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NONSTATIONARY MODEL OF HEAT AND MASS TRANSFER IN ELECTROCHEMICAL SYSTEMS

V. G. Anisimovich[a], **N. N. Grinchik**[b],
V. A. Zhuk[c], **S. I. Sakovets**[a],
A. A. Khmyl'[a], **and V. A. Tsurko**[c]

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A system of partial differential equations for a macroscopic description of the transfer in complex electrochemical systems is proposed. A numerical algorithm for finding an approximate solution is constructed. Computational experiments for copper plating by means of electrolysis are carried out.

Technological processes that involve electrochemical systems are widely used in nonferrous metallurgy, galvanoplastics, the production of chemical current sources, and metal treatment. Their successful design has now become inefficient without the development and analysis of physicomathematical models of the processes and the carrying out of computational experiments. The current work proposes a physicomathematical model of transfer phenomena in an electrochemical medium taking into account the interaction of diffusion fluxes, electromagnetic waves, and the Joule heating of the material.

State-of-the-art technologies are characterized by a pulsed electrical action on the medium. Here, the solute concentration has a noticeable effect on the electrical conductivity, and a timing analysis of the physicochemical processes becomes important. Some models of electrochemical systems were examined previously [1-5]. Works [1-3] deal with modeling of the electrolysis in a steady-state case disregarding the material diffusion; in [4, 5], the models of transfer in electrolytes were considered based on a separate description of the cation and anion diffusion but disregarding the heating of the medium. Here, a good many of the parameters for ion fluxes are introduced, whose determination procedure is complicated. Moreover, the interactions between the cations and anions of the solute and between the solvent molecules are ignored.

The Joule heating in an electrochemical cell was considered in [6] using the Nernst–Planck equations. According to [6], the solution of the problem necessitates the knowledge of a number of additional characteristics, such as the electric potential in supernatant layers, a horizontal fall of the volume electric potential at an electrode, etc. Here, only an approximate solution of the stationary problem is presented.

The model of the processes in electrochemical systems given below requires a relatively small number of input data and represents a higher level of physicomathematical description of phenomena. It is based on the method that was first examined in [7, pp. 147-148] and elaborated in [8-10].

Model. For modeling the diffusion electric phenomena, we consider an approach that is based on an integral description of the diffusion and heating of the medium. A separate description of the diffusion electrochemical processes requires an appropriate "recognizer" for identifying the actual cation and anion fluxes. In practice, only observed mass, charge, and heat fluxes are usually recorded. The equation of electric neutrality of the medium does not provide independence of a variation in the cation and anion differentials, since in the electrolytic solution even in a double electric near-electrode layer their variations are functionally related.

A macroscopic description of the electromagnetic field in a distributed system must draw on the Maxwell equations that take the vector form

$$\partial \mathbf{D}/\partial t + \mathbf{j}_q = \operatorname{rot} \mathbf{H}\,, \quad \operatorname{div} \mathbf{D} = \rho\,, \tag{1}$$

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[a]Belarusian State University of Informatics and Radioelectronics; [b]Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute," National Academy of Sciences of Belarus; [c]Institute of Mathematics, National Academy of Sciences of Belarus, Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 73, No. 3, pp. 561-566, May–June, 2000. Original article submitted June 18, 1999.

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$$-\partial\mathbf{B}/\partial t = \operatorname{rot}\mathbf{E}\,, \quad \operatorname{div}\mathbf{B} = 0\,, \tag{2}$$

where $\mathbf{D} = \varepsilon\varepsilon_0\mathbf{F}$ and $\mathbf{B} = \mu\mu_0\mathbf{H}$. According to [7, p. 161], the mass, charge, and heat-flux densities are

$$\mathbf{q}_j = -D_A\nabla n + D_A^*\lambda\mathbf{E}\,, \quad \mathbf{j}_q = \lambda\,(\mathbf{E} - \lambda_A^*\nabla n)\,, \quad \mathbf{j}_\tau = -k\nabla T\,.$$

If the medium is homogeneous, its properties can be characterized by the parameters ε, μ, λ, and D_A. The coefficients λ and k in the general case are functions of n and T.

The elimination of the magnetic-field strength from the system of equations (1) and (2) yields the equation for the vector of the electric-field strength

$$\frac{\varepsilon}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2} + \mu_0\frac{\partial\mathbf{j}_q}{\partial t} = \frac{1}{\mu}\,(\Delta\mathbf{E} - \operatorname{grad}\operatorname{div}\mathbf{E})\,. \tag{3}$$

To allow for the mass transfer, Eq. (3) is supplemented by the diffusion equation

$$\partial n/\partial t = -\nabla\mathbf{q}_j\,. \tag{4}$$

The passage of the electric current entails the Joule heating of the medium. On the assumption that it is stationary, the heat-conduction equation is of the following form [11, p. 169]:

$$c_p\,\rho\,\frac{\partial T}{\partial t} = -\nabla\mathbf{j}_\tau + \mathbf{j}_q\cdot\mathbf{E}\,. \tag{5}$$

For phenomenologically independent processes, Eqs. (3)-(5) permit a simplification of the analysis of the diffusion electric phenomena, since recorded parameters for the observed phenomena are used in lieu of the hydrodynamic theory of ion diffusion.

With a component-by-component treatment, the obtained system (3)-(5) is a three-dimensional system of five equations in five unknowns. A numerical realization of this problem in the presence of mixed derivatives is very complicated. Many physical processes permit natural assumptions that simplify the initial problem.

As has been demonstrated in [12, p. 27], for conductors it can be assumed with a sufficient degree of certainty that the volume charge density is equal to zero. This is stipulated by the following factors: (1) if the initial charge density was equal to zero, it remains equal to zero subsequently and (2) the charge, which was initially distributed over the entire conductor, decreases with time at each point exponentially. In all, even poor, conductors, the relaxation time is extremely short. Therefore, div $\mathbf{D} = 0$ and, hence, div $\mathbf{E} = 0$.

On these assumptions, the system of equations (3)-(5) in a one-dimensional case takes the form

$$\frac{\varepsilon}{c^2}\frac{\partial^2 E}{\partial t^2} + \mu_0\frac{\partial}{\partial t}\left(\lambda\,(n, T)\left(E - \lambda_A^*\,(n, T)\,\frac{\partial n}{\partial x}\right)\right) = \frac{1}{\mu}\frac{\partial^2 E}{\partial x^2}\,, \tag{6}$$

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial x}\left(D_A\frac{\partial n}{\partial x} - D_A^*\,(n, T)\,\lambda\,(n, T)\,E\right), \tag{7}$$

$$c_p\,\rho\,\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left(k\,(n, T)\,\frac{\partial T}{\partial x}\right) + \lambda\,(n, T)\left(E - \lambda_A^*\frac{\partial n}{\partial x}\right)E\,. \tag{8}$$

It follows from the Onsager reciprocal relation for kinetic coefficients that cross terms must be equal up to a factor [7, pp. 139-140], and therefore we need factual knowledge of the coefficient of ambipolar diffusion D_A^*, which can be determined from the polarization curve, and also from ε, μ, and D_A.

With a one-dimensional modeling, system (6)-(8) is considered in a certain confined region $G = [0 \le x \le l] \times [0 \le t \le \overline{T}]$, where l is the anode–cathode spacing and $\overline{T}$ is the process time. The initial conditions are of the form

$$n(x,0) = n_0(x)\,,\quad E(x,0) = \varphi_1(x)\,,$$
$$\partial E(x,0)/\partial t = \varphi_2(x)\,,\quad T(x,0) = T_0(x)\,, \tag{9}$$

and the boundary conditions are in most cases defined by the fluxes $\mathbf{q}_j$, $\mathbf{j}_q$, and $\mathbf{j}_\tau$ at the boundaries.

Computational Scheme. To solve numerically the system of equations (6)-(8), we use the method of finite differences. In the region G, we introduce the spatial and time grids of nodes:

$$\overline{\omega}_h = \left\{x_i = ih\,,\ \ i = 0, 1, \ldots, N\,,\ \ h = l/N\right\},$$
$$\overline{\omega}_\tau = \left\{t_j = j\tau\,,\ \ j = 0, 1, \ldots, j_0\,,\ \ \tau = \overline{T}/j_0\right\},$$

where N and j_0 are integral parameters that determine the calculation accuracy. Let y, v, and w denote approximate values at the nodes $\overline{\omega}_h$ and $\overline{\omega}_\tau$ of the functions E, n, and T, respectively. Approximating the derivatives by their difference analogs, we obtain the following difference scheme for the system of equations (6)-(8):

$$(\varepsilon\mu/c^2)\, y_{\bar{t}t} + \mu\mu_0\left(\lambda(v,w)\left(y - \lambda_A^*(v,w)\, v_{2\overset{\circ}{x}}\right)\right)_{\overset{\circ}{t}} = y_{\bar{x}x}^{(\sigma_1,\sigma_2)}\,, \tag{10}$$

$$v_{\overset{\circ}{t}} = (D_A v_{\bar{x}})_x^{(\sigma_1,\sigma_2)} - (D_A^*(v,w)\,\lambda(v,w)\, y)_{\overset{\circ}{x}}^{(\sigma_1,\sigma_2)}\,, \tag{11}$$

$$c_p\rho w_{\overset{\circ}{t}} = (k(v,w)\, w_{\bar{x}})_x^{(\sigma_1,\sigma_2)} + \lambda(v,w)\left(y - \lambda_A^*(v,w)\, v_{\overset{\circ}{x}}\right) y\,. \tag{12}$$

For y at fixed i, here $y_t = (y^{j+1} - y^j)/\tau$, $y_{\bar{t}} = (y^j - y^{j-1})/\tau$, and $y_{\overset{\circ}{t}} = (y_{j+1} - y_{j-1})/\tau$, and on the time layer j, $y_x = (y_{i+1} - y_i)/h$, $y_{\bar{x}} = (y_i - y_{i-1})/h$, and $y_{\overset{\circ}{x}} = (y_{i+1} - y_{i=1})/h$; σ_1 and σ_2 are the weight parameters for time layers: $y^{\sigma_1,\sigma_2} = \sigma_1 y^{j+1} + (1 - \sigma_1 - \sigma_2)y^j + \sigma_2 y^{j-1}$.

With a sufficient smoothness of the functions $E = E(x, t)$, $n = n(x, t)$, and $T = T(x, t)$, the difference scheme (10)-(12) approximates differential equations (6)-(8) with the order $O(\tau^2 + h^2)$ at $\sigma_1 = \sigma_2$ and with the order $O(\tau + h^2)$ when the values of the weight factors are at variance. The boundary conditions are approximated so that the order of approximation is consistent with the equations [13, p. 309].

An approximate solution of the nonlinear system of equations (10)-(12) with appropriate boundary conditions is found with the aid of the following iteration process:

$$(\varepsilon\mu/c^2)^{k+1}\, y_{\bar{t}t} + \mu\mu_0\left(\lambda(\overset{k}{v},\overset{k}{w})\left(\overset{k+1}{y} - \lambda_A^*(\overset{k}{v},\overset{k}{w})\, \overset{k}{v}_{\overset{\circ}{x}}\right)\right)_{\overset{\circ}{t}} = \overset{k+1}{y}{}_{\bar{x}x}^{(\sigma_1,\sigma_2)}\,, \tag{13}$$

$$\overset{k+1}{v}_{\overset{\circ}{t}} = \left(D_A\, \overset{k+1}{v}_{\bar{x}}\right)_x^{(\sigma_1,\sigma_2)} - \left(D_A^*(\overset{k}{v},\overset{k}{w})\,\lambda(\overset{k}{v},\overset{k}{w})\,\overset{k}{y}\right)_{\overset{\circ}{x}}^{(\sigma_1,\sigma_2)}\,, \tag{14}$$

$$c_p\rho\, \overset{k+1}{w}_{\overset{\circ}{t}} = \left(k(\overset{k}{v},\overset{k}{w})\, \overset{k+1}{w}_{\bar{x}}\right)_x^{(\sigma_1,\sigma_2)} + \lambda(\overset{k}{v},\overset{k}{w})\left(\overset{k}{y} - \lambda_A^*(\overset{k}{v},\overset{k}{w})\, \overset{k}{v}_{\overset{\circ}{x}}\right)\overset{k}{y}\,. \tag{15}$$

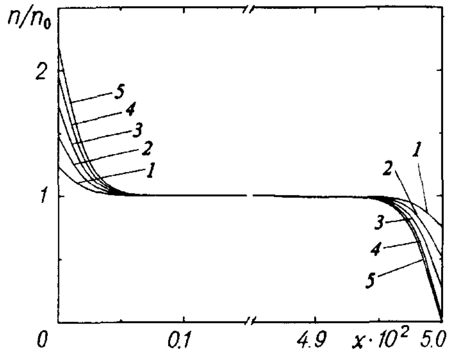

Fig. 1. Distribution of the relative concentration of salt for various current densities: 1) 100, A/m^2; 2) 200; 3) 300; 4) 400; 5) 500. n/n_0, dimensionless quantity; x, m.

For $k = 0$, the values of the grid functions on the preceding time layer are chosen as initial approximations. Each iteration reduces to the solution of three systems of linear algebraic equations with a three-diagonal matrix using the factorization method.

A theoretical study of the constructed difference scheme leads to extremely cumbersome calculations. Here, a priori evaluations do not always adequately reflect the quality of the proposed algorithm, which, however, is characteristic of the investigation of nonlinear difference problems. Therefore, the propounded numerical method was tested on model problems by varying the time and space steps and the weight and iteration parameters.

Example of Modeling of Diffusion Electric Phenomena in Electrolytes. Let us consider the process of copper plating with an electric current with a constant density J traversing the solution of copper sulfate $CuSO_4 \cdot 5H_2O$. Copper Cu (99.78%) is used as the anode. It deposits from the solution at the cathode. The coefficients of current efficiency for copper are taken to be 100%. The electrochemical equivalent of copper $Cu^{++} + 2e^-$ is assumed to be $k_e = 0.6588 \cdot 10^{-6}$ kg/C [9]. The electrical conductivity $\lambda(n)$ of the copper-plating electrolyte as a function of the concentration of copper sulfate in water is presented in [9], and the temperature dependence of the coefficients λ and k is regarded as insignificant. In calculations for $CuSO_4$ we set $D_A = 5 \cdot 10^{-10}$ m^2/sec, $D_A^*(n) = \lambda(n) \cdot 10^{-11}$ kg/(A·sec), $\lambda_A^*(n) = \lambda(n) \cdot 10^{-4}$ V·m^2/kg, $\varepsilon = 70$, and $\mu = 1$. The anode–cathode spacing is $l = 0.05$ m. The values of c_p, ρ, and k are taken to be $4.2 \cdot 10^3$ J/(kg·K), 10^3 kg/m^3, and 0.6 W/(m·K), respectively.

The passage of the electric current through the solution is described by the system of differential equations (6)-(8). For a numerical solution, it is supplemented by the boundary conditions, which for the process in question are of the form

$$\mathbf{q}_j = k_e J\,, \quad \mathbf{j}_q = J\,. \tag{16}$$

Equations (16) define the mass and charge fluxes that go from the anode into the copper-plating solution at $x = 0$ or arrive at the cathode at $x = l$.

The heat transfer as a consequence of electrochemical reactions at the electrodes is taken into account by the relations $-\mathbf{j}_\tau = \alpha(T - T_0)$ at the anode and $\mathbf{j}_\tau = \alpha(T - T_0)$ at the cathode. The initial conditions have the form (9) with $\varphi_1(x) = \varphi_2(x) = 0$, $n_0(x) =$ const being the initial concentration of copper sulfate, and $T_0 =$ const being the initial temperature of the process.

We next present the results of numerical modeling of the concentration redistribution and unsteady-state Joule heating of an electrochemical cell in copper plating for various densities of the direct current. It is seen from Fig. 1 that as early as within a minute after the commencement of copper plating, the electrolyte concentration changes noticeably, which, evidently, is the cause of a nonsymmetrical heating of the electrochemical cell.

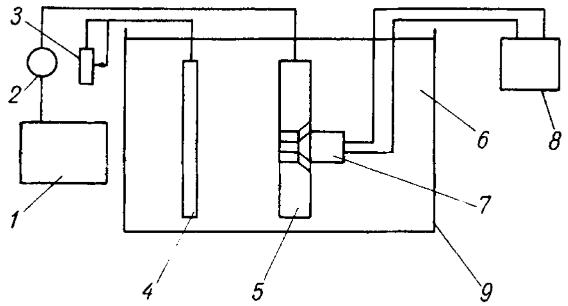

Fig. 2. Diagram of an experimental setup for measuring the temperature in a near-cathode layer.

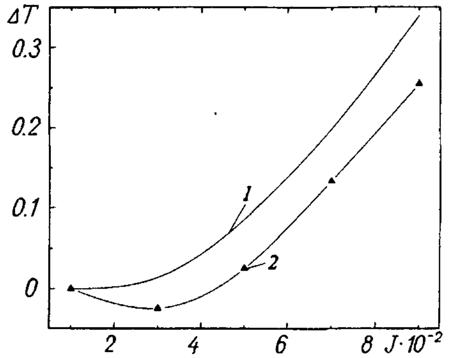

Fig. 3. Superheating of a near-cathode region vs. current density: 1) numerical modeling; 2) experiment. ΔT, K; I, A/m^2.

To measure the temperature in the surface layer of the electrolytic solution near the cathode and to compare it with calculated results, an experimental setup was developed and manufactured that is diagrammed in Fig. 2. Copper anode 4 and cathode 5 were placed in a galvanic bath 9 with sulfuric-acid copper-plating electrolyte 6. The cathode of thickness 1 mm had an opening into which temperature pickup 7 was inserted, in whose capacity a thermal resistor with a temperature coefficient of resistance of 365 Ω/deg was used. The resistance of the thermal resistor was measured via ohmmeter 8. The bath was energized from stabilized dc source 1. The current strength in the bath was assigned by variable resistor 3 and measured by ammeter 2.

The temperature was measured within 60 sec after the energization. Figure 3 presents experimental data for the superheating of the near-cathode region as a function of the density of the direct current and the results of numerical modeling. Clearly, an increase in the current density leads to a rise in the near-surface temperature. The near-surface temperature obtained from solving Eqs.(6)-(8) is 10-15% higher than the temperature recorded experimentally. The discrepancy is most likely explained by the errors in determining the coefficients and by the assumptions made. In the future, the electrolyte motion and also the heat transfer of the electrolyte, electrodes, and surrounding medium should be taken into account. Nevertheless, the calculated results and the experimental data are in good qualitative agreement, which makes it possible to use the proposed approach for modeling the transfer in complex electrochemical systems.

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NOTATION

B, magnetic induction, T; c_p, specific heat, J/(kg·K); **D**, electric displacement, C/m^2; D_A, coefficient of molecular diffusion, m^2/sec; D_A^*, coefficient of ambipolar diffusion, kg/(A·sec); **E**, electric field strength, V/m;

$\mathbf{H}$, magnetic field strength, A/m; J, current density, A/m^2; $\mathbf{j}_q$, charge flux density, C/(m^2·sec); $\mathbf{j}_T$, heat flux density, J/(m^2·sec); k, thermal conductivity, W/(m·K); k_e, electrochemical equivalent, kg/C; n, concentration of electrolytic solution, kg/m^3; $\mathbf{q}_j$, mass flux density, kg/(m^2·sec); t, time, sec; T, temperature, K; x, distance, m; α, heat transfer coefficient, W/(m^2·K); ε, dielectric constant; ε_0, electric constant, F/m; λ, electrical conductivity, 1/(Ω·m); λ_A^*, electrical ambipolar conductivity, V·m^3/kg; μ, magnetic permittivity; μ_0, magnetic constant, H/m; ρ, density, kg/m^3; c, electrodynamic constant.

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