The effect of electrodeposition process parameters on the current density distribution in an electrochemical cell

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Cell voltage – current density dependences for a model electrochemical cell of fixed geometry were calculated for different electrolyte conductivities, Tafel slopes and cathodic exchange current densities. The ratio between the current density at the part of the cathode nearest to the anode and the one furthest away were taken as a measure for the estimation of the current density distribution. The calculations reveal that increasing the conductivity of the electrolyte, as well as increasing the cathodic Tafel slope should both improve the current density distribution. Also, the distribution should be better under total activation control or total diffusion control rather than at mixed activation-diffusion-Ohmic control of the deposition process. On the contrary, changes in the exchange current density should not affect it. These results, being in agreement with common knowledge about the influence of different parameters on the current distribution in an electrochemical cell, demonstrate that a quick estimation of the current distribution can be performed by a simple comparison of the current density at the point of the cathode closest to anode with that at furthest point.

Keywords: current density distribution, electrochemical cell.

INTRODUCTION

Recently, the new concept of current line division for the analysis of the current distribution in electrochemical cells was introduced and evaluated by considering, as an example, the phenomenon known in electroforming as "corner weakness".[1] It was shown that it is possible to explain not only this phenomenon, but also the origin of a crack appearing in the deposit along the bisector of the angle between a plain electrode surface and a protrusion perpendicular to it. It was also shown that the complete current density (c.d.) distribution, along the cathode profile, as shown in Fig. 1, can be calculated using the values of the c.d. at the front part of the cathode elevation and the c.d. at the front part of plain cathode surface outside the "shadow" of the elevation. It should be noted that just this ratio between these current densities is a criterion for the estima-

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tion of the c.d. distribution, *i.e.*, for a brief judgment about the c.d. distribution it is not obligatory to calculate the complete distribution along the cathode profile. Hence, the purpose of this communication is to demonstrate how the effect of different parameters on the c.d. distribution can be estimated by analysis of the ratio between the current densities at the points of the cathode nearest to and furthest from the anode.

In the case of total Ohmic control of the deposition process, it is obvious that the c.d. at the elevation near to the anode, j_n, can be expressed as

$$j_n \quad j_f \ \frac{l \quad h}{l} \tag{1}$$

where j_f is the current density at the plain cathode surface far from the anode, l – the interelectrode distance and h – the height of the elevation as denoted in Fig. 1.

In the case of activation-Ohmic control, the situation is somewhat different. The voltage imposed on an electrochemical cell, E_{cell}, can be expressed not only as a function of j_f for the part of the cathode far from the anode (2), but also as a function of j_n for the cathode segment near to anode (3):

$$E_{cell} = \frac{b_a}{2.3} \ \ln \frac{j_f}{j_{oa}} \quad \frac{b_c}{2.3} \ \ln \frac{j_f}{j_{oc}} \quad \frac{j_L}{j_L \quad j} \qquad (l \quad h) \ j_f \tag{2}$$

$$E_{cell} = \frac{b_a}{2.3} \ \ln \frac{j_n}{j_{oa}} \quad \frac{b_c}{2.3} \ \ln \frac{j_n}{j_{oc}} \quad \frac{j_L}{j_L \quad j} \qquad l \ j_n \tag{3}$$

where b_a and b_c and j_{0a} and j_{0c} are the anodic and cathodic Tafel slopes and exchange current densities, respectively, j_L the limiting diffusion current density for the cathodic process and   the resistivity of the solution.

Using the above equations and the assumption that the diffusion layer,   , is uniform all over the cathode surface and much thinner than the height of the elevation

$$h \gg \tag{4}$$

the metal deposit profile in the "shadow" of the elevation (dashed region in Fig. 1) can be effectively calculated, as was shown recently.[1]

However, an estimation of the effects of different parameters on the current density distribution can be made by simply plotting the dependencies (2) and (3), *i.e.*, E_{cell} as function of current densities at the parts of the cathode near to, j_n, and far from the anode, j_f, respectively.

Hence, the effect of the solution resistivity can be estimated by comparing the $E_{cell} - j_n$ with the $E_{cell} - j_f$ dependencies calculated for different resistivities ($_1 = 2$ cm; $_2 = 5$ cm; $_3 = 10$ cm), while all the other cell parameters are kept constant: $h = l = 5$ cm, $b_a = 40$ mV/dec, $b_c = 120$ mV/dec, $j_{0a} = j_{0c} = 0.1$ mA/cm^2 and $j_L = 7$ mA/cm^2. The calculated dependences are plotted in Fig. 2 from which it can be seen that, besides the conductivity of the electrolyte, the kind of the control of the deposition process also determines the current distribution.
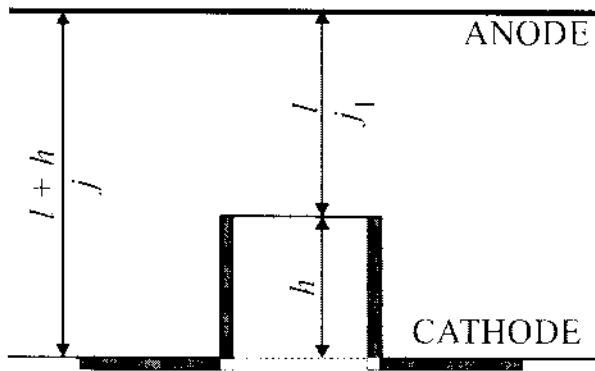
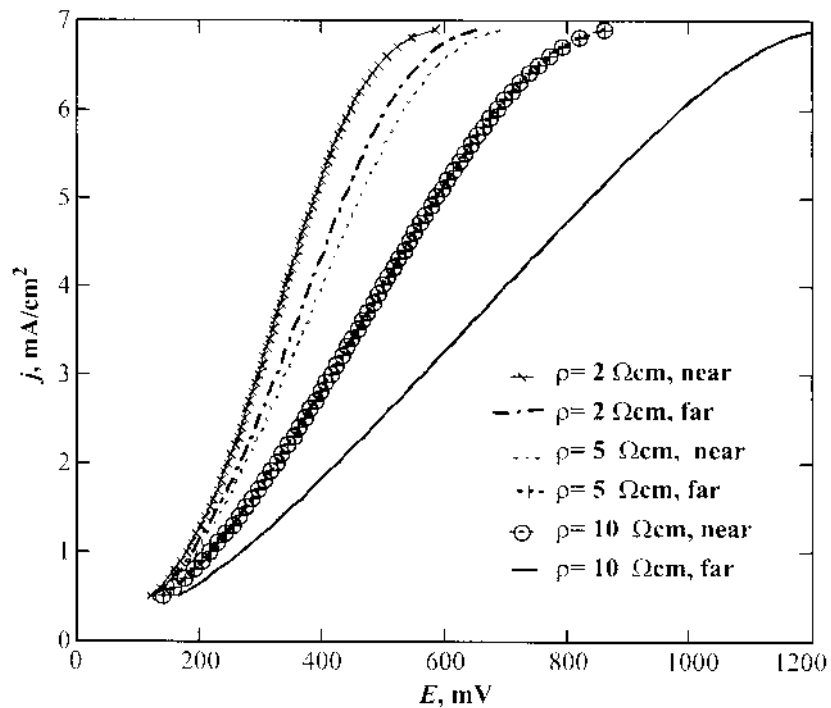Fig. 1. Schematic representation of an electrochemical cell.

Fig. 2. Dependencies of the current densities at the near and at the far part of the cathode on the cell voltage, for different solution resistivities.

From the diagrams in Fig. 2, the dependencies of the current density at the near on the current density at the far part of the cathode can be derived. The result is shown in Fig. 3, together with the boundary dependences calculated using Eq. (1). As can be
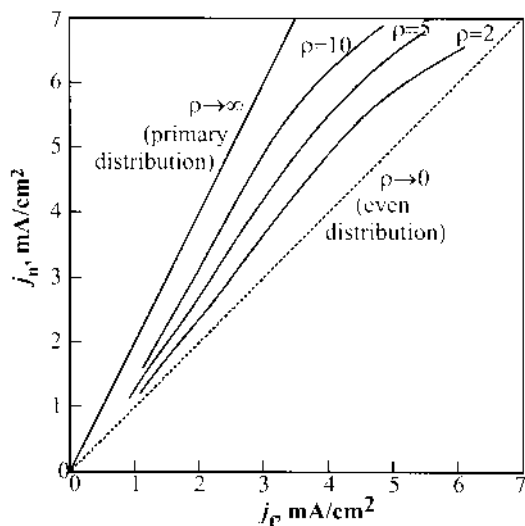
Fig. 3. Depencencies of the current density at the near on the current density at the far part of the cathode for different solution resistivities.
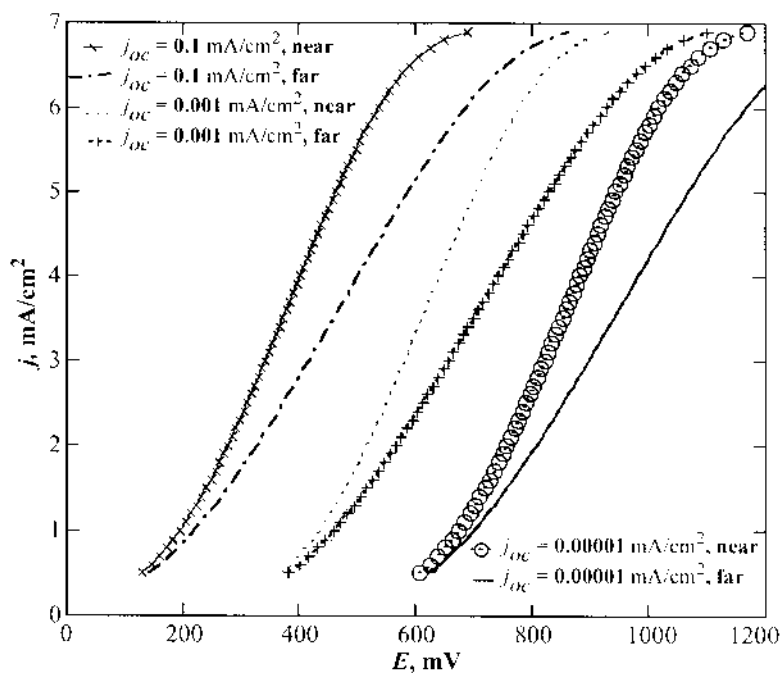

Fig. 4. Dependensies of the current densities at the near and at the far part of the cathode on the cell voltage for different cathodic exchange current densities.

seen, the larger the conductivity of the electrolyte, the better is the current density distribution. Also, the distribution is better under total activation control at low cell voltages and under total diffusion control at high cell voltages than under mixed activation-diffusion-Ohmic control, at medium cell voltages.
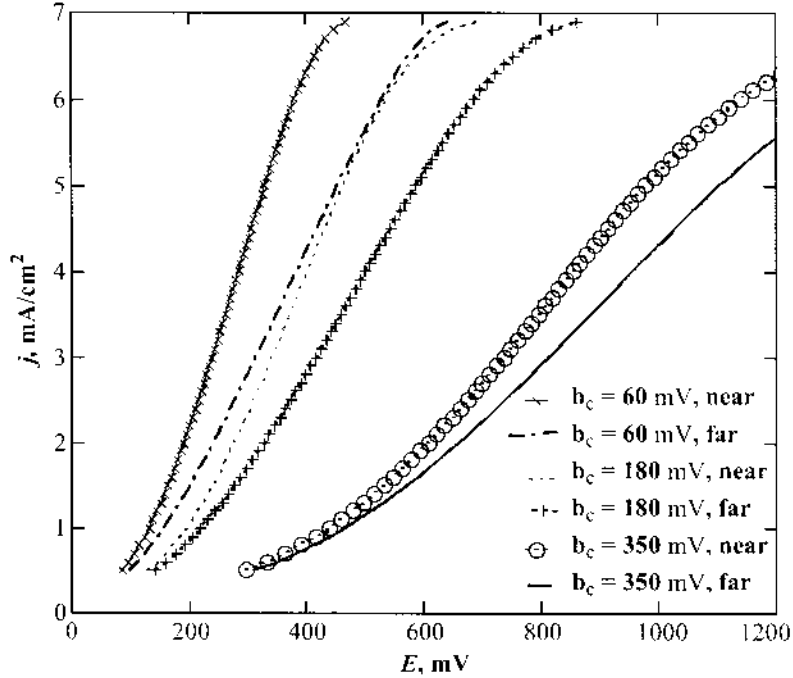
Fig. 5. Dependencies of the current densities at the near and at the far part of the cathode on the cell voltage for different cathodic Taffel slopes.
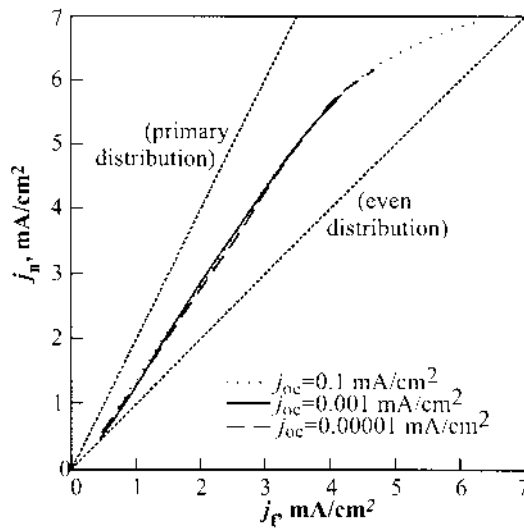

Fig. 6. Dependencies of the current density at the near on the current density at the far part of the cathode for different cathodic exchange current densities.

The effect of the cathodic exchange current density, j_{0c}, can be analyzed in the same manner. The $E_{cell} - j_n$ and $E_{cell} - j_f$ dependencies were calculated for different cathodic exchange c.d.s ($j_{oc1} = 0.1$ mA/cm², $j_{0c2} = 10^{-3}$ mA/cm², $j_{0c1} = 10^{-5}$ mA/cm²), keeping other parameters constant: $b_a = 40$ mV/dec, $b_c = 120$ mV/dec, $j_{0a} = 0.1$
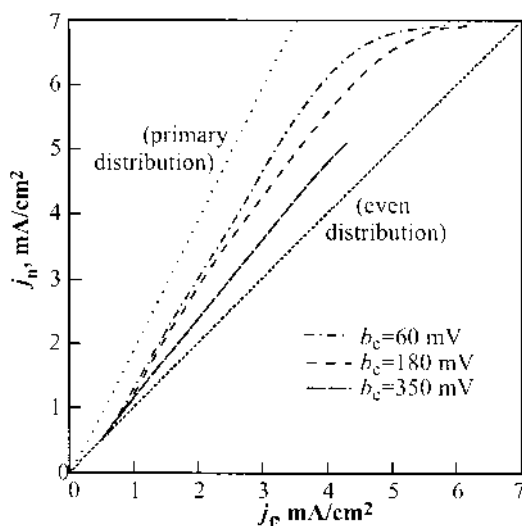
Fig. 7. Dependencies of the current density at the near on the current density at the far part of the cathode for different cathodic Taffel slopes.

mA/cm^2, $j_L = 7$ mA/cm^2 and $= 5$ cm. The result of this analysis is shown in Fig. 4. The corresponding derived dependencies of the current density at the near on the current density at the far part of the cathode are given in Fig. 5. It can be seen that a change in the cathodic exchange current density does not effect the current density distribution (Fig. 5). The same should be expected for changes in the anodic exchange current density (*cf.* Eqs. (2) and (3)).

Finally, the effect of the cathodic Tafel slope, b_c, is illustrated in Fig. 6 where E_{cell} $- j_n$ and $E_{cell} - j_f$ dependencies are plotted for b_c ranging between 60 and 350 mV/dec and $b_a = 40$ mV/dec, $j_{0c} = j_{0a} = 0.1$ mA/cm^2, $j_L = 7$ mA/cm^2 and $= 5$ cm. The corresponding $j_n - j_f$ dependensies are given in Fig. 7.

From Fig. 7 it can be concluded that increasing the cathodic Tafel slope considerably improves the current density distribution.

It must be stressed that the above considerations do not require experimental verification because it has been clearly shown that the current density – cell voltage dependencies can be successfully calculated using the corresponding kinetic parameters, interelectrode distances and solution conductivity, for different distances at the electrode surface.[2]

CONCLUSION

The results of above the considerations are in harmony with common knowledge about the influence of the solution resistivity and cathode polarizability (Tafel slope) on the c.d. distribution during metal deposition. The lack of influence of the exchange c.d. could also be expected. The exchange c.d. could be of importance only if its value exceeds that of the limiting diffusion c.d., which is characteristic of extremely fast cathodic deposition processes (*e.g.* the deposition of Ag).[3] All this speaks in favor of the validity of the here performed estimation of the current density distribution, which comprises the simple comparison of the cathodic c.d. at the cathode point closest to the anode with that at the furthest point.

И З В О Д

УТИЦАЈ ПАРАМЕТАРА ЕЛЕКТРОХЕМИЈСКОГ ТАЛОЖЕЊА МЕТАЛА НА РАСПОДЕЛУ СТРУЈЕ У ЕЛЕКТРОХЕМИЈСКОЈ ЋЕЛИЈИ

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Зависности напона на ћелији од густине струје, за модел електрохемијске ћелије фиксне геометрије, рачунате су за различите проводљивости електролита, Тафелове нагибе као и за различите катодне густине струје измене. Однос између густине струје на делу катоде најближем аноди и оне на најудаљенијем делу узет је као мера за процену расподеле струје. Резултати прорачуна указују на то да је расподела струје боља код електролита са већом проводљивошћу као и код процеса које карактеришу већи Тафелови нагиби. Такође расподела је боља у условима чисте активационе и чисте дифузионе контроле него у условима мешовите активационо-дифузионо-омске контроле. Насупрот томе, промене густине струје измене не утичу на расподелу струје. Ови резултати су у складу са добро познатим правилима о утицају различитих параметара на расподелу струје и указују да се расподела струје може проценити простим поређењем густине струје на делу катоде најближем аноди са оном на најудаљенијем делу.

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