Reacting metal ion concentration in the vicinity of small disk electrodes computed at the voltammetric peak current
2. Concentration in the plane perpendicular to the electrode

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Concentration changes in the plane perpendicular to the electrode surface were calculated by digital simulation, using implicit finite difference method depending on diffusion and kinetic factors. On this basis, the features of diffusion layer formation at small disk electrodes were studied and discussed. It has been determined that the steady state diffusion conditions are realised in the peak current region at a sufficiently small electrode radius r_o and low potential sweep rate v. A maximum diffusion layer thickness is observed in this situation. The effective diffusion layer thickness, which is evaluated assuming the linear concentration changes in the diffusion layer with the distance from the electrode surface, was found to show the maximum value equal to $\pi r_o/2$ at the electrode centre and was decreased to some low value at its edge.

Key words:

INTRODUCTION

In the previous work [1], concentration changes at the disk electrode surface and in the radial direction outside the electrode at peak current have been studied depending on the electrode dimensions, diffusion and kinetic factors. This work deals with the concentration changes in the direction perpendicular to the disk electrode surface.

Evaluation of concentration changes in the perpendicular direction to the electrode, i. e. determination of the diffusion layer thickness, is a rather complicated problem in the common case, which not always can be solved to sufficient accuracy at all. Difficulties of evaluation lie mainly in the fact that transport of reacting ions often is defined not only by diffusion but also by migration and convection. Migration is usually eliminated by adding to the solution a large quantity of indifferent electrolyte. Stirring the solution at a known rate may control convection. The best known means of convection control is the use of rotating disk electrode, since a simple analytical association has been found betwe-

en the diffusion layer thickness and electrode rotation rate [2].

A much more complicated situation is observed in the unstirred solutions where, in addition to diffusion, natural convection begins to act. Since natural convection depends on some factors that are hard to evaluate, exact determination of its size and action area is unfeasible. Therefore, experiments in such cases are conducted to avoid expansion of diffusion layer up to the influence area of natural convection. To attain this aim, non-stationary methods with short electrolysis time are used.

Rate and distance of expansion of the diffusion layer are important in the study of small electrodes, especially their arrays. Therefore, this problem has been examined in some works.

It has long been known that there is an association between diffusion current and diffusion layer thickness at large electrodes, where linear diffusion exists. Later, the equation has been derived which showed a relation between the diffusion current and time of electrolysis at small electrodes [2, 3]. From these two relationships, an expression for the limiting

expansion of diffusion layer with time at sufficiently short time intervals has been obtained [4, 5]:

$$\delta_l = (\pi Dt)^{1/2}. \tag{1}$$

It has been also found that the steady state current i_{ss} varies at small disk electrodes in direct proportion to the electrode radius r_o [6,7]:

$$i_{ss} = 4nFDc^o r_o. \tag{2}$$

From this, the steady state diffusion layer thickness has been obtained to be as follows [5]:

$$\delta_{ss} = (\pi/4) \, r_o \tag{3}$$

As can be seen, the diffusion layer thickness at sufficiently small disk electrodes, where the steady state conditions are generally achieved in a short time after starting the electrolysis, has been obtained to be somewhat below the electrode radius.

The aim of this work is to compute the concentration changes at disk electrode in the direction perpendicular to the electrode surface and thus to evaluate the diffusion layer thickness at the peak current depending on the electrode radius, diffusion and kinetic factors.

COMPUTATIONAL PROCEDURE

A disk electrode inlaid in a coplanar insulator and placed in an infinite hemisphere solution containing metal ions was considered. Diffusion was the only transport mode to the electrode surface.

Computation was carried out by an implicit finite difference method. The details of computation have been presented in [8].

The dimensionless diffusion factor p and dimensionless kinetic factor q were defined as

$$p = \log(\alpha nFvr_o^2 / RTD), \tag{4}$$

$$q = \log [r_o \, k_s / D(c^o)^\alpha]. \tag{5}$$

The dimensioned values of the reaction rate constant k_s and potential sweep rate v were calculated using the following data: $\alpha = 0.5$, $n = 2$, $T = 298$ K, $D = 7 \times 10^{-6}$ cm^2 s^{-1}, $c^o = 1 \times 10^{-5}$ mol cm^{-3}.

RESULTS AND DISCUSSION

Curves of concentration changes in the area of electrode edge depending on the distance from the electrode surface are presented in Fig. 1. The data obtained show a strong dependence of concentration changes on p and q. This could be expected, since

p is associated directly with the potential sweep rate v and electrode radius r_o, and q is associated with r_o (see equations 4 and 5). The surface concentration c^s at peak current is still high, and the diffusion layer thickness is small at high p and q. For example, c^s is only about 2.5 times lower than the bulk concentration c^o and the diffusion layer is much smaller than r_o at $p = 2$ and $q = 3$ (Fig.1 a). The reason for this effect is the short time it takes to reach the peak current. As the results in [1] have shown, this time t_p becomes shorter to some extent with an increase in r_o and predominantly with an increase in v, i. e. on the whole with increase in p.

The surface concentration c^s becomes lower with a decrease in p and q and thus with an increase in t_p (Fig. 1 b) and approaches zero at negative p (Fig.
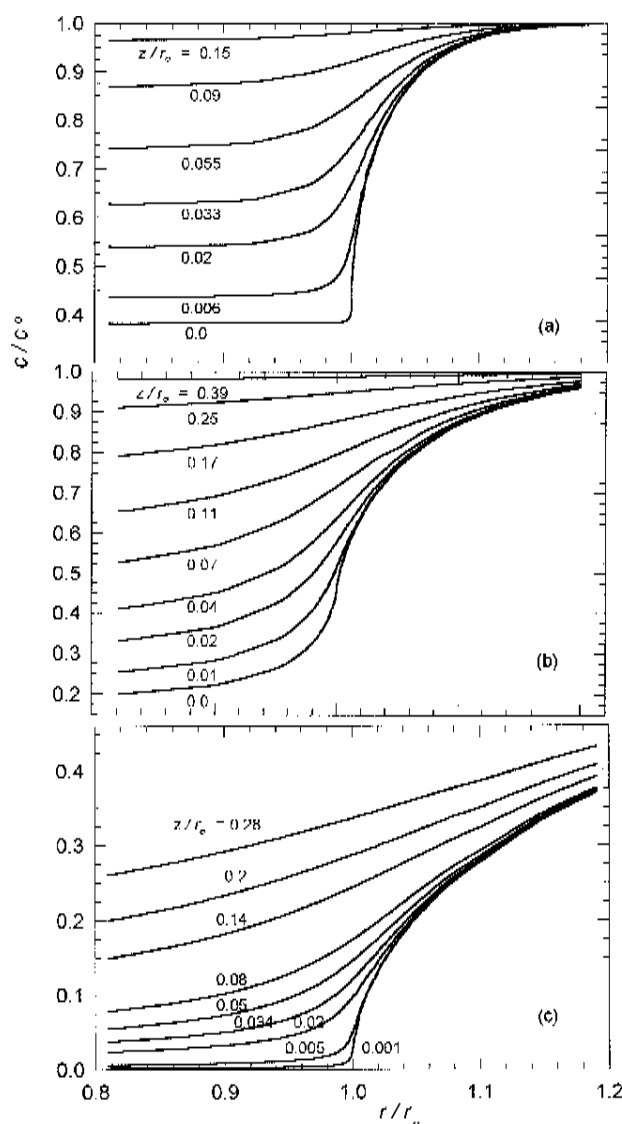

Fig. 1. Concentration along the electrode radius in the edge area depending on distance from the electrode surface at: (a) $p = 2$ and $q = 3$; (b) $p = 2$ and $q = 0$, and (c) $p = -2$ and $q = 0$. The normalized distances (z/r_o) are shown at the curves

1 c), showing the diffusion to approach the steady state conditions. The concentration also grows slower with the distance from the electrode.

It is well known that c^s is an important parameter of electrochemical reactions. Some results on c^s have been reported in the previous work [1], where it has been determined that this concentration at peak current is a rather complicated function of t_p at small disk electrodes. This work presents some more detailed data. Figure 2 shows a profile of c^s from the centre to the edge of small electrode (2 µm) depending on v. Very small electrodes make it possible to establish steady state diffusion conditions shortly after the start of electrolysis and to maintain them in a wide v range. As can be seen in Fig. 2, c^s is independent of v up to 0.045 V s^{-1} at $q = 2$ and up to 0.45 V s^{-1} at $q = -2$. These values correspond to $\log k_s$ equal to –0.45 and –4.45, respectively, when the units of k_s are (cm s^{-1})(mol cm^{-3})$^{1/2}$ and the dimensioned values needed for calculation are taken as indicated in the computational procedure. Moreover, c^s is approximating zero. These results are known as an evidence for the existence of steady state diffusion. The surface concentration c^s begins to increase with an increase in v and, at sufficiently high v, attains the values characteristic of large electrodes.

An increase in r_o leads to a decrease in the values of v required for an increase in c^s. This effect of r_o follows the rules specified by equation 4.

Figure 2 also shows that the c^s is virtually constant in the most part of the electrode area and a steep rise in c^s is observed only at the extreme edge. This is especially obvious at high q. With a decrease in q, an increase in c^s is observed farther from the electrode edge.

Figure 3 presents some evidence of concentration changes in the direction perpendicular to the electrode centre ($r/r_o = 0$) depending on r_o, v and k_s. One can see that the diffusion layer achieves the steady state and the bulk concentration values are approached at the distances many times higher than r_o at small electrodes, when v is low (Fig. 3 a and b). The diffusion layer becomes progressively dependent on v with an increase in r_o and is thinner at a higher v (Fig. 3, c to f).
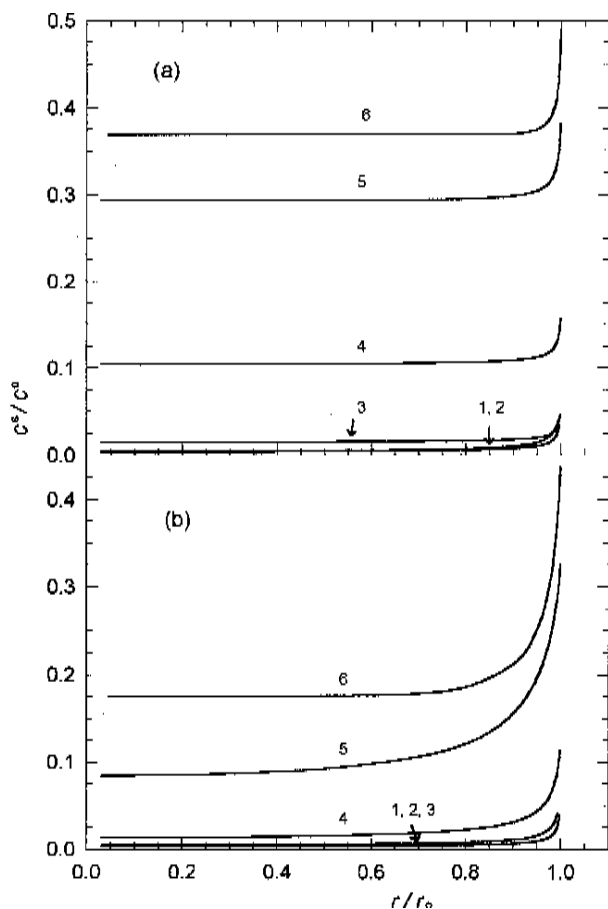

Fig. 2. Distribution of surface concentration along the electrode radius. $q = 2$ (a) and $q = -2$ (b). v (Vs^{-1}): 0.0045 (1), 0.045 (2), 0.45 (3), 4.5 (4), 45 (5) and 450 (6). $r_o = 2$ µm
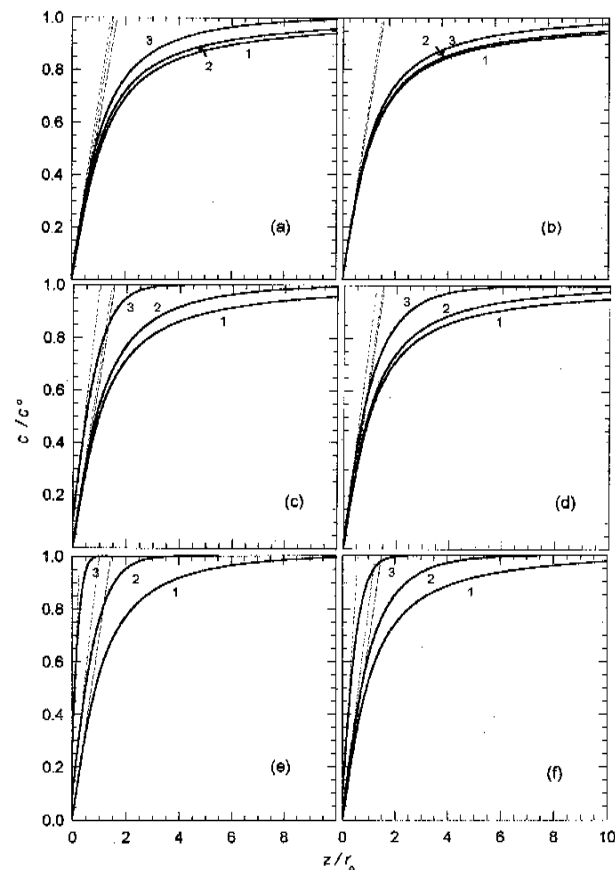

Fig. 3. Concentration changes in the direction perpendicular to the electrode surface at $r/r_o = 0$. r_o (µm): 2 (a, b), 8 (c, d) and 32 (e, f). $q = 2$ (a, c, e) and $q = -2$ (b, d, f). v (Vs^{-1}): (a) and (b) – 4.5 (1), 45 (2) and 450 (3); (c) and (d) – 2.8 (1), 28 (2) and 280 (3); (e) and (f) – 1.75 (1), 17.5 (2) and 175 (3)

Profiles of the diffusion layer are dependent on the distance from the electrode centre (Fig. 4). A steeper rise in the concentration with the distance from the electrode is observed at the edge area. This effect was found to exist even at not a great change in c^o at the edge of the electrode, as is the case at small r_o and low v, i. e. under conditions close to steady state (Fig. 4 a). The difference in diffusion layer profiles becomes greater with an increase in v and partially in k_s (Fig. 4 b and c).

The calculated real diffusion layer, as is seen from the above data, comprises two main parts: a steep rise in concentration at near-surface layers and a slow change to bulk concentration at farther distances.

The second part of diffusion layer is only of some theoretical importance, however, it has no real influence on the current value, i. e. on the electrochemical reaction rate. The current is defined by the first part of diffusion layer. Here a linear dependence of concentration changes on the distance from the electrode is obtained at the distances close to the electrode surface. This is identical with a derivative of concentration with respect to the distance from the electrode at the point $z = 0$, which is proportional to the current according to the known equation:

$$(\partial c/\partial z)_{z=0} = j/nFD. \tag{6}$$

Linearity between the concentration changes and z obtained in the solution layer near to the electrode surface was extrapolated to c^o. In this manner a

diffusion layer thickness was obtained, which is known as an effective diffusion layer thickness δ_{eff}. Such a diffusion layer thickness is obtained when the concentration changes with z are taken to be linear in the diffusion layer, i. e. the Nernst diffusion model is assumed. These linear dependences are shown in Figs. 3 and 4 by dotted lines. They cut off the δ_{eff} values at the upper abscissa for each diffusion case presented in the Figures.

As can be seen, δ_{eff} obtained at the electrode centre is increased to some constant value with a decrease in r_o and v, i. e. approaching the steady state conditions (Fig. 3 a to d). This value was found to be equal to

$$\delta_{eff, ss} = 1.57 \, r_o = \pi r_o/2. \tag{7}$$

A drop in c^s to zero in this case also supports the existence of steady state conditions.

Thus, the peak current is obtained under steady state diffusion at a sufficiently small r_o and low v. This is a well-known feature of the microelectrode behaviour [8]. The current peak becomes independent of v in such a situation and the voltammograms look like ordinary polarisation curves. The δ_{eff} takes the maximum value under steady state diffusion conditions. Its value is decreased with increase in r_o and v. This means that the system is moving away from the steady state diffusion conditions.

The data obtained also show (Fig. 4) that the maximum value of δ_{eff} was determined at the electrode centre. This value decreased, initially very slowly and at the end rapidly, when moving to the electrode edge.
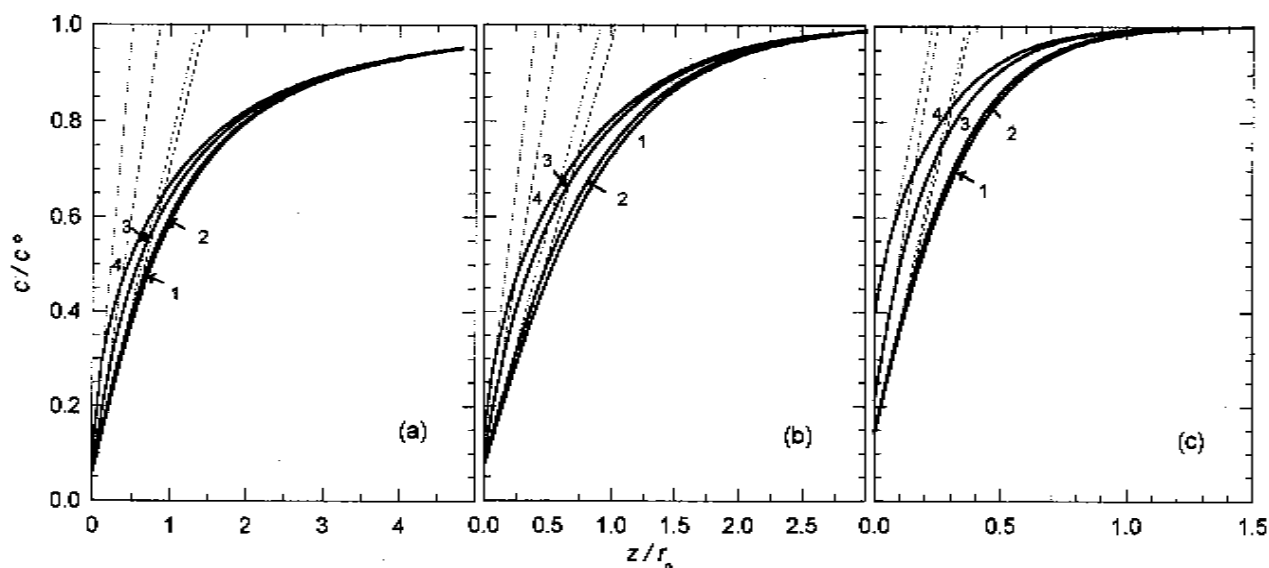

Fig. 4. Concentration changes in the direction perpendicular to the electrode surface depending on the normalized distance from the electrode centre at r / r_o: (a) 0 (1), 0.4 (2), 0.8 (3) and 0.99 (4); (b) 0 (1), 0.5 (2), 0.84 (3) and 0.96 (4); (c) 0 (1), 0.5 (2), 0.9 (3) and 0.99 (4). v (Vs^{-1}): 0.01 (a), 0.18 (b) and 4 (c). , logk_s [k_s / (cm s^{-1})(mol cm^{-3})$^{1/2}$]: −0.65 (a),−2.15 (b) and −3.65 (c). r_o = 10 μm

The above results differ from those in [5]. It is evident that such a distinction is associated with a different approach to this problem, since the average value of δ_{eff} has been derived in [5] and the local one was calculated in this work. The local value of δ_{eff}, as is seen from the above data, is not constant along the electrode surface and decreases from the centre to the edge.

An attempt was made to derive the expression for local δ_{eff} depending on the position at the electrode surface.

To this end, the diffusion equation with corresponding boundary conditions must be solved. The cylindrical coordinate system is generally used in investigations of diffusion at disk electrodes, where the base of a cylinder is taken as the electrode surface. The diffusion equation in this system is

$$\frac{\partial c}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial^2 c}{\partial z^2}\right]. \tag{8}$$

The solution of this equation can be simplified in the coordinate system of oblate ellipsoid of rotation, which is obtained by rotation of ellipse around its minor axis. The major semi-axis of the ellipsoid is equal to the electrode radius r_o. The disk surface is obtained when the minor semi-axis of the ellipsoid $b \rightarrow 0$.

The association between the two above coordinate systems is as follows:

$$r^2 = x^2 + y^2 = f^2(1 + \sigma^2)(1 - \tau^2), \tag{9a}$$

$$z = f\,\sigma\,\tau, \tag{9b}$$

where:

$$\sigma^2 = [(v\ w)^{1/2} + u]\,/\,2f^2 \tag{10a}$$

$$\tau^2 = [(v\ w)^{1/2} - u]\,/\,2f^2 \tag{10b}$$

$$v = (f + r)^2 + z^2 \tag{10c}$$

$$w = (f - r)^2 + z^2 \tag{10d}$$

$$u = r^2 - f^2 + z^2 \tag{10e}$$

$$f = (a^2 - b^2)^{1/2} \tag{10f}$$

$$\varphi_{cyl} = \varphi_{ellip} = \varphi = \operatorname{arctg}(y/x) \tag{10g}$$

a and b are the major and the minor semi-axes of the ellipsoid, respectively.

The diffusion equation in the ellipsoidal coordinate system is of the form

$$\frac{\partial c}{\partial t} = \frac{D}{f^2(\sigma^2 + \tau^2)}\left\{\frac{\partial}{\partial \sigma}\left[(1 + \sigma^2)\frac{\partial c}{\partial \sigma}\right] + \right.$$
$$\left. + \frac{\partial}{\partial \tau}\left[(1 - \tau^2)\frac{\partial c}{\partial \tau}\right]\right\}. \tag{11}$$

When $t \rightarrow \infty$, i. e. at the steady state diffusion, the boundary conditions were taken as follows:

at the electrode surface ($\sigma = \sigma^s = b/f$): $c = c^s = $ const $\tag{12a}$

away from the electrode surface ($\sigma = \sigma^o$): $c = c^o = $ const $\tag{12b}$.

Based on a symmetry of boundary conditions with respect to τ, a conclusion may be made that the concentration is independent also on τ. Then the 1st term of the sum in the right side of eq. (11) is equal to zero:

$$\frac{\partial}{\partial \sigma}\left[(1 + \sigma^2)\frac{\partial c}{\partial \sigma}\right] = 0 . \tag{13}$$

It follows that:

$$(1 + \sigma^2)\frac{dc}{d\sigma} = A \tag{14a}$$

and

$$\frac{dc}{d\sigma} = \frac{A}{1 + \sigma^2} . \tag{14b}$$

Then $c = A\,\operatorname{arctg}\sigma + B$. $\tag{15}$

Here, A and B are the constants. They may be found from boundary conditions (12):

$$A = (c^o - c^s)\,/\,(\operatorname{arctg}\sigma^o - \operatorname{arctg}\sigma^s), \tag{16a}$$

$$B = (c^s \operatorname{arctg} \sigma^o - c^o \operatorname{arctg} \sigma^s)\,/\,(\operatorname{arctg} \sigma^o - \operatorname{arctg} \sigma^s). \tag{16b}$$

The local current density at the electrode surface is equal to

$$i = nFD\left(\frac{\partial c}{\partial \vec{n}}\right)_{\sigma = \sigma^s}, \tag{17}$$

where $\vec{n}$ is a normal to the electrode surface.

The derivative of the concentration with respect to the normal may be written in terms of a tensor component [9]:

$$\frac{\partial c}{\partial \vec{n}} = \sqrt{g^{\sigma\sigma}}\, \frac{\partial c}{\partial \sigma} \qquad (18)$$

Here, $g^{\sigma\sigma}$ is a component of a contravariant metric tensor, which is expressed as

$$g^{\sigma\sigma} = (\partial\sigma/\partial x)^2 + (\partial\sigma/\partial y)^2 + (\partial\sigma/\partial z)^2, \qquad (19),$$

where

$$x = r\cos\varphi \text{ and } y = r\sin\varphi. \qquad (20)$$

After some transformation we obtain from (18)

$$\frac{\partial c}{\partial \vec{n}} = \frac{\left(1+\sigma^2\right)^{1/2}}{f\left(\sigma^2+\tau^2\right)^{1/2}}\, \frac{\partial c}{\partial \sigma} \quad . \qquad (21)$$

It follows from (14b) and (21) that

$$\frac{\partial c}{\partial \vec{n}} = \frac{A}{f\left[\left(\sigma^2+\tau^2\right)\left(1+\sigma^2\right)\right]^{1/2}} \quad . \qquad (22)$$

We obtain at the electrode surface ($z = 0$), when $b \rightarrow 0$: $\sigma = \sigma^s = 0$, $f \rightarrow a = r_o$ and, from (10), $\tau = (r_o^2 - r^2)^{1/2} / r_o$. Then

$$\left(\frac{\partial c}{\partial \vec{n}}\right)_{\sigma=\sigma^s} = \frac{A}{\left(r_o^2 - r^2\right)^{1/2}} \qquad (23)$$

We assume at $t = \infty$ that $c^s = 0$ and $\sigma \rightarrow \infty$. Then from (16)

$$A = c^o / \text{arctg } \sigma^o = 2c^o / \pi \text{ and } B = 0. \quad (24)$$

Substitution of expression A into (23) gives:

$$\left(\frac{\partial c}{\partial \vec{n}}\right)_{\sigma=\sigma^s} = \frac{2c^o}{\pi\left(r_o^2 - r^2\right)^{1/2}} \quad . \qquad (25)$$

Then the local current density is equal to

$$i = 2nFDc^o / \pi\,(r_o^2 - r^2)^{1/2}. \qquad (26)$$

The average current density is expressed as

$$i_{av} = \frac{\int_0^1 i\tau d\tau}{\int_0^1 \tau d\tau} = 4nFDc^o / \pi r_o \quad . \qquad (27)$$

According to the definition of effective diffusion layer thickness δ_{eff}, we have:

$$\left(\frac{\partial c}{\partial \vec{n}}\right)_{\sigma=\sigma^s} = \left(\frac{\partial c}{\partial z}\right)_{z=0} = \frac{c^o}{\delta_{eff}} \quad . \qquad (28)$$

Then we obtain from (25) and (28) that the steady state diffusion layer thickness $\delta_{eff,ss}$ is equal to:

$$\delta_{eff,ss} = (\pi/2)(r_o^2 - r^2)^{1/2} \qquad (29)$$

The average effective diffusion layer thickness according to (27) and (28) is:

$$\delta_{eff,ss,av} = \pi r_o/4. \qquad (30)$$

The results obtained show that the value of $\delta_{eff,ss}$ at the electrode centre ($r = 0$) is twice as large as the average $\delta_{eff,ss}$, however, it decreases moving to the electrode edge.

The profile of $\delta_{eff,ss}$ from the centre to edge of the electrode calculated using equation 29 is presented in Fig. 5. Points at the curve represent the simulated values of $\delta_{eff,ss}$. One can see that the $\delta_{eff,ss}$ values calculated using analytical expression and obtained by digital simulation agree sufficiently well.
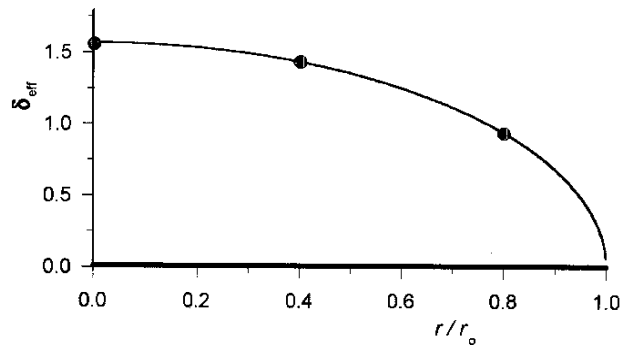

Fig. 5. Thickness of the effective steady state diffusion layer along the radius of small electrode calculated using eq. 29 (solid line) and obtained by digital simulation (points)

CONCLUSIONS

Concentration changes in the plane perpendicular to the electrode surface at a peak current are dependent mostly on the diffusion factor p, which defines the time taken to peak current. Steady state diffusion conditions are realised in the peak current area and the maximum diffusion layer thickness is formed at a sufficiently small r_o and low v.

An effective diffusion layer thickness evaluated assuming the linear changes in concentration in the diffusion layer with the distance from the electrode surface is characterized by the maximum value equ-

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al to $\pi r_{\mathrm{o}}/2$ at the electrode centre and decreases to some low value at its edge.

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REAGUOJANČIŲ METALŲ JONŲ KONCENTRACIJA ARTI MAŽŲ DISKO ELEKTRODŲ, APSKAIČIUOTA VOLTAMPEROMETRINĖS SROVĖS MAKSIMUME 2. KONCENTRACIJA STATMENOJE ELEKTRODUI PLOKŠTUMOJE

S a n t r a u k a

Neišreikštinių baigtinių skirtumų metodu apskaičiuoti koncentracijos pokyčiai statmena elektrodo paviršiui krypti-mi, esant maksimumo srovei priklausomai nuo difuzinio ir kinetinio veiksnių ir tuo pagrindu išnagrinėtos difuzijos sluoksnio susidarymo prie mažų disko elektrodų ypatybės. Nustatyta, kad esant pakankamai mažam elektrodo radiusui r_{o} ir lėtam potencialo skleidimo greičiui v maksimalios srovės srityje yra realizuojamos stacionarios difuzijos sąlygos. Šioje būsenoje susidaro maksimalus difuzijos sluoksnio storis. Nustatyta, kad efektyvusis difuzijos sluoksnio storis, kuris buvo įvertintas priėmus tiesinį koncentracijos kitimą difuzijos sluoksnyje atstumo nuo elektrodo atžvilgiu, turi didžiausią vertę, lygią $\pi r_{\mathrm{o}}/2$, elektrodo centre ir mažėja iki tam tikros mažos vertės jo pakraštyje.

В. Скоминас, П. В. Стасюкайтис

КОНЦЕНТРАЦИЯ РЕАГИРУЮЩИХ ИОНОВ МЕТАЛЛОВ ВБЛИЗИ МАЛЫХ ДИСКОВЫХ ЭЛЕКТРОДОВ, ВЫЧИСЛЕННАЯ ПРИ ВОЛЬТАМПЕРОМЕТРИЧЕСКОМ ПИКЕ ТОКА 2. КОНЦЕНТРАЦИЯ В ПЕРПЕНДИКУЛЯРНОЙ К ЭЛЕКТРОДУ ПЛОСКОСТИ

Р е з ю м е

Методом неявных конечных разностей вычислены изменения концентрации в направлении, перпендикулярном к поверхности электрода, в зависимости от диффузионного и кинетического факторов и на этой основе рассмотрены особенности образования диффузионного слоя при малых дисковых электродах. Установлено, что при достаточно малом радиусе электрода r_{o} и медленной скорости развертки потенциала v в области пика тока реализуются условия стационарной диффузии. В этом положении наблюдается наибольшая толщина диффузионного слоя. Установлено, что эффективная толщина диффузионного слоя, которая была оценена приняв прямолинейное изменение концентрации в диффузионном слое с расстоянием от электрода, имеет наибольшее значение, равное $\pi r_{\mathrm{o}}/2$, в центре электрода и уменьшается до некоторого малого значения на его краю.