# Mathematical Modeling of Non-linear Electrochemical Circuits with Pulse Sources of Voltage

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***Abstract* — Mathematical model of the system «power supply – electrolyzer» in conditions of non-stationary electrolysis has been submitted in the work. Numerical calculations have been made and the processes in the system with electrolyzer of nickel plating has been analyzed.**

## I. INTRODUCTION

THE present work is extension and development of the researches [1] on mathematical modelling of non-linear electrochemical circuits replacing pulse electrolysis processes.

The obtaining of quantitative regularity describing non-stationary modes of electrolysis is important both at study of mechanisms of electrochemical processes and with the applied object – for the creation of new current sources and processing of technological modes in electroplating, hydrometallurgy, chemotronics etc. And the most complete analysis is possible at complex consideration of non-linear electromagnet chemical system the power supply is electrolyzer.

The experimental and analytical determination of necessary sizes is complicated and sometimes it is impossible by some reasons. In this connection, in our opinion the mathematical modelling of all the system with subsequent analysis of its output characteristics (system analysis) is nearly a unique method to solve the tasks of put complexity. The mathematical model is built on the basis of the Kirchhoff laws and known kinetic equations of electrolysis processes.

However essentially dynamic volt - ampere characteristic of borders electrode / electrolyte can be entered in the computer and from the diagrams or tables received experimentally. This approach is effective at modelling of processes proceeding in electrolytes with surface - active substances or at the account of non-linear dependence of capacity of double layer from potential.

Generally mathematical model of electrochemical system represents the system of non-linear integro-differential equations concerning output values - electrochemical and power characteristics of the system: electrode overvoltage, partial density of current, forms of primary current of power supply etc. A part of these values allows to expect influence of power supply operations and electrolyzer on the basic properties of metals and parameters of electrolysis process, others - to determine economic and power parameters of the system (efficiency, power factor and etc.).

## II. EQUIVALENT CIRCUIT DIAGRAM OF THE SYSTEM.

In fig. 1 equivalent circuit of diagram of the system «power supply voltage - electrolyzer» is submitted. A source voltage is recognised as widespread transformer-thyristor pulse shaper. One phase is given in the figure.

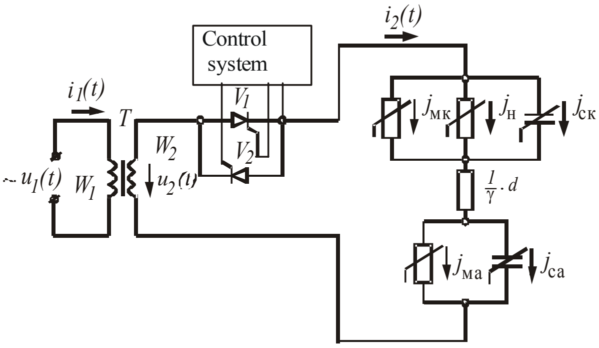

Fig. 1.

The working pulses of voltage on electrolyzer are formed of sinusoid voltage $u_2(t)$ of commercial frequency by cutting off a front of semisinusoid with the help of thyristors V1 and V2 and control system of source. At work of only thyristor V1 proceeding through electrolyzer current $i_2(t)$ as well as voltage will be unipolar. As thyristor V2 starts working there is an opportunity to form a range of main and reverse pulses. The amplitude of pulses depends on a number of coils of primary winding W1 or secondary one W2 of the transformer T and duration of pulses is regulated by the moment of unlocking the thyristors.

The power supply allows to obtain various forms of voltage on electrolyzer; in the given work the researches for one and two-halfcycle voltage with cuts-off [2].

## III. MATHEMATICAL MODEL OF SYSTEM.

At construction of equivalent circuit diagrams of electrodes (fig. 1) is accepted, that their surfaces are flat, homogeneous; cathode reactions of the discharges of metal and hydrogen are one-phased and replaced by

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parallel non-linear resistive elements, by which in its turn capacity of double layer of electrode also is connected simultaneously. The process of oxygen formation on the anode was not taken into account. On the grounds [3] it is accepted, that moderating stages at electroplating and metal dissolution in electrolyte are correspondingly discharge and ionisation phases and capacity of double layer does not depend on overvoltage and frequency.

Taking into account accepted assumptions, mathematical model of the system according to fig. 1 is:

$$j_k(t) = \frac{i_2(t)}{S_k} = j_{\text{МК}}(t) + j_{\text{СК}}(t) + j_{\text{Н}}(t)\,, \tag{1}$$

$$j_a(t) = \frac{i_2(t)}{S_a} = j_{\text{Ма}}(t) + j_{\text{са}}(t)\,, \tag{2}$$

$$j_{\text{МК}}(t) = \dot{j}^{0}_{\text{МК}}\left[\exp\left(-\alpha_{\text{М}}\frac{nF}{RT}\eta_{\text{МК}}\right) - \exp\left((1-\alpha_{\text{М}})\frac{nF}{RT}\eta_{\text{МК}}\right)\right], \tag{3}$$

$$j_{\text{Ма}}(t) = \dot{j}^{0}_{\text{Ма}}\left[\exp\left(\beta\frac{nF}{RT}\eta_a\right) - \exp\left(-(1-\beta)\frac{nF}{RT}\eta_a\right)\right], \tag{4}$$

$$j_{ck}(t) = C_k\frac{d\eta_k}{dt} \tag{5}$$

$$j_{ca}(t) = C_a\frac{d\eta_a}{dt}\,, \tag{6}$$

$$\eta_{\text{НК}}(t) = \begin{cases} R_{\text{П}} j_{\text{Н}}(t), & \text{at } |\eta_{\text{НК}}| \le \dfrac{RT}{F} \\ j_{\text{Н}}(t) = \dot{j}^{0}_{\text{Н}}\exp\left(\alpha_{\text{Н}}\dfrac{F}{RT}\eta_{\text{НК}}\right), & \text{at } |\eta_{\text{НК}}| > \dfrac{RT}{F} \end{cases} \tag{7}$$

$$u_1(t) = i_1(t)r_1 + W_1F_c\frac{dB}{dt}\,, \tag{8}$$

$$0 = \eta_a(t) - \eta_k(t) + \left(R_2 + \frac{\rho d}{S}\right)i_2(t) \pm W_2F_c\frac{dB}{dt}\,, \tag{9}$$

$$i_1W_1 \mp i_2W_2 = H(t)l_{cp} \tag{10}$$

Here $S = \sqrt{S_k \cdot S_a}; S_k : S_a = 1:2$, where indexes "k" and "a" are values of cathode and anode; $j_k, j_a$ – complete density of current of electrodes; $j_{\text{Мк}}, j_{\text{Н}}$ – partial density of current of ion discharges of metal and hydrogen; $j_{\text{Ма}}$ – partial density of ionisation current; $\dot{j}^{0}_{\text{МК}}$, $\dot{j}^{0}_{\text{Ма}}$, $\dot{j}^{0}_{\text{Н}}$ – density of exchange current; $j_{ck}, j_{ca}$ – density of capacitive current of electrodes; $C_k, C_a$ – capacity of double layers of electrodes; $\eta_{\text{Мк}}, \eta_{\text{Н}}$ – overvoltage of metal and hydrogen formation; $\eta_k$ – cathode overvoltage; $i_2$ – strength of electrolyzer current; $R_{\text{П}}$ – resistance to polarization; $\rho$ – specific resistance of electrolyte; $d$ – distance between electrodes; $S_k, S_a$ – electrode areas; $u_1, i_1$ – input voltage and current of system; – parameters and magnetic characteristics of power supply. Other symbols are generally-adopted.

The signs "minus" and "plus" in last component equations (9) and (10) correspond to positive and negative half-cycles of sinusoid voltage $u_1(t)$.

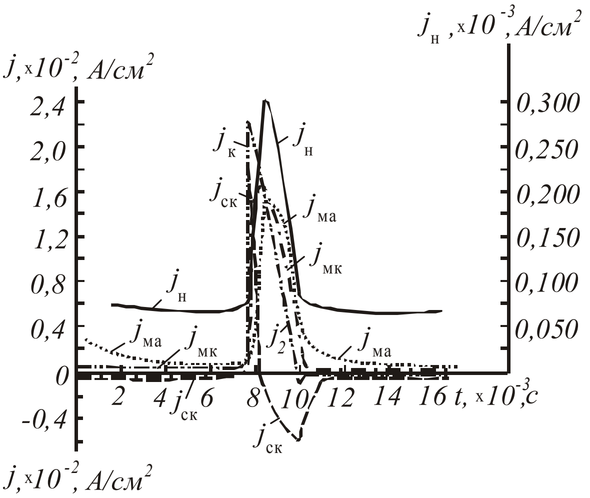

Fig. 2.

The dependences of complete and partial density of current electrolyzer nickel plating at supply of one half-cycle voltage 50 Hz with cut off and pulse duration $t_i$ = 5 ms (the symbols are explained in the text).

## IV. RESULTS OF CALCULATIONS.

Numerical integration of the system (1) - (10) was performed for the process of sulphite nickel plating by the method Runge-Kutt of the fourth order and generalized method Adams at the zero primary conditions for the first pulse voltage. During the calculations both instantaneous and average values of basic electrical and electrochemical quantities were determined. The calculations have been performed for the data:

$\dot{j}^{0}_{\text{МК}} = 3{,}1\cdot 10^{-7}$ A/sm², A/sm², $\dot{j}^{0}_{\text{Н}} = 3{,}9\cdot 10^{-9}$ A/sm²,

$\alpha_{\text{М}} = 0{,}3$; $\beta = 0{,}4$; $\alpha_{\text{Н}} = 0{,}62$; F/sm²;

$\rho d = 400$ Om·sm²; $n = 2$; V; $T_{\text{И}} = 20\cdot 10^{-3}$ s;

$W_1 = 110$; $W_2 = 8$; $F_c = 10^{-2}$ m²; $l_{cp} = 160$ sm²;

$S = 10^4$ sm²; $r_1 = 0.04$ Om; $R_2 = 8.5\cdot 10^{-3}$ Om.

The results of calculations are submitted in fig. 2 - 4. The adequacy of constructed mathematical model has been checked up by industrial introduction of nickel plating process and also by comparison of calculated data to experimental researches (the divergence of results does not exceed 5 %).

The analysis of received results of calculations allows to make the following basic conclusions.

1. The polarizing dependences are distinct under the form from volt-ampere characteristics $u_в$ (fig. 2, 3). It is explained by significant non-linear volt-ampere characteristics phase boundaries of electrodes, and also large values $C_к$ and $C_l$. In this connection it’s impossible to consider identification of (with the subsequent introduction to industrial practice) form of

temporary dependence polarising current of a cell used in laboratory conditions at halvanostatical researches or electrode potential, supported potentiostatically in those conditions with the form having a place in real electrolysis of voltage on a bath.

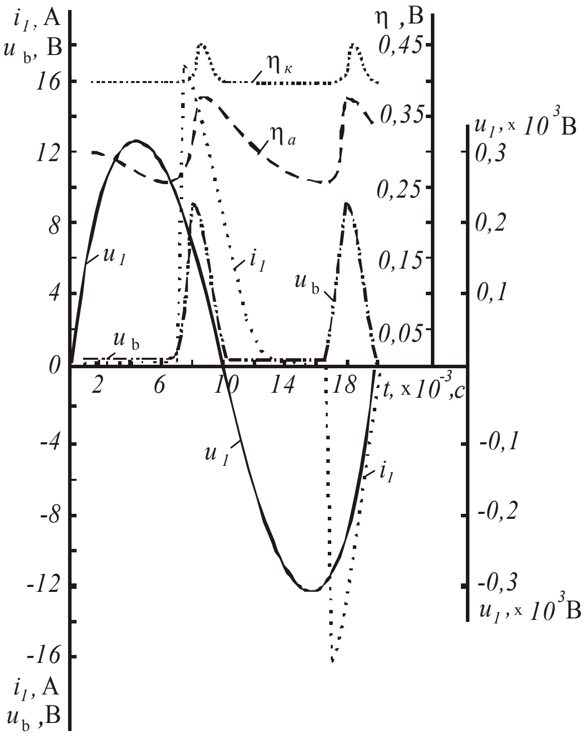

Fig. 3. Electrochemical characteristics of the power supply system – electrolyzer (the symbols are explained in the text).

The large values $C_\kappa$ and $C_l$ also conditions that $j_k(t)$ exceeds $u_в(t)$ on t ≥ 0,25 ms.

Cathode and anode polarizing characteristics for various forms of voltage $u_в(t)$ are similar to each other, however the last, as a rule, are lower the ones (fig. 3).

2. Instantaneous $\eta_\kappa$, and maximum $\eta_{kmax}$, for max values of electrode overvoltage in a mode of pulsating voltage (fig. 3) in relation to stationary process move to electronegative area and also grow at reduction of pulse duration $t_i$ for the same average current density: at $t_i$ = 10 ms (one half-cycle voltage with the period 20 ms) $\eta_{kmax}$ = 0,466, max = 0,355 V, and at $t_i$ = 1,25 ms — 0,556 and 0,461 correspondently. The similar nature of change is also observed at amplitudes of oscillations of electrode polarizations $D_\eta$: at $t_i$ = 10 ms, $D_{\eta\kappa}$ = 0,086 B, $D_{\eta a}$ = 0,138 B, and for $t_i$ = 1,25 ms, $D_{\eta k}$ = 0,13 B, $D_{\eta a}$ = 0,222 B. Simultaneously, steeper front of polarizing voltage cause faster increase of potential from minimum up to maximum value also makes up 5,5 ms at speed of voltage increase on electrolyzer 1500 V/s and 0,2 ms at - $3{,}14\cdot10^5$ V/s (fig. 3). The indicated factors promote increasing and redistribution of the crystallization centres and is known to influence on the structure of deposit: the grain size decreases from 0,6 up to 0,10 microns, and density dislocations increases from $5\cdot10^{10}$ $sm^{-2}$ up to $6{,}6\cdot10^{11}$ $sm^{-2}$ (experimental researches).

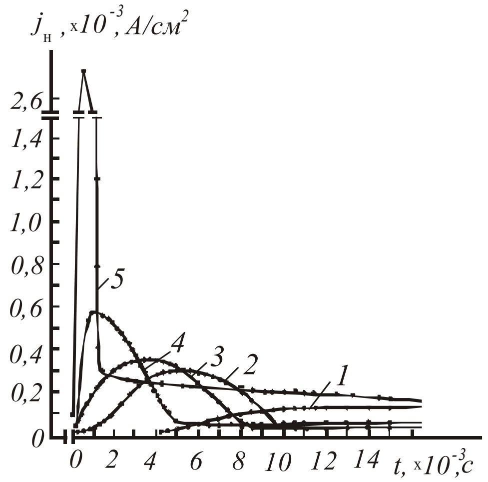

Fig. 4. Temporary dependences of change of partial speeds of ions discharge of hydrogen at various modes of electrolyzer: 1 - at a constant voltage 2,8 V; 2 - one half-cycled rectified one, 50 Hz; 3 - one half-cycled, 50 Hz, with cut off $t_i$ = 8,25 ms; 4 – the same at $t_i$ = 5 ms; 5 – the same at $t_i$ = 2,5 ms; 6 – the same at $t_i$ = 1,25 ms.

3. When frequency of polarizing pulses increases up to $10^3$ Hz and higher, amplitude of oscillations of cathode potential decreases and the structure of deposit also becomes more equilibrium. It is proved experimentally that the period of crystal lattice of nickel deposit at 50 Hz is equal to 3,518 E, and at $10^4$ Hz – 3,521 E; accordingly the size of mosaic blocks increased from 250 up to 583 E.

4. During pauses of polarizing current exponential reduction of electrode potentials is observed (fig. 3). Therefore it's possible to observe discharge of ions of hydrogen called internal electrolysis on cathode at the indicated period. It is necessary to tell, that reaction of internal electrolysis begins before the termination(of) polarising pulse - at once after electrode potential has maximum value (fig. 3)

5. For the same form of voltage $u_в(t)$ and constant average value $j_k(t)$ with increase of amplitude and reduction of pulses, duration $u_в(t)$ not only maximum (fig. 4), but also average value of partial density of current of hydrogen increases. Owing to it output of nickel on a current (Vt) decreases from 98,2 % at $t_i$ = 10 ms and $t_p$ = 10 ms up to 94,5 % at $t_i$ = 1,25 ms and $t_p$ = 18,75 ms.

The comparison of values V for one half-cycle and two half-cycle with cuts off of polarizing current speaks for the benefit of the last – 94 % against 98,7 % under other identical conditions.

6. Owing to large values electrode capacity $C_\kappa$ of change in each period of density symbol $j_{ck}$, and also final time of processes in electronic elements of power supply the short-term transition through zero of complete current $j_k$ (fig. 2) takes place. However partial density of current of discharge $Ni_2$ + and $H_30$ + do not change polarity. These phenomena are

observed and in experimental conditions on industrial baths energizing from semi-conductor units.

Duration of electrode charging and the moment of symbol change of $j_{ск}$ are defined by amplitude of voltage on electrolyzer with its increase the indicated effects proceed faster.

Besides the time when complete density of current $j_k$ has maximum value lags behind on 0,05 - 0,15 ms time when by polarization of electrode has the greatest values.

7. The considered system (power supply – electrolyzer) working in a non-stationary mode, is a complex loading for factory electric system and substantially deforms the form of primary current $i_I(t)$ in comparison with input voltage $u_I(t)$. It has negative effect for the factor of capacity (cos φ) of all the device. At a supply of bath by two half-cycled rectified voltage by frequency 50 Hz and duration cut off $t_o$ = 1,75 ms cos φ = 0,97, however, already at $t_o$ = 5 ms and $t_i$ = 5 ms factor of capacity is sharply reduced to 0,7.

At the same time efficiency of all the system at a supply of electrolyzer nickel plating from a source of periodic current and any change of bath loading is not lower than 90 %, that on 15 - 20 % is higher than this factor of standard generating sources of constant current.

## V. CONCLUSION.

Thus information received as a result of calculation on the computer is extensive and allows sufficiently to consider the basic processes proceeding in all the system power supply - electrolyzer.

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