

Optimal control of oxidation-reduction processes in electrochemical reactors with flowing volumetric - porous electrodes. Mathematical models

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Abstract - As to the solution of problems control of electrochemical reactors with VPE, two directions of research seem to be the most promising ones. The first direction is in the optimization of construction items of the reactor at the expense of precise selection of electrical conductivity of an electrode, as the function dependent on one of spatial coordinate. The second direction is in optimal process control of an electrochemical deposition in the situation when the relation of the dimensional current density on electrodes of reactor to the temporary coordinate of process is selected as a control parameter. To work on these topics, it is necessary to use methods of mathematical modeling of electrochemical processes in porous media, as well as mathematical methods of solutions of problems of optimal control. In addition, an experimental verification of mathematical findings is necessary. To do this, it is proposed to elaborate methods for obtaining of carbon fibrous materials with given properties, such as, for example with given electrical conductivity.

MATHEMATICAL MODELS

Electrochemical systems with flowing volumetric - porous electrodes (VPE) of graphitic carbon fibrous materials (CFM) attract attention of researchers. One of the main reasons is a well developed reactionary surface (4000-5000 sm^2/g) which in combination with a sufficiently high electrical conductivity, high porosity (90 - 98 %) and high values of the material transfer factors 10^{-1} - 10^{-2} sm/s provides an essential intensification of electrochemical processes, as well as deposition of significant amount of metal per unit weight of material (till 30 - 40 kg on kg CFM). This is true even from electrolytes with low concentrations of metals (10^{-2} - 10^{-7} mol / l).

A number of different designs of industrial and experimental reactors with the usage of carbon fibrous electrodes are currently in place. They are used in a

number of processes, such as withdrawal of metals from weak solutions, creation of self-contained local processes in galvanotechnic, etc. It has been also shown, however that the capabilities of intensification of the above electrochemical processes on flowing three-dimensional electrodes made of CFM are not completely utilized.

To find the optimal conditions of functioning of electrolytic cells with VPE, one should rely on mathematical modeling, which includes in particular optimization and optimal control of electrochemical processes occurring in pores of volumetric - porous electrodes. Major contributions in the field of physical and mathematical simulations of processes of electro deposition of metals on VPE are due to the works of V. Daniel-Bek [1] and A. Frumkin [2]. Using an approach of I. Zeldovich [3] for the description structurally - composite systems, they approximated a volumetric - porous electrode by a quasi-homogeneous model, which is characterized by a set of effective parameters. Works of O. Ksengek [4], N. Gurevich [5], V. Bagotsky [5], Ju. Chizmadgiev [6], R. Sioda [7], Kreysa G [8,9], Coeuret F. [10], Newman J. [11], Pollar R., Trainham J. [12], Bek R.J. [13], Doherty T. [14], Soleh M.M. [23], Kuhn A. [24], Oren J. [25] and others have demonstrated the feasibility of an effective recovery of active materials of VPE at small concentrations of components.

Developing further the above theoretical results, the authors of the project have elaborated physical and mathematical models of electrochemical processes in volumetric - porous electrodes, which take into account the three-dimensional nature of processes and their time dependence. Systems of integro - differential equations are obtained, which describe electro chemical processes in VPE, as well as connections between the potential of electrical field (E) at an arbitrary spatial point ($x=(x_1, x_2, x_3)$) of pseudo-homogeneous environment,

partial current densities (J_k) and concentrations (C_k) of electro-fissile components (k) [15]:

$$-F \frac{\partial \sum_k z_k C_k}{\partial t} + \nabla \bullet \left[-\frac{1}{r_{\text{ac}} + r_{\text{TB}}} \nabla E \right] + \sum_k S J_k = 0 \quad (1)$$

$$|W| \frac{\partial C_k}{\partial n} = \frac{S}{z_k F} J_k \quad (2)$$

$$J_k = f(C_k, \exp(p(E))) \quad (3)$$

$$\int_V J_k(z) dz = I(t). \quad (4)$$

Where ∇ , $\nabla \bullet$, Δ are gradient, divergence and Laplace operator accordingly, W is the speed of the passage of the electrolyte, n is the direction of the passage, D_k , S , Z_k , F are electrochemical parameters, f and p are given functions, Γ is the boundary of medium, and t denoted time, $I(t)$ are given density of a dimensional current given on the electrode V .

It is stipulated in the mathematical model, that the electrical conductivity of a solid phase $d_T = 1/r_{\text{TB}}$ can change in time due to the filling of electrode by metal in accordance with the equations obtained by the authors [16]:

$$r_T = \frac{r_{\text{yT}} (1-P)^{2/3} + \frac{SP}{F} \sum_{k=1}^N \frac{r_{\text{M,k}}}{Z_k q_k} \int_0^t J_k(x,t) dt}{(1-P)^{2/3} + \frac{SP}{F} \sum_{k=1}^N \frac{1}{q_k Z_k} \int_0^t J_k(x,t) dt}. \quad (5)$$

The electrical conductivity of a fluid phase changes in time with the change of the gas-filling factor. This change is described by the following equation [17]:

$$P \cdot \frac{\partial C}{\partial t} + \nabla \bullet (W \cdot C) - (1-P)M = 0. \quad (6)$$

Here C is the concentration of the gaseous Hydrogenium; Z is a constant describing the degree of porosity of the electrode, M is the gas source intensity, $x=(x_1, x_2, x_3)$ denotes spatial point in the electrode.

By solving these equations (together with initial and boundary conditions) one can calculate electrochemical processes in pores of three-dimensional flowing volumetric - porous electrodes for non-stationary processes.

Our theoretical and experimental studies have demonstrated that one of major constructional characteristics of electrolytic cells with VPE is the spatial distribution of electrical conductivity of the graphitic carbon fibrous material of cathode (r_T). In addition, the most essential feature allowing one to control the process, is the dependence of the density of the current (I), from time t [18].

Thus, in order to solve the problem of the optimization of the process of an electrolysis on VPE, one should focus on the following topics: (a) elaboration of mathematical models, methods and algorithms of determination of optimal relations $r_T(x)$ and $I(t)$, and (b) elaboration of the technology for obtaining of graphitic carbon fibrous materials of the cathode with prescribed electric conductive properties.

To solve the first problem, the general system (1) - (4), which models electrochemical processes in VPE, is converted into the following system of ordinary differential equations [19]:

$$\frac{dE}{dx} = Z(x) \quad (7)$$

$$\frac{dr_T}{dx} = u(x) \quad (8)$$

$$\frac{dZ}{dx} = -Z(x) \cdot u(x) \cdot \frac{r_{\text{ac}}}{r_T(x)(r_T(x) + r_{\text{ac}})} + Sv \left(\frac{1}{r_T(x)} + \frac{1}{r_{\text{ac}}} \right) J(x) \quad (9)$$

$$\frac{dC}{dx} = \frac{Sv}{wzF} J(x) \quad (10)$$

$$Z(0) = -\frac{I}{r_T(0)}, \quad Z(L) = -\frac{I}{r_{\text{ac}}}. \quad (11)$$

Here L the thickness of the electrode.

Note that unlike the three-dimensional time dependent equations (1) - (4), equations (7) - (11) are one-dimensional and time dependence is not included in them. Such a simplification is quite natural in the case when lines of the electrical field are parallel to the streamline of solution. The systems with this property of electrochemical processes are widespread and will be considered in this project. Besides, the model (7)-(11) reflects the situation, when density of a dimensional current on the electrode does not change in time. In this case the process can be defined, as pseudo-stationary, which enables one to assume that the time derivatives of function C equal zero $\left(\frac{\partial C}{\partial t} = 0 \right)$.

The optimization functional is selected as

$$s^2 = \int_0^L \left(\frac{I}{L} - J(E, C) \right)^2 dx \rightarrow \min. \quad (12)$$

Minimum of this functional corresponds to the most uniform distribution of the electrochemical process within the volume of an electrode, which is the main characteristics of the efficiency of the electro-deposition process of metals on VPE.

As a control function, the relation $u(x) = \frac{dr_T}{dx}$ is selected. After optimization of this function, one can easily calculate the target electrical conductivity $r_T(x)$.

In principle, this optimization problem can be solved by the maximum principle of L. Pontrjagin. There are, however some essential features of this problem, which complicate an application of this principle. First, the problem of optimal control is ill-posed, since the objective functional (12) depends only on phase variables ($E(x), C(x)$). Second, the system of differential equations (7) - (11) is unstable with respect to its right hand sides. This means that a small change in functions in the right hand sides of these equations can cause substantial changes in the solution. The same is true for small changes in the initial conditions.

Therefore, it is necessary to develop new and effective numerical methods for the solution of the problem (7) - (11). These methods should take into account the ill-posed nature of this problem.

Another direction of this investigations is mathematical modeling, analytical studies and development of methods and algorithms for calculation of optimal control of the electrochemical reactor at the expense of correct choice of the relation of dimensional electrode's current from time t . In this case the condition (4) in the problem (1) - (4) should be written as

$$\int_{V_K} J_k(z) dz = I(t)$$

Here z - a point of a surface of the cathode V_K .

The authors have an idea on how to reduce the problem (1) - (4) to a non-linear boundary value inverse problem. In this case the problem of optimization would be solved as an inverse problem of the determination of the function $I(t)$, involved in the boundary conditions (4). Thus, the control function $I(t)$ is determined as a boundary condition satisfying to a minimum of the functional:

$$g(I(t)) = \frac{1}{2} \sum_{i=1}^N \int [E(I, x_i, t) - \text{const}_i]^2 dt$$

Minimum of this functional provides the most uniform distribution of the potential with respect to the linear coordinate x of the electrode during the entire process.

To use this method, it is necessary to rewrite the problem as a non-linear inverse problem of mathematical physics. Questions of uniqueness and existence for this inverse problem will be addressed. Naturally, a numerical method of minimization of the functional (12) will also be developed.

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