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MATHEMATICAL MODELING OF A SECONDARY CELL BREAKDOWN CURRENT CURVE THROUGH FIXED RESISTANCE.

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ABSTRACT

In the context of linear theory a pair of plates of lead -acid accumulator, discharged on dc Ohmic resistance are under consideration. Operator expression for the accumulator discharge voltage has been obtained as a result of joint studying both concentration and electric fields in electrolytic solution. Assumption for homogeneous distribution of current density along electrode surface is applied/. Representation of accumulator's discharge curve on fixed resistance has a form of a complex transcendental function. Representation reversal is performed numerically using terminal search procedure. Terminals proved to be real negative numbers, thus determining monotonous descending character of the breakdown current curve. Temporal curve of the breakdown current is represented as an infinite series replaced by a finite sum, with uncertainty calculation being given. The expected calculation technique for the breakdown current curve can be applied at the secondary cell's short-circuit current estimation.

Index Terms- mathematical modeling, electrochemical system, electrodes, current representation.

Voltage representation on a accumulator cell is defined through the following expression [1]

$$\overset{\circ}{U}(p)=\frac{E_0}{p}-\overset{\circ}{I}(p)\left(R_Э+R^{+}+R^{-}\right)-$$
$$-\overset{\circ}{I}(p)\frac{1}{hd}\cdot\frac{g_{11}\left(N_1+N_2 ch\sqrt{\frac{p}{D}}l\right)-g_{21}\left(N_1 ch\sqrt{\frac{p}{D}}l-N_2\right)}{\sqrt{\frac{p}{D}}sh\sqrt{\frac{p}{D}}l},$$

where E_0 is the initial voltage ; $R_Э$ - electrolytic resistance; R^{+} -positive electrode resistance; R^{-} -negative electrode resistance ; h -height of the cell plate; d – width of the cell plate; l –distance between electrodes of the cell; $g_{11}>0, g_{21}<0$ - characteristics of Nernst equation approximation; $N_1>0, N_2>0$ - electrode-kinetic coefficients*;* D- diffusion coefficient; $\overset{\circ}{I}(p)$ - representation of current.

Ohmic resistance voltage is determined by Ohm's law:

$$\overset{\circ}{U}(p)=\overset{\circ}{I}(p)R_H \qquad (2)$$

From the correlations (1) and (2) we obtain:

$$\overset{\circ}{I}(p)=\frac{E_0}{p\left(R_H+R_Э+R^{-}+R^{+}+\frac{g_{11}(N_2 ch\sqrt{\frac{p}{D}}l+N_1)-g_{21}(N_2+N_1 ch\sqrt{\frac{p}{D}}l)}{hd\sqrt{\frac{p}{D}}sh\sqrt{\frac{p}{D}}l}\right)} \qquad (3)$$

Designating $R_H + R_э + R^- + R^+ = R$,
$\frac{g_{11}N_1 - g_{21}N_2}{hd} = B_1 > 0, \frac{g_{11}N_2 - g_{21}N_1}{hd} = B_2 > 0,$

we receive .

$$\overset{\circ}{I}(p) = \frac{E_0}{\sqrt{p}\left(R\sqrt{p} + B_1\sqrt{D}\frac{1}{sh\sqrt{\frac{p}{D}}l} + B_2\sqrt{D}cth\sqrt{\frac{p}{D}}l\right)} \quad (4)$$

Using limit theorems of operational calculus for initial and finite values of the original we find

$$I(0) = E_0/R; I(\infty) = 0.$$

To define the original $I(t)$ with $0 < t < \infty$ we use Mellin's inversion formula. First we find all roots of the denominator of the right-hand side (4). From (4) it follows that $p=0$ is not an image terminal $\overset{\circ}{I}(p)$. Terminals $I(p)$ are found from the following equation

$$\sqrt{p}\left(R\sqrt{p} + \frac{B_1\sqrt{D}}{sh\sqrt{\frac{p}{D}}l} + B_2\sqrt{D}cth\sqrt{\frac{p}{D}}l\right) = 0$$

Introducing a new complex variable Z into the last equation according to the rule $\sqrt{\frac{p}{D}}l = jZ$ we invert it into

$$ctgZ + \frac{B_1}{B_2} \cdot \frac{1}{\sin Z} = \frac{R}{B_2 l}Z \quad (5)$$

where $j = \sqrt{-1}; Z = x + jy; x, y$ are real independent variables of a complex plane ($x;y$).

One can show that equation (5) has only prime real roots. To find them it is convenient to solve an equation equivalent to (5):

$$\frac{\cos x + \frac{B_1}{B_2}}{\sin x} = \frac{R}{B_2 l}x \quad (6)$$

Procedure of finding equation roots (6) is fulfilled either graphically or numerically by calculator, using iteration approach.

Graphic calculation of equation (6) proves that all its roots are prime ones. The obtained roots $\boldsymbol{x_k}$ allow recording function poles $\overset{\circ}{I}(p)$ with the help of pre-introduced permutation:

$$p_k = -\frac{D}{l^2}x_k^2, \quad k = 1,2,3,...$$

Note that terminals p_k as well as x_k are prime. To apply Mellin's formula we find beforehand the residue of function $e^{pt}\overset{\circ}{I}(p)$ in terminals $p = p_.$:

$$\operatorname{Res}_{pk}\left[e^{pt}\overset{\circ}{I}(p)\right] = \left.\frac{E_0 e^{pt}}{\frac{d}{dp}\left(\sqrt{p}\left(R\sqrt{p} + B_1\sqrt{D}\frac{1}{sh\sqrt{\frac{p}{D}}l} + B_2\sqrt{D}cth\sqrt{\frac{p}{D}}l\right)\right)}\right|_{p=p_k} =$$

$$= \frac{2E_0 \sin^2 x_k e^{-\frac{D}{l^2}x_k^2 t}}{R\sin^2 x_k + (B_1 + B_2)l} = \frac{2E_0 l(B_2\cos x_k + B_1)^2 e^{-\frac{D}{l^2}x_k^2 t}}{Rl(B_2\cos x_k + B_1)^2 + (B_1 + B_2)R^2 x_k^2}$$

According to the obtained residue the current original is determined: (7)

$$I(t) = \sum_{k=1}^{\infty}\frac{2E_0 l(B_2\cos x_k + B_1)^2}{Rl(B_2\cos x_k + B_1)^2 + (B_1 + B_2)R^2 x_k^2}e^{-\frac{D}{l^2}x_k^2 t}$$

Each harmonic component of this expression represents a positive decreasing time function t, so the whole curve of discharge I*(t) is a* monotone decreasing function, that is the transient process in the external circuit of accumulator has a acyclic monotone character.

In the calculations according to (7) the infinite series is substituted for a finite sum.

The number of summands M in it is set by current valuation error Δ_I. The difference

R_M between accurate value of the current and approximate one has a form of

$$R_M = \sum_{k=M+1}^{\infty} \frac{2E_0 l(B_2 \cos x_k + B_1)^2}{Rl(B_2 \cos x_k + B_1)^2 + (B_1 + B_2)R^2 x_k^2} e^{-\frac{D}{l^2} x_k^2 t}$$

Let's assume that $R_M \le \Delta_I$.

Consider the flowing series:

$$I(0) = \sum_{k=1}^{\infty} \frac{2E_0 l(B_2 \cos x_k + B_1)^2}{Rl(B_2 \cos x_k + B_1)^2 + (B_1 + B_2)R^2 x_k^2} e^{-\frac{D}{l^2} x_k^2 t}$$

Between its residual

$$Q_M \equiv \sum_{k=M+1}^{\infty} \frac{2E_0 l(B_2 \cos x_k + B_1)^2}{Rl(B_2 \cos x_k + B_1)^2 + (B_1 + B_2)R^2 x_k^2} = \frac{E_0}{R} - \sum_{k=1}^{M} \frac{2E_0 l(B_2 \cos x_k + B_1)^2}{Rl(B_2 \cos x_k + B_1)^2 + (B_1 + B_2)R^2 x_k^2}.$$

and R_M there exists a correlation $R_M \le Q_M$ So, condition $Q_M \le \Delta_I$ being observed, the correlation $R_M \le \Delta_I$ will be executed. Thus, the number of summands in the partial sum during the current calculation according to the formula (3,271) is determined under the following condition:

$$\frac{E_0}{R} - \sum_{k=1}^{M} \frac{2E_0 l(B_2 \cos x_k + B_1)^2}{Rl(B_2 \cos x_k + B_1)^2 + (B_1 + B_2)R^2 x_k^2} \le \Delta_I$$

With the help of formulas (7), (8) the calculation of current in the accumulator cell circuit with the following characteristics was done:

D=2,328*10^{-9} m^{2}c^{-1}; N_1=1,67 kmol*A^{-1}м$^{-2}$; N_2=2,78 kmol*A^{-1}м$^{-2}$; g_{10}=1,582 B; g_{20}= -0,264 B; g_{11}=0,028 B*(kmol/м^3)$^{-1}$; g_{21}= -0,021 B*(kmol/м^3)$^{-1}$; $\gamma_э$=1,65 Ом$^{-1}$*м$^{-1}$; h =0,143 м; d =0,125 м; l =1,0*10^{-3} м; C_0=3,84 kmol/м^3; R_H=0,1 Ом; S=2,6*10^{-3} m; r=3,4*10^{-3} м; γ^+=1,34*10^4 Ом$^{-1}$*м$^{-1}$; γ^- =5,56*10^5 Ом$^{-1}$*m$^-$

The calculation and experimental results are shown in the figure 1.

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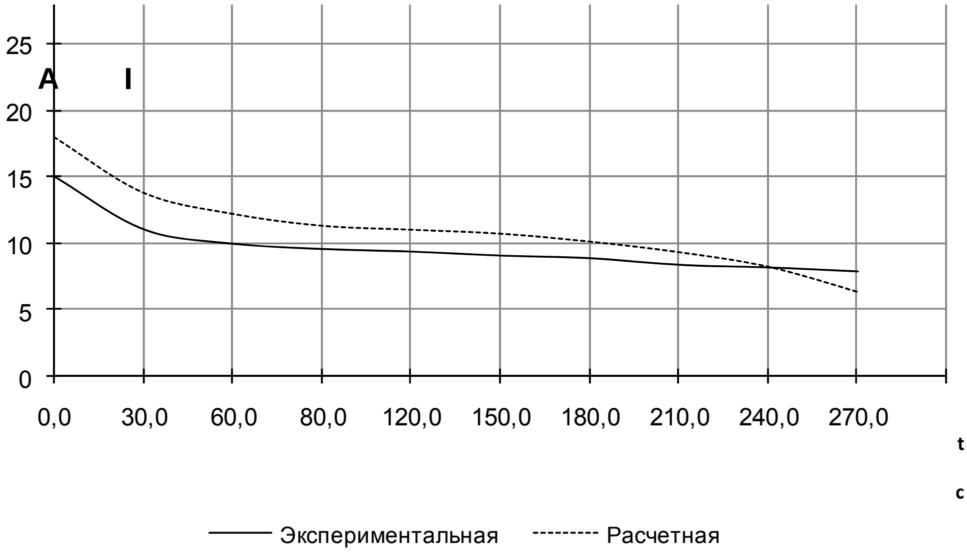

Figure 1. Current curves of the accumulator cell breakdown through fixed Resistance Rн=0,1м