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Abstract

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THEORY OF THE ELECTROCHEMICAL DIODE

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In recent years new elements of electrical circuits have been proposed—electrochemical diodes ([1–5]), which make it possible to carry out nonlinear transformations of weak electrical signals of low and infralow frequencies. The increased sensitivity, economy, reliability, and cheapness of these devices open up new possibilities for creating highly efficient information converters ([6,7]). The circuit element under consideration is an electrolytic cell consisting of two indifferent (platinum) electrodes placed in a sealed ampoule with an oxidation–reduction system, for example an aqueous solution of potassium ferrocyanide with a small addition of potassium ferricyanide. The ions present in the solution, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and K^+, are charge carriers. When an external emf is applied, reduction occurs at the cathode:

$$Fe(CN)_6^{3-} + \ominus \to Fe(CN)_6^{4-},$$

and oxidation at the anode:

$$Fe(CN)_6^{4-} - \ominus \to Fe(CN)_6^{3-}.$$

If, under the acting emf, there are no side reactions, the concentration of the initial substances does not change, and such a cell is stable in time. In the general case, the current through the cell is determined by the processes of diffusion, migration, natural convection of carriers in the bulk, as well as by the rate of the chemical reaction and by charging of the electrical double layer at the electrodes ([8,9]). With a large difference in areas, the current is practically controlled by processes at the microelectrode (([8]), pp. 96—97). If the solution is purified of surface-active substances and the signal spectrum is bounded from above, then the charging of the double layer can be neglected ([10,2]). For small emf values or with the addition of an indifferent electrolyte, migration may be neglected (([8]), pp. 96—97; ([9]), p. 262). Reducing the size of the microelectrode (Péclet number $\ll 1$) also makes it possible to neglect convection (([9]), p. 60). Under the assumptions made, the current through the diode is therefore determined by the processes of diffusion and chemical transformation of carriers at the microelectrode. Below, a theory of such a diode with a spherical microelectrode is given.

Let, in the course of the reaction, the oxidant A_1 and the reductant A_2 exchange n electrons: $A_1 + n\ominus \rightleftarrows A_2$. If r denotes the distance from the center of the hemispherical electrode (radius a), then in the half-interval $a \leq r < \infty$ the concentrations of the oxidant $C_1(r,t)$ and reductant $C_2(r,t)$ obey the equations of symmetric spherical diffusion:

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

where D_ν are diffusion coefficients, and t is time. Let us write the boundary conditions necessary for solving system (1):

$$C_\nu(r,-0) = C_\nu(\infty,t) = \overline{C}_\nu \qquad (\nu = 1, 2), \tag{2}$$

$$D_1 \frac{\partial}{\partial r} C_1(a,t) = -D_2 \frac{\partial}{\partial r} C_2(a,t) = \frac{i(t)}{nFS}, \tag{3}$$

where $\overline{C}_\nu$ are the equilibrium concentrations at $t < 0$; S is the area of the microelectrode; F is Faraday' s number; $i(t)$ is the current.

The Tafel equation gives one more condition:

$$\frac{i(t)}{i_0} = \frac{C_1(a,t)}{\overline{C}_1} \exp \bar{\alpha} E(t) - \frac{C_2(a,t)}{\overline{C}_2} \exp \bar{\beta} E(t), \tag{4}$$

where $\bar{\alpha} = \alpha nF/RT$, $\bar{\beta} = -\beta nF/RT$; $\beta = 1 - \alpha$; $i_0 = nFSk\bar{C}_1^{\beta}\bar{C}_2^{-\alpha}$; R is the gas constant; T is the absolute temperature; k is the rate constant at the normal potential; $E(t)$ is the e.m.f. applied to the diode (relative to the microelectrode). Conditions (2)–(4) uniquely define the boundary-value problem and make it possible to find the functional relation between the e.m.f. $E(t)$ and the current through the diode $i(t)$.

We shall do this as follows. Assuming $i(t)$ known, we solve (1) by the operational method ([11]) under the boundary conditions (2)–(3), separately for each type of carrier. We find the dependences $C_\nu(r,t)$ on $i(t)$. Substituting further the value $C_\nu(a,t)$ into (4), we obtain the desired relation:

$$\frac{i(t)}{i_0} = \frac{\exp \bar{\alpha} E(t)}{U_1} \left[U_1 - \frac{d}{dt} \int_0^t F_1(t-\tau) i(\tau)\, d\tau \right] - \frac{\exp \bar{\beta} E(t)}{U_2} \left[U_2 + \frac{d}{dt} \int_0^t F_2(t-\tau) i(\tau)\, d\tau \right], \tag{5}$$

where

$$U_\nu = nFS\bar{C}_\nu, \qquad F_\nu(t) = \frac{a}{D_\nu} \left[1 - \exp \frac{tD_\nu}{a^2} \operatorname{erfc} \sqrt{\frac{tD_\nu}{a^2}} \right] \qquad (\nu = 1, 2).$$

If the diode is connected to a current generator, then to find the voltage drop $E(t)$ we obtain an algebraic equation, and the problem is solved comparatively simply. Of greatest interest is connection to a source of e.m.f. Then, with respect to $i(t)$, we obtain an integral equation that is easily solved in two cases: 1) for a stepwise e.m.f., which makes it possible to find the principal characteristics of the diode—the transient and the current-voltage characteristics; and 2) for small signals, when linearization of (5) with respect to the variable component of the e.m.f. is possible. Let us consider these cases.

Fig. 1. Transient characteristic

$$\frac{h(t)}{h_0} = 1 - \frac{H_1 + H_2}{h + H_1 + H_2}\left[1 - \exp(h + H_1 + H_2)^2 t \;\mathrm{erfc}(h + H_1 + H_2)\sqrt{t}\right]$$

If at $t = 0$ the diode is connected to a source of constant e.m.f. $\bar{E}$, then (5) can be solved by the operational method ([12]), and after simple transformations we obtain the transient characteristic of the diode:

$$h(t) = h_0\left[1 + B_1\left(1 - \exp\alpha_1^2 t \;\mathrm{erfc}\,\alpha_1\sqrt{t}\right) + B_2\left(1 - \exp\alpha_2^2 t \;\mathrm{erfc}\,\alpha_2\sqrt{t}\right)\right]. \quad (6)$$

Here $h(t)$ is the transient current,

$$h_0 = i_0\left(\exp\bar{\alpha}\bar{E} - \exp\bar{\beta}\bar{E}\right),$$

$$B_1 = \frac{h_1 H_2 + h_2 H_1 - \alpha_1(H_1 + H_2)}{\alpha_1(\alpha_1 - \alpha_2)}, \qquad B_2 = \frac{h_1 H_2 + h_2 H_1 - \alpha_2(H_1 + H_2)}{\alpha_2(\alpha_2 - \alpha_1)},$$

$$\alpha_{1,2} = (h_1 + h_2 + H_1 + H_2)/2 \mp \sqrt{\frac{1}{4}(h_1 + h_2 + H_1 + H_2)^2 - (h_1 h_2 + h_1 H_2 + h_2 H_1)};$$

$$H_1 = i_0 U_1^{-1} D_1^{-1/2} \exp\bar{\alpha}\bar{E}, \qquad H_2 = i_0 U_2^{-1} D_2^{-1/2} \exp\bar{\beta}\bar{E},$$

$$h_\nu = a^{-1}\sqrt{D_\nu} \qquad (\nu = 1, 2).$$

The course of the curve is easier to trace for $D_1 = D_2 = D$ (Fig. 1). If one takes into account that the transient component of the current is

$$h_{\mathrm{p}}(t) = [h_0(H_1 + H_2)/(h + H_1 + H_2)] \times$$

Fig. 2. Current-voltage characteristic. I $-\mu = 1$; II $-\mu = e^{-1}$; III $-\mu = e$

Figure 1: Fig. 2. Current-voltage characteristic. I $-\mu = 1$; II $-\mu = e^{-1}$; III $-\mu = e$

$$\times \exp(h + H_1 + H_2)^2 t \ \mathrm{erfc}(h + H_1 + H_2)\sqrt{t}, \tag{7}$$

then the duration of the process may be estimated by the time constant $\tau = (h + H_1 + H_2)^{-2}$, which we define as the time during which h_{p} falls to 0.43 ($\simeq$ exp 1 erfc 1) of its maximum value. Another constant—the establishment time $\bar{\tau}$—defined as the interval during which h_{p} falls to a small fraction σ of the maximum, is related to τ by the simple dependence: $\bar{\tau} = \pi\sigma^2\tau$. We note that τ and $\bar{\tau}$ decrease (the upper frequency limit of the diode increases) when fast reactions ($k \to \infty$) and small electrode sizes are used. Thus, for $k \geqslant 1$ cm $\cdot$ sec^{-1}, $a = 10^{-5}$cm, $\bar{C}_1 = \bar{C}_2$, $\bar{E} \to 0$, $D = 10^{-5}$ cm$^2 \cdot$ sec^{-1}, $\sigma = 0.05$, $\tau \ll 10^{-6}$ sec, $\bar{\tau} \leq 1.3 \cdot 10^{-4}$ sec. In the general case, when $D_1 \neq D_2$, characteristic (6) has a similar form (since usually $D_1 \simeq D_2$).

Fig. 2. Current-voltage characteristic. $I -\mu = 1$; $II -\mu = e^{-1}$; $III -\mu = e$

The steady-state value of the current

$$h(\infty) \equiv \bar{i} = h_0(1 + B_1 + B_2) \tag{8}$$

gives the current-voltage characteristic of the diode. In the particular case $k \to \infty$

$$\bar{i} = nFSa^{-1}\sqrt{D_1 D_2 \bar{C}_1 \bar{C}_2}\ \mathrm{ch}\,\gamma E_0[\mathrm{th}\,\gamma(\bar{E} - E_0) + \mathrm{th}\,\gamma E_0], \tag{9}$$

where $E_0 = (2\gamma)^{-1} \ln \mu$, $\gamma = nF/2RT$, $\mu = D_1\bar{C}_1/D_2\bar{C}_2$.

Figure 2 gives three curves for different μ, showing, in particular, the possibility of creating (by choosing $\bar{C}_v$) specialized diodes operating without initial bias in a specified region of the characteristic. A feature of the characteristics is also a sharply pronounced nonlinearity in the region E_0: all changes in current at 298°K occur (to within 0.5% of the maximum) in the narrow region $\delta E = 0.261/n$ V. The finiteness of the rate k and radius a always worsens the nonlinear properties of the diode, reducing the steepness of the characteristic (dashed curve, for $\bar{C}_1 = \bar{C}_2$, $D_1 = D_2$, $a = \beta$, $D = 2ak$). This effect is negligibly small if $2ak \gg D$.

Let us find the solution of (5) for $E(t) = \bar{E} + \Delta E(t)$, where $\bar{E} =$ const, $\Delta E(t)$ is the variable component of the emf, and $|\Delta E(t)| \ll RT/nF$. Then $i(t) = \bar{i} + \Delta i(t)$, where $\bar{i} =$ const. We transform (5), expanding the exponentials in powers of $\Delta E(t)$ and restricting ourselves to quantities of first order of smallness:

Fig. 3. Equivalent circuit*

Figure 2: Fig. 3. Equivalent circuit*

$$\Delta E(t) = \frac{\Delta i(t)}{i_0 B} + \frac{H_1 \sqrt{\bar{D}_1}}{i_0 B} \frac{d}{dt} \int_0^t F_1(t-\tau)\, \Delta i(\tau)\, d\tau +$$

$$+ \frac{H_2 \sqrt{\bar{D}_2}}{i_0 B} \frac{d}{dt} \int_0^t F_2(t-\tau)\, \Delta i(\tau)\, d\tau, \tag{10}$$

where

$$B = \bar{\alpha}(1 - \bar{\alpha} i / U_1 D_1) \exp \bar{\alpha}\bar{E} - \bar{\beta}(1 + \bar{\alpha} i / U_2 D_2) \exp \bar{\beta}\bar{E}.$$

Transforming (10) according to Laplace–Carson ([11], p. 129, No. 2.8), we obtain:

$$\frac{\Delta E(p)}{\Delta i(p)} = Z(p) = R_k + \frac{R_1 Z_1(p)}{R_1 + Z_1(p)} + \frac{R_2 Z_2(p)}{R_2 + Z_2(p)}. \tag{11}$$

Here $\Delta E(p)$ and $\Delta i(p)$ are transformed functions; $R_k = 1/i_0 B$, $R_1 = aU_1^{-1} B^{-1} D_1^{-1} \exp \bar{\alpha} E$, $Z_1(p) = U_1^{-1} B^{-1} D_1^{-1/2} p^{-1/2} \exp \bar{\alpha} E$, $R_2 = aU_2^{-1} B^{-1} D_2^{-1} \exp \bar{\beta} E$, $Z_2(p) = U_2^{-1} B^{-1} D_2^{-1/2} p^{-1/2} \exp \bar{\beta} E$.

Using the convolution theorem and formula (12), we find the general solution of (10):

$$\Delta i(t) = \frac{1}{h_0 R_k} \int_0^t h(t-\tau)\, \Delta E(\tau)\, d\tau, \tag{12}$$

where $h(t)$ coincides with (6), if in the expressions for α_ν, h_0, B_ν, $\bar{E}$ is understood as the constant component of the applied emf.

From (11) we also obtain the equivalent circuit of the diode when operating with a small signal; it is completely determined by five resistances R_k, R_1, R_2, Z_1, and Z_2 (Fig. 3).

Fig. 3. Equivalent circuit*

In conclusion, I consider it my pleasant duty to express gratitude to Acad. A. N. Frumkin, Corresponding Member of the Academy of Sciences of the USSR V. G. Levich, and Prof. P. D. Lukovtsev for valuable discussion.

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* An operator resistance of the form $\sqrt{R/Cp}$, where C and R are distributed capacitance and resistance, is possessed by a semi-infinite RC-cable ([13]), conventionally denoted by two straight lines.

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