

## MATHEMATICAL MODELS OF THE NONSTATIONARY ELECTROCHEMICAL PROCESSES IN VOLUMETRIC POROUS FLOW ELECTRODES

*Model representations of the nonstationary processes caused by the nonstationary electrolysis regimes on three-dimensional flow electrodes (TFEs) were developed. A change in the electrode and electrolyte parameters with time was taken into account. As an illustration of the efficiency of a model of two-dimensional electrochemical system, co-electrodeposition of two metals with hydrogen evolution on TFE was considered for the case of mutually perpendicular directions of current and electrolyte flow.*

### Introduction

Electrochemical mechanism of the reactions occurring in electrochemical reactors designed for metal electrodeposition is, obviously, a unifying principle of their operation. The electrode potential and potential jump at the interface in the electrochemical system are crucial characteristics controlling both the transformation rate and nature of the end product. For many types of electrochemical systems, in particular, for threedimensional flow electrodes (TFEs), the problem arises of assuring uniform potential distribution in different electrode areas and, as a consequence, limitation of the useful electrode size and thickness. The potential distribution is determined by the following main factors: kinetics of electrode process, conductivities of the solid and liquid phases of the electrochemical system, and electrolysis regime (voltage, stirring, temperature).

Evidently, to improve operation of the electrochemical reactors, irrespective of their destination and principles of organization of the electrochemical reactions, it is, essential, first, to develop scientific notions of the nature of electrochemical reaction and the influence of the current, hydrodynamic, diffusional, and other characteristics of the electrochemical process on its efficiency and, second, to construct and develop the appropriate mathematical models and computational methods for the most favorable deposition regimes with allowance for the energetic and hydrodynamic possibilities of the reactors and their elements and construction.

Among the promising three-dimensional flow electrodes intensifying electrochemical processes, especially in diluted solutions, fiber carbon electrodes have found practical use [1 – 4].

Because of a variety of factors influencing the operation efficiency of TFEs, the optimal operating conditions can be determined only through the mathematical modeling, optimization, and optimal control of the electrochemical processes occurring in the pores of volumetric porous electrodes, in conjunction with the experimental study of the nonstationary processes and properties of carbographite fiber materials.

Although the general problems of the mathematical modeling of electrochemical processes are well-documented in the works of electrochemists and mathematicians, e.g., in [5–36], we did not find any publications devoted to the mathematical modeling of the processes occurring on three-dimensional porous flow electrodes in the nonstationary electrolysis regimes.

The purpose of this work was to develop model representations for the nonstationary electrochemical TFEs in the nonstationary electrolysis regimes. In doing so, a change in the electrode and electrolyte parameters was taken into account as in [21–23]. As an illustration of the efficiency of a model of two-dimensional electrochemical system, the current and flow directions were chosen to be mutually perpendicular, without discussing advantages and disadvantages of such an organization of the process. This issue will be the subject of our further publications.

### Basic equations

The basic equations used for constructing and studying the mathematical model of electrodeposition in various electrochemical systems are presented below. We assume that the flow  $N_i$  ( $i = 1, \dots, n$ ) of charged particles of the sort  $i$  in the electrolyte volume is determined by the migrative and convective components, as is the case in the majority of electrochemical systems,

$$N_i = z_i \mu_i F c_i \nabla E + c_i V. \quad (1)$$

Here,  $z_i, c_i$ , and  $\mu_i$  are, respectively, the charge, concentration, and mobility of the  $i$ th electroactive species in a pseudohomogeneous medium;  $\nabla E$  is the gradient of electric potential; and  $V$  is the velocity vector of the convective solution transfer. The current in the electrode/ electrolyte volume is expressed by the formula

$$J = F \sum z_i N_i \quad (2)$$

The material balance in the absence of a homogeneous electrochemical reaction is expressed as

$$\partial c_i / \partial t = -\nabla \cdot N_i \quad (3)$$

Where  $\nabla \cdot N_i$  is the divergence of the  $N_i$  flow. For the stationary system, one has

$$\nabla \cdot N_i = 0 \quad (4)$$

From (1) and (2) it follows that

$$J = F^2 \sum_i^n z_i^2 u_i c_i \nabla E + FV \sum_i^n z_i c_i \quad (5)$$

or

$$J = \chi \nabla E + FV \sum_i^n z_i c_i \quad (6)$$

Where  $\chi = F^2 \sum_i^n z_i^2 u_i c_i$  is the conductivity of the pseudohomogeneous medium. The conductivity can be considered constant if a change in the concentrations of electroactive species has only little effect on it (e.g., in the presence of a base electrolyte).

By multiplying each term in (4) by  $z_i F$ , summing over  $i$ , one obtains, in combination with (2),

$$\nabla \cdot J = 0 \quad (7)$$

or

$$\nabla \cdot \left[ \chi \nabla E + FV \sum_i^n z_i c_i \right] = 0 \quad (8)$$

#### Generalized mathematical models

Further transformation of (8) depends on whether the electroneutrality condition

$$\sum z_i c_i = 0 \quad (9)$$

is fulfilled in the system or not. It is commonly supposed that this condition is fulfilled over all volume of the electrolyte solution, except for the electric double layer near the electrodes and other interfaces [34, p. 261].

However, the condition (9) does not hold in the case of metal electrodeposition in the pseudohomogeneous systems, e.g., in volumetric porous electrodes, where, from the macrokinetic standpoint, one can assume the presence of a potential jump at the solid electrode/electrolyte boundary in each elementary volume of the electrode space.

In the mathematical modeling and calculation of the electrochemical systems with volumetric porous flow electrodes designed for metal extraction, one can arbitrarily recognize two approaches: with (1) mutually parallel electric-field and electrolyte-flow lines in reactor and (2) mutually perpendicular or angular arrangement of the current and flow directions. The electrolysis regime is either galvanostatic or potentiostatic (dynamic).

In this work, an attempt was undertaken to describe the electrolysis process on a TFE for an arbitrary arrangement of the current- and electrolyte-supply boundaries, i.e., for both galvanostatic and galvanodynamic regimes in a three-dimensional electrochemical system.

Breaking of electroneutrality at any point indicates, generally, that either a positive or negative source of charged particles is situated at this point. As mentioned above, we consider the case of a pseudohomogeneous electrochemical system, e.g., of a volumetric porous electrode filled with a homogeneous electrolyte with the averaged effective characteristics. Such an approach was originally proposed by Ya.B. Zel'dovich and today is successively used for modeling pseudohomogeneous systems [8].

It would appear natural that the potential in such a model medium suffers jump at the solid electrode/electrolyte boundary in each elementary volume of the electrode space, where electrode reactions can proceed, thereby breaking the (9) condition. By transforming (3) with allowance for this fact, one gets

$$\partial c_i / \partial t = -\nabla \cdot (z_i u_i F c_i \nabla E + c_i V) \quad (10)$$

or

$$Fz_i \partial c_i / \partial t = -\nabla \cdot (z_i^2 F^2 u_i c_i \nabla E + Fz_i c_i V) \quad (11)$$

The summation over  $i = 1, \dots, n$  in (11) gives

$$\sum Fz_i \partial c_i / \partial t = \nabla \cdot [-\kappa \nabla E - FV \sum z_i c_i] \quad (12)$$

or

$$F \partial \sum z_i c_i / \partial t = \nabla \cdot [-\kappa \nabla E] - F \nabla \cdot [V \sum z_i c_i] \quad (13)$$

After removing from (13) the terms  $z_i c_i$  corresponding to the electrolyte components not involved in the electrochemical reactions, one arrives at the relation similar to (13), however, with the summation only over the electroactive species (indexed  $k$ ) that are involved in the reactions:

$$F \partial \sum z_k c_k / \partial t = \nabla \cdot [-\kappa \nabla E] - F \nabla \cdot [V \sum z_k c_k] \quad (14)$$

The second sum on the right-hand side of (14) has the form

$$\begin{aligned} & \sum \left( \frac{\partial c_k}{\partial x} V_x + \frac{\partial c_k}{\partial y} V_y + \frac{\partial c_k}{\partial z} V_z \right) \\ &= \sum |V| \left( \frac{\partial c_k}{\partial x} \cos \alpha + \frac{\partial c_k}{\partial y} \cos \beta + \frac{\partial c_k}{\partial z} \cos \gamma \right) \\ &= \sum |V| \frac{\partial c_k}{\partial r}, \end{aligned} \quad (15)$$

where  $r$  is directed along the solution flow.

As in [25], one can readily obtain the following relation:

$$\frac{\partial c_k}{\partial r} = -\frac{S_V}{|V| z_k F} J_{sk} \quad (16)$$

where  $S_V$  is the reaction surface and  $J_{si}$  is the density of polarizing current for the  $i$ th species.

Substitution of (15) and (16) into (14) gives

$$F \partial \sum z_k c_k / \partial t = \nabla \cdot [-\kappa \nabla E] + S_V \sum J_{sk}.$$

The conducting properties in each elementary volume of the pseudohomogeneous medium considered can naturally be modeled by two series-connected conductors [2] characterizing the solid and liquid phases of the system;  $\rho = \rho_L + \rho_s$ . Considering that  $\rho_s = 1/\chi_s$ ;  $\rho_L = 1/\chi_L$ ; and  $\chi = 1/\rho = 1/(\rho_L + \rho_s)$ , one gets

$$F \partial \sum z_k c_k / \partial t = \nabla \cdot [-(\kappa_s \kappa_L / (\kappa_s + \kappa_L)) \nabla E] + S_V J_{sk} \quad (17)$$

The set of (17), in conjunction with (16) and kinetic equations relating  $J_{sk}$  with  $E_{\bar{c}_k}$ ,

$$J_{sk}(x) = j_{0k} \frac{\exp(\alpha_k z_k F (E - \varphi_{Rk}) / RT) - \exp((\alpha_k - 1) z_k F (E - \varphi_{Rk}) / RT)}{1 + j_{0k} \exp(\alpha_k z_k F (E - \varphi_{Rk}) / RT) / z_k F K_m c_k} \quad (18)$$

can be used to calculate the potential, current density, and concentration distributions for the electroactive species in the volume of a porous electrode. This set of equations should be supplemented by the natural boundary conditions

$$\begin{aligned} \frac{\partial E}{\partial n}(t) \Big|_{\sigma_c} &= J(t) \rho_s; & \frac{\partial E}{\partial n}(t) \Big|_{\sigma_A} &= -J(t) \rho_L; \\ \frac{\partial E}{\partial n}(t) \Big|_{\sigma_I} &= 0; & c(t) \Big|_{\sigma_{sur}} &= c_0, \end{aligned} \quad (19)$$

where  $n$  is directed along the normal to the boundary  $\sigma = \sigma_c + \sigma_A + \sigma_I + \sigma_{sur}$  of the reaction region. The terms in the latter of the reaction region. The terms in the latter sum stand for the outer boundaries of electrode, which are generally characterized by, respectively, the following components: current feed, current removal, insulator, and electrode surface through which electrolyte flows in.

One variant of the spatial orientation of a three-dimensional TFE is schematically shown in figure 1.

**Mathematical models for calculations**

In the case where only one electroactive component is present in the electrolyte solution and the electrolyte flow is directed along the current, the set of (16)–(19) takes the form

$$zF \frac{\partial c}{\partial t} = -\frac{\partial^2(1/\rho)E}{\partial x^2} + S_V J_S \tag{20}$$

$$|V| zF \frac{\partial c}{\partial x} = -S_V J_S \tag{21}$$

$$J_S(x) = j_0 \frac{\exp(\alpha z F (E - \varphi_R) / RT) - \exp((\alpha - 1) z F (E - \varphi_R) / RT)}{1 + j_0 \exp(\alpha z F (E - \varphi_R) / RT) / z F K_m c} \tag{22}$$

$$c(0, \tau) = c_0, \quad c(x, 0) = c_0, \quad \frac{\partial E}{\partial x}(0, t) = \rho_S I(t) \\ \frac{\partial E}{\partial x}(L, t) = \rho_L I(t), \quad E(x, 0) = \varphi_R \tag{23}$$

Note that the resistivity of a pseudohomogeneous medium in (20) is generally not constant across the whole width of the electrode and can change during the electrolysis because of the inclusion of a metal sediment into the conductance of the carbographite material. These variations can be included into the mathematical model as shown in [21]. In this case, (20) can be written in the expanded form,

$$zF \frac{\partial c}{\partial t} = -\frac{\partial^2 E}{\partial x^2} - \frac{\partial E}{\partial x^2} - \frac{\partial E}{\partial x} \frac{\rho_S \rho_L}{(\partial \rho_S / \partial x)(\rho_S + \rho_L)} \\ + \frac{\rho_S \rho_L}{(\rho_S + \rho_L)} S_V J_S. \tag{24}$$

By introducing time grid for  $0 \leq t \leq T: \Omega_t = \{t_i: t_0=0; t_i=i\Delta t, i=1, \dots, m; t_m=T\}$  and spatial grid for

$$0 \leq x \leq L: \Omega_x = \{x_j: x_0=0; x_j=j\Delta x, j=1, \dots, q; x_q=L\}$$

and replacing partial derivatives by their discrete analogs, one obtains, at each grid point, the set of equations whose solution enables one to determine all electrochemical functions of interest.

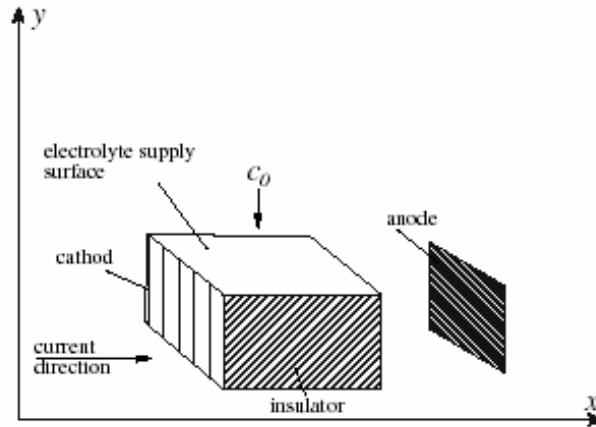


Figure 1. Scheme of a volumetric porous flow electrode

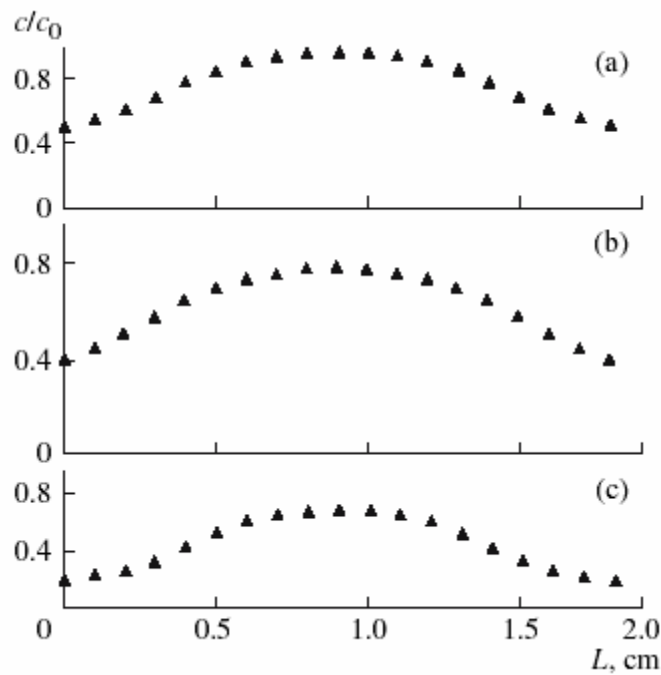


Figure 2. Profile of the relative Au concentration along electrode height  $h$  for the mutually perpendicular directions of current and electrolyte flow; electrode height  $h$  (cm): (a) 0.2; (b) 1, and (c) 2

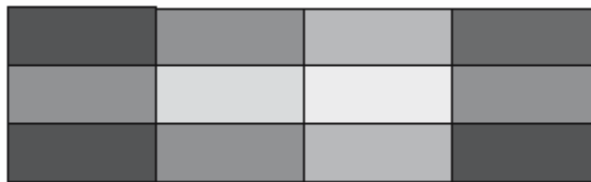


Figure 3. Distribution of the deposited metal over the volume of porous electrode, where dark-colored areas correspond to the larger amount of metal deposited on electrode.

One-dimensional nonstationary problem (16)–(19) can be solved in a similar manner for the electrochemical reaction involving several species. In this case, the relevant set of equations can be obtained by the appropriate transformation of Eqs. (20)–(23). In the case where the organization of the electrochemical process cannot be described by a one-dimensional model, numerical computations become much more complicated. The electrolysis on a TFE with mutually perpendicular directions of current and solution flow is a practically important electrochemical process. The corresponding numerical solution can be obtained by the method described above with a grid along the height of carbographtite electrode:  $\Omega_h = \{h_j : h_0 = H; h_j = h_0 - j\Delta h, j = 1, \dots, M; h_M = 0\}$ . The solution for each preceding layer can be used to approximate derivatives of the functions of  $h$  that are involved in the mathematical model.

### Results and discussion

The computational results obtained for the Au distribution in width and height of a volumetric porous flow electrode are presented in figure 2 for the case of gold and silver co-electrodeposition from a thiourea solution in sulfuric acid with concentrations

$$[\text{Au}] = 10^{-7} \text{ mol/cm}^3 \text{ and } [\text{Ag}] = 10^{-5} \text{ mol/cm}^3,$$

with allowance for the evolution of gaseous hydrogen. The following parameters were taken for the electrode and the electrolysis process:

$$|V| = 0.55 \text{ cm/s}, S_V = 260 \text{ cm}^2/\text{cm}^3, h = 2 \text{ cm}, I = -0.3 \text{ A/cm}^2, T = 293 \text{ K},$$

porosity

$$\varepsilon = 0.92, L = 2 \text{ cm}, \text{ and } \chi_s = \chi_l = 0.1 \text{ (}\Omega \text{ cm)}^{-1}.$$

One can see in figures 2 and 3 that the distribution of deposited metal over the electrolyzer volume is not homogeneous. The inner layers of the carbographtite material are poorly filled with the sediment, and, hence, the electrolyzer operates inefficiently.

One way to enhance the TFE efficiency consists in choosing the optimal parameters for the process, in particular, for the electrolysis current regime  $J(t)$ . Contrary to our previously published data and other publications, we consider in this work the nonstationary electrolysis regime. We consider the effect of a time-varying current and compare it with the data characterizing the dc process with a current passing through the electrode.

Clearly, the process of metal electrodeposition in this case would be nonstationary, and all electrochemical functions and some of the parameters of electrolyzer and process would depend not only on the spatial coordinate in the electrode volume but also on time.

The homogeneity index of metal distribution over the electrode depth was chosen as an optimization criterion, e.g.,

$$K(t) = \sigma(t)/[\bar{J}(t) \times L] \quad (25)$$

where

$$\begin{aligned} \sigma^2(t) &= \int_0^L [\bar{J}(t) - \sum_{i=1}^n J_i(x, t)]^2 dx/L \text{ and } \bar{J}(t) \\ &= \int_0^L [\sum_{i=1}^n J_i(x, \tau)] dx/L. \end{aligned}$$

To illustrate the effect of the control function  $J(t)$  on the amount and homogeneity of the distribution of deposited metals, calculations were performed for the co-precipitation of gold

$$(0.2 \times 10^{-5} \text{ mol/cm}^3)$$

and silver

$$(0.1 \times 10^{-6} \text{ mol/cm}^3)$$

from a thiourea solution in sulfuric acid

$$(0.25 \text{ mol/l H}_2\text{SO}_4, 80 \text{ g/l thiourea}).$$

The solutions of this type are used in the sorption technology for extracting gold and silver from an ore [3].

The variants of current regimes used in the calculations for different electrolysis times are presented in figure 4. Note that the control function  $J(t)$  has the same integrated characteristic in all variants: the overall current

$$\int_0^t I(t) dt$$

fed into the electrode.

The computational results indicate that the amount of deposited metals, their ratio, and the homogeneity of their distribution over the TFE depth depend on the deposition regime. Obviously, this is so primarily because of the distinctions in the nonstationary electrode states arising under different external actions; in the case at hand, for different types of time variation chosen for the overall current passing through the electrode. It follows from the results presented in figure 4 that different deposition regimes have different effects on the amounts of deposited metals. Whereas the amount of deposited gold tends to decrease upon passing from one regime to the other, the amount of silver, conversely, increases. For instance, the fourth variant is one of the best for the electrode-deposited gold and one of the worst for silver, while the directly opposite conclusion can be drawn for the sixth variant (figures 5a, 5b).

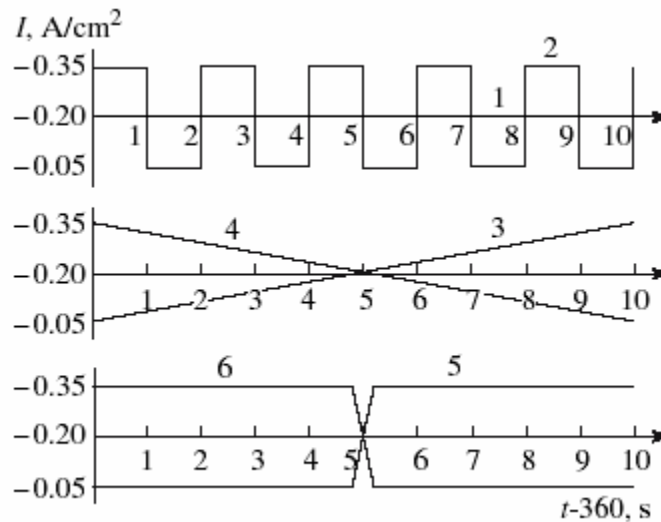


Figure 4. Variants of current regimes used in the calculations

The variations in the homogeneity of the metal-distribution indexes  $K_1$  and  $K_2$  are illustrated in figures 5c and 5d for different  $I(t)$  regimes. These figures demonstrate the tendency to equalize the distribution of metal sediments upon passing from regime 1 to regime 6. The exception is provided by regime 4, which is unfavorable to the homogeneous gold deposition on TFE.

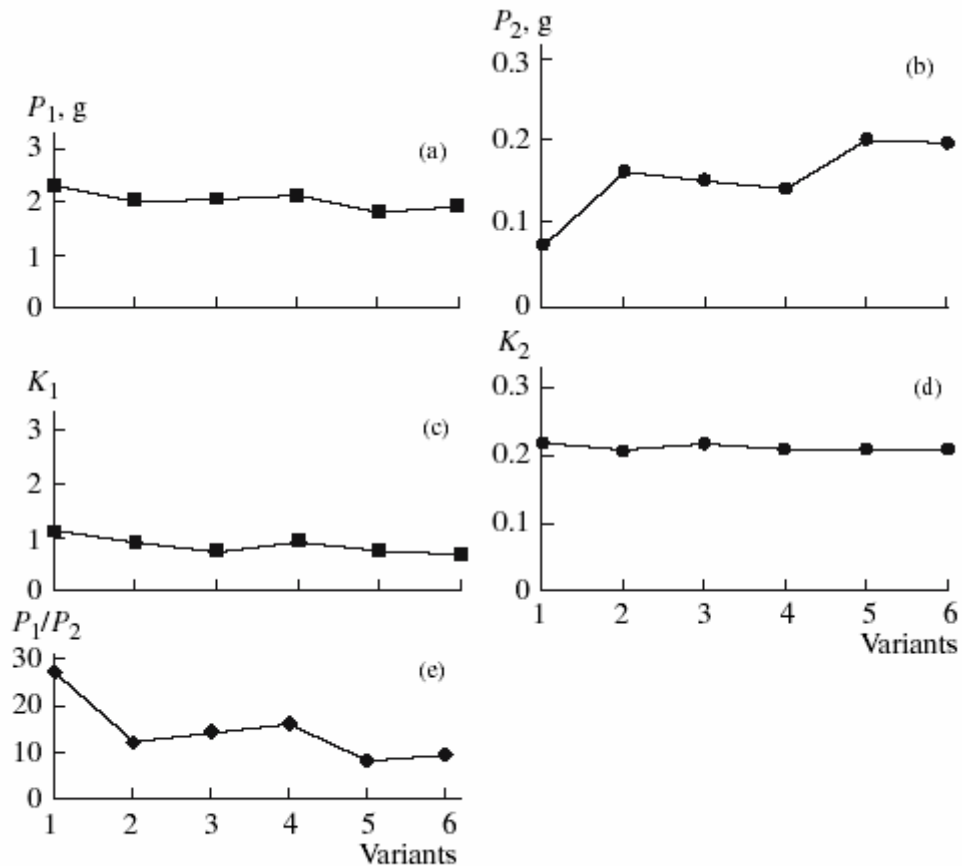


Figure 5. (a) Gold ( $P_1$ ) and (b) silver ( $P_2$ ) weights for the different variants of  $I(t)$ . Homogeneity of the (c) gold ( $K_1$ ) and (d) silver ( $K_2$ ) distributions for the different variants of  $I(t)$ . (e) Weight ratios of the deposited metals for the different variants of  $I(t)$

The effect of the deposition regime  $I(t)$  on the metal weight ratio is demonstrated in figure 5e. This index becomes important if there is a need to deposit mainly one of the metals from the electrolyte solution, or if the technological conditions require the deposition of alloy with a given composition. One can see in figure 5e that regime 1 is the best for the preferred gold deposition from the electrolyte, while variant 5 is favorable to the deposition of an alloy saturated mostly with silver.

The computational results presented in this work suggest that the problem of optimizing metal electrodeposition on TFE can be solved for various technological demands imposed on the results of the deposition process.

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