TRANSIENT CONVECTIVE DIFFUSION ON A CONVEX ELECTRODE IN THE PRESENCE OF ANOMALOUS WALL EFFECTS

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The effect of the shape of an electrode on the course of electrochemically driven transient mass transfer at potentiostatic conditions is investigated for the case of a nonlinear velocity profile in the region of the concentration boundary layer. Particular results for circular electrodes are given.

In our earlier paper[1] we have considered the theory of transient convective diffusion for the case of a nonlinear velocity profile and with the assumption that the working electrode is an infinite straight band of a width L oriented in the bypassed planar wall perpendicularly to the flow direction. Here, we generalize this theory[1] to the case of an arbitrary planar convex electrode of finite dimensions.

THE GENERAL THEORY

Let us consider a transient mass-transfer process in an unidirectionally flowing fluid with the velocity field

$$v_x = u(z) = Az^p, \quad v_y = v_z = 0 \tag{1}$$

over a planar wall, $z = 0$, in which the mounted electrode covers a simply connected domain $\mathscr{R}$ (Fig. 1). The mathematical model of the transient process considered is described by the transport equation

$$D\,\partial^2_{zz}c - Az^p\,\partial_x c - \partial_t c = 0 \tag{2}$$

with the boundary conditions

$$c = c_0: \quad \text{for} \quad t < 0 \quad \text{or} \quad z \to \infty \quad \text{or} \quad (x, y) \in \mathscr{N} \tag{3a}$$

$$c = 0: \quad \text{for} \quad t > 0 \quad \text{and} \quad z = 0 \quad \text{and} \quad (x, y) \in \mathscr{R} \tag{3b}$$

Due to the neglection of the y-th component of diffusional flows, *i.e.*, of the term $D\,\partial_{yy}^2 c$ in the transport equation (*2*), this simplified formulation of the problem contains the coordinate y only as a parameter. This, together with the neglection of the corresponding x-th component of diffusional flows, belongs to usual simplifications of equations of convective diffusion[2], which is justified at sufficiently high Péclet numbers,

$$Pé = L^{2(1-q)}(A/D)^{2q} = u(\delta)\,L/D \tag{4}$$

with

$$q = 1/(2 + p)\,, \tag{5}$$

L is characteristic length of the electrode, D is the diffusion coefficient and δ is the Nernst thickness of the concentration boundary layer related to the mean current density $\bar{I}$,

$$\delta = \nu c_0 F D/\bar{I}\,. \tag{6}$$

The concentration field, which is the solution of the 4-dimensional boundary-value problem (*2*), (*3a,b*), can be expressed as $c = c(z;\, t,\, \xi)$, where ξ is a new longitudinal coordinate measured from the leading edge of the electrode at a given $y =$ = const. (Fig. 1). At $\xi = x$, this field is the solution to the problem for the above mentioned band electrode[1]. According to known results[1], the corresponding field of instantaneous local current densities can be expressed explicitly also here:

$$I(t, y, \xi) = \begin{cases} I_s(\xi)\,; & \xi < \lambda(t) \\ I_i(t)\,; & \xi > \lambda(t)\,, \end{cases} \tag{7a,b}$$

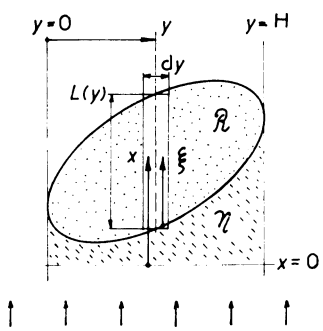

FIG. 1

Geometry of the working electrode. x, y Cartesian coordinates in the plane $z = 0$, H = total width of the electrode, $L(y)$ local length of the electrode, ξ local longitudinal distance from the leading edge of the electrode, de, $\mathscr{R}$ region of the electrode, $\mathscr{N}$ region before the electrode; the arrows mark the direction of the liquid stream along the wall $z = 0$

where transient, I_i, and steady, I_s, current densities are given by the relations

$$I_i(t) = vc_0F^{-1/2}D^{1/2}t^{-1/2}\,, \tag{8}$$

$$I_s(\xi) = vc_0F\pi^{-1/2}C^{1-q}(\beta A/\xi)^q\,. \tag{9}$$

The coordinate of the instantaneous distance of the boundary between the transient and steady zone from the leading edge of the electrode, $\xi = \lambda$, is given by the relation

$$\lambda(t) = \beta AD^{p/2}t^{1+p/2} \tag{10}$$

with

$$\beta = q^2(\pi^{1/2}/\Gamma(q+1))^{1/q}\,. \tag{11}$$

By the method employed in our earlier work[1] we can also find the expression for instantaneous mean current densities, I, for a given longitudinal line $y =$ const. of length $L = L(y)$:

$$\bar{I}_x(t, y) = \frac{1}{L}\int_0^L I(t, y, \xi)\,d\xi = \begin{cases} \bar{I}_s(L)\,; & L < \lambda(t) \\ \bar{I}_i(L)\,; & L > \lambda(t) \end{cases} \tag{12a,b}$$

with

$$\bar{I}_s(L) = \frac{2+p}{1+p} I_s(L) \tag{13}$$

$$\bar{I}_i(t, L) = T^{-1/2}\left(1 + \frac{1}{1+p}T^{1+p/2}\right)I_s(L) \tag{14}$$

$$T = t/t_\infty(L) \tag{15}$$

$$t_\infty(L) = D^{-pq}(\beta A/L)^{-2q}\,. \tag{16}$$

The parameters $I_s(L)$ and $t_\infty(L)$ in these equations represent the steady local current density at the end of the longitudinal line ($y =$ const., $0 < \xi < L(y)$), and the corresponding local time of stabilization of diffusion fluxes, resp.

Thus, the calculation of instantaneous mean current densities, $\bar{I}$, over the entire surface of the electrode, becomes a simple mechanical task of calculating the integral

$$\bar{I}(t) = \int_R I(t, y, \xi)\,dy\,d\xi \bigg/ \int_R dy\,d\xi = \int_0^H \bar{I}_x(t, y)\,L(y)\,dy \bigg/ \int_0^H L(y)\,dy \tag{17a,b}$$

since $\bar{I}_x(t, y)$ is given explicitly by relations (*12a,b*). Specifically it holds for finite convex electrodes

$$\int_0^H L(y)\,\bar{I}(t, y)\,dy = \int_{\varkappa_s} L(y)\,\bar{I}_s(L(y))\,dy + \int_{\varkappa_i} L(y)\,\bar{I}_i(t, L(y))\,dy\,, \qquad (18)$$

where $\varkappa_i = \varkappa_i(t)$ is a simple finite interval,

$$y \in \varkappa_i(t) \Rightarrow t < t_\infty(L(y)) \qquad (19)$$

and the complement $\varkappa_s = \{(0; H) - \varkappa_i\}$ is for convex electrodes the union of at most two simple finite intervals. The coordinate $y = h(t)$ of the boundary between $\varkappa_i$ and $\varkappa_s$ at time t is the root of the equation

$$I_s(L(h)) = I_i(t)\,. \qquad (20)$$

A Circular Electrode

For a circular electrode of radius R, the dependence $L = L(y)$ can be expressed in a simple parametric form as

$$L = L(\alpha) = 2R\cos(\alpha)\,, \quad y = y(\alpha) = R\sin(\alpha)\,. \qquad (21a,b)$$

The minimum steady local current density, I_c, and the corresponding total time of stabilization of the process, t_c, are given by the relations

$$I_c = I_s(2R) = c_0 F \pi^{-1/2} D^{1-q} (\beta A/2R)^q \qquad (22)$$

$$t_c = t_\infty(2R) = D^{-pq} (\beta A/2R)^{-2q}\,. \qquad (23)$$

We will use them for introducing the normalized variables

$$T = t/t_c\,, \quad N = \bar{I}/I_c\,. \qquad (24a,b)$$

In our case of the circular electrode, expressions (*12a,b*), (*13*), (*14*) can be rearranged to read

$$\bar{I}_x(T, \alpha)/I_c = \begin{cases} \dfrac{2+p}{1+p}\cos^{-q}(\alpha)\,; & \alpha > \varkappa \\[2ex] T^{-1/2}\left(1 + \dfrac{\cos(\varkappa)}{(1+p)\cos(\alpha)}\right); & \alpha < \varkappa \end{cases}, \qquad (25a,b)$$

where $\varkappa \in (0; \pi/2)$ is, for a given T, the root of the equation

$$\cos(\varkappa) - T^{1+p/2} = 0\,. \qquad (26)$$

On inserting these expressions into relations (*18*)–(*20*), we obtain the following result for $T \leqq 1$:

$$N(T) = \frac{4}{\pi}\int_0^{\pi/2} I_c^{-1}\bar{I}_x(T, \alpha)\cos^2(\alpha)\,d\alpha =$$

$$= \frac{4}{\pi}\left[\frac{2+p}{1+p}\int_{\varkappa}^{\pi/2}\cos^{2-q}(\alpha)\,d\alpha + T^{-1/2}\int_0^{\varkappa}\left(1 + \frac{1}{1+p}\frac{\cos(\varkappa)}{\cos(\alpha)}\right)\cos^2(\alpha)\,d\alpha\right], \qquad (27)$$

where $\varkappa = \varkappa(T) = \arccos(T^{1+p/2})$. For $T = 1$, the mean current density assumes its steady-state value $\bar{I}(\infty) = I_c N(1)$ and, in accordance with Eq. (*27*) for $T = 1$, it holds

$$N(1) = \frac{2+p}{1+p}\frac{2}{\sqrt{\pi}}\frac{\Gamma[(5+3p)/(4+2p)]}{\Gamma[(7+4p)/(4+2p)]}\,. \qquad (28)$$

The corresponding asymptotic representations can be found in the form

$$T^{1/2}N(T) \approx \begin{cases} 1 + \dfrac{4}{\pi}\dfrac{T^s}{1+p} - \dfrac{2}{3\pi}\dfrac{T^{3s}}{3p+5}\,; & T \to 0_+ \\[2ex] T^{1/2}N(1) + \dfrac{\sqrt{2}}{\pi}\dfrac{16}{15}\dfrac{2+p}{1+p}(1-q^2)(1-T^s)^{5/2}\,; & T \to 1_- \end{cases} \qquad (29a,b)$$

with

$$s = 1 + p/2 = 1/(2q)\,. \qquad (30)$$

RESULTS AND DISCUSSION

Relation (*27*), in spite of the relative simplicity of necessary calculations, is not suitable for a common treatment of experimental data. Thus, we attempted to replace it with a simple empirical formula for $N_E(T)$, which would represent the course of $N(T)$ as defined by relation (*27*) with sufficient accuracy in the entire relevant interval of $T \in (0; 1)$. The final form of such a formula as found by an empirical modification of the asymptotic representation according to Eq. (*29a*) is

$$T^{1/2}N_E(T) = 1 + \frac{4}{\pi}\frac{T^s}{1+p} - \frac{0{\cdot}047568}{1+0{\cdot}5943p}T^{3s}\,, \qquad (31)$$

which guarantees deviations from the exact $N(T)$ curve according to (27) lower than 0·005% (*i.e.*, 5 significant digits) for $p \in \langle 0; 1 \rangle$. The closeness of the empirical representation (31) and the exact relation (27) is illustrated in Fig. 2*b*, where $\Delta_E = (N_E/N - 1)$.

TABLE I

Exact and approximate values of the normalized steady current densities on the circular electrode

p	$N(1)$	$N_E(1)$	$N_L(1)$
0	2·225 672	2·225 672	2·220
1/6	2·048 070	2·048 067	2·045
1/3	1·915 229	1·915 227	1·915
1/2	1·812 157	1·812 155	1·813
2/3	1·729 875	1·729 874	1·732
5/6	1·662 682	1·662 682	1·665
1	1·606 783	1·606 783	1·610

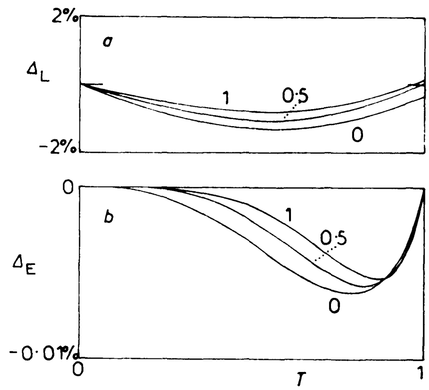

FIG. 2

The relative accuracy of the linearized (*a*) and empirical (*b*) transient function $N(T)$. The numeric labels in the figure are values of the parameter p

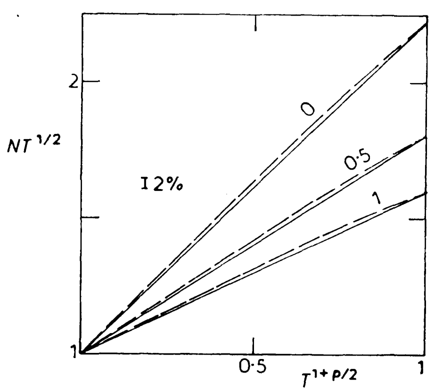

FIG. 3

The $N-T$ transient characteristic for a circular electrode in the linearized coordinates. ——— Linearized courses according to Eq. (32), ----- exact courses according to Eq. (27). The numeric labels are values of the parameter p. The line segment in the figure denotes a 2% deviation in $NT^{1/2}$

A more crude, but in most practical cases sufficient approximation $N_L(T)$ of the function $N = N(T)$, is offered by the relation

$$T^{1/2}N_L(T) = 1 + T^s/[0.82(1 + p)] . \qquad (32)$$

The relative error of this approximation, $\Delta_L = (N_L/N - 1)$, does not exceed 1% of the exact value according to (31) (Fig. 2a). For a better orientation, Table I contains exact values of the parameter $N(1)$ and their approximations by $N_E(1)$, $N_L(1)$.

By using the approximation $N_L(T)$ according to Eq. (32) we can – within a relative error of 1% – process any transient data graphically by linear regression methods employing the linear regression formula

$$Y = a(1 + bX) \qquad (33)$$

with

$$Y = It^{1/2} , \quad X = t^{1+p/2} \qquad (34a,b)$$

$$a = t_c^{1/2}I_c = \nu c_0 \boldsymbol{F} \sqrt{(D/\pi)} , \qquad (35a)$$

$$b^{-1} = 0.82(1 + p)\, t_c^s = 1.64(1 + p)\,(\beta A/R)^{-1}\, D^{-p/2} . \qquad (35b)$$

To this purpose, however, we must know the values of parameter p preliminarily. Since the value of a can be determined from independent measurements, *e.g.*, by investigating transient currents in an unmoving fluid, the parameter p can be estimated with a good accuracy from the slope of the $\ln(Y/a - 1)$ *vs* $\ln t$ dependence. A comparison between the linearized course $N_L(T)$ and the exact courses $N(T)$ of the transient characteristic is shown in Fig. 3. The linearized relation (33) is analogous to the exact theoretical result for a band electrode[1] and it becomes identical with it for an equivalent length dimension of the circular electrode of radius R equal to

$$L = 1.64R . \qquad (36)$$

In coordinates $Y - X$, the parameter t_c defined by Eq. (23) can again be found as the intersection of the transient curve and the horizontal straight line $Y = N(1)\, a$.

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