PHYSICAL CHEMISTRY

Corresponding Member of the USSR Academy of Sciences V. G. LEVICH, B. M. GRAFOV

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

Corresponding Member of the USSR Academy of Sciences V. G. LEVICH, B. M. GRAFOV

FARADAIC RECTIFICATION IN A SOLUTION OF A BINARY ELECTROLYTE

Recently, in studying the kinetics of electrochemical reactions, the effect of Faradaic rectification has begun to be used (1). When a cell is polarized by a sinusoidal current, in addition to an alternating voltage, a certain constant shift of the potential arises at the cell, caused by the nonlinearity of the electrochemical cell. From this potential shift one can draw definite conclusions concerning the rate constant and the so-called transfer coefficients of the electrochemical reaction. The existing theory of Faradaic rectification (1, 2) applies to a cell in which there is an excess of indifferent electrolyte. At the same time, the rectification effect in a cell without a supporting electrolyte, in a cell with a binary electrolyte, is of undoubted interest. We shall consider the polarization of a cell with a stationary solution of a binary electrolyte by a current of relatively low frequency, so that it is possible to neglect the presence of the double-layer capacitance and retardation effects in the diffuse part of the double layer. In what follows we shall use the notation adopted in (3, 4).

We shall consider the case of a sufficiently large equilibrium value of the potential in the plane of closest approach, $|\bar{\psi}^*| \gg 1$. Then it may be assumed that the electric charge in the diffuse part of the double layer is determined mainly by the charge of only one type of ions, for example, by the charge of negative ions.

Let us first consider the case when the negative ions participate in the electrode reaction. For the density of the electric current flowing through the electrode, in accordance with the theory of slow discharge (5), one may write

$$i\_ = z\_en^0_\_v\_ \left[e^{\alpha \Delta\psi z\_ n^*_\_/\bar{n}^*_\_} - e^{-\beta\Delta\psi z\_}\right], \tag{1}$$

where the quantity $z\_en^0_\_v\_$ is equal to the exchange current of the electrochemical reaction, and $v\_$ is the rate constant of the reaction. We shall assume, as is usually done in considering the Faradaic rectification effect (1, 2), that polarization of the cell occurs near the equilibrium state by a sinusoidal current of sufficiently small amplitude. Therefore, retaining only terms of first and second order of smallness in the current amplitude, expression (1) may be rewritten in the form

$$\tilde{i}_- = z_- e n_-^0 v_- \left[z_- \Delta\tilde{\psi} + \tilde{n}_-^*/\bar{n}_-^* + \frac{1}{2}(\alpha-\beta) z_-^2 \Delta\tilde{\psi}^2 + \alpha z_- \Delta\tilde{\psi}\, \tilde{n}_-^*/\bar{n}_-^* \right]. \qquad (2)$$

We are interested in the value of the potential averaged over the period of the sinusoidal current, in particular the mean value $\langle \Delta\tilde{\psi} \rangle$ of the voltage drop in the compact part of the double layer

$$\langle \Delta\tilde{\psi} \rangle = \frac{\omega}{2\pi} \int_0^{2\pi/\omega} \Delta\tilde{\psi}\, dt. \qquad (3)$$

Averaging expression (2) with respect to time, we obtain

$$\langle \Delta\tilde{\psi} \rangle = \frac{1}{2}(\beta-\alpha) z_- \langle \Delta\tilde{\psi}^2 \rangle - \alpha \langle \Delta\tilde{\psi}\, \tilde{n}_-/n_-^0 \rangle - \frac{1}{z_-} \langle \tilde{n}_-/n_-^0 \rangle. \qquad (4)$$

In computing mean values of quantities of the second order of smallness of the type $\langle \Delta\tilde{\psi}^2 \rangle$, $\langle \Delta\tilde{\psi} \tilde{n}_- \rangle$, one may use expressions obtained while retaining only terms of the first order of smallness, i.e., the expressions that were used in finding the impedance of the cell $(^{3,4})$. In what follows, the calculation of mean values of quantities representing the product of two alternating quantities will be carried out only in this way.

To calculate the mean shift of the potential in the diffuse part of the double layer $\langle \psi^* - \psi^{(d)} \rangle$, one may use expression $(^3)$

$$\frac{1}{2}\mathcal{E}^{*2} = \chi^2 \frac{n_-^{(d)}}{n_-^{(0)}} e^{z_-(\psi^* - \psi^{(d)})},$$

from which, to within quantities of the second order of smallness, it follows that

$$\overline{\mathcal{E}}^* \tilde{\mathcal{E}}^* + \frac{1}{2}\tilde{\mathcal{E}}^{*2} = \chi^2 e^{z_- \psi^*} \left\{ \tilde{n}_-^{(d)}/n_-^0 + z_-(\tilde{\psi}^* - \tilde{\psi}^{(d)}) + \frac{1}{2} z_-^2 (\tilde{\psi}^* - \tilde{\psi}^{(d)})^2 + z_-(\tilde{\psi}^* - \tilde{\psi}^{(d)}) \tilde{n}^{(d)}/n_-^0 \right\}.$$

Averaging with respect to time gives

$$\langle \psi^* - \tilde{\psi}^{(d)} \rangle = \frac{e^{-z_- \psi^*}}{2\chi^2 z_-} \langle \tilde{\mathcal{E}}^{*2} \rangle + \overline{\mathcal{E}}^* \frac{\varepsilon_r}{\varepsilon D_r} e^{-z_- \psi^*} \langle \Delta\tilde{\psi} \rangle - \frac{1}{2} z_- \langle (\tilde{\psi}^* - \tilde{\psi}^{(d)})^2 \rangle - \langle (\tilde{\psi}^* - \tilde{\psi}^{(d)}) \tilde{n}^{(d)}/n_-^0 \rangle. \qquad (5)$$

To calculate the mean shift of the potential in the diffusion region, we use the transport equation

$$j_- D_-^{-1} = -\frac{\partial n_-}{\partial x} - z_- \mathcal{E} n_-,$$

from which, to within terms quadratic in the current amplitude, it follows that

$$\langle z_- \tilde{\mathcal{E}} \rangle = \frac{1}{n_-^0} \left\langle \frac{\tilde{n}_-}{n_-^0} \frac{\partial \tilde{n}_-}{\partial x} \right\rangle + \frac{1}{n_-^0 D_-} \langle \tilde{j}_- \tilde{n}_- / n_-^0 \rangle. \tag{6}$$

If (6) is integrated with respect to the coordinate and, in the averaging, quantities computed to within first order of smallness are used, one can obtain

$$\langle \tilde{\psi}^{(d)} - \tilde{\psi}^{(L)} \rangle = \frac{1}{4n_-^0} \left(\frac{i^{(0)}}{z_- e(1 + z_-/z_+) k'_\omega D_-} \right)^2 \frac{z_-(D_+ - D_-)}{z_+ D_+ + z_- D_-}, \tag{7}$$

where i^0 is the amplitude of the sinusoidal current and

$$k'_\omega = \sqrt{\frac{z_+ D_+ + z_- D_-}{D_- D_+ (z_+ + z_-)} \omega}.$$

The appearance of a mean potential shift in the region adjacent to the diffuse layer (where the condition of electroneutrality is satisfied) is physically connected with a change in the fraction of current carried by one or the other kind of ion. Directly near the diffuse layer, the current is carried mainly only by the ions participating in the electrode reaction. Far from the electrode, the fraction of the current carried by one or the other kind of ion is determined by Ohm' s law. If the diffusion coefficients of the ions are equal to one another, there is no potential shift in the diffusion region.

In the region where Ohm' s law is satisfied, the mean potential shift is equal to zero because of the presence of a linear relation between the field strength and the electric current.

Using (7), (4), (5), and the results of (4), one can obtain the following expression for the average shift of the total voltage drop:

$$\langle \widetilde{V} \rangle = \langle \Delta \widetilde{\psi} \rangle + \langle \widetilde{\psi}^* - \widetilde{\psi}^{(d)} \rangle + \langle \widetilde{\psi}^{(d)} - \widetilde{\psi}^{(L)} \rangle =$$

$$= \frac{1}{4z_-} \left(\frac{i^{(0)}}{z_- e n_-^0} \right)^2 \left\{ \frac{\beta - \alpha}{v_-^2} + \frac{1}{D_- \omega} \left(\frac{z_+ D_+}{z_+ D_+ + z_- D_-} \right)^2 \right\}. \tag{8}$$

In writing (8) we have omitted the quantity $\varepsilon_r (\varepsilon \delta_r \tilde{\sigma}^*)^{-1}$ as small in comparison with the difference $(\beta - \alpha)$.

It is more convenient to write the expression for the potential shift in a binary electrolyte in terms of the amplitude of the sinusoidal current $i^{(0)}$, and not the amplitude of the sinusoidal voltage $V^{(0)}$, equal to the voltage drop across the cell after subtracting purely ohmic losses. This is connected with the fact that the ohmic losses in a cell with a binary electrolyte are very large, and it may prove difficult to separate out against their background the part associated with the nonlinearity of the cell (double layer, etc.). However, it is meaningful to rewrite expression (8) in terms of the voltage amplitude $V^{(0)}$, so that the rectification effect in a binary electrolyte can be compared with Faradaic rectification in the presence of an indifferent electrolyte.

For $\omega \ll v_-^2/D_-$, it follows from (8) and (4) that

$$\langle \widetilde{V} \rangle = \frac{1}{4}\, z_- \,\frac{z_+ D_+ + z_- D_-}{D_+(z_+ + z_-)}\, V^{(0)2}. \tag{9}$$

Expression (9) differs from the corresponding expression for the voltage shift in the presence of a supporting electrolyte (^{1,2}) only by the factor $(z_+ D_+ + z_- D_-)/[D_+(z_+ + z_-)]$. If the diffusion coefficients are equal, this difference disappears.

At high frequencies, when $\omega \gg v_-^2/D_-$, expression (8) becomes

$$\langle \widetilde{V} \rangle = \frac{z_-}{4}(\beta - \alpha) V^{(0)2}, \tag{10}$$

which exactly coincides with the corresponding formula for high frequencies in the case of the presence of an indifferent electrolyte. This is a quite natural result, since at high frequencies the finite value of the discharge rate is manifested. In this case the main voltage drop falls in the region of the Helmholtz layer, and the distinction between a binary electrolyte and an electrolyte with addition of an indifferent electrolyte disappears.

Using the same method of calculation and the results of (^{3,4}), one can obtain an expression for Faradaic rectification for the case in which the discharging ions (positive) are repelled from the electrode. It has the form:

$$\langle \widetilde{V} \rangle = \langle \Delta \widetilde{\psi} \rangle + \langle \widetilde{\psi}^* - \widetilde{\psi}^{(d)} \rangle + \langle \widetilde{\psi}^{(d)} - \widetilde{\psi}^{(L)} \rangle =$$

$$= \frac{1}{4}\,\frac{i^{(0)2}}{z_+^3 e^2 n_+^{0\,2} D_+^2} \left\{ -\frac{z_-^2 D_-^2 D_+}{(z_+ D_+ + z_- D_-)^2 \omega} + \sqrt{2}\,\frac{-L_{\mathrm{dv}} + L_p(\beta - 1)}{k'_\omega} + \right.$$

$$\left. + (L_p^{\sim} + L_{\mathrm{dv}})\bigl[L_{\mathrm{dv}} + (2\beta - 1) L_p\bigr] \right\}, \tag{11}$$

where L_p is the effective reaction length, and L_{dv} is the effective diffusion length in the double layer:

$$L_p = \frac{D_+}{v_+}, \qquad L_{\mathrm{dv}} = e^{(z_+ - z_-/2)\psi^*} \left[\chi_\omega^- - \sqrt{2}\,(z_+ - z_-/2)\right]^{-1},$$

v_+ is the reaction-rate constant. The quantity $z_+ e n_+^0 v_+$ represents the exchange current of the electrode reaction.

Expression (11) is valid only in the case where the doubled charge

the positive ions exceeds the valence of the negative ions that determine the charge in the diffusion layer, i.e., if the inequality

$$z_+ > z_-/2. \tag{12}$$

is satisfied.

If, instead of inequality (12), the reverse inequality is satisfied, then for Faradaic rectification one obtains the expression

$$\langle \widetilde{V} \rangle = \langle \Delta\widetilde{\psi} \rangle + \langle \widetilde{\psi}^* - \widetilde{\psi}^{(d)} \rangle + \langle \widetilde{\psi}^{(d)} - \widetilde{\psi}^{(L)} \rangle =$$

$$= \frac{1}{4} \frac{\widetilde{i}^{(0)2}}{z_+^3 e^2 n_+^{0\,2} D_+^2} \left\{ - \frac{z_-^2 D^2 D_+}{(z_+ D_+ + z_- D_-)^2 \omega} + \sqrt{2}\, \frac{L_p(\beta - 1)}{k'_\omega} + (2\beta - 1) L_p^2 \right\}. \tag{13}$$

Expression (13) is obtained formally from (11) if in (11) the effective diffusion length in the double layer is set equal to zero.

In conclusion, we note that the results obtained are readily generalized to the case when the charge of the diffusion layer is determined mainly by the charge of the positive ions.

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
30 VII 1962

CITED LITERATURE

1. G. C. Barker, *Trans. Symposium on Electrode Processes*, Philadelphia, 1959.
2. Yu. A. Vdovin, DAN, **120**, 554 (1958).
3. V. G. Levich, B. M. Grafov, DAN, **146**, No. 2 (1962).

4. V. G. Levich, B. M. Grafov, DAN, **146**, No. 3 (1962).
5. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, B. N. Kabanov, *Kinetics of Electrode Processes*, Moscow State University Press, 1952.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.