CALCULATION OF ALTERNATING DIFFUSION CURRENT ON A VIBRATING ELECTRODE ALLOWING FOR THE ELECTRODE REACTION RATE

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The problem of the diffusion on a vibrating spherical electrode operating under limiting-current conditions was previously quantitatively examined, and expressions (valid with respect to order of magnitude) for the degree of sensitivity of the electrode ξ [1] were obtained:

$$\xi = \Delta J / J^{(0)}, \tag{1}$$

where ΔJ and $J^{(0)}$, respectively, are the amplitude of the periodic diffusion current and the value of the steady-state diffusion current. It is therefore of interest to evaluate the effect of the rate of the electrode reaction on the degree of sensitivity of the electrode.

We will consider the case of mixed kinetics for a vibrating spherical electrode, on the surface of which an irreversible electrochemical reaction, characterized by rate constant k, takes place. This system is described by the nonsteady-state equation of convective diffusion [2]

$$\frac{\partial c}{\partial t} + \mathbf{v}\nabla c = D\Delta c. \tag{2}$$

We will limit ourselves to an examination of the case where the rate amplitude U_0 is small, viz.,

$$U_0 / \omega \ll R, \delta_\nu, \delta_D, \tag{3}$$

where ω is the vibrational frequency of the electrode, $\delta_\nu \sim (\nu/\omega)^{1/2}$, $\delta_D \sim (D/\omega)^{1/2}$, ν and D are the viscosity and diffusion coefficients, and R is the electrode radius.

Expanding the concentration of the reacting substance with respect to the small parameter U_0

$$c = c^{(0)} + c^{(1)} + \ldots, \tag{4}$$

and considering the effect of convection only in first order with respect to U_0, we obtain the following expression for $c^{(1)}$:

$$\frac{\partial c^{(1)}}{\partial t} + \mathbf{v}\nabla c^{(0)} = D\Delta c^{(1)}, \tag{5}$$

where $\mathbf{v}$ is the hydrodynamic velocity, $c^{(0)}$ is the steady-state distribution of concentrations, c_0 is the concentration of substance in the volume of the electrolyte, and $\varepsilon = D/kR$. According to Eq. (5), the problem reduces to the solution of the equation

$$\frac{\partial c^{(1)}}{\partial t} + c_0 \frac{R}{r^2} \frac{v_r}{1+\varepsilon} = D\Delta c^{(1)} \tag{6}$$

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with boundary conditions

$$\lim_{r\to\infty} c^{(1)} = 0, \qquad kc^{(1)}|_{r=R} = D\frac{\partial c^{(1)}}{\partial r}\Big|_{r=R} \tag{7}$$

where v_r is the radial component of the velocity of the liquid moving far off from the sphere according to the law [3]

$$\lim_{r\to\infty} v = -U_0 e^{-i\omega t}. \tag{8}$$

Considering the periodic dependence of the velocity on the time as well as the geometry of the problem, the solution of Eq. (8) can be represented in the form

$$c^{(1)} = c_0\frac{U_0 R}{D}\frac{1}{1+\varepsilon}\lambda(r)\cos\theta e^{-i\omega t} \tag{9}$$

where θ is the angle between vectors U_0 and r. The λ (r) function is a solution of the heterogeneous Bessel equation

$$r^2\lambda''(r)+2r\lambda'(r)-(r^2n_D^2/R^2+2)\cdot\lambda(r) = \left(\frac{3R^3}{n_\nu r^2}-\frac{3R^3}{n_\nu^2 r^3}\right)e^{n_\nu(r/R-1)}+\frac{R^3}{r^3}\left(1-\frac{3}{n_\nu}+\frac{3}{n_\nu^2}\right)-1, \tag{10}$$

where

$$n_\nu^2 = -i\omega R^2/\nu, \qquad n_D^2 = -i\omega R^2/D,$$

with boundary conditions

$$\lim_{r\to\infty}\lambda(r)=0, \qquad \lambda(R)=\varepsilon R\lambda'(R)$$

In the process, ξ is determined by the following expression:

$$\xi = 1/2\cdot R\lambda'(R)U_0 R/D. \tag{11}$$

From Eq. (10), for $R\cdot\lambda'(R)$ we find

$$R\lambda'(R)=\left\{\frac{3(n_D^2-n_\nu^2)}{n_D n_\nu^2}e^{-(n_D+n_\nu)}\mathrm{Ei}(n_D+n_\nu)+\frac{n_D^2}{8}\right.$$
$$\left.+\frac{n_D}{8}-\frac{n_D^3}{8}(1-3/n_\nu+3/n_\nu^2)e^{-n_D}\mathrm{Ei}(n_D)-\frac{3n_D^2}{8n_\nu}-\frac{3n_\nu}{8n_D}+5/8+3/8n_D\right\}\left[\frac{(2\varepsilon+1)}{n_D}+\varepsilon n_D-(2\varepsilon+1)\right]^{-1} \tag{12}$$

The dependence $\xi(n_D, n_\nu, \varepsilon)$, determined by expression (12), is very complex, and it is therefore expedient to examine several limiting cases:

a. $\delta_\nu > \delta_D \gg R$ (during a single half-cycle the diffusion process has time to propagate at distances greater than the dimensions of the electrode R, and the flow is Stokesian in nature).

b. $\delta_\nu \gg R \gg \delta_D$ (the diffusion process during one half-cycle has time to propagate at distances of the order $\delta_D \ll R$, and the flow is Stokesian in nature).

c) $R \gg \delta_\nu > \delta_D$ (the diffusion process has time to propagate at distances of the order $\delta_D \ll R$, and there is a hydrodynamic boundary layer).

In the case of a type a electrode ($|n_D| \ll 1, |n_\nu| \ll 1$), we obtain the limiting expression

$$\xi_{\infty} = \frac{3}{16}\frac{U_0 R}{D}(1+2\varepsilon)^{-1} \tag{13}$$

for ξ. In limiting cases b and c, which take advantage of the asymptotic expansion of the integral exponent, we arrive at the following result:

$$R\lambda'(R) = 3(1 - n_\nu)n_D^{-3}(\varepsilon n_D - 1)^{-1}. \tag{14}$$

Thus, for a type b electrode, ξ takes on the form

$$\xi_b = \frac{3}{2}\frac{U_0 R}{D} n_D^{-3}(\varepsilon n_D - 1)^{-1}, \tag{15}$$

while for a type c electrode ($|n_\nu| \gg 1$, $|n_D| \gg 1$),

$$\xi_c = \frac{3}{2}\frac{U_0 R}{D}\left(\frac{D}{\nu}\right)^{1/3} n_D^{-3}(\varepsilon n_D - 1)^{-1}. \tag{16}$$

If the electrode reaction is rapid, i.e., if the mass-transfer process is the determining factor, then Eqs. (13), (15), and (16) (when $\varepsilon \to 0$) transform to the corresponding expressions for the degree of sensitivity of the electrode operating under limiting-current conditions [1].

Estimating expressions can be obtained for ξ for complex-shaped electrodes. We will consider an electrode with characteristic hydrodynamic dimension H, on the surface of which an irreversible electrochemical reaction occurs. A substance impinging upon the electrode as a result of vibrational motion is consumed in the reaction, while the unchanged ions accumulate in the near-electrode zone of thickness δ_D. The balance of the substance impinging in unit time on a unit area of the electrode can be written with respect to order of magnitude in the following way

$$v_\nu(\delta_D) \cdot j^{(\nu)} \delta_D D^{-1} \sim (kc_s^{(1)} + \omega c_s^{(1)}\delta_D), \tag{17}$$

where $v_y(\delta_D)$ is the value of the normal component of velocity at distance δ_D, and $c_s^{(1)}$ is the correction for the near-electrode concentration due to vibrations. The second term in the right-hand side of expression (17) describes the accumulation of substance in the near-electrode zone. Considering that $j^{(1)} = kc_s^{(1)}$ and $\delta_D \sim (D/\omega)^{1/2}$, we find

$$\xi \sim v_\nu(\delta_D) \cdot \delta_D \cdot D^{-1}(1 + D/k\delta_D)^{-1}. \tag{18}$$

In writing expression (17), it was assumed that the thickness of the steady-state diffusion layer considerably exceeds the thickness of the periodic diffusion layer.

Depending on the vibrational frequency of the electrode, there are three different cases:

a) $\delta_D \gg H$, $\delta_\nu \gg H$. From expression (18) for ξ we obtain the expression:

$$\xi_a \sim \frac{U_0 \delta_D}{D}\left(1 + \frac{D}{k\delta_D}\right)^{-1}, \tag{19}$$

b) $\delta_D \ll H$, $\delta_\nu \gg H$. For ξ we find

$$\xi_b \sim \frac{U_0 H}{D}\left(\frac{\delta_D}{H}\right)^3 (1 + D/k\delta_D)^{-1} \tag{20}$$

c) $\delta_D < \delta_\nu \ll H$. In this case, $v_y(\delta_D) \sim U_0\, \delta_D H^{-1} (D/\nu)^{1/2}$, and, consequently,

$$\xi_c \sim \frac{U_0 H}{D}\left(\frac{D}{\nu}\right)^{1/3}\left(\frac{\delta_D}{H}\right)^3 (1 + D/k\delta_D)^{-1} \tag{21}$$

Comparing expressions (15) and (16), and, respectively, (20) and (21), one can be convinced of their coincidence from the point of view of a functional dependence on the determining parameters.

LITERATURE CITED

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