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R. Sh. NIGMATULLIN

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Abstract

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R. Sh. NIGMATULLIN

GENERAL EQUATION AND ELECTRICAL ANALOG OF AN ELECTROLYTIC CELL WITH A SPHERICAL STATIONARY MICRO-ELECTRODE

(Presented by Academician A. N. Frumkin, 5 IV 1963)

The development of the theory of modern polarographic methods and electrochemical converters of electrical signals is associated with the study of the functional relation between the e.m.f. applied to an electrolytic cell and the current flowing ([1]).

Below, on the basis of the laws of diffusion kinetics, the dependence of the current $i(t)$ on an e.m.f. $\mathcal{E}(t)$ of arbitrary form is established for a cell with a spherical stationary microelectrode. It is assumed that: 1) the oxidation-reduction reaction at the electrode obeys the Tafel equation; 2) the capacitance of the double electric layer C_0 is a prescribed function of the electrode potential; 3) ion migration is taken into account through the volume resistance of the solutions R_0 ([2]). The paper also proposes an electrical model for investigating processes in the circuit of such a cell.

Fig. 1

Let the oxidant A_1 and the reductant A_2 on the surface of a microelectrode of radius a (Fig. 1) exchange n electrons: $A_1 + n\ominus \rightleftarrows A_2$. Let A_1 in this case always remain in the solution, while A_2 either also remains in the solution (case I), or dissolves in the electrode material (II), or in its thin surface layer of thickness $\bar{a} \ll a$ (III), i.e. we consider, respectively, a solid electrode, a mercury drop, or a solid electrode coated with a mercury film. In all these cases, finding the relation between $i(t)$ and $\mathcal{E}(t)$ reduces to solving a boundary-value problem for a system of two parabolic equations:

$$\frac{\partial}{\partial t}C_\nu(r,t) = D_\nu\left[\frac{\partial^2}{\partial r^2}C_\nu(r,t) + \frac{2}{r}\frac{\partial}{\partial r}C_\nu(r,t)\right] \quad (\nu = 1,2), \tag{1}$$

where $t \geq 0$, for $C_1 : r \geq a$; $\quad C_2 :$ I—$r \geq a$, II—$0 \leq r \leq a$, III—$a - \bar{a} \leq r \leq a$;

$$C_\nu(r,-0) = \bar{C}_\nu = \text{const} \quad (\nu = 1,2); \tag{2}$$

$$C_1(\infty,t)=\bar{C}_1;\quad \text{I—}C_2(\infty,t)=\bar{C}_2,\quad \text{II—}\frac{\partial}{\partial r}C_2(0,t)=0,$$

$$\text{III—}\frac{\partial}{\partial r}C_2(a-\bar{a},t)=0; \tag{3}$$

$$\frac{\partial}{\partial r}C_1(a,t)=\frac{i_d(t)}{nFSD_1};\quad \text{I—}\frac{\partial}{\partial r}C_2(a,t)=-\frac{i_d(t)}{nFSD_2};$$

$$\text{II, III—}\frac{\partial}{\partial r}C_2(a,t)=\frac{i_d(t)}{nFSD_2}; \tag{4}$$

$$\frac{i_d(t)}{i_0}=\frac{C_1(a,t)}{\bar{C}_1}\exp\bar{\alpha}\mathcal{E}_d(t)-\frac{C_2(a,t)}{\bar{C}_2}\exp\bar{\beta}\mathcal{E}_d(t); \tag{5}$$

$$\text{a)}\quad i(t)=i_d(t)+\frac{d}{dt}[\mathcal{E}_dC_0(\mathcal{E}_d)],\qquad \text{b)}\quad \mathcal{E}(t)=R_0i(t)+\mathcal{E}_d(t). \tag{6}$$

where C_1 and C_2 are the concentrations of A_1 and A_2; $\bar{C}_1$ and $\bar{C}_2$ are their initial, equilibrium values; i_d is the faradaic current; $\mathcal{E}_d$ is the electrode potential (with the opposite sign), measured relative to a macroelectrode of the same material; $\bar{\alpha}=\alpha nF/RT$, $\bar{\beta}=-\beta nF/RT$, $\beta=1-\alpha$, $i_0=nFSk\bar{C}_1^{\beta}\bar{C}_2^{\alpha}$. The remaining notation is standard.

Fig. 2

The problem is solved as follows. From (1)–(4), by the operational method [3], we find the dependence of the boundary concentrations $C_\nu(a,t)$ on the current $i(t)$. Substituting $C_\nu(a,t)$ into the Tafel equation (5), we establish the relation between $\mathcal{E}_d$ and i_d. Next, using Kirchhoff' s laws (6), we obtain the desired dependence:

$$\begin{aligned}\frac{i_d}{i_0}=&\frac{\exp\bar{\alpha}\mathcal{E}_d}{u_1}\left[u_1-\frac{d}{dt}\int_0^t F_1(t-\tau)i_d(\tau)\,d\tau\right]\\&-\frac{\exp\bar{\beta}\mathcal{E}_d}{u_2}\left[u_2+\frac{d}{dt}\int_0^t F_2(t-\tau)i_d(\tau)\,d\tau\right],\end{aligned} \tag{7}$$

where

$$i_d=i-\frac{d}{dt}\left[\mathcal{E}_dC_0(\mathcal{E}_d)\right],\qquad \mathcal{E}_d=\mathcal{E}-R_0i,\qquad u_\nu=nFSC_\nu\ (\nu=1,2),$$

$$F_1(t) = \frac{a}{D_1}\left[1 - \exp\frac{tD_1}{a^2}\,\operatorname{erfc}\sqrt{\frac{tD_1}{a^2}}\right],$$

and $F_2(t)$ is different for the three cases:

$$F_2^{\mathrm{I}} = \frac{a}{D_2}\left(1 - \exp\delta\,\operatorname{erfc}\sqrt{\delta}\right), \qquad F_2^{\mathrm{II}} = \frac{a}{D_2}\left[3\delta + \frac{1}{5} - \sum_{m=1}^{\infty}\frac{2}{\mu_m^2}\exp(-\mu_m^2\delta)\right],$$

$$F_2^{\mathrm{III}} = \frac{a}{D_2}\left[\bar{\delta} + \frac{1}{3} - \sum_{m=1}^{\infty}\frac{2}{\mu_m^2}(-1)^m\cos\mu_m\exp(-\mu_m^2\bar{\delta})\right]; \qquad \delta = \frac{tD_2}{a^2}; \qquad \bar{\delta} = \frac{tD_2}{a^2};$$

μ_m are the positive roots of the equation $\operatorname{tg}\mu_m = \mu_m$.

The nonlinear integral equation of Volterra type that has been found establishes the dependence between the current $i(t)$ and an arbitrary (within the class of functions of bounded variation) emf $\mathcal{E}(t)$. In the general case, the solution of (7) cannot be expressed in closed form, i.e., in quadratures, through functions characterizing the original equation, without the use of infinite processes. Since the accuracy of electrochemical measurements rarely exceeds 1–5%, i.e., is lower than the accuracy of electrical analog computers, the question of an electrical model of equation (7) naturally arises.

Proceeding from the analogy between the processes of diffusion and potential equalization in RC circuits with distributed parameters, one can show that the operational "diffusion resistance"

$$f_\nu(p) = p\int_0^\infty F_\nu(t)\exp(-pt)\,dt = (-1)^\nu nFS\,\frac{[c_\nu(a,p) - \bar{C}_\nu]}{i(p)} \qquad (\nu = 1,2)^*$$

is equivalent to the electrical resistance of a two-terminal network $Z_\nu(p)$, composed in the general case of a homogeneous RC-cable and an active resistance (see Table 1).

The derivative convolution of the functions $F_\nu(t)$ and $i_d(t)$ in (7) corresponds to the voltage at the output of a certain linear four-terminal network when the input voltage follows the law of variation $i_d(t)$. Using (4), it is easy to show that, as such a four-terminal network, one may take an operational amplifier in which negative feedback is provided through a circuit with resistance $Z_\nu(p)$. The results obtained make it possible to construct a structural model of equation (7) from RC-cables and standard blocks of analog computers: amplifiers, nonlinear

converters, as well as differentiating, multiplying, and summing devices (Fig. 2).

Fig. 3. Oscillopolarograms of Cd^{2+} in KCl, obtained on the model for three values of R_0: 16.2; 273 and 1000 ohms ($C_1 = 10^{-6}$ g-ion $\cdot$ cm^{-3}, $E = 0.5t_B$, $T = 298^{\circ}$K, $S = 3 \cdot 10^{-2}$ cm^2, $D_1 = 0.72 \cdot 10^{-5}$ cm$^2 \cdot$ sec^{-1})

Equations for the voltages in the model circuit:

$$\frac{U_{Mi}}{K_{M0}} = \frac{\exp(\theta K_{M\alpha} U_{Me})}{r_{M1}} \left[\frac{r_{M1}}{\theta} - \frac{d}{dt_M} \int_0^{t_M} F_{M1}(t_M - \tau_M) U_{Mi}(\tau_M)\, d\tau_M \right] - \frac{\exp(\theta K_{M\beta} U_{Me})}{r_{M2}} \left[\frac{r_{M2}}{\theta} + \frac{d}{dt_M} \int_0^{t_M} F_{M2}(t_M - \tau_M) U_{Mi}(\tau_M)\, d\tau_M \right], \tag{8}$$

where

$$U_{Mi} = U_M - \frac{d}{dt_M} \left[\vartheta U_{Me} \psi_M(\theta K_{M\gamma} U_{Me}) \right], \qquad U_{Me} = \mathcal{E}_M - K_{MR} U_M,$$

$$F_{M1} = R_{M1} \left(1 - \exp \delta^{\mathrm{I}}_{M1} \operatorname{erfc} \sqrt{\delta^{\mathrm{I}}_{M1}} \right), \qquad F^{\mathrm{I}}_{M2} = R_{M1} \left(1 - \exp \delta^{\mathrm{I}}_{M2} \operatorname{erfc} \sqrt{\delta^{\mathrm{I}}_{M2}} \right),$$

$$F^{\mathrm{II}}_{M2} = R^{\mathrm{II}}_{M2} \left[3\delta^{\mathrm{II}}_{M2} + \frac{1}{5} - \sum_{m=1}^{\infty} \frac{2}{\mu_m^2} \exp(-\mu_m^2 \delta^{\mathrm{II}}_{M2}) \right],$$

$$F^{\mathrm{III}}_{M2} = R^{\mathrm{III}}_{M2} \left[\delta^{\mathrm{III}}_{M2} + \frac{1}{3} - \sum_{m=1}^{\infty} \frac{2}{\mu_m^2} (-1)^m \cos \mu_m \exp(-\mu_m^2 \delta^{\mathrm{III}}_{M2}) \right],$$

$$\delta^{(N)}_{M\nu} = t_M \beta^{-1}_{M\nu} (R^{(N)}_{M\nu})^{-2} \qquad (N = 0,\ \mathrm{I},\ \mathrm{II},\ \mathrm{III};\ \nu = 1, 2), \qquad \theta = 1b^{-1}, \quad \vartheta = 1\,\mathrm{sec}.$$

Comparing the equations of the original system (7) and of the model (8), by known methods ([5]) it is easy to introduce similarity constants and to find similarity invariants.

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* The concentration transformed according to Laplace–Carson is

$$c_\nu(a,p) = p\int_0^\infty C_\nu(a,t)\exp(-pt)\,dt \qquad (\nu = 1,2).$$

The proposed electrical analog of the cell makes it possible to obtain $i(t)$, $i_d(t)$, $\mathcal{E}_d(t)$, as well as the time dependence of the change in the boundary concentrations of the oxidant and reductant for specified $\mathcal{E}(t)$ and cell parameters. The corresponding voltages in the circuit are taken (relative to ground) from terminals 2-6 (Fig. 2).

Table 1

Operational "diffusion resistance" $f_\nu(p)$	Electrical analog and operational resistance of the two-terminal network $Z_\nu(p)$
$f_1(p) = \dfrac{1}{\sqrt{pD_1} + \dfrac{D_1}{a}}$	**A** Semi-infinite RC-cable. $R_{M1} > 0$– active resistance. $Z_1 = \dfrac{1}{\sqrt{p\beta_{M1}} + 1/R_{M1}}$ $\beta_{M1} = \bar{c}_{M1}/\bar{r}_{M1}{}^*$
$f_2^{\mathrm{I}}(p) = \dfrac{1}{\sqrt{pD_2} + \dfrac{D_2}{a}}$	**B** Semi-infinite RC-cable. $R_{M2}^{\mathrm{I}} > 0$– active resistance. $Z_2^{\mathrm{I}} = \dfrac{1}{\sqrt{p\beta_{M2}} + 1/R_{M2}}$ $\beta_{M2} = \bar{c}_{M2}/\bar{r}_{M2}{}^*$
$f_2^{\mathrm{II}}(p) = \dfrac{1}{\sqrt{pD_2}\,\mathrm{cth}\left(\dfrac{a}{D_2}\sqrt{pD_2}\right) - \dfrac{D_2}{a}}$	**V** Short-circuited segment of an RC-cable (length l). $R_{M2}^{\mathrm{II}} < 0$ active negative resistance. $Z_2^{\mathrm{II}} = \dfrac{1}{\sqrt{p\beta_{M2}}\,\mathrm{cth}\left(\lvert R_{M2}^{\mathrm{II}}\rvert\sqrt{p\beta_{M2}}\right) + 1/R_{M2}}$ $\lvert R_{M2}^{\mathrm{II}}\rvert = r_{M2}l.$
$f_2^{\mathrm{III}}(p) = \dfrac{1}{\sqrt{pD_2}\,\mathrm{th}\left(\dfrac{a}{D_2}\sqrt{pD_2}\right)}$	**G** Segment of an RC-cable (length l), open at the end. $Z_2^{\mathrm{III}} = \dfrac{1}{\sqrt{p\beta_{M2}}\,\mathrm{th}\left(R_{M2}^{\mathrm{III}}\sqrt{p\beta_{M2}}\right)}$

* $\bar{r}_{M\nu}$ and $\bar{c}_{M\nu}$ are the distributed resistance and capacitance of the RC-cable ($\nu = 1,2$).

For the special case of semi-infinite linear diffusion ($D_\nu t \ll a^2$) and reversible processes ($i_0 \to \infty$), the model was implemented.* The circuit used operational amplifiers from the IPT-5 integrator, a multiplication unit, and BN-3 universal functional converters. The external emf was specified by an NGPK-3 generator. As the semi-infinite RC-cable there was used an equivalent6, in the working

frequency region, chain RC-line made up of a finite number of links. On the model, with an accuracy of 1.5-9%, the influence of R_0 on the potential shift and the peak current of the polarographic wave (Fig. 3) under application of a linearly varying emf was studied.

In conclusion, I consider it a pleasant duty to express my gratitude to Academician A. N. Frumkin and Corresponding Member of the Academy of Sciences of the USSR V. G. Levich for their unfailing attention to the work and valuable discussion.

Kazan Aviation Institute

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CITED LITERATURE

1. Ya. P. Gokhshtein, DAN, **126**, No. 3, 598 (1959); N. Matsuda, Y. Ayabe, *Zs. Elektrochem.*, **59**, 494 (1955); R. Sh. Nigmatullin, DAN, **150**, No. 1, 138 (1963).

2. A. N. Frumkin, V. S. Bogotskii, Z. A. Iofa, B. N. Kabanov, *Kinetics of Electrode Processes*, Moscow, 1952, p. 96; V. G. Levich, *Physicochemical Hydrodynamics*, Moscow, 1959, p. 262.

3. V. A. Ditkin, P. I. Kuznetsov, *Handbook of Operational Calculus*, Moscow-Leningrad, 1951.

4. A. A. Feldbaum, *Computing Devices in Automatic Systems*, Moscow, 1959, p. 209.

5. I. M. Telbaum, *Electrical Modeling*, Moscow, 1959, p. 42.

6. E. F. Bazlov, R. Sh. Nigmatullin, *Transactions of the Kazan Aviation Institute*, issue 79, 65 (1963).

* The subsequent part of the work was carried out jointly with E. F. Bazlov.

Note: Figure translations are in progress. See original paper for figures.