LITERATURE CITED

1. V. I. Odelevskii, "Generalized conductivity of heterogeneous systems," Zh. Tekh. Fiz., 21, No. 6, 667-685 (1951).
2. G. N. Dul'nev and Yu. P. Zarichnyak, "Heat conduction of multicomponent mixtures," Inzh.-Fiz. Zh., 12, No. 4, 419-425 (1967).
3. K. I. Martyushov, Electrical Conduction of Composite Resistive Materials. Reviews in Electronic Engineering, Series 5 [in Russian], TsNII Élektronika, Moscow (1982), No.8 (910).
4. K. I. Martyushov, Cermet Thick-Film Resistors. Reviews in Electronic Engineering, Series 5 [in Russian], TsNII Élektronika, Moscow (1981), No. 4(837).
5. D. Smith and J. Anderson, "Theory of electrical conduction in particulate systems," Philos. Mag., 43, No. 5, 797-810 (1981).
6. A. Malliaris and D. Turner, "Influence of particle size on the electrical resistivity of compacted mixtures of polymeric and metallic powders," J. Appl. Phys., 42, No. 2, 614-618 (1971)
7. D. A. Bruggeman, "Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen. 1, 11," Ann. Phys., 24, Nos. 7-8, 636-679 (1935).
8. S. Kirkpatrick, "Percolation and conduction," in: Theory and Properties of Disordered Materials [Russian translation], Mir, Moscow (1977), p. 249-289.
9. E. V. Kharitonov, Dielectric Materials with Inhomogeneous Structure [in Russian], Radio i Svyaz', Moscow (1983), pp. 84-89.
10. C. Marshall, "Temperature coefficients of resistance: A new approach," IEEE Trans. Comp. Hybrids Manuf. Technol., CHMT-2, 265-269 (1979).

MASS TRANSFER WITH "MEMORY" IN ELECTROCHEMICAL PROCESSES

L. S. Kalashnikova

UDC 541.138:66.015.3

Diffusion processes in porous electrodes are investigated on the basis of mass-transfer equation with "memory." The equation is analyzed with the application of the Laplace transform.

The analysis of mass-transfer processes in porous electrodes is of major importance in the investigation of many electrochemical processes, in particular the operation of electrochemical current sources. A complicated interaction takes place between the electric and concentration fields in a porous electrode, where mass transfer is accompanied by electrochemical reactions. The large difference between the characteristic time constants of the diffusion and electrical processes means that they can be considered independently. The variation of the concentration field in the diffusion mode of operation of a porous electrode is described by an equation of the form [1]

$$\frac{\partial c}{\partial \tau} = D^* \Delta c - k_0 c. \tag{1}$$

This equation has been derived on the assumption that the expenditure or accumulation of active substance as a result of electrochemical reactions takes place uniformly. However, this assumption is an idealization, and in real electrodes the instantaneous mode of operation of the electrode is observed to depend on the nature of the process at previous times, i.e., on the history of the process.

Mass transfer of this nature can be modeled if the following expression is used to describe the transfer flux [2]:

$$q_m = -D^* \operatorname{grad} c - \int_0^\tau D^* D'(\tau - \theta) \operatorname{grad} c(\mathbf{r}, \theta)\, d\theta. \tag{2}$$

Institute of the National Economy, Irkutsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 49, No. 3, pp. 481-486, September, 1985. Original article submitted July 4, 1984.

 0022-0841/85/4903- 1108$09.50

Proceeding from (2), we can obtain an equation for the mass transfer in materials with "memory"; in the two-dimensional case it has the form

$$\frac{\partial c}{\partial \tau} = D^* \frac{\partial^2 c}{\partial x^2} + \int_0^\tau D^* D'(\tau - \theta) \frac{\partial^2 c}{\partial x^2} d\theta. \quad (3)$$

The function $D(\tau - \theta)$, which characterizes the relaxation properties of the process in the porous electrode, must be of the "fading memory" type [3]:

$$D(\theta) = \alpha \exp(-\lambda\theta). \quad (4)$$

We can always make $\lambda = 1$ by a suitable choice of time scale.

In regard to many important practical problems it is interesting to analyze the operation of a planar porous electrode of thickness 2d under the conditions of mass transfer with "memory" [4]. The initial and boundary conditions for (3) in this case are

$$\begin{aligned} &\tau = 0: \ c(x) = c_0; \\ &\tau > 0: \ x = \pm d, \ c(x, \tau) = 1. \end{aligned} \quad (5)$$

For the ensuing analysis we write Eq. (3) in the form

$$\frac{\partial c}{\partial \tau} - D^* \frac{\partial^2 c}{\partial x^2} = \int_0^\tau D'(\tau - \theta) \frac{\partial c}{\partial \theta} d\theta - \int_0^\tau D'(\tau - \theta) \left[\frac{\partial c}{\partial \theta} - D^* \frac{\partial^2 c}{\partial x^2} \right] d\theta.$$

Denoting $q(x, \tau) = \partial c/\partial \tau - D^* \partial^2 c/\partial x^2$, we obtain

$$q(x, \tau) + \int_0^\tau D'(\tau - \theta) q(x, \theta) d\theta = \int_0^\tau D'(\tau - \theta) \frac{\partial c}{\partial \theta} d\theta.$$

Taking the Laplace transform, we obtain the following equation for the transformed functions:

$$\bar{q}(x, p) + \bar{D}'(p) \bar{q}(x, p) = \bar{D}'(p) [p\bar{C}(x, p) - c_0],$$

whereupon

$$\bar{q}(x, p) = \frac{p\bar{D}'(p)}{1 + \bar{D}'(p)} \left[\bar{C}(x, p) - \frac{c_0}{p} \right]. \quad (6)$$

After taking the inverse transforms, we obtain Eq. (6) in the form

$$\frac{\partial c}{\partial \tau} - D^* \frac{\partial^2 c}{\partial x^2} = \Pi(\tau)^* [c(x, \tau) - c_0], \quad (7)$$

where the asterisk * denotes the convolution of functions, and $\bar{\Pi}(p) = p\bar{D}'(p)/[1 + \bar{D}'(p)]$. We represent the operator $\bar{\Pi}(p)$ in the form $\bar{\Pi}(p) = B + \bar{\Pi}_0(p)$. Then Eq. (7) is rewritten as

$$\frac{\partial c}{\partial \tau} - D^* \frac{\partial^2 c}{\partial x^2} = B[c(x, \tau) - c_0] + \int_0^\tau \Pi_0(\tau - \theta) [c(x, \theta) - c_0] d\theta. \quad (8)$$

Equation (8) can be regarded as a diffusion equation with sources of a special type, where the first term on the right-hand side determines the instantaneous power of the source and the second term characterizes the stored power. If $D(\theta)$ satisfies (4), the operators $\bar{\Pi}(p)$ and $\bar{\Pi}_0(p)$ acquire specific forms:

$$\bar{\Pi}(p) = -\frac{p\alpha}{p + 1 - \alpha}; \ \bar{\Pi}_0(p) = \frac{\alpha(1 - \alpha)}{p + 1 - \alpha}. \quad (9)$$

Using these expressions, we obtain the following transform from Eqs. (7) and (8):

$$\bar{C}(x, p) = \frac{c_0}{p} + (1 - c_0) \frac{\operatorname{ch} R(p) x}{p \operatorname{ch} R(p) d}, \quad (10)$$

$$R(p) = \sqrt{\frac{p(p+1)}{D^*(p + 1 - \alpha)}}.$$

The inverse (original) of this transform can be found by using Cauchy's theorem of residues to invert the Laplace integral:

$$c(x,\ \tau) = 1 + \frac{2(1-c_0)}{d^2} \sum_{m=1}^{\infty} \sum_{j=1}^{2} A_{jm} e^{p_{jm}\tau} \cos \frac{\pi\left(m-\frac{1}{2}\right)x}{d}, \tag{11}$$

where

$$A_{jm} = \frac{(-1)^{m+1}\pi\left(m-\frac{1}{2}\right)}{p_{jm}\left[1+\frac{\alpha(1-\alpha)}{(p_{jm}+1-\alpha)^2}\right]},$$

and p_{1m} and p_{2m} are the roots of the equation $R(p)d = i\pi(m - 1/2)$.

In the limit $\tau \to \infty$ it follows from (11) that $c(x) = 1$. Autonomous chemical current sources have a finite total power, i.e.,

$$Q(x) = \int_0^{\infty} q(x,\ \tau)\, d\tau < \infty. \tag{12}$$

From (7) we obtain the following expression for $\bar{q}(x, p)$:

$$\bar{q}(x,\ p) = \bar{\Pi}(p)\left[\bar{C}(x,\ p) - \frac{c_0}{p}\right]$$

or $\bar{q}(x, p) = \bar{\Pi}(p)\bar{\phi}(x, p)$, where $\phi(x, \tau) = c(x, \tau) - c_0$.

It follows from the condition of finiteness of $Q(x)$ that $\bar{\Pi}(p)\bar{\phi}(x, p) \to Q(x) < \infty$, if $\bar{\Pi}(p)\bar{\phi}(x, p)$ is analytic for $\mathrm{Re}\ p > 0$ and is bounded as $p \to 0$. In this case $q(x, \tau) \to 0$ as $\tau \to \infty$. For the case of a planar electrode

$$\bar{\varphi}(x,\ p) = (1-c_0)\frac{\mathrm{ch}\, R(p)x}{p\,\mathrm{ch}\, R(p)d}.$$

Here the condition of analyticity of $\bar{\Pi}(p)\bar{\phi}(x, p)$ is equivalent to the requirement that $\alpha < 1$. The boundedness of the maximum local capacitance of the electrode follows from the relation

$$q = (1-c_0)\lim_{p\to 0}\frac{\bar{\Pi}(p)}{p} = \frac{\alpha(1-c_0)}{\alpha-1} < \infty.$$

For $\bar{\Pi}(0) \neq 0$ condition (12) is not satisfied, and it is only sensible to consider the case $\bar{\Pi}(0) = 0$.

The most interesting problem is to analyze the operation of a porous electrode under the conditions of a constant polarization and discharge of the electrode by a constant current. The prinicpal characteristic of the potentiostatic mode of operation is the value of the current taken from the electrode:

$$i(\tau) = \int_{-d}^{d} q(x,\ \tau)\, dx. \tag{13}$$

Using the expressions for $\bar{q}(x, p)$, we obtain

$$\bar{i}(p) = 2\varphi_0 \frac{\bar{\Pi}(p)}{pR(p)}\, \mathrm{th}\, R(p)\, d,$$

$$i(\tau) = \frac{4D^*\varphi_0\alpha}{d}\sum_{m=1}^{\infty}\sum_{j=1}^{2}\frac{e^{p_{jm}\tau}(p_{jm}+1-\alpha)}{\alpha(2p_{jm}+1)-(p_{jm}+1)^2}, \tag{14}$$

where p_{1m} and p_{2m} are the roots of the equation

$$R(p)d = i\pi(m - 1/2).$$

The total capacitance of the electrode is given by the expression

$$\int_0^{\infty} i(\tau)\, d\tau = \lim_{p\to 0}\bar{i}(p) = \frac{2\varphi_0\alpha d}{\alpha-1}.$$

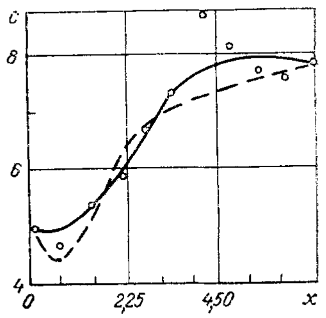

Fig. 1

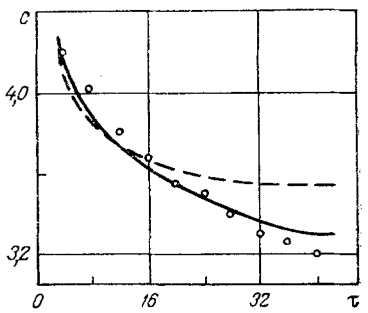

Fig. 2

Fig. 1. Distribution of KOH concentration c (N) along the thickness x (mm) of a nickel–nickel oxide electrode during discharge, i_0 = 0.0167 A/cm², c_0 = 5 N, t = 25°C, d = 0.75 m, D^* = 1.39·10⁻⁶ cm²/sec, α = 0.637, λ = 0.058 h⁻¹, discharge depth factor 2 A· h.

Fig. 2. Variation of KOH concentration c (N) with time τ (sec) after the discharge of a nickel–nickel oxide electrode, i_0 = 0.0143 A/cm², c_0 = 5 N, t = 25°C, d = 0.075 cm, D^* = 1.39·10⁻⁶ cm²/sec, α = 0.637, λ = 0.058 h⁻¹, discharge depth factor 0.5 A·h.

If the electrode is discharged by a constant current, the potentials on the outer surfaces of the electrode are $\varphi(\tau)/_{x=\pm d} = \varphi(\pm d, \tau)$ for a given discharge current. Under symmetrical conditions of operation of the electrode, the expression for $\bar{\varphi}(x, p)$ must be symmetrical:

$$\bar{\varphi}(x, p) = A(p)\,\mathrm{ch}\,R(p)\,x,$$

whereupon

$$\bar{q}(x, p) = \bar{\Pi}(p)\,A(p)\,\mathrm{ch}\,R(p)\,x. \tag{15}$$

Substituting (15) into (13), we obtain

$$\bar{i}(p) = 2\frac{\bar{\Pi}(p)\,A(p)}{R(p)}\,\mathrm{sh}\,R(p)\,d.$$

It follows from the condition of a constant discharge current $\bar{i}(p) = I/p$, where I is the value of the discharge current, that

$$A(p) = \frac{I}{2}\,\frac{R(p)}{p\bar{\Pi}(p)\,\mathrm{sh}\,R(p)d}.$$

The distribution of the potential in the electrode is given by the expression

$$\bar{\varphi}(x, p) = \frac{I}{2}\,\frac{R(p)}{p\bar{\Pi}(p)}\,\frac{\mathrm{ch}\,R(p)\,x}{\mathrm{sh}\,R(p)\,d},$$

where the values of the potential on the surface of the electrode are

$$\bar{\varphi}(\pm d, p) = \frac{I}{2}\,\frac{R(p)}{p\bar{\Pi}(p)}\,\mathrm{cth}\,R(p)\,d.$$

The electrode discharge curve $\phi(\tau)$ is described by the equation

$$\varphi(\tau) = -\frac{Id}{6\alpha D^*} - \frac{I(\tau + 1 - \tau d)}{2\alpha d} + \frac{I\pi^2 D^*}{\alpha d^3}\sum_{m=1}^{\infty}\sum_{j=1}^{2} B_{jm}e^{p_{jm}\tau}, \tag{16}$$

where

$$B_{jm} = \frac{m^2(p_{jm} + 1 - \alpha)}{p_{jm}^2\left[1 + \frac{\alpha(1-\alpha)}{(p_{jm}+1-\alpha)^2}\right]};$$

p_{1m} and p_{2m} are the roots of the equation $R(p)d = i\pi m$.

For asymmetrical conditions at the boundaries of the electrode, the boundary conditions for Eq. (3) have the form

$$\begin{aligned} &\tau = 0: \quad c(x) = c_0; \\ &\tau > 0: \quad x = 0, \qquad c(x, \tau) = c_0; \\ &\qquad\qquad x = d, \qquad c(x, \tau) = 1. \end{aligned} \tag{17}$$

The following expressions for the discharge current $i(\tau)$ and the discharge curve $\phi(\tau)$ can be obtained for such boundary conditions:

$$\begin{aligned} i(\tau) &= \frac{\varphi_0 \alpha D^*}{d} \sum_{m=1}^{\infty} \sum_{j=1}^{2} \frac{e^{p_{jm}\tau}(p_{jm} + 1 - \alpha)}{\alpha(2p_{jm} + 1) - (p_{jm} + 1)^2}, \\ \varphi(\tau) &= -\frac{2Id}{3\alpha D^*} - \frac{8I(\tau + 1 - \tau\alpha)}{\alpha d} + \frac{32I\pi^2 D^*}{\alpha d^3} \sum_{m=1}^{\infty} \sum_{j=1}^{2} B_{jm} e^{p_{jm}\tau}, \end{aligned} \tag{18}$$

where p_{1m} and p_{2m} are the roots of the equation $R(p)d = 2i\pi(m - 1/2)$.

As examples, the experimental data of [5] are compared with the solution of Eqs. (1) and (3) in Figs. 1 and 2. The results calculated according to Eq. (3) with the "memory" term are represented by solid curves in the figures, those calculated according to Eq. (1) without the "memory" term are represented by dashed curves, and the experimental potassium hydroxide concentrations determined in [5] are indicated by dots. The calculated values of the parameters D^*, α, and λ of the model (3) are given in each case.

NOTATION

c, concentration; D^*, diffusion coefficient; τ, time; θ, variable of integration; c_0, equilibrium concentration; 2d, thickness of electrode; α, λ, parameters of relaxation function; $D(\theta)$ relaxation function; p, variable of Laplace transform.

LITERATURE CITED

1. O. S. Ksenzhek, "Diffusion of the operation of porous electrodes," Zh. Fiz. Khim., 36, No. 2, 243-248 (1962).
2. L. S. Kalashnikova and I. N. Taganov, "Mass-transfer equation in materials with 'memory'," Teor. Osn. Khim. Tekhnol., 15, No. 6, 914-917 (1981).
3. J. M. Finn and L. T. Wheeler, "Wave propagation aspects of the generalized theory of heat conduction," Z. Angew. Math. Phys., 23, No. 6, 927-931 (1981).
4. L. S. Kalashnikova and I. N. Taganov, "Mass-transfer with 'memory' in the operation of porous electrodes," in: Mathematical Modeling and Optimization of Chemical Technological Processes [in Russian], Leningrad (1982); Abstract No. 1316-82 deposited at ONIITÉKhIM, Cherkassy.
5. A. L. Rotinyan and V. B. Uvarov, Determination of the Alkali Concentration at the Surface of a Porous Electrode by the Method of Measuring the Potential Difference between Its Polarizable and Nonpolarizable Sides. Analytical Study of the Variation of the Alkali Concentration in the Pores by the Composite-Electrode Method [in Russian], NTK Leningr. Tekhnol. Inst. im. Lensoveta, Brief Communications, Leningrad (1972).