Mathematical modeling and synthesis of an electrical equivalent circuit of an electrochemical device

Yuriy Yakovlevich Gerasimenko, Nikolay Iosifovich Tsygulev, Alla Nikolaevna Gerasimenko, Evgeny Yurievich Gerasimenko, Dmitry Dmitrievich Fugarov, Olga Andreevna Purchina

Don State Technical University, Gagarina square, 1, Rostov-on-Don, 344010, Russia

Abstract. Mathematical modeling of an electrochemical device is performed as a result of system research of concentration and electric fields in a two-electrode electrochemical system. The object of the study is considered to be linear with constant parameters. Object dimensions are considered negligible, therefore density of electric current on the surface of electrodes is considered to be evenly distributed. The limiting stage of electrode processes in the system is diffusion in electrolyte with finite mass transfer rate. Analytical formulas have been obtained for calculating separate discrete parameters of these branches. For the purpose of engineering calculations, the number of branches in electric substitution scheme may be limited by a finite number, depending on desired accuracy of the calculations.

[Gerasimenko Y.Y., Tsygulev N.I., Gerasimenko A.N., Gerasimenko E.Y., Fugarov D.D., Purchina O.A. **Mathematical modeling and synthesis of an electrical equivalent circuit of an electrochemical device.** *Life Sci J* 2014;11(12s):265-269] (ISSN:1097-8135). http://www.lifesciencesite.com. 53

Keywords: boundary conditions, electrolyte concentration, electric potential surge, Nernst equation, electrical equivalent circuit

Introduction

For the purpose of rigorous calculation and study of electrochemical devices' dynamics, their advanced mathematical models are required. The latter may only be obtained as a result of dynamical system study of electric and mass transfer in them. An important aspect of this study is the closed relation between concentration and electric fields with the help of the processes occurring at the electrode - electrolyte interface of electrode processes. The ultimate goal of an electrochemical device system research is to obtain its mathematical model as an element of an electrical circuit.

An electrochemical device that consisted of two identical plane-parallel electrodes was studied. Current *I(t)* flows through this device, while current density is uniformly distributed on the surface of electrodes. The electrodes area is s, and the distance between the electrodes is ℓ. The limiting stage of electrode process kinetics is molecular-hyperbolic diffusion in electrolyte that occurs with constant rate $V = \sqrt{D/\tau}$, where D is diffusion coefficient and [tau] is relaxation constant. Let us consider spatiotemporal concentration field of electrolyte *C (x; t)* as monadic, with the x coordinate normal to electrodes surfaces. Coordinates x = 0 and x = ℓ correspond to the electrodes (fig. 1).

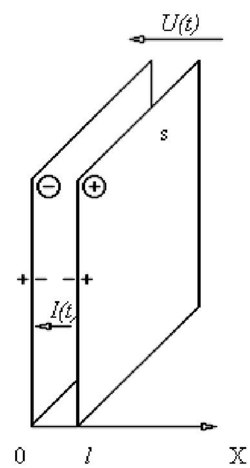

Fig1. Geometry of an electrochemical device

In relation to concentration field of the electrolyte $C_{(x;\, t)}$ the following initial boundary value problem [3, 4] is set [1, 2] in the interval [0; ℓ]:

$$\frac{\partial C}{\partial t} + \tau \frac{\partial^2 C}{\partial t^2} = D \frac{\partial^2 C}{\partial x^2}, \qquad (1)$$

$$C(x;0) = C_0, \qquad (2)$$

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

$$\frac{\partial C}{\partial x}(0;t) = N \frac{I(t)}{s}, \qquad (4)$$

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

where $N>0$ is the kinetic constant [5, 6] of the electrode reaction; C_0 is the initial concentration of electrolyte.

Main part

The problem (1) — (5) can be easily solved using the Laplace operational method [7]. Let there be correspondences $C(x;t) \overset{\circ}{\underset{\circ}{=}} \mathring{C}(x;p)$, $I(t) \overset{\circ}{\underset{\circ}{=}} \mathring{I}(p)$.

In relation to the image $\mathring{C}(x;p)$, we get the following boundary problem:

$$\frac{d\mathring{C}(x;p)}{dx^2} - \frac{p(\tau\cdot p+1)}{D}\mathring{C}(x;p) = -\frac{C_0(\tau\cdot p+1)}{D}, \qquad (6)$$

$$\frac{d\mathring{C}(0;p)}{dx} = N\frac{\mathring{I}(p)}{s}, \qquad (7)$$

$$\frac{d\mathring{C}(l;p)}{dx} = N\frac{\mathring{I}(p)}{s}. \qquad (8)$$

General solution of a differential equation (6) has the following structure:

$$\mathring{C}(x;p) = \mathring{\tilde{C}}(x;p) + \mathring{C}_н(x;p), \qquad (9)$$

Where $\mathring{\tilde{C}}(x;p)$ is the general solution of a homogeneous differential equation

$$\frac{d^2\mathring{\tilde{C}}(x;p)}{dx^2} - \frac{p(\tau\cdot p+1)}{D}\mathring{\tilde{C}}(x;p) = 0, \qquad (10)$$

$\mathring{C}_н(x;p)$ is some partial solution of the initial inhomogeneous equation (9).

In order to solve (10) let us compose a secular equation

$$k^2 - \frac{p(\tau\cdot p+1)}{D} = 0, \qquad (11)$$

Roots of equation (11)

$$k_{1,2} = \pm\sqrt{\frac{p(\tau\cdot p+1)}{D}}$$

make it possible to write the general solution of (10) as:

$$\mathring{\tilde{C}}(x;p) = A(p)sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}x + B(p)ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}x, \qquad (12)$$

where *A(p) and B(p)* are arbitrary constants of integrating that are to be defined.

Partial solution $\mathring{C}_н(x;p)$ of equation (6) can be written as:

$$\mathring{C}_н(x;p) = \frac{C_0}{p}. \qquad (13)$$

Insertion of (12) and (13) into (9) leads to the following result:

$$\mathring{C}(x;p) = A(p)sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}x + B(p)ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}x + \frac{C_0}{p}. \qquad (14)$$

Coefficients *A(p)* and *B(p)* can be found from boundary conditions (7) and (8).

To do so, let us differentiate (14) by x:

$$\frac{d\mathring{C}(x;p)}{dx} = \sqrt{\frac{p(\tau\cdot p+1)}{D}}\left(A(p)ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}x + B(p)sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}x\right). \qquad (15)$$

From (15) with x=0, we have:

$$\frac{d\mathring{C}(0;p)}{dx} = A(p)\sqrt{\frac{p(\tau\cdot p+1)}{D}}/ \qquad (16)$$

Collating (12) and (13) into (9) leads to the following result:

$$A(p) = N\frac{\mathring{I}(p)}{s\sqrt{\frac{p(\tau\cdot p+1)}{D}}}. \qquad (17)$$

Insertion of (17) and x=l into (15) results in:

$$\frac{d\mathring{C}(l;p)}{dx} = \frac{N\mathring{I}(p)}{s}ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}l + B(p)\sqrt{\frac{p(\tau\cdot p+1)}{D}}sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}l. \qquad (18)$$

Collating (8) and (18), we define coefficient *B(p).*

$$B(p) = N\frac{\mathring{I}(p)sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}{s\sqrt{\frac{p(\tau\cdot p+1)}{D}}ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}. \qquad (19)$$

General solution $\mathring{C}(x;p)$ set by expression (14) with regard to (17) and (19) gets the following form:

$$\mathring{C}(x;p) = \frac{C_0}{p} + \frac{N\mathring{I}(p)sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}\left(x-\frac{l}{2}\right)}{s\sqrt{\frac{p(\tau\cdot p+1)}{D}}ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}. \qquad (20)$$

In any electrochemical system at the electrode-electrolyte interface there is a surge [8,9] of electric potential that is uniquely defined with accepted allowances by the value of electrolyte concentration on the interface surface. This dependence is set by Nernst equations that are defined in the case studied by the following linear relations [1]:

$$\Delta^{-}(t) = g_0 + g_1 C(0;t), \qquad (21)$$

$$\Delta^{+}(t) = g_0 + g_1 C(l;t), \qquad (22)$$

where [delta] − *(t)* is the potential surge on the cathode; [delta] + *(t)* − s the potential surge on the anode; $g_0>0$, $g_1>0$ are parameters of linear approximation of the Nernst equation.

Applying the Laplace transformation to relations (21) and (22), we obtain [10, 11] the following operator dependencies:

$$\overset{\circ}{\Delta}{}^{-}(t) = \frac{g_0}{p} + g_1 \overset{\circ}{C}(0;p), \qquad (23)$$

$$\overset{\circ}{\Delta}{}^{+}(t) = \frac{g_0}{p} + g_1 \overset{\circ}{C}(l;p). \qquad (24)$$

Voltage $U(t)$ at the electro-chemical device is calculated using the 2-d Kirchhoff's Law

$$\Delta^{+}(t) + I(t)r_э - \Delta^{-}(t) - U(t) = 0,$$

where $r_э = \dfrac{l}{\gamma s}$ is the resistance of the electrolyte column between the plates. Here [gamma] is specific conductivity of the electrode.

From the 2-d Kirchhoff's Law we get:

$$U(t) = \Delta^{+}(t) - \Delta^{-}(t) + I(t)r_э\,. \qquad (25)$$

$$\overset{\circ}{U}(p) = \overset{\circ}{\Delta}{}^{+}(p) - \overset{\circ}{\Delta}{}^{-}(p) + \overset{\circ}{I}(p)r_э\,. \qquad (26)$$

Let us insert (23) and (24) into (26).

$$\overset{\circ}{U}(p) = g_1\left(\overset{\circ}{C}(l;p) - \overset{\circ}{C}(0;p)\right) + \overset{\circ}{I}(p)r_э\,. \qquad (27)$$

We get $\overset{\circ}{C}(0;p)$ and $\overset{\circ}{C}(l;p)$ from (20):

$$\overset{\circ}{C}(0;p) = \frac{C_0}{p} + \frac{N\overset{\circ}{I}(p)}{s}\cdot\frac{sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}{\sqrt{\frac{p(\tau\cdot p+1)}{D}}\,ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}, \qquad (28)$$

$$\overset{\circ}{C}(l;p) = \frac{C_0}{p} + \frac{N\overset{\circ}{I}(p)}{s}\cdot\frac{sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}{\sqrt{\frac{p(\tau\cdot p+1)}{D}}\,ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}. \qquad (29)$$

From (27), using (28), (29), we obtain:

$$U(p) = \frac{2Ng_1 sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}{s\sqrt{\frac{p(\tau\cdot p+1)}{D}}\,ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}\cdot\overset{\circ}{I}(p) + r\overset{\circ}{I}(p). \qquad (30)$$

Synthesis of an electrical equivalent circuit. The obtained correlation (30) is the basis for synthesis [12, 13, 14] of an electrical equivalent circuit.

Coefficient $\overset{\circ}{I}(p)$ of the first summand in (30) is the diffusion-hyperbolical impedance:

$$Z(p) = \frac{2Ng_1 sh\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}{s\sqrt{\frac{p(\tau\cdot p+1)}{D}}\,ch\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}}.$$

The value inverse to it, i.e., conductivity, is expressed as:

$$Y(p) = \frac{s}{2Ng_1}\sqrt{\frac{p(\tau\cdot p+1)}{D}}\,cth\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2}. \qquad (31)$$

Let us decompose [2] the hyperbolic function included into (31) into the following sequence:

$$cth\sqrt{\frac{p(\tau\cdot p+1)}{D}}\frac{l}{2} = \frac{2}{l\sqrt{\frac{p(\tau\cdot p+1)}{D}}} + \sqrt{\frac{p(\tau\cdot p+1)}{D}}\cdot\frac{l}{\pi^2}\sum_{k=1}^{\infty}\frac{1}{\frac{p(\tau\cdot p+1)}{4D\pi^2}l^2 + k^2}.$$

Inserting the last decomposition into (31) and omitting intermediate calculations, we obtain:

$$Y(p) = \frac{s}{2Ng_1 l} + \sum_{k=1}^{\infty}\frac{\frac{2s}{g_1 Nl}p^2 + \frac{2s}{g_1 Nl\tau}p}{p^2 + \frac{1}{\tau}p + \frac{4k^2\pi^2 D}{l^2\tau}}. \qquad (32)$$

Conductivity *Y(p)* defined by formula (32) meets requirements [8, 15] of physical feasibility using passive electric elements.

Let us show that each member of the series in formula (32) can be modeled using the electrical circuit (Fig.2).

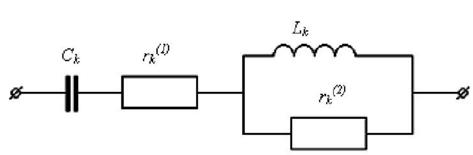

Fig. 2. Substitution branch electric drawing

Impedance of the circuit shown in fig.2 has the form:

$$Z_k(p)=\frac{p^2L_kC_k\left(r_k^{(1)}+r_k^{(2)}\right)+p\left(L_k+C_kr_k^{(1)}r_k^{(2)}\right)+r_k^{(2)}}{pC_k\left(pL_k+r_k^{(2)}\right)}$$

.

Accordingly, conductivity of the branch is given by expression:

$$Y_k(p)=\frac{pC_k\left(pL_k+r_k^{(2)}\right)}{p^2L_kC_k\left(r_k^{(1)}+r_k^{(2)}\right)+p\left(L_k+C_kr_k^{(1)}r_k^{(2)}\right)+r_k^{(2)}} \quad (33)$$

Let us reduce expression (33) to (32):

$$Y_k(p)=\frac{p^2\frac{1}{r_k^{(1)}+r_k^{(2)}}+p\frac{r_k^{(2)}}{L_k\left(r_k^{(1)}+r_k^{(2)}\right)}}{p^2+p\frac{L_k\left(r_k^{(1)}+r_k^{(2)}\right)}{L_kC_k\left(r_k^{(1)}+r_k^{(2)}\right)}+\frac{r_k^{(2)}}{L_kC_k\left(r_k^{(1)}+r_k^{(2)}\right)}} \quad (34)$$

Comparing the corresponding coefficients in (32) and (34), we obtain the system of equations for determining parameters of an electrical equivalent circuit branch:

$$\begin{cases}\dfrac{1}{r_k^{(1)}+r_k^{(2)}}=\dfrac{2s}{g_1Nl},\\ \dfrac{r_k^{(2)}}{L_kC_k\left(r_k^{(1)}+r_k^{(2)}\right)}=\dfrac{2s}{g_1Nl\tau},\\ \dfrac{L_k+C_kr_k^{(1)}r_k^{(2)}}{L_kC_k\left(r_k^{(1)}+r_k^{(2)}\right)}=\dfrac{1}{\tau},\\ \dfrac{r_k^{(2)}}{L_kC_k\left(r_k^{(1)}+r_k^{(2)}\right)}=\dfrac{4k^2\pi^2D}{l^2\tau}.\end{cases}$$

Solving the latter system of equations leads to the following results:

$$C_k=\frac{sl}{2g_1Nk^2\pi^2D};$$

$$r_k^{(1)}=\frac{g_1N4k^2\pi^2\tau D}{2sl};\; r_k^{(2)}=\frac{2g_1Nk^2\pi^2\tau D}{sl};$$

$$L_k=\frac{2g_1Nk^2\pi^2\tau^2D}{sl}.$$

Taking into account the structure of expressions (32) and (30), we obtain a complete electrical equivalent circuit of an electrochemical device (Fig. 3).

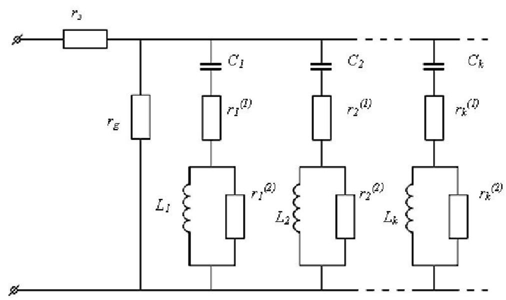

Fig. 3. Electrical equivalent circuit of an electrochemical device

In this scheme, resistance r_g that models ohmic losses in the process of electrode polarization is calculated as follows:

$$r_g=\frac{g_1Nl}{s}.$$

With initial data

s = 0.01 m^2; *l* = 0.01 *m*; g_1 = 0.025 *V/(Kmol/*m^3*); N* = 5.45 *(Kmol/*m^3*)m·*A^{-1}*;* $\tau_2 = 1\cdot10^{-6}$ *sec;*

γ = 35 $Ohm^{-1}\cdot m^{-1}$; D = $1.65\cdot10^{-6}$ $m^2\cdot s^{-1}$

we obtain the following values of electrical equivalent circuit parameters:

r_e = 0.029 Ohm; r_g = 0.136 Ohm;

C1 = 22.52 farad; $r_1^{(1)}$ = $4.44\cdot10^{-8}$ Ohm; $r_1^{(2)}$ = $4.44\cdot10^{-8}$ Ohm; L1 = 4.44·10-8 µHenry;

C2 = 5.63 farad; $r_2^{(1)}$ = $1.775\cdot10^{-7}$ Ohm; $r_2^{(2)}$ = $1.775\cdot10^{-7}$ Ohm; L2 = $1.775\cdot10^{-7}$ µHenry;

C3 = 2.50 farad; $r_3^{(1)}$ = $3.99\cdot10^{-7}$ Ohm; $r_3^{(2)}$ = $3.99\cdot10^{-7}$ Ohm; L2 = $3.99\cdot10^{-7}$ µHenry

Discussion

If a scientific calculation is needed for a transient current process with given input voltage, calculation result is represented as a partial sum of an infinite series. The number of summands in partial sum of the series is determined by a predetermined current calculation error. In engineering calculations of transient current, an electrochemical device with a finite number of parallel branches with reactive elements is used.

Conclusions

1. Rigorous scientific calculations of an electrochemical device are possible only in case of a system study of its physical fields (concentration and electrical ones).

2. A mathematical model of an electrochemical device as an element of an electric circuit can be built after calculating operating voltage at its electrodes.

3. The electrical equivalent circuit of an electrochemical device contains an infinite number of

parallel branches containing active and reactive elements.

4. When calculating the current in an external circuit of an electrochemical device connected to a voltage source, there is the problem of numerical inversion of the integral Laplace transformation for a complex transcendental expression.

5. The obtained expression for operating impedance of an electrochemical device makes it possible to synthesize all kinds of its particular characteristics and to study the dynamics of any transition process.

Corresponding Author:
Dr.Gerasimenko Yuriy Yakovlevich
Don State Technical University
Gagarina square, 1, Rostov-on-Don, 344010, Russia

References

1. Gerasimenko, Yu.Ya. and E.Yu. Gerasimenko, 2009. Mathematical Modeling of a Secondary Cell Breakdown Current Curve Through Fixed Resistance. In the Proceedings of IWK Information Technology and Electrical Engineering – Devices and Systems, Materials and Technology for the Future, Germany, Ilmenau, pp: 389-390.
2. Gerasimenko, Yu.Ya. and E.Yu. Gerasimenko, 2009. Mathematical Modeling of Electrochemical System with Diffusive Hyperbolic Control of Electrode Kinetics. In the Proceedings of IWK Information Technology and Electrical Engineering – Devices and Systems, Materials and Technology for the Future, Germany, Ilmenau, pp: 391-392.
3. Farlow, S, 1985. Partial Differential Equations for Scientists and Engineers. Moscow: Mir, pp: 384.
4. Polyanin, A.D., 2001. Handbook of Linear Equations in Mathematical Physics. Moscow: Publishing House “Physico-Mathematical Literature”, pp: 576.
5. Qin, X.Y. and Y.P. Sun, 2014. Approximate analytical solutions for a shrinking core model for the discharge of a lithium ion-phosphate electrode by the Adomian decomposition method. Applied Mathematics and Computation, V.230: 267-275.
6. Gerasimenko, Y.Y., 2009. Mathematical modeling of electrochemical systems. South Russian State technical University (NPI). Novocherkassk SRSTU (NPI), pp: 306.
7. Privalov, I.I., 1977. Introduction to the theory of functions of a complex variable. Moscow: Nauka, pp: 444.
8. Gerasimenko, Y.Y., S.M. Kucherenko, S.M. Lipkin and M.S. Lipkin, 2014. Potential Step Study of Intercalation Processes. Electrochemical Society Transaction., 58(14): 89-94.
9. Legrand, N., S. Raël, B. Knosp, M. Hinaje, P. Desprez and F. Lapicque, 2014. Including double-layer capacitance in lithium-ion battery mathematical models. Journal of Power Sources, V.251: 370-378.
10. Gerasimenko, Y.Y. and G.N. Rasteryaev, 2001. Modeling an electric field in an electrolytic bath. Scientific Thought of the Caucasus. South Caucasus Higher Education Scientific Center, 6: 54-58.
11. Gerasimenko, Y.Y., G.N. Rasteryaev, E.V. Shishkin et al., 2002. Modeling of an electric field in an electrolytic system with parallel-plate electrodes iro boundary effects. Scientific Thought of Caucasus. South Caucasus Higher Education Scientific Center, 2(Special issue): 34-40.
12. Allu, S., B. Velamur Asokan, W.A. Shelton, B. Philip and S. Pannala, 2014. A generalized multi-dimensional mathematical model for charging and discharging processes in a super capacitor. Journal of Power Sources, V.256: 369-382.
13. Momma, T., M. Matsunaga, D. Mukoyama and T. Osaka, 2012. Ac impedance analysis of lithium ion battery under temperature control. Journal of Power Sources, V.216: 304-307.
14. Ye, Y., Y. Shi and A.A.O. Tay, 2012. Electro-thermal cycle life model for lithium ion-phosphate battery. Journal of Power Sources, V.217: 509-518.
15. Tolstov, Y.G., 1978. The Theory of Linear Circuits. Moscow: Vysshaya Shkola, pp: 280.

7/25/2014