NOTE

A new dimensionless group for the estimation of the current density distribution in an electrochemical cell

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(Received 14 May 2004)

Abstract: A new dimensionless group for the estimation of the current density distribution in an electrochemical cell is defined as the ratio of the sum of the absolute values of the anodic and cathodic overpotentials to the overall cell voltage.

Keywords: dimensionless group for the estimation of the current density distribution.

INTRODUCTION

It is known that electrodeposited metal can have different morphologies at different positions on the electrode surface. This means that the local current density during electrodeposition of metals varies from point to point on an electrode surface. Even for a simple electrode configuration, calculation of the current distribution is a complex problem and the difficulties increase further with increasing complexity of the geometry, especially if the limiting diffusion curent varies over the electrode due to different geometric and hydrodynamic conditions.

If a complete calculation can not be performed, it is possible to estimate certain trends, using a dimensionless group called the Wagner number, *Wa*, given by:

$$Wa = \frac{\mathrm{d}\eta_c}{\mathrm{d}j} \frac{k}{l} \tag{1}$$

where $d\eta_c/dj$ is the slope of the cathodic activation potential – current density dependence, k is the conductivity of the solution and l is a characteristic length. The Wagner number represents the ratio of the cathodic polarization resistance to the solution resistance.¹

Recently, a new method for the determination of the current density distribution, based on a simple equation of the electrode kinetics, was developed.² The aim

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of this note was to derive a more general, dimensionless group for the estimation the current density distribution in electrochemical cells from this simple equation.

DISCUSSION

It was shown in a previous paper² that the maximum length of the current line l' due to current propagation between the electroce edges and side wall of the cell can be related to the interelectrode distance I_h by:

$$l' = \frac{l_{\rm h}}{1 - \frac{\rho l_{\rm h} j_{\rm h}}{\eta_{\rm a,h} + \eta_{\rm c,h} + \rho l_{\rm h} j_{\rm h}}}$$
(2)

where j_h is the current density in the homogeneous current field and $\eta_{a,h}$ and $\eta_{c,h}$ are the absolute values of the corresponding anodic and cathodic overpotentials, respectively. Equation (2) can be rewritten in the form:

$$S = \frac{\eta_{a,h} + \eta_{c,h}}{\eta_{a,h} + \eta_{c,h} + \rho l_h j_h}$$
(3)

where

$$S = \frac{l_{\rm h}}{l'} \tag{4}$$

S in the above equation indicates to which extent the primary current distribution is corrected by the secondary one. It follows from Eq. (3) that $\rho l_h j_h \to \infty$, $S \to 0$ means primary current distribution, $\rho l_h j_h \to 0$, $S \to 1$, means secondary current distribution.

If

$$\eta_{a,h} + \eta_{c,h} = E_e \tag{5}$$

and

$$\eta_{a,h} + \eta_{c,h} + \rho l_h j_h = U \tag{6}$$

where $E_{\rm e}$ is the sum of the absolute values of the anodic and cathodic overpotentials and U is the cell voltage, it follows from Eq. (3):

$$S = \frac{E_e}{U} \tag{7}$$

which has an excellent physical meaning.

In addition, S defined in this way can be easily determined for each particular curent density by a single galvanostatic pulse.

Acknowledgements: This work was supported by the Ministry of Science, Technology and Development of the Republic of Serbia under the research project "Electrochemical analysis and characterization of alloys composites and micro structured materials" (H1821).

ИЗВОД

НОВА БЕЗДИМЕНЗИОНА ГРУПА ЗА ПРОЦЕНУ РАСПОДЕЛЕ ГУСТИНЕ СТРУЈЕ У ЕЛЕКТРОХЕМИЈСКОЈ ЋЕЛИЈИ

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Нова бездимензиона група за процену расподеле густине струје у електрохемијској ћелији дефинисана је као однос збира апсолутних вредности анодне и катодне пренапетости, према укупном напону на ћелији.

(Примљено 14. маја 2004)

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