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PRINCIPLES OF CONSTRUCTING EQUIVALENT CIRCUITS FOR NONLINEAR ELECTROCHEMICAL ELEMENTS: ANALYSIS AND EXPERIMENTAL PARAMETER DETERMINATION

Annotation. The paper proposes a generalized scheme for replacing the electrolyzer for the deposition of metal coatings. As nonlinear elements of the specified scheme, the dependences of the partial currents of metal dissolution and deposition on the near-anode or near-cathode voltage drop are considered, respectively. The possibility of applying certain simplifications in the general scheme, depending on the peculiarities of the deposition process of one or another metal, was also analyzed.

At the same time, the general structure of approximating expressions is proposed and the approximation coefficients for individual nonlinear electrochemical elements are determined. The specified expressions differ from the previously known ones in that their structure is suitable for obtaining the general regularities of electromagnetic processes that take place in systems of pulse electrodeposition of metals in an explicit form.

Key words: pulse electrolysis, nonlinear circuits, electrochemical elements, cathode polarization, deposition current, analytical approximation, cubic polynomial.

Introduction

The analysis of nonlinear electrical circuits is one of the most complex and critically important tasks in modern electrical engineering and electronics. Unlike linear circuits, where the relationship between current and voltage is described by linear differential equations, nonlinear circuits are characterized by much more complex dependencies. These dependencies can be exponential, power-law, logarithmic, or of other types, complicating their analytical solutions and requiring the use of numerical methods and computer modeling.

Nonlinear components, such as diodes, transistors, thyristors, as well as various electrochemical components (batteries, supercapacitors), are widely used in modern electronic devices and energy systems. For example, batteries, which are typical nonlinear elements, have complex dependencies of internal resistance and voltage on the state of charge and temperature. This makes their modeling and analysis crucial for the development of efficient energy storage and management systems.

One of the main problems in analyzing nonlinear electrical circuits is the absence of universal solution methods. Each nonlinear system requires an individual approach that considers its specifics and operating conditions. To address this problem, various methods are employed: analytical, nu-

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merical, graphical, and combined. Each of these methods has its advantages and disadvantages, and the choice of method depends on the specific task.

Analytical methods, such as the Volterra method or perturbation method, allow obtaining exact solutions but are effective only for certain types of nonlinearities and usually require significant simplifications. Numerical methods, such as the Newton-Raphson method or finite difference method, are more universal and can be applied to a wide range of nonlinear problems, but they demand significant computational resources. Graphical methods, such as phase diagram analysis, enable visualizing the system's behavior but do not always provide quantitative results.

Besides analysis methods, an important aspect is the construction of adequate models of nonlinear elements. For this, various approaches are used: physical modeling, empirical models, as well as machine learning methods, which allow building models based on large volumes of data.

Thus, the problems of analyzing nonlinear electrical circuits are multifaceted and require a comprehensive approach that combines theoretical knowledge, experimental data, and modern computational methods. Solving these problems is key to developing new technologies and improving the efficiency of existing systems.

1. Analysis of the features and construction of equivalent circuits with nonlinear electrochemical elements

As noted in [1], the first problem that arises in the analysis of nonlinear electrical circuits is the adequate description of the system being studied. That is, it is necessary to construct an adequate equivalent circuit, determine its parameters, and choose the characteristics of the nonlinear elements. This fully applies to electrochemical circuits as well. Therefore, it is advisable first to focus on the specific features inherent to these circuits, to note which phenomena and under what conditions are taken into account, and also how this determines the equivalent circuit.

In electrical engineering, electrical circuits containing only electronic conductors, i.e., conductors of the first kind, which are metals or semiconductors, are predominantly considered. The former, as is well known, have a specific electrical conductivity of more than 107 S/m, while the latter have a conductivity ranging from 10-8 to 106 S/m. In contrast, an electrochemical circuit is understood as a circuit that contains at least one ionic conductor (a conductor of the second kind). An ionic conductor is an aqueous solution of one or more electrolytes, which can be salts, acids, or bases. This conductor contains positively MZ+ and negatively MZ- charged metal ions. A characteristic feature of ionic conductors is the ability to vary their specific electrical conductivity over a wide range from 5·10-6 S/m (pure water) to 80 S/m (a concentrated solution of a strong acid) by changing the concentration of the electrolyte [2].

Metal immersed into an electrolyte is called an electrode. The electrode from which current conventionally enters the electrolyte is called an anode, and the one from which it enters from the electrolyte is called a cathode (see Fig. 1). The anode can be either soluble or insoluble. Therefore, the current passes through the following path: external circuit – anode – electrolyte – cathode and returns to the external circuit. A structurally designed electrochemical circuit is called an electrochemical (galvanic) cell. In the case where processes in this cell occur with the release of electrical energy into the external circuit, the cell is called a chemical power source or galvanic cell. If the processes in the cell are accompanied by energy absorption from an external source, the cell is called an electrolytic bath or electrolyzer. In practice, electrolyzers are widely used for electrolytic deposition of metals and alloys, metal refining, as well as in chemistry. Electromagnetic processes in circuits with electrolyzers are distinguished for electroplating metals in stationary and pulse electrolysis modes. In the stationary mode, the applied input voltage or current is constant, while in the non-stationary mode, they are non-sinusoidal.

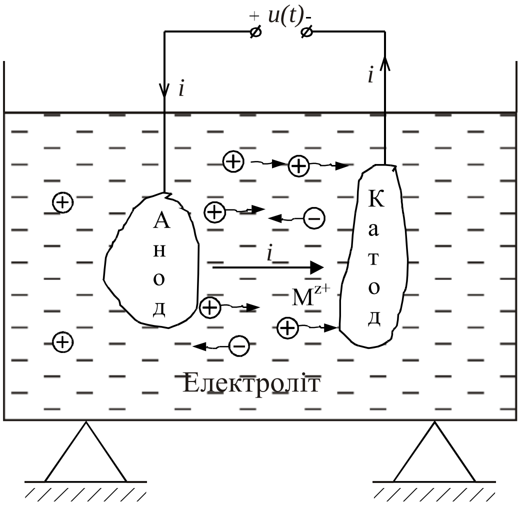


Figure 1 - Scheme of an electrochemical cell

When the voltage u(t) is applied to the electrolyzer (Fig. 1), the discharge of MZ+ cations to the metal coating M occurs at the cathode according to the reaction:

$$M^{z+} + ze^{-} \rightarrow M \text{ ("metal")}, \tag{1}$$

where ē is the charge of the electron; z is the valency of the metal.

Simultaneously, the anode dissolves (if it is soluble) according to the reaction:

$$\text{M-}ze^{-} \rightarrow M^{z+}, \tag{2}$$

resulting in the replenishment of the electrolyte solution with MZ+ cations, which diffuse to the cathode and discharge on its surface according to reaction (1).

During the current flow through the circuit (Fig. 1) and at the interphase boundaries of the anode-electrolyte and electrolyte-cathode, electrode potential drops uк and ua arise, which in electrochemistry are respectively called anodic and cathodic polarizations. If the anode is insoluble, then $u_a = 0$.

In addition to the main "working" reactions (1) and (2), to which portions of the current i(t) are expended, denoted respectively as ia and ik, accumulation and retention of electric charges occur at the interfacial electrode boundaries, forming their double layer. Thus, the interphase boundary between the electrode and the electrolyte can be represented (replaced) by a nonlinear resistive element NR, which is equivalent to one of the reactions (1) or (2) with currents ia or ik, and a capacitance element C connected in parallel to it with a current is (Fig. 2). Moreover, as demonstrated by the practice of electrochemical research, the dependencies ua(ia), uk(ik), i.e., the volt-ampere characteristics (VAC) of these resistors are nonlinear. Classical analytical expressions for them are provided in [2 – 4]. These expressions are determined by the features of the processes occurring in the electrolyzer (electrolysis processes), namely the main stage of the process. For example, if the main (slow) stage of the process at the cathode is reaction (1), i.e., the so-called activation polarization of the cathode occurs [2 – 4], then the VAC of the nonlinear resistor are described by the expression:

$$i_к(u_к) = j_0 S_к \exp\left(-\alpha \frac{z\cdot F}{R\cdot T} u_к\right), \qquad (3)$$

where j0 is the so-called partial current density of metal ion discharge; Sк is the cathode area; α is the so-called transfer coefficient of the cathodic reaction; z is the valency of the metal; F is Faraday's constant; R is the universal gas constant; T is the temperature of the cathode.

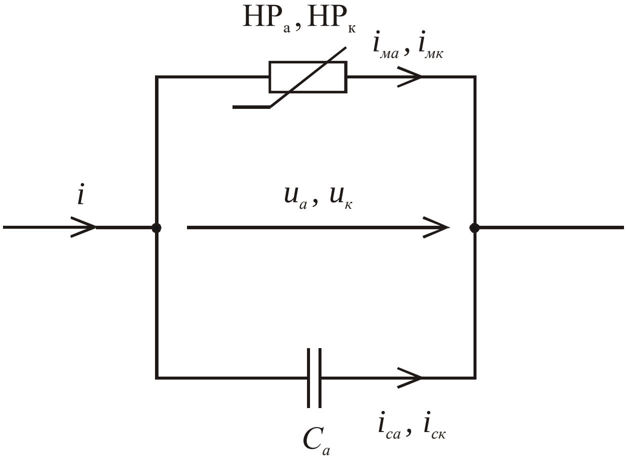


Figure 2 - Electrical equivalent circuit of an electrode

If the slow stage of the cathodic process is the diffusion of cations to the cathode (Fig. 1), i.e., the so-called concentration polarization occurs, then the volt-ampere characteristics (VAC) have an analytical form

$$u_к(i_к) = \frac{R\cdot T}{z\cdot F} ln\left(1 - \frac{i_к}{i_{diff}}\right), \qquad (4)$$

where idiff is the so-called limiting diffusion current of the cathode.

If the deceleration stage (1) is overlapped by the deceleration of cation diffusion to the cathode, the analytical expression of the I-V characteristic is described as follows:

$$i_к(u_к) = j_0 S_к \left[\left(1 - \frac{i_к}{i_{гр}}\right) exp\left(-\alpha \frac{z\cdot F}{R\cdot T} u_к\right)\right]. \qquad (5)$$

In a number of electrolysis processes, the adsorption of various substances present in the electrolyte on the cathode surface is decisive. In this case, the I-V characteristic of the nonlinear resistive element in Figure 2 has an N-shaped appearance (Figure 3).

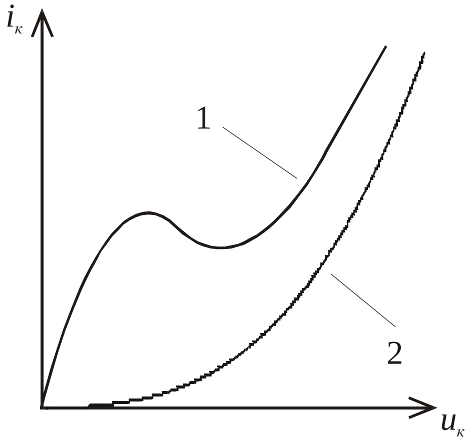


Figure 3 - Qualitative view of the I-V characteristic at the cathode-electrolyte interface in the presence of surfactants in the electrolyte (1) and in their absence (2)

In practical tasks involving the analysis of nonlinear electrochemical circuits—electrolyzers—the main quantity of interest is the cathodic voltage drop u_k or $u_k(t)$ or its amplitude, which determines the quality of the deposited electroplating. Another important quantity is the current $ik(t)$ and its average value, which is directly proportional to the process rate (according to Faraday's law) and thus to the rate of the coating deposition.

Another process occurring at the cathode is hydrogen evolution, which also consumes part of the total current. This process is represented in the equivalent circuit by adding another nonlinear resistor to the section that represents the cathode (Fig. 2). The characteristic of this resistor is described by the expression [4]

$$i_H(u_к) = j_{0H} S_к \exp\left(-\alpha_H \frac{z \cdot F}{R \cdot T} u_к\right), \qquad (6)$$

where j_{0H} is the partial current density of hydrogen ion discharge; α_H is the transfer coefficient of the hydrogen ion discharge reaction.

At the same time, in the general case, two reactions occur at the anode [3]: dissolution of the anode metal and charge concentration around it. Therefore, its equivalent circuit can also be represented as in Fig. 2. The I-V characteristic of the nonlinear resistor in this case is described by a formula similar to (3), with a different transfer coefficient.

As mentioned earlier, the specific active conductivity of the electrolyte can vary widely, but in any case, it is a finite value. This means that there will be thermal energy losses in the electrolyte, which is represented in the equivalent circuit by the presence of an active resistance RR. Additionally, if an alternating current flows through the electrolyte, it will create a varying magnetic field, implying that the electrolyte (as a large conductive medium) possesses inductance L.

Therefore, summarizing the above, the overall schematic of the electrolyzer is shown in Fig. 4.

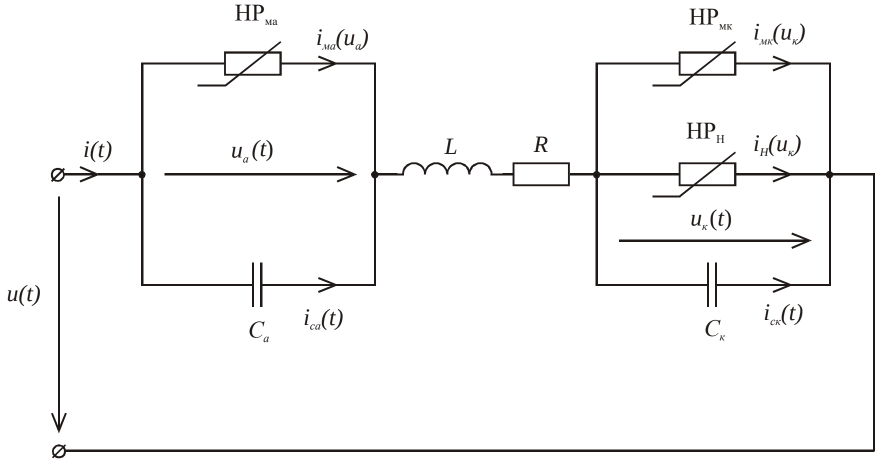
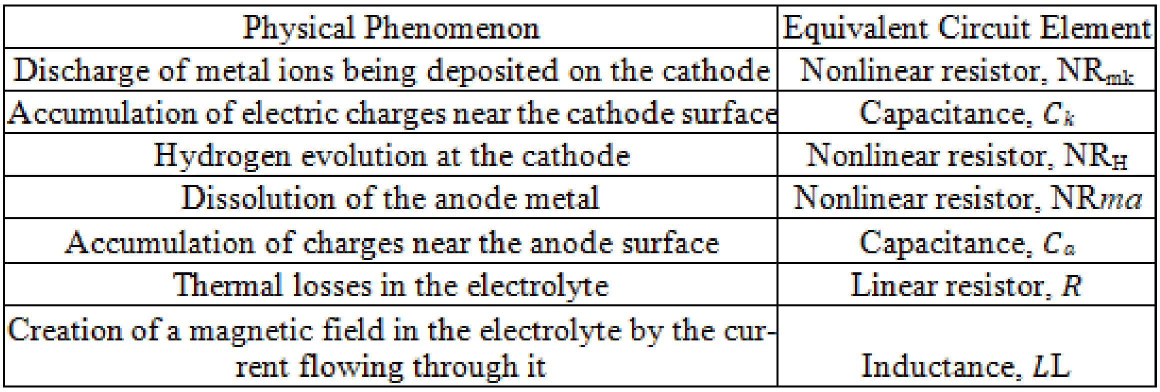


Figure 4 - General electrical equivalent circuit of the processes involved in electrochemical metal deposition (electrolyzer deposition)

Below (Table 1) is presented the correspondence between the processes in the deposition electrolyzer and the electrical elements that represent them.

Table 1

Correlation between phenomena in the electrolyzer and the elements of the equivalent circuit



Physical Phenomenon	Equivalent Circuit Element
Discharge of metal ions being deposited on the cathode	Nonlinear resistor, NR_{mk}
Accumulation of electric charges near the cathode surface	Capacitance, C_k
Hydrogen evolution at the cathode	Nonlinear resistor, NR_H
Dissolution of the anode metal	Nonlinear resistor, NR_{ma}
Accumulation of charges near the anode surface	Capacitance, C_a
Thermal losses in the electrolyte	Linear resistor, R
Creation of a magnetic field in the electrolyte by the current flowing through it	Inductance, LL

From the perspective of theoretical electrical engineering, the circuit in Fig. 4 represents a circuit with nonlinear electrochemical elements. Since it contains three energy-storing elements, the processes within it need to be described by a system of nonlinear differential equations, which can be reduced to a nonlinear third-order differential equation. At the same time, in practice, it is not always necessary to consider all these phenomena. As a rule, researchers analyze second-order electrochemical circuits [5–7], neglecting certain phenomena. In this work, we also consider circuits with nonlinear electrochemical elements that can be adequately described by nonlinear second-order differential equations. However, unlike previous works, the aim here is to obtain a general solution.

We will analyze possible simplifications, starting with the equivalent circuits of the cathode and anode. Metal deposition on the cathode is the "working" process of the electrolyzer, so it cannot be neglected under any circumstances. However, the concurrent hydrogen evolution does not always occur—an example is copper electroplating. In this case, the corresponding nonlinear resistor will be absent. Depending on the material used, the anode may be insoluble or non-polarizable, or both. Assuming the anode is insoluble allows the exclusion of the corresponding nonlinear resistor from its equivalent circuit. Non-polarizability of the anode reduces the order of the differential equation describing the circuit's state to the second order, as the capacitance Ca is not considered. In practice, non-polarizable anodes, such as platinum, are usually used under laboratory conditions.

Another simplification widely used by researchers [5–7] is neglecting the inductance of the electrolyte. Thus, the processes in the electrochemical circuit are also described by a second-order differential equation. However, in certain cases, such as deposition with rectangular pulses, the inductances of the power supply, the electroplating bath, and the connecting wires have a significant negative impact on the metal deposition process. For instance, in [8], the authors note the "slumping" of the leading edge of current pulses, thereby reducing its peak density while maintaining the same pulse length in the nickel plating electrolyzer. Ultimately, this necessitates loading the electrolyzer to only 30–35% of the normal level. The same work also suggests ways to mitigate this impact, such as using capacitor power supplies for electroplating baths. However, it is impossible to completely eliminate the bath's inherent inductance, so it needs to be considered. In general, calculating this inductance is a complex task involving the computation of the bath's electromagnetic field. Nevertheless, for the reasons mentioned above, a simplified method is needed to estimate the inductance of the electrolyzer. To estimate the inductance of the electroplating bath with electrolyte, we will consider it as a straight conductor of rectangular cross-section and limited length (Fig. 5).

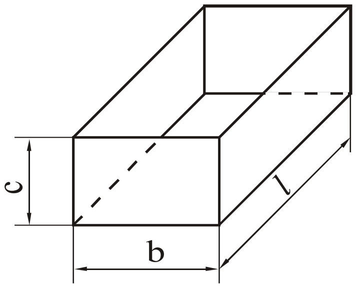


Figure 5 - General view of the electroplating bath for determining the inductance of its electrolyte

Then, according to [9-11], its inductance under the influence of direct current and low frequencies is equal to

$$L_1 = \frac{\mu_0 \ell}{2 \cdot \pi}\left(ln\frac{2\ell}{b+c} + \frac{1}{2}\right), \tag{7}$$

where ℓ is the length of the bath; b and c are the width and height, respectively; μ_0 is the magnetic constant.

If it is necessary to account for the uneven current distribution across the bath's cross-section, then the inductance obtained from formula (7) should be increased by

$$\Delta L = -\frac{-\mu_0 \ell}{2 \cdot \pi} \cdot \frac{x^4}{24} \cdot f(\varepsilon), \tag{8}$$

where $x = 0{,}2 \cdot k \cdot c, k = \sqrt{\omega \cdot \mu_0 \cdot \gamma}, \varepsilon = \frac{c-b}{c+b}$;

$$f(\varepsilon) = \frac{(1-\varepsilon)^3 \cdot \left(1 - \frac{\varepsilon^2}{3}\right) \cdot (1+4\varepsilon^2+\varepsilon^4)}{1+\varepsilon}.$$

where γ – he specific conductivity of the electrolyte.

Formula (8) can be used when $k(b+c)<7$ [9].

We will also consider the active resistance of the electrolyte in all cases, based on the finite value of its specific conductivity γ. Thus, the resistance of the electrolyte will be determined by the formula

$$R=\frac{d}{\gamma\cdot S}. \tag{9}$$

where d is the distance between the electrodes; S is the average area of the electrodes.

All calculations, both numerical and analytical, in the work were performed for nonlinear circuits of industrial electrolyzers. At the same time, experimental verification of the obtained results was carried out in laboratory conditions on a scaled-down model of the setup, based on similarity theory [12]. Therefore, let us formulate the main principles on which it is based and the requirements for this model.

The electrical equivalent circuit of the model and the real circuit must be identical, while the model and the actual system will be described by similar differential equations, differing only in similarity constants.

The model must be synchronous, meaning it operates in real-time scale.

Voltage drops at the anode and cathode, as well as current densities in the model and the real setup, should be the same to ensure consistent coating quality and deposition rate.

The electrolyte composition, temperature, and specific interfacial capacitances between the cathode-electrolyte and anode-electrolyte must also be the same. Consequently, the specific resistances of the electrolyte, the current-voltage characteristics at the interfacial boundaries, which in turn provide the same distribution of partial deposition current densities, should be identical.

The implementation of these principles using technical means is provided below.

2. Methods and equipment for experimental verification of calculated results

The verification of calculated results obtained by the proposed method was conducted experimentally in laboratory conditions by studying processes, particularly the cathodic voltage drop, in a series of electrochemical circuits of the "power supply – metal electroplating electrolyzer" system.

When supplying electric circuits from a constant voltage source, the circuit in Fig. 6 was used. It consists of two loops: polarizing and potentiometric (or measuring). The polarizing loop, intended for the flow of working current, consists of a battery AB with a voltage of 100–200 V, resistor R, ammeter A, and electrolytic cell K_0. Standard cells of type YASE-2 or EYA-3 were used, where A is the anode, K is the cathode, and EP is the reference electrode. The potentiometric loop, designed for measuring the cathodic potential V(t) or the cathodic voltage drop uк(t) in addition to electrodes K and EP, also includes a cathode voltmeter V, an oscilloscope with a direct current amplifier, and a potentiometer P, which compensates for the DC component of the voltage between the studied electrode K and the reference electrode EP. The cathode voltmeter V and the oscilloscope had high input resistances (the current in the measuring loop did not exceed 10^{-8} A).

The circuit in Fig. 6 was also used to obtain volt-ampere characteristics of the subsystems cathode-electrolyte and anode-electrolyte as nonlinear elements of the electrochemical circuit.

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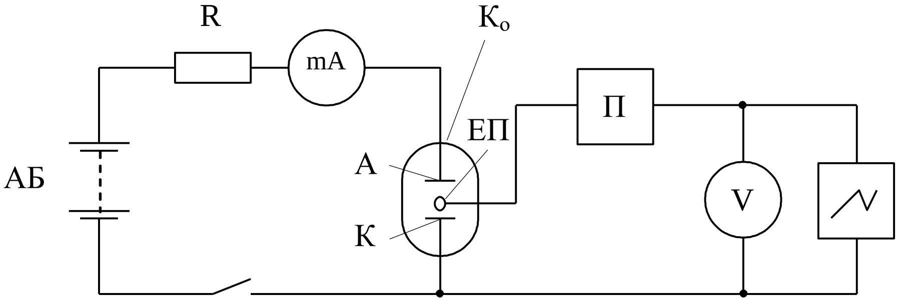
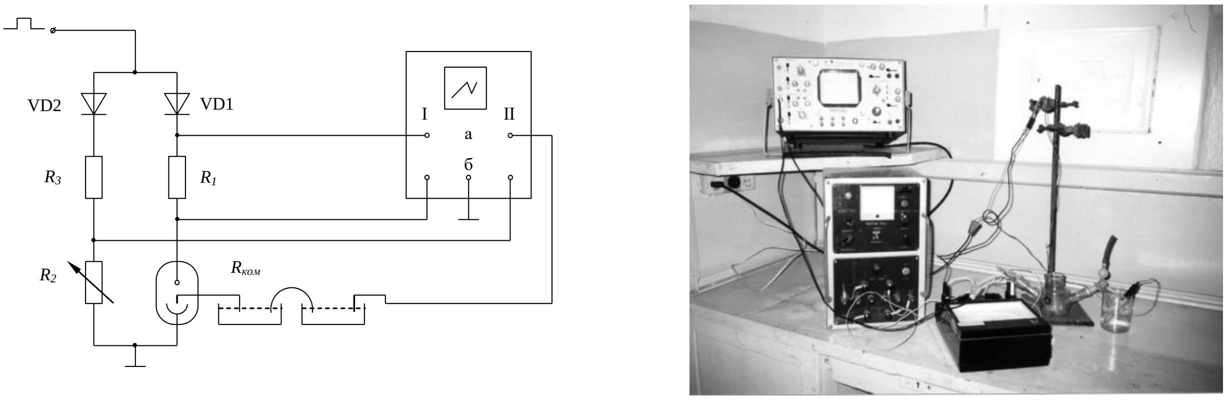


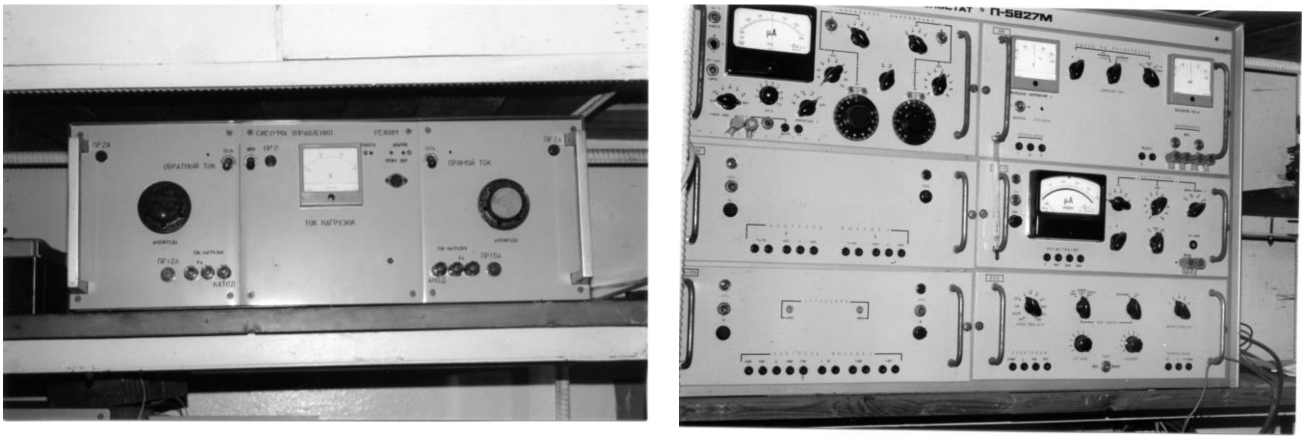
Figure 6 - Scheme of the setup for studying processes under direct current

Measurements of the cathodic voltage drop uк(t) (or cathodic potential) when supplying the electrodeposition electrolyzer from a non-sinusoidal current or voltage source (in the so-called pulse electrolysis [1]) were carried out on a setup that compensates for the voltage drop in the active resistance of the electrolyte (Fig. 7). The cell was switched on in a two-electrode configuration. As known [1], if the condition $R_1R_2 = R_3R_{ком}$ is satisfied in the circuit of Fig. 8, then the mentioned voltage drop is equal to the voltage across R_2, and the differential input 1 of the oscilloscope registers the potential of the cathode relative to a standard silver chloride electrode. The second input II of the device records the voltage drop u_{ab}, which is proportional to the cell current. The equality of currents in both branches was achieved by adjusting the resistances of resistors R_1 and R_3 and the volt-ampere characteristics of diodes VD_1 and VD_2.



a) b)

Figure 7 - Scheme of the setup for studying processes during pulse electrolysis (a); photograph of the laboratory setup for pulse metal deposition (b)



a)

b)

Figure 8 - Photographs of laboratory power sources for pulse electrolysis

As laboratory sources of pulsed current, serial pulse generators (G5-54, G3-34) in combination with a single-stage transistor amplifier or specially designed energy sources were used (Fig. 8). A reversible block of output cascades served as the power amplifier. Pulse transformers of the output cascade block were designed considering the possibility of transmitting pulse lengths longer than the supply pulse length. The generator and output cascade block were powered from stabilized constant voltage sources of the "Agat" type.

The registration of the time dependencies of the current and electrode potential was performed by photographing them from the screens of electronic oscilloscopes C1-68, C1-83, C8-14 with a sensitivity of 1 mV/cm. The input resistance of the voltage amplifiers used for potential measurements was not less than 10^9 Ohms. The average current value was determined by integrating the voltage drop curves across R_1 and in some cases using sample magnetoelectric instruments of the M253, M254 type with an accuracy class of 0.5. At low pulse frequencies, the use of magnetoelectric milliammeters for small measurement ranges leads to distortion of the supply pulse shape. Consequently, the average current values measured by the device and found from the oscillograms do not coincide. The reason for this phenomenon lies in the influence of the inherent inductance of the built-in shunts of the ammeters. Therefore, electronic measuring devices (oscilloscopes and digital voltmeters B7-21, B7-21A) that record the voltage drop on the combined non-inductive shunt, which was connected in the electrochemical cell circuit, were used for measuring pulse currents, including the average value. Meanwhile, in the case of pulse mode experiments, the use of typical constant current shunts is impractical due to their overheating caused by the thermal losses of higher harmonic currents and the skin effect phenomenon. These phenomena progress with the compression of pulses, increasing their amplitude and frequency. Therefore, special measuring shunts were fabricated, the use of which did not lead to the mentioned negative phenomena. The value of the cathodic potential was recorded relative to a standard silver chloride electrode of the EVL-1MX type with subsequent recalibration to the hydrogen reference electrode. Experiments under identical conditions were conducted at least three times, and the results were considered reproducible if they coincided within ±3%. Each experimentally obtained volt-ampere characteristic was recorded in a fresh portion of the electrolyte.

The measurement of the so-called stationary potential of a de-energized electrode, which gives its initial value, was carried out using a technique elements of which were borrowed from [1]. For this purpose, a special cell was used. The stationary potential of freshly deposited coating was recorded in the electrolyte of its own ions automatically 3 - 5 ms after the current was switched off.

The value of the electrode capacitance $C_\text{к}$ was determined from the known Frumkin-Kolotyrkin relationship [1]:

$$u_\text{к}(t_p) = u_\text{к}(0) - b_\text{м} \cdot ln\left(1 + \frac{j(0)}{b_\text{м} \cdot C_\text{к}} \cdot t\right), \tag{10}$$

where $u_\text{к}(0)$, $j(0)$ are the cathodic voltage drop and current density before circuit disconnection; $u_\text{к}(t_p)$ is the cathodic voltage drop after time t_p following circuit disconnection; $b_\text{м}$ is the Tafel equation constant.

Since for the initial segment of the voltage drop

$$t << \frac{b_\text{м} \cdot C_\text{к}}{j(0)}, \tag{11}$$

Then

$$C_\text{к} = \frac{j(0) \cdot t_p}{u_\text{к}(t_p) - u_\text{к}(0)}. \tag{12}$$

The specific resistance of the electrolytes was measured using the bridge method in a special electrolytic cell according to [13]. All electronic measuring instruments had standardized metrological characteristics and were regularly subjected to verification and calibration.

3. Approximation of volt-ampere characteristics of nonlinear electrochemical elements

To perform an analytical calculation of a circuit containing nonlinear elements, it is necessary to have functions that describe the volt-ampere characteristics of these nonlinear elements. In this work, these characteristics were obtained in tabular form experimentally, using the methodology described in the previous section. To approximate the data from the table or graph, constructed from experimental data, we first define the general structure of the approximating function, and then determine the parameters that enter into this expression. Since the ultimate goal of analytical calculations in this work is primarily to obtain functions of partial deposition currents and cathode overvoltage as a function of time in explicit form, the main criterion in choosing the general structure of the approximating expression is its suitability for obtaining the solution of the mentioned form when applying the method of variable transformation. In addition, it is logical to seek maximum simplicity and conciseness of the chosen structure. These considerations practically make widely known analytical expressions that relate cathode overvoltage to the partial cathode current unsuitable for application in this work.

Therefore, we mainly apply polynomial approximation, particularly for the case of activation polarization (cathode overvoltage) in the form of an incomplete cubic polynomial

$$j_\text{к}(u_\text{к}) = z_{01}u_\text{к} + z_{03}u_\text{к}^3, \tag{13}$$

If there are regions of negative differential resistance on the specified volt-ampere characteristics (VAC), a complete cubic polynomial is used.

$$j_\text{к}(u_\text{к}) = z_{01}u_\text{к} + z_{02}u_\text{к}^2 + z_{03}u_\text{к}^3. \tag{14}$$

The expressions (13) and (14) mentioned above satisfy the criteria mentioned earlier and are consistent with the qualitative appearance of the volt-ampere characteristics (VAC) of the nonlinear electrochemical elements used in this work (Fig. 3). The criterion of accuracy of the approximation in this case is the criterion of root-mean-square approximation [14].

$$\left(\frac{1}{b-a}\cdot\int_a^b\left(\tilde{f}(x)-f(x)\right)^2dx\right)^{\frac{1}{2}}\leq\delta \quad , \qquad (15)$$

where $f(x)$– the value of the approximating function; $f(x)$ – the value of the function being approximated; a, b – the limits of the approximation interval; δ – the permissible deviation value.

In general, as noted in [14], the accuracy requirements in approximation problems are usually not high; the approximation accuracy should be of the same order as the accuracy of the given characteristic.

To conduct analytical calculations in this work, the following approximations of the VACs of electrochemical elements are necessary:

- Anode dissolution current density from the anodic voltage drop $j_{\text{ma}}(u_{\text{a}})$.
- Copper deposition current density from the cathodic voltage drop $j_{\text{Cu}}(u_{\text{c}})$.
- Copper deposition current density from the cathodic voltage drop in the presence of PAR in the electrolyte $j_{\text{mp}}(u_{\text{c}})$.
- Nickel deposition current density from the cathodic voltage drop $j_{\text{Ni}}(u_{\text{c}})$.
- Iron deposition current density from the cathodic voltage drop $j_{\text{Fe}}(u_{\text{c}})$.
- Hydrogen evolution current density from the cathodic voltage drop $j_{\text{H}}(u_{\text{c}})$.

For the first two characteristics, we will use linear approximation, aiming for the simplest approximating expression. We will approximate the third characteristic with a complete cubic polynomial since it will allow us to represent the region of negative differential resistance. Characteristics 5 and 6 will be approximated by an incomplete cubic polynomial to facilitate the solution process. For the hydrogen approximation, we will use the classical electrochemical approach, using the Tafel equation (6). The coefficients for this approximation are borrowed from [9-11].

Since the method outlined in the previous section involves obtaining the total VAC:

$$j_{к}(u_{к}) = j_{мк}(u_{к}) + j_{H}(u_{к}), \qquad (16)$$

it is need to separate the parts of the current density that contribute to the deposition of metal and the evolution of hydrogen. We will do this according to formula (2.16), using the experimental results $j_{\text{os}}(u_{\text{c}})$ and formula (6) for $j_{\text{H}}(u_{\text{c}})$. The results of the approximation for each of the six characteristics will be summarized in Table 2.2.

Table 2

Approximation of experimentally obtained VACs of nonlinear electrochemical elements

Nonlinear dependence	Electrolyte composition, conditions	Structure of the approximating expression	Approximation coefficients	Argument, V	Function (experimental), A/cm²	Function (approximated), A/cm²
1	2	3	4	5	6	7
$j_{an}(u_a)$	$NiSO_4 \cdot 7H_2O$–200 g/L, NaCl–10 g/L, H_3BO_4–30 g/L, $t^\circ_{ел}$= 20°C.	$j_a(u_a) = \frac{u_a}{R_a S_a}$	R_a=0,06 Ohm	0,00	0,00	0,000
				0,05	$5{,}13 \cdot 10^{-5}$	$8{,}333 \cdot 10^{-5}$
				0,10	$1{,}09 \cdot 10^{-4}$	$1{,}667 \cdot 10^{-4}$
				0,15	$1{,}51 \cdot 10^{-4}$	$2{,}500 \cdot 10^{-4}$
				0,20	$2{,}74 \cdot 10^{-4}$	$3{,}333 \cdot 10^{-4}$
				0,25	$3{,}66 \cdot 10^{-4}$	$4{,}167 \cdot 10^{-4}$
				0,30	$5{,}98 \cdot 10^{-4}$	$5{,}000 \cdot 10^{-4}$
				0,35	$6{,}99 \cdot 10^{-4}$	$5{,}833 \cdot 10^{-4}$
				0,40	$7{,}44 \cdot 10^{-4}$	$6{,}667 \cdot 10^{-4}$
				0,45	$7{,}80 \cdot 10^{-4}$	$7{,}500 \cdot 10^{-4}$
				0,50	$9{,}08 \cdot 10^{-4}$	$8{,}333 \cdot 10^{-4}$
				0,60	$1{,}12 \cdot 10^{-3}$	$1{,}000 \cdot 10^{-3}$
1	2	3	4	5	6	7
$j_{Cu}(u_K)$	$CuSO_4$–250 g/L, H_2SO_4–70 g/L, $t^\circ_{ел}$= 20°C.	$j_{Cu}(u_K) = \frac{u_K}{R_{Cu} S_K}$.	R_{Cu}=6,667× ×10^{-4} Ohm.	0,00	0,00	0,00
				0,05	$9{,}0 \cdot 10^{-4}$	$7{,}5 \cdot 10^{-4}$
				0,10	$6{,}9 \cdot 10^{-3}$	$15 \cdot 10^{-3}$
				0,15	$16{,}1 \cdot 10^{-3}$	$22 \cdot 10^{-3}$
				0,20	$24{,}9 \cdot 10^{-3}$	$30 \cdot 10^{-3}$
				0,25	$48{,}6 \cdot 10^{-3}$	$37 \cdot 10^{-3}$
				0,30	$50{,}9 \cdot 10^{-3}$	$45 \cdot 10^{-3}$
				0,35	$56{,}4 \cdot 10^{-3}$	$52 \cdot 10^{-3}$
				0,40	$66{,}7 \cdot 10^{-3}$	$60 \cdot 10^{-3}$
				0,45	$69{,}6 \cdot 10^{-3}$	$67 \cdot 10^{-3}$
				0,50	$70{,}3 \cdot 10^{-3}$	$75 \cdot 10^{-3}$
1	2	3	4	5	6	7
$j_{лм}(u_K)$	$CuSO_4$–250 g/L, H_2SO_4–70 g/L, тіоацеталь –1,0 g/L, $t^\circ_{ел}$= 20°C.	$j_{лм}(u_K) = z_{01} u_K + z_{02} u_K^2 + z_{03} u_K^3$.	z_{10}=1,053 S/cm², z_{20}=-6,202 S/(V·cm²), z_{30}=10,691 См/(В²·см²).	0,00	0,00	0,00
				0,05	$58 \cdot 10^{-3}$	$38 \cdot 10^{-3}$
				0,10	$88 \cdot 10^{-3}$	$54 \cdot 10^{-3}$
				0,15	$55 \cdot 10^{-3}$	$54 \cdot 10^{-3}$
				0,20	$28 \cdot 10^{-3}$	$48 \cdot 10^{-3}$
				0,25	$21 \cdot 10^{-3}$	$43 \cdot 10^{-3}$
				0,30	$17 \cdot 10^{-3}$	$46 \cdot 10^{-3}$
				0,35	$49 \cdot 10^{-3}$	$67 \cdot 10^{-3}$
				0,40	$143 \cdot 10^{-3}$	$113 \cdot 10^{-3}$
				0,45	$216 \cdot 10^{-3}$	$192 \cdot 10^{-3}$
				0,50	$317 \cdot 10^{-3}$	$312 \cdot 10^{-3}$
	2	3	4	5	6	7
$j_{Ni}(u_K)$	$NiSO_4 \cdot 7H_2O$–200 g/L, NaCl–10 g/L, H_3BO_4–30 g/L, $t^\circ_{ел}$= 20°C.	$j_{Ni}(u_K) = z_{01} u_K + z_{03} u_K^3$.	z_{01}=8,0·10^{-4} S/cm², z_{03}=0,061 См/(V²·cm²).	0	0	0
				0,05	$0{,}5 \cdot 10^{-4}$	$0{,}48 \cdot 10^{-4}$
				0,10	$5{,}1 \cdot 10^{-4}$	$1{,}4 \cdot 10^{-4}$
				0,15	$5{,}5 \cdot 10^{-4}$	$3{,}3 \cdot 10^{-4}$
				0,20	$9{,}1 \cdot 10^{-4}$	$6{,}5 \cdot 10^{-4}$
				0,25	$1{,}8 \cdot 10^{-3}$	$1{,}3 \cdot 10^{-3}$
				0,30	$1{,}9 \cdot 10^{-3}$	$1{,}9 \cdot 10^{-3}$
				0,35	$2{,}2 \cdot 10^{-3}$	$2{,}9 \cdot 10^{-3}$
				0,40	$3{,}7 \cdot 10^{-3}$	$4{,}2 \cdot 10^{-3}$
				0,45	$5{,}4 \cdot 10^{-3}$	$5{,}9 \cdot 10^{-3}$
				0,50	$7{,}3 \cdot 10^{-3}$	$8{,}0 \cdot 10^{-3}$
				0,55	$10{,}7 \cdot 10^{-3}$	$11{,}0 \cdot 10^{-3}$
				0,60	$12{,}2 \cdot 10^{-3}$	$14{,}0 \cdot 10^{-3}$

1	2	3	4	5	6	7
$j_H(u_к)$	-	$j_H(u_к) = j_{0H}\, e^{\left(-\alpha_H \frac{z \cdot F}{R \cdot T} u_к\right)}$	α_H=0,62 $\frac{z \cdot F}{R \cdot T}$= =25,7·$10^3$ V^{-1}, j_{0H}=3,9·10^{-9} A/sm^2.	0	-	3,9·10^{-9}
				0,05		1,303·10^{-8}
				0,10		4,353·10^{-8}
				0,15		1,454·10^{-7}
				0,20		4,858·10^{-7}
				0,25		1,623·10^{-6}
				0,30		5,423·10^{-6}
				0,35		1,812·10^{-5}
				0,40		6,052·10^{-5}
				0,45		2,022·10^{-4}
				0,50		6,755·10^{-4}
				0,55		2,257·10^{-3}
				0,60		7,54·10^{-3}
				0,65		0,025
				0,70		0,084
				0,75		0,281
				0,80		0,939

Figures 9-14 show the corresponding approximated current-voltage characteristics (CVC) with experimental points plotted, which visually allows for the assessment of the approximation accuracy. From Figure 14, it is evident that significant hydrogen evolution begins at cathodic overpotentials greater than 0.6 V. Accordingly, this process can be neglected if the maximum value of the cathodic overpotential during metal deposition does not exceed this value.

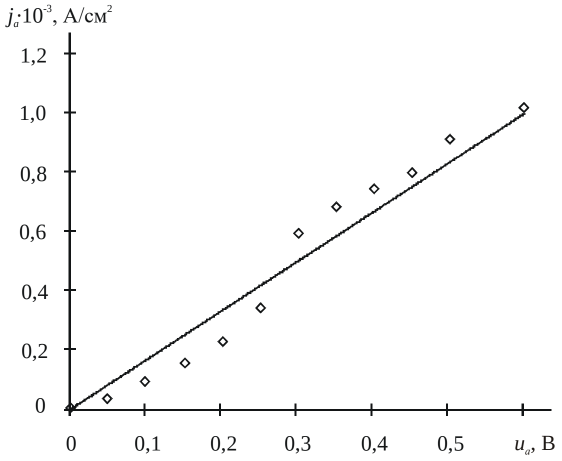


Figure 9 - Dependence of the current density of anode dissolution on the anodic overpotential $j_a(u_a)$: ◇–experiment, ― –approximation

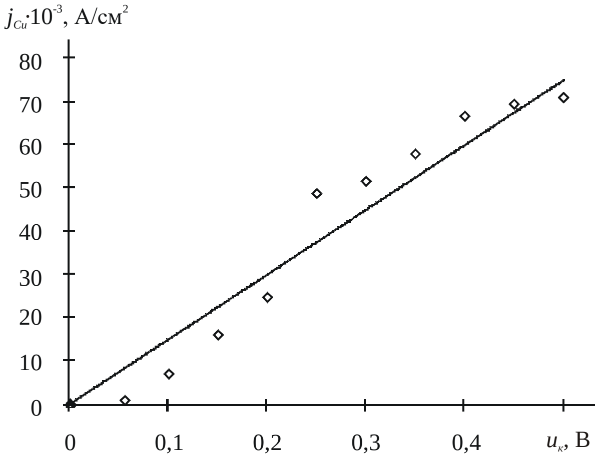


Figure 10 - Dependence of the current density of copper deposition on the cathodic overpotential $j_{Cu}(u_k)$:◇ – experiment, ― – approximation

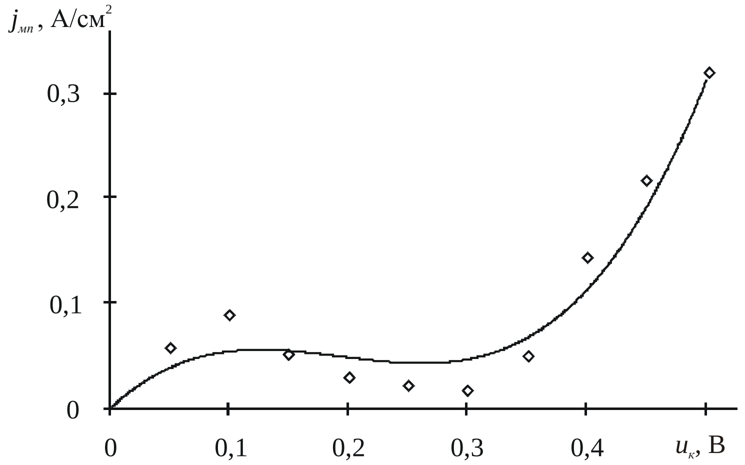


Figure 11 - Dependence of the current density of copper deposition
on the cathodic overpotential in the presence of PAR in the electrolyte $j_{mp}(u_k)$:
◇ – experiment, — – approximation

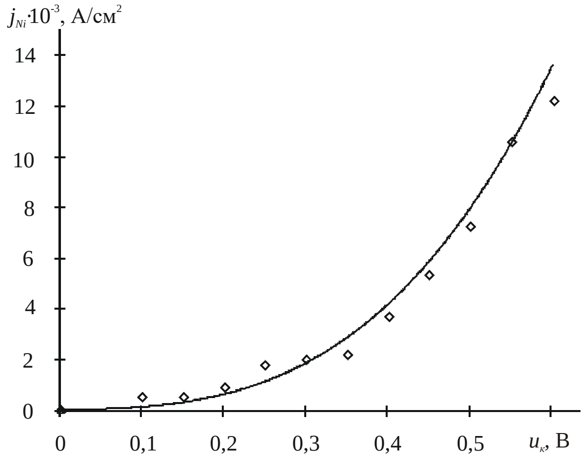


Figure 12 -Dependence of the current density of nickel deposition
on the cathodic overpotential $j_{Ni}(u_k)$: ◇ – experiment, — – approximation

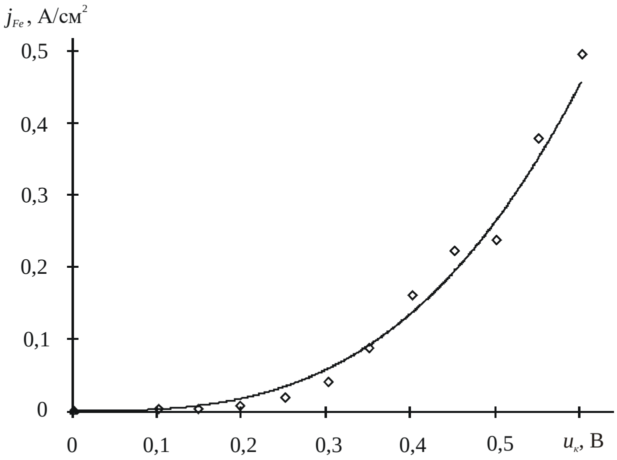


Figure 13. Dependence of the current density of iron deposition
on the cathodic overpotential $j_{Fe}(u_k)$: ◇ – experiment, — – approximation

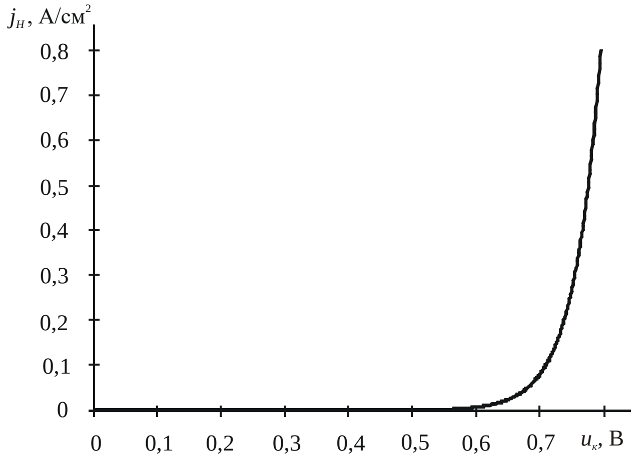


Figure 14. Dependence of the current density of hydrogen evolution on the cathodic overpotential $j_H(u_k)$

Conclusions

As seen from Section 1, from the standpoint of theoretical electrical engineering, the electrical circuit of the electrolyzer represents an electrical circuit with at least one nonlinear electrochemical element, which is described by the volt-ampere characteristic of the phase boundary between the cathode and the electrolyte.

Even considering possible simplifications, for an adequate representation of processes in the electrolyzer, the mentioned circuit should contain no fewer than two energy-consuming elements (two capacitors or an inductance and a capacitor).

The methodology of experimental research described in Section 2 is quite complex, requiring a specially equipped laboratory, equipment, and the availability of electrolyte components. Similar experiments in industrial plants are generally prohibitively expensive. This underscores the general necessity of widespread use of mathematical modeling to explore new metal deposition regimes in pulse electrolysis with significantly reduced experimental research. However, only the presence of an analytical solution for the specified circuit can ensure a wide variation of circuit parameters in this case.

The approximating expressions (13), (14) proposed in Section 3 for the CVCs of nonlinear electrochemical elements, while not "classical" for electrochemistry, are suitable for describing the obtained experimental data. These expressions are sufficiently simple in structure, and their accuracy is of the same order as the accuracy of the characteristics themselves.

From Section 3, it is evident that the process of hydrogen evolution can be disregarded for cathodic overpotentials up to 0.55 V, as its partial current within these limits is small relative to the current of deposition of any of the considered metals.

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Principles of constructing equivalent circuits for nonlinear electrochemical elements: analysis and experimental parameter determination

The analysis of nonlinear circuits is one of the most important tasks of modern electrical engineering and electronics. Unlike linear circuits, which are characterized by linear relationships between voltages and currents on the elements, in non-linear circuits the corresponding dependencies are more complex. Accordingly, in the general case, electromagnetic processes in the specified circles are characterized by systems of nonlinear differential equations. At the same time, one of the main problems in the field of analysis of nonlinear circles is the lack of universal calculation methods. First of all, this applies to analytical methods that actually allow you to obtain general laws that allow you to study the effect of changing various parameters on the nature of the process in the circle.

Thus, the task of developing and adapting existing methods of calculating nonlinear systems for the analysis of processes in circles with nonlinear elements of various natures arises. In particular, this work is devoted to the issue of developing equivalent schemes for replacing electrotechnical complexes of electrolytic deposition of metals, as well as experimental research on obtaining current-current characteristics of nonlinear elements of these schemes.

The paper proposes a generalized scheme for replacing the electrolyzer for the deposition of metal coatings. As nonlinear elements of the specified scheme, the dependences of the partial cur-

rents of metal dissolution and deposition on the near-anode or near-cathode voltage drop are considered, respectively. The possibility of applying certain simplifications in the general scheme, depending on the peculiarities of the deposition process of one or another metal, was also analyzed.

At the same time, the general structure of approximating expressions is proposed and the approximation coefficients for individual nonlinear electrochemical elements are determined. The specified expressions differ from the previously known ones in that their structure is suitable for obtaining the general regularities of electromagnetic processes that take place in systems of pulse electrodeposition of metals in an explicit form.

Key words: pulse electrolysis, nonlinear circuits, electrochemical elements, cathode polarization, deposition current, analytical approximation, cubic polynomial.

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