dominant at large cell voltages,\textsuperscript{8,9} which leads to a uniform current density distribution.

All the above facts can be explained by discussing \( L' \), the depth of current line penetration between the electrode edges and cell side wall. It was shown\textsuperscript{10,11} that

\[
L' = \frac{l}{2} \left[ \frac{\eta_a - \eta_e + \rho l}{\eta_a - \eta_e + \rho l \frac{\sqrt{2}}{2}} \right]^{1/2} - 1
\]  

(1)

for \( l \leq 2A \) and \( A \) instead \( l/2 \) in Eq. (1) fol \( l > 2A \). Obviously, Eq. (1) is valid if
where $L$ is the electrode edges – cell side wall distance. If $L = 150$ mm, condition (2) is satisfied and $L'$ from Eq. (1) should be used in Eq. (3).

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

$U$ in the above relations represents the cell voltage, $\eta_a$ and $\eta_c$ the anodic and cathodic overpotentials, respectively, $l$ the interelectrode distance, $\rho$ the resistivity of the solution, $A$ the electrode width and $j$ the current density.

For one and the same current density in the cell, the electrochemical part of the cell voltage does not depend on the interelectrode distance, but the Ohmic drop in a homogeneous field is strongly dependent on it, which leads to an increase of $L'$ with increasing $l$. This produces a decrease in the cell voltage at a fixed current density, because of the decrease of the overall Ohmic resistance. Hence, at a fixed cell voltage, the increase of $L'$ will produce an increase of the current density relative to the cell with $L = 0$ for the same $l$ and hence a worse current density distribution. The effect will be the same with increasing $L$ at $l = 150$ mm, if condition (2) is not satisfied.

In a similar way, in cells with the same $l = 150$ mm and $L = 150$ mm, $L'$ will depend on the fraction of Ohmic drop $\rho lj$ in the cell voltage. At a value of fixed $l$, the product $\rho lj$ increases faster with increasing $j$ than the electrochemical part of the cell voltage. Hence, increasing the depositing ion concentration and the stirring rate decreases the ability of the electrolyte to distribute the current density uniformly, as does decreasing the supporting electrolyte concentration. Increasing the Tafel slopes and, probably, decreasing the exchange current densities will improve the current distribution.

Obviously, diffusion control of the deposition process produces a uniform distribution of current density.

Changing the temperature also produces a significant effect, because the decrease of $\rho$ is larger than the increase of $j$ with increasing temperature.

As was shown in previous papers, polarization curves can be easily calculated using the data from simple polarization measurements. Hence, the current density distribution in cells with plane parallel electrodes can be calculated without experimental determination.

The above conclusions are derived from the results presented in Refs. 8 and 9. It should be noted that in plotting the dependencies in Figs. 2–4 it was assumed that the limiting current density of the deposited ions is always the same even in the situations when dendritic growth or hydrogen evolution take place and that the measured current density is larger than the limiting diffusion one, as is the case when $l = 150$ mm and $L = 150$ mm, for example.

In this way the possibilities of the method developed in this series of papers are clearly demonstrated.
ИЗВОД

РАСПОДЕЛА СТРУЈЕ У ЕЛЕКТРОХЕМИЈСКОЈ ЋЕЛИЈИ. ДЕО VII.

ЗАКЉУЧНЕ НАПОМЕНЕ

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Предложен је нови метод за одређивање способности електролита за равномерну расподелу струје у електрохемијској ћелији. Метод је заснован на поређењу густине струје у ћелији у којој електроде додирuju ћидове суда, са густином струје у ћелији са променљивим растојањем ћидова суда од ивице електроде. Утицаји геометрије ћелије, параметара пропаси и густине струје разматрану су и илустровани користећи резултате дате у претходним радовима из ове серије.

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