Calculating Optimal Mode in the Electrolysis of Metals on a Flow of Three-Dimensional Electrode

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Abstract

The paper presents the mathematical model in the form of systems of differential and algebraic equations for the calculation of one of the most common in the industry technological schemes functioning of the electrolyzer with flow three-dimensional electrodes. This scheme corresponds to the processing solution circulation mode when oxidation or reduction of electroactive components and recovery of metals from solutions hydrometallurgical and electrochemical production. The solutions of the problem of practically important cases - of linear dependence of performance of the electrolyzer from the inlet concentration of metal ions and in the case of a electrolyzer in the limiting diffusion current mode. An algebraic formula for the estimation processing time required for extracting a predetermined quantity of metal from solution, the degree of its extraction and electrolyzer productivity

Keywords: Electrolyzer, Flow Three-Dimensional Electrode, Recycling, Mathematical Model, Differential Equations, Control
1 Introduction

Flow Three-Dimensional electrodes (FTDE) is widely used in various electrochemical processes including intensification oxidation-reduction reactions in solutions with low concentration of electroactive components. For example, on the basis of three-dimensional flow-through electrodes made of carbon fiber materials developed technological processes of extraction of gold and silver, platinum and non-ferrous metals from solutions in hydrometallurgy, electroplating, film - photocopier and jewelry industry [1-3].

An important issue in the organization of the process of extraction of metals or coating the surface elements FDE metals and their compounds is the development of technology, one of the main elements of which is the connection diagram of the electrolyzer and the container with a solution to be treated. The possible connection diagrams: circulation, co-current, co-current with recycling and other.

Along with experimental studies one of the main methods for solving these issues are the studies using physical and mathematical modeling both the individual electrochemical processes and wiring diagrams electrolyzer - container with treated a solution of. An important point is the possibility of optimizing the process parameters and schema elements: container volume, dimensions, and characteristics of the electrolytic cell, the electrode elements, etc.

This work is devoted to the development of a mathematical model to calculate the circulation process scheme technological scheme of the electrodeposition of metals in the FTDE, in particular, of carbon fiber materials.

One of the possible schemes of the circulation process is shown in Figure 1.

![Figure 1. Circulation scheme of metal electrodeposition process. E - electrolyzer, c - concentration of the metal, V - volumetric flow rate of the solution, B - containers with a solution.](image)

Solution to be treated with a metal concentration c0 and speed V0 enters in the container V1, then from tank B1 with a metal concentration c1 and velocity V1 is supplied to the electrolyzer E, in which the electrodeposition of metal on a PTE,
and then with a metal concentration \( f(c_1) \) and the speed \( V_1 \) flows into container B2. Solution, depending on the degree of metal extraction, is removed from the system (with a concentration \( c_2 \) and speed \( V_3 \)) or through the container B1 again enters into the electrolyzer E.

2 Mathematical Model

Written the conservation laws in the form of discrete for the volume of the solution \( Q_1, Q_2 \), for the amount of metal ions in solution in the containers B1,B2, considering the precipitated metal in an electrolyzer E at time points \( \tau \) and \( \tau + \Delta \tau \), where \( \Delta \tau \) - a small increment of time. Productivity of electrolyzer E us known - \( f(c) \), and hence the concentration of metal in the solution after its passage through the electrolyzer is also us known \( c_2 = f(c_1) \), if the input to the electrolyzer the concentration was \( c_1 \). Obviously, the values \( c_1, c_2 \) must be equal to the value of metal concentration in the containers \( B_1, B_2 \). Obtain the following system of algebraic equations, relating the volume of solution and amount of electroactive substances in containers \( B_1, B_2 \):

\[
Q_1(\tau+\Delta \tau) = Q_1(\tau) + V_0(\tau)\Delta \tau - V_1(\tau)\Delta \tau + V_2(\tau)\Delta \tau \\
Q_2(\tau+\Delta \tau) = Q_2(\tau) + V_1(\tau)\Delta \tau - V_2(\tau)\Delta \tau + V_3(\tau)\Delta \tau \\
c_1(\tau+\Delta \tau) = c_1(\tau) Q_1(\tau) + c_0(\tau) V_0(\tau)\Delta \tau - c_1(\tau) V_1(\tau)\Delta \tau + c_2(\tau) V_2(\tau)\Delta \tau \\
c_2(\tau+\Delta \tau) = c_2(\tau) Q_2(\tau) + f(c_1(\tau)) V_1(\tau) - c_2(\tau) V_2(\tau)\Delta \tau - c_2(\tau) V_3(\tau)\Delta \tau
\]

Grouping expressions in these equations and taking the limit for \( \Delta \tau \to 0 \), we obtain a system of differential equations, describing the material balance for the scheme shown in figure 1:

\[
\begin{align*}
\frac{dQ_1}{d\tau} &= V_0 - V_1 + V_2 \\
\frac{dQ_2}{d\tau} &= V_1 - V_2 - V_3 \\
\frac{dc_1}{d\tau} &= c_0 V_0 - C_1 V_1 + c_2 V_2 \\
\frac{dc_2}{d\tau} &= f(c_1(\tau)) V_1 - c_2 V_2 - c_2 V_3
\end{align*}
\]

Note that the system (1) consists of four differential equations for the determination of four unknown functions (in (1) \( V_0(\tau), c_0(\tau) \) and the form of depending \( f(c_1(\tau)) \) must be given). In general, when the \( n \) electroactive component participating in the electrochemical reaction, we obtain a system of \( 2+2n \) differential equations and the same number of unknown functions, that we do not give, because the system is bulky.

It is obvious that the solution of (1) need to use the specified initial conditions for the volume of the electrolyte and the initial values of the concentration of electroactive substances in containers \( B_1, B_2 \): \( Q_i(0), \dot{Q}_i(0), c_1(0), c_2(0) \). When calculating the practical embodiment of the circulating mode of electrolysis in most cases can be considered \( V_0 = V_3 = 0 \) and \( V_1 = V_2 \), a \( \dot{Q}_i = \dot{Q}_i(0) \), \( \dot{Q}_i = \dot{Q}_i(0) \). Then the system (1) takes the form:
\[
\begin{align*}
Q_1 \frac{dc_1}{d\tau} &= V(c_2 - c_1), \\
Q_2 \frac{dc_2}{d\tau} &= V(-c_2 + f(c_1)).
\end{align*}
\tag{2}
\]

The task can be solved under the condition where the function \( f(c) \) is defined. In general, when there is the electrodeposition of metal on three dimensional flow electrodes, the function can be calculated using a mathematical model, described in the publications [4-6]. In this paper, we consider the form of the \( f(c) \) for two special cases: a linear relationship when \( f(c) = (1 - \gamma)c \), when \( 0 \leq \gamma \leq 1 \) and for the case where the electrode works in the limiting diffusion current across its volume, that is, when at each point of the electrode the speed of the process is limited by the diffusion of discharging the ions of metal. Each of these cases corresponds to a specific technological situation which is of practical importance. The first of these describes the problem, when the metal is necessary to precipitate most evenly over the thickness of the electrode on the FTDE (coordinate \( 0 \leq x \leq L \), where \( L \) - thickness of the FTDE). The second case involves the possibility to precipitate on the electrode metal as much as possible in a given time, regardless of the uniform precipitation at FTDE.

Consider a one-dimensional stationary model of FTDE, which is a system of ordinary differential equations and describes the distribution of polarization \( E \), current density distribution \( j_S \), of the concentration of the electroactive component \( c \) in the flow three-dimensional electrode for many technological situations adequately [4]:

\[
\begin{align*}
\frac{d^2 E}{dx^2} &= \left( \frac{1}{\kappa_T} + \frac{1}{\kappa_{\kappa}} \right) S_V j_S \tag{3} \\
\frac{dE}{dx}(0) &= -\frac{I}{\kappa_T}; \quad \frac{dE}{dx}(L) = \frac{I}{\kappa_{\kappa}}; \tag{4} \\
\frac{dC}{dx}(x) &= -\frac{S_V}{VZF} j_S(x) \tag{5}
\end{align*}
\]

Here \( V \) - linear velocity of solution flow, \( \kappa_T, \kappa_{\kappa} \) - electrical conductivity of the electrode and the electrolyte, respectively, \( S_V \) – specific reaction surface, \( Z \) – the number of electrons, participating in the electrochemical reaction, \( F \) - Faraday number, \( I \) - the overall density of the current passing through the electrode.

Consider these particular cases of the form of function \( f(c) \) and the corresponding solutions of modeling equations.
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3 Modeling of the recycling process with a linear dependence of the performance of the electrode on the concentration of metal

We assume that the defined operating conditions of the FTDE at which the metal sludge is evenly distributed through the thickness of the electrode. This can be achieved, for example, by calculating the optimum conductivity of the carbon material cathode as a function of the coordinates \( x \) and by proper selection of overall current density as a function of the inlet concentration, that in the first approximation can be considered linear \( I(c_0)=k c_0 \) with some empirical factor \( k \).

The current density of the reaction electrodeposition of metal \( j_s(x) \) should be uniform at all points of the electrode, in case of uniform distribution of the process over the electrode thickness \( x \) and must be equal to the average of the overall density, that is \( j_s(x)=I/L \). Then, by direct integration of equation (5) in the range from 0 to \( L \) is easy to obtain the expression:

\[
c(L) = c(0) - \frac{S_j k}{VZF} c(0)
\]

which implies a linear relationship \( f(c) = (1-\gamma)c \).

System (2) in this case takes the form:

\[
\begin{align*}
\frac{dc_1}{d\tau} &= -\frac{V}{Q_1} c_1 + \frac{V}{Q_1} c_2, \\
\frac{dc_2}{d\tau} &= -\frac{V(1-\gamma)}{Q_2} - \frac{V}{Q_2} c_2
\end{align*}
\]

with the characteristic equation

\[
\begin{vmatrix}
-\frac{V}{Q_1} - \lambda & \frac{V}{Q_1} \\
\frac{V(1-\gamma)}{Q_2} & -\frac{V}{Q_2} - \lambda
\end{vmatrix} = 0.
\]

It is easy to find the roots of this equation:

\[
\lambda_{1,2} = -\frac{V(Q_1+Q_2)}{2Q_1Q_2} \pm \frac{1}{2} \sqrt{\frac{V^2(Q_1+Q_2)^2}{Q_1^2Q_2^2} - \frac{4V^2\gamma}{Q_1Q_2}}.
\]

We denote the radical expression as \( D \) and performing simple transformations, we obtain:

\[
D = \frac{V^2(Q_1^2+Q_2^2+2Q_1Q_2(1-2\gamma))}{Q_1^2Q_2^2}.
\]
This shows that $D > 0$ (with $Q_1 > 0$ and $Q_2 > 0$) and characteristic equation always has real roots. In general, when $0 < \gamma < 1$ the task of finding the values $c_1(\tau)$ and $c_2(\tau)$ represented in the form:

$$c_1(\tau) = D_1 \exp[\psi_1(\tau)] + D_2 \exp[\psi_2(\tau)], \quad c_2(\tau) = D_1 \frac{S - Q_1 - Q_2}{2Q_2} \exp[\psi_1(\tau)] + D_2 \frac{Q_2 - Q_1 - S}{2Q_2}$$

(8)

where $\psi_1(\tau) = \frac{V(S - Q_1 - Q_2)}{2Q_1Q_2} \tau; \quad \psi_2(\tau) = \frac{-V(Q_1 + Q_2 + S)}{2Q_1Q_2} \tau; \quad D_1 = \frac{c_1(0)(S + Q_1 - Q_2) + 2Q_2c_2(0)}{2S}; \quad D_2 = \frac{c_1(0)(S - Q_1 + Q_2) - 2Q_2c_2(0)}{2S};

$$S = \sqrt{(Q_1 + Q_2)^2 - 4\gamma Q_1Q_2}.$$

Thus, $c_1(\tau) = A_1 \exp(-K_1\tau) + B_1 \exp(-K_2\tau), \quad c_2(\tau) = A_2 \exp(-K_1\tau) + B_2 \exp(-K_2\tau).$

Herein $A_1, A_2, B_1, B_2, K_1, K_2$ - constants, $K_1 > 0, K_2 > 0$. We denote $\min(K_1, K_2) = K, \max(A_1, A_2, B_1, B_2) = M$. After transformations we obtain the estimates:

$$|c_1(\tau)| \leq \varepsilon, \quad |c_2(\tau)| \leq \varepsilon, \quad \text{with} \quad \tau \geq \frac{1}{K} \ln \frac{2M}{\varepsilon}$$

(9)

Estimates are important for the practical organization of the recycling process, because, when an performance of electrode is known, can estimate the time of the technological process, which is necessary for extracting a predetermined quantity of metal from a solution of. On the other hand, the use of inequalities (9) at a given time of the process to determine the performance of the electrolizer, which is necessary to produce the desired effect of the electrolysis process in the FTDE.

4 Modeling of the recycling process with operation electrolyzer with electrode in the conditions of the limiting diffusion current

In solving the technological problems usually required to determine an overall current density $I$, the thickness of the electrode $L$, ensure the operation of the entire electrode in the mode limiting diffusion current, when a given degree of metal extraction $R = 1 - \frac{C_L}{C_0}$, where $C_0, C_L$ - concentration of precipitated metal values at the inlet and outlet of the FTDE. If the electrode at $x$ operates under the limiting diffusion current, in order to calculate the current density is known relation:

$$j_s(x) = j_{np}(x) = ZFk_m c(x)$$

(10)
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Herein $K_m$, mass transfer coefficient, whose value is determined by the configuration and diameter of particles constituting the FTDE and by the hydrodynamics of the process.

Integrating equation (3) from 0 to $L$ in view of equation (10) we obtain:

$$
\frac{I}{\chi_\infty} = -\frac{I}{\chi_T} + \left(1 + \frac{1}{\chi_\infty}\right) \frac{V}{S_v k_m} \left(1 - \exp \left(-\frac{S_v k_m L}{V}\right)\right)
$$

(11)

And, as $J_{np}(L) = \frac{Z F k_m}{V} c_0 \exp\left(-\frac{S_v k_m L}{V}\right)$,

$$
\frac{I}{\chi_\infty} = -\frac{I}{\chi_T} + \left(1 + \frac{1}{\chi_T}\right) \frac{V}{\chi_\infty} \frac{Z F C_0}{S_v k_m} \left(1 - \frac{J_{np}(L)}{Z F k_m C_0}\right)
$$

(12)

From the relation (12), taking into account the relation (10) it is easy to obtain an estimate of overall current density $I^*$, which provides the limiting diffusion current at the end point of the electrode $L$, and therefore the work of total FTDE in conditions of the limiting current, as well, can be obtained the thickness of the electrode, providing the work of total electrode in mode of the limiting current.

$$
I^* = Z F C_0 V R
$$

(13)

$$
L^* = -\frac{V \ln(1 - R)}{S_v k_m}
$$

(14)

Equations (13) and (14) indicate as for a given degree of metal extraction $R$, the conditions of the process, that ensure the electrolizer work on the limiting diffusion current, can be found.

We give a solution to the problem for the practically important case of electrodeposition of metal on the FTDE when recycling solutions is carried out using a buffer container $Q$. This is consistent with the scheme of Fig. 1 with $Q_1 = Q_2 = \frac{Q}{2}$, $V_1 = V_2 = V$, $c_1(\tau) = c_2(\tau) = c(\tau)$. In this case, the system (2) is transformed into one equation:

$$
Q \frac{dc}{d\tau} = V (f(c) - c).
$$

And, since $f(c) = c_L = (1 - R)c$, then $Q \frac{dc}{d\tau} = -V R c$. If the entire electrode in the mode current limiting diffusion works, then $Q \frac{dc}{d\tau} = -V \left(1 - \exp \left(-\frac{k_m S_v L}{V}\right)\right) c$.

Solving this equation, we obtain the relation:

$$
\ln \left(\frac{c_0}{c(\tau)}\right) = \frac{V \left(1 - \exp \left(-\frac{k_m S_v L}{V}\right)\right)}{Q} \tau,
$$

(15)
which makes it possible to calculate the concentration of metal $c(\tau)$ in the buffer tank during $\tau$. If a task is to reduce the concentration in the buffer tank to a predetermined value $c_\tau$ for some time $\tau$, then from (15) we can calculate the amount of buffer capacity $Q$, needed to solve the problem:

$$Q = \frac{V \left(1 - \exp\left(-\frac{k_m S_0 L}{V\Theta}\right)\right)}{\ln\left(c_0 / c_\tau\right)} \tau .$$

**Conclusion**

Presented in this paper, mathematical models and relationships allow us to calculate the main parameters of the circulation schemes of the organization of the electrolysis process with flow carbon electrodes. During deposition of metal on electrodes of carbon fibrous material into consideration physical parameters of these electrodes (porosity, specific surface area, etc.), electrolysis mode (current, hydrodynamic).

Have the opportunity to review the problem of optimizing the technological scheme, the parameters of the electrolysis process, the structural elements of the flow-through electrode. Note that in this paper we consider the simplest scheme of electrolyte recirculation using electrolyzers with FTDE, however, given the results and reasoning can be generalized to more complex process flow scheme, using once-through and circulation modes of electrolysis.

All the findings can be divided into cases of electrodeposition of several metals, with regard to side electrochemical reactions and reactions recovery of metal ions to the not metallic forms. In these cases it is not always possible to bring the solution to an analytic formula, however, possible to develop a computational algorithm and software, allowing the calculate the elements of the construction electrolyzer and technological conditions of its operation. To solve the problem in the most general form, you can use mathematical models and algorithms presented in publications [4-6].

**Acknowledgements.** This work was financially supported by the Ministry of Education of Russia within the base portion.

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Received: February 9, 2015; Published: April 4, 2015