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MATHEMATICAL MODELING OF ELECTROCHEMICAL SYSTEM WITH DIFFUSIVE-HYPERBOLIC CONTROL OF ELECTRODE KINETICS

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ABSTRACT

A two-electrode electrochemical system with equal parallel-plate electrodes is considered. Electrode kinetics is controlled through electrolyte diffusion stage, described by differential equation of hyperbolic kind. . Electric field in the electrolyte is considered to be potential. Concentration and electric fields in electrolyte are connected through boundary condition on electrodes in the form of the 2-d Fick's law and linearized Nernst equation. According to the results of teamwork study of physical fields in the electrochemical system an operator equation was formed for electrode system electrodes which allow synthesizing its electric system circuit. The circuit obtained allows to calculate transient processes in electrical devices containing the described electrochemical system. This study has been performed in the context of linear theory for electrochemical systems

Index terms- electrochemical system, boundary conditions, electrolyte concentration.

In this paper an electrochemical system (ECS), consisting of two similar plane-parallel electrodes is under consideration.

Current I(t), is flowing through (ECS) with current density being uniformly distributed.

Electrode processes limiting phase is represented by electrolyte molecular-hyperbolic diffusion proceeding with terminal velocity equal to $V = \sqrt{D/\tau_r}$, where D is a diffusion coefficient, τ_r- relaxation constant. Relatively to the electrolyte concentration field C(x;t) on the stretch [0;l] the following boundary-value problem is posed:

$$\frac{\partial C}{\partial t} + \tau_r \frac{\partial^2 C}{\partial t^2} = D\frac{\partial^2 C}{\partial x^2}; \quad (1)$$

$$C(x;0) = C_0; \quad (2)$$

$$\frac{\partial C}{\partial t}(x;0) = 0; \quad (3)$$

$$\frac{\partial C}{\partial x}(0;t) = N\frac{I(t)}{S}; \quad (4)$$

$$\frac{\partial C}{\partial x}(l;t) = N\frac{I(t)}{S}, \quad (5)$$

where N is the electrode kinetic constant, C_0 – the initial electrolyte concentration.

Solution of the task (1)-(5) through Laplace approach results in the representation of

$$\overset{0}{C}(x;p)$$

of the concentration field of the following form:

$$\overset{0}{C}(x;p) = \frac{C_0}{p} + \overset{0}{I}(p)\frac{N}{S}\cdot\left(\left(sh\left(\sqrt{\frac{p+p^2\tau_r}{D}}\right)\left(x-\frac{l}{2}\right)\right)\Big/\left(\sqrt{\frac{p+p^2\tau_r}{D}}ch\left(\sqrt{\frac{p+p^2\tau_r}{D}}\frac{l}{2}\right)\right)\right)$$

where $\overset{0}{I}(p)$ - representation by Laplace of current $I(t)$.

The ECS electrode voltage $\overset{0}{U}(p)$ in the operator form is the following : [1]:

$$\overset{0}{U}(p) = \overset{0}{\Delta^+}(p) - \overset{0}{\Delta^-}(p) + \overset{0}{I}(p)r_э, \qquad (7)$$

where $r_э = \frac{\rho_э l}{S}$ - is the electrolyte column resistance.

Representation of potential steps on electrodes is defined through the following correlations

$$\overset{0}{\Delta}{}^{+}(p)=g_0+g_1\overset{0}{C}(l;p),$$

$$\overset{0}{\Delta}{}^{-}(p)=g_0+g_1\overset{0}{C}(0;p),$$

Where positive constants ' are approximation characteristics of Nernst's equation for the selected electrochemical system.
From formula (6) it is easy to find

$$\overset{0}{C}(l;p)=\frac{C_0}{p}+\overset{0}{I}(p)\frac{N}{S}\cdot\left(\left(th\left(\sqrt{\frac{p+p^2\tau_r}{D}}\frac{l}{2}\right)\right)/\left(\sqrt{\frac{p+p^2\tau_r}{D}}\right)\right),$$

$$\overset{0}{C}(0;p)=\frac{C_0}{p}-\overset{0}{I}(p)\frac{N}{S}\cdot\left(\left(th\left(\sqrt{\frac{p+p^2\tau_r}{D}}\frac{l}{2}\right)\right)/\left(\sqrt{\frac{p+p^2\tau_r}{D}}\right)\right).$$

(11)

With regard to (8)-(11) the correlation (7) yfs th following form:

$$\overset{0}{U}(p)=\overset{0}{I}(p)\frac{2Ng_1}{S}\cdot\left(\left(th\left(\sqrt{\frac{p+p^2\tau_r}{D}}\frac{l}{2}\right)\right)/\left(\sqrt{\frac{p+p^2\tau_r}{D}}\right)\right)+\overset{0}{I}(p)r_э.$$

(12)

With $\overset{0}{I}(p)$ in the first summand of the expression (12), the coefficient comes as a diffusion-hyperbolic impedance $Z(p)$
Its inverse value, conductivity, looks like

$$Y(p)=\frac{S}{2Ng_1}\cdot\sqrt{\frac{p+p^2\tau_r}{D}}cth\left(\sqrt{\frac{p+p^2\tau_r}{D}}\frac{l}{2}\right).$$

(13)

To obtain the equivalent electrical circuit for ECS with the help of discrete units , let's factorize(13) into series [2].

$$Y(p)=\frac{S}{lNg_1}+\sum_{k=1}^{\infty}\left(\left(\frac{2S}{\lg_1 N}p^2+\frac{2S}{\lg_1 N\tau_r}p\right)/\left(p^2+\frac{p}{\tau_r}+\frac{4D\pi^2k^2}{\tau_r l^2}\right)\right)$$

(14)
Formula (14) indicates that diffusion-hyperbolic conductivity will be modeled(simulated) by infinite set of parallel branches with conductivity

$$Y_k(p)=\left(\frac{2S}{\lg_1 N}p^2+\frac{2S}{\lg_1 N\tau_r}p\right)/\left(p^2+\frac{p}{\tau_r}+\frac{4D\pi^2k^2}{\tau_r l^2}\right).$$

(15)

$Y_k(p)$ represented in formula (15) can be simulated by the following electrical circuit:

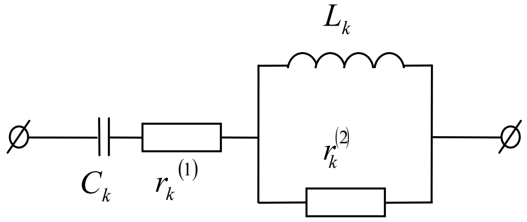

Fig.. 1. Electrical circuit of a brunch

Elements of separate brunches are calculated by formulas

$$C_k=\frac{Sl}{2D\pi^2g_1Nk^2},$$

$$C_k=\frac{Sl}{2D\pi^2g_1Nk^2},$$

$$L_k=\frac{2D\pi^2g_1Nk^2}{Sl},$$

$$r_k^{(1)}=\frac{\left(l^2-4\tau_rD\pi^2k^2\right)g_1N}{2Sl},$$

$$r_k^{(2)}=\frac{2\tau_rD\pi^2g_1Nk^2}{Sl}$$

In the expression for $r_k^{(1)}$ with $k\le 5\cdot10^4$ the bracket remains a positive value. This condition is always fulfilled in p practice. With $k>5\cdot10^4$ the electrical model of a brunch will be represented by an other circuit. Studying this problem doesn't belong to our task of investigation.
Taking into account the foresaid the electric circuit can be represented in a form in the figure 2

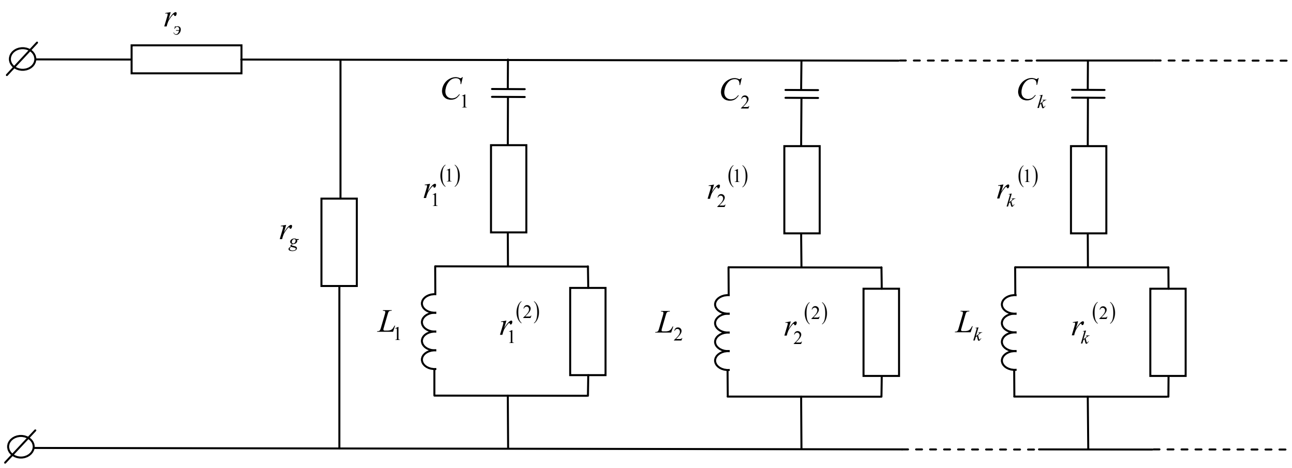

Fig.2. Electrical equivalent circuit of ECS

The produced equivalent circuit satisfies the physics of process occurring in ECS and has been developed for the first time.

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