NONSTATIONARY MODEL OF HEAT AND MASS TRANSFER IN ELECTROCHEMICAL SYSTEMS

V. G. Anisimovich, N. N. Grinchik, V. A. Zhuk, S. I. Sakovets, A. A. Khmyl, and V. A. Tsurko

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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

\[ \partial D / \partial t + j_d = \nabla H, \quad \text{div} \ D = \rho, \]

(1)

\[-\partial \mathbf{B}/\partial t = \text{rot} \mathbf{E}, \quad \text{div} \mathbf{B} = 0,\]  

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

\[ \mathbf{q}_m = -D_A \nabla n + D_A^* \lambda \mathbf{E}, \quad \mathbf{j}_q = \lambda (\mathbf{E} - \lambda \nabla n), \quad \mathbf{j}_h = -k \nabla T. \]

If the medium is homogeneous, its properties can be characterized by the parameters \( \varepsilon, \mu, \lambda, \) and \( D_A \). The coefficients \( \lambda \) 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

\[ \frac{\varepsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \mu_0 \frac{\partial \mathbf{j}_h}{\partial t} = \frac{1}{\mu} (\Delta \mathbf{E} - \text{grad} \text{ div} \mathbf{E}). \]  

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

\[ \frac{\partial n}{\partial t} = -\nabla \mathbf{q}_m. \]

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]:

\[ c_p \rho \frac{\partial T}{\partial t} = -\nabla \mathbf{j}_h + \mathbf{j}_q \cdot \mathbf{E}. \]

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, \( \text{div} \mathbf{D} = 0 \) and, hence, \( \text{div} \mathbf{E} = 0 \).

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

\[ \frac{\varepsilon}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2} + \mu_0 \frac{\partial \mathbf{j}_h}{\partial t} \left[ \lambda (n, T) \left( \mathbf{E} - \lambda^* (n, T) \frac{\partial n}{\partial x} \right) \right] = \frac{1}{\mu} \frac{\partial^2 \mathbf{E}}{\partial x^2}. \]

\[ \frac{\partial n}{\partial t} = \frac{\partial}{\partial x} \left[ D_A \frac{\partial n}{\partial x} - D_A^* (n, T) \lambda (n, T) \mathbf{E} \right]. \]

\[ c_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[ k (n, T) \frac{\partial T}{\partial x} \right] + \lambda (n, T) \left( \mathbf{E} - \lambda^* \frac{\partial n}{\partial x} \right) \mathbf{E}. \]

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 \( \varepsilon, \mu, \) and \( D_A \).

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