RECTIFICATION EFFECT ON AN IDEALLY POLARIZABLE ELECTRODE

Corr. Member, AN SSSR V. G. Levich and B. M. Grafov

Institute of Electrochemistry, Academy of Sciences, USSR

Translated from Doklady Akademii Nauk SSSR, Vol. 146, No. 6,
pp. 1372-1373, October, 1962
Original article submitted May 26, 1962

It is of essential importance to carry out a quite complete, quantitative study on the passage of a current through the simplest electrochemical system: a stagnant solution of a binary electrolyte. In this paper, a calculation is given of the average potential shift caused by a sinusoidal current passing through a cell with an ideally polarizable electrode. As will be shown below, the passage of a sinusoidal signal is accompanied by a rectification effect. In principle, measuring of this effect permits finding of the potential value in the plane of closest ion approach (the so-called psi-primed potential).

Passage of a sinusoidal current through an ideally polarizable electrode produces periodic charging and discharging of the double layer and, in particular, sinusoidal variations of the field strength in the Helmholtz layer. The change of the potential drop in the Helmholtz layer is proportional to the variations of the field strength, and for this very reason possesses a sinusoidal character. Therefore, the average value of the potential drop in the Helmholtz layer is equal to zero.

The value of the psi-primed potential is supposed to be quite high, so that it may be taken that the charge in the diffusion layer is virtually determined by one type of ions only. For the sake of concreteness, the latter ions are assumed to be negative. Then, the average potential drop in the diffusion layer [1] can be calculated with the following equation:

$$\frac{1}{2}\mathscr{E}^{*2} = \varkappa_-^2 \frac{n_-^{(d)}}{n_-^0} e^{z_-(\psi^* - \psi^{(d)})}. \tag{1}$$

Here and further, the notation of [1] is employed. In discussions on Faraday rectification the cell is usually [2] taken to be polarized by a current of quite a small amplitude. We shall assume that the amplitude is small enough. Equation (1) then yields, with an accuracy up to second-order terms,

$$\mathscr{E}^*\tilde{\mathscr{E}}^* + \frac{1}{2}\tilde{\mathscr{E}}^{*2} = \varkappa_-^2 e^{z_-\bar{\psi}^*}\left[\frac{\tilde{n}_-^{(d)}}{n_-^{(0)}} + z_-(\tilde{\psi}^* - \tilde{\psi}^{(d)}) \right.$$
$$\left. + \frac{\tilde{n}_-^{(d)}}{n_-^0} z_-(\tilde{\psi}^* - \tilde{\psi}^{(d)}) + \frac{1}{2} z_-^2 (\tilde{\psi}^* - \tilde{\psi}^{(d)})^2\right]. \tag{2}$$

The average of $\langle\tilde{\psi}^* - \tilde{\psi}^{(d)}\rangle$

$$\langle\tilde{\psi}^* - \tilde{\psi}^{(d)}\rangle = \frac{\omega}{2\pi}\int_0^{2\pi/\omega} [\tilde{\psi}^* - \tilde{\psi}^{(d)}]\,dt$$

has to be calculated over the period $2\pi/\omega$ of the sinusoidal current. Averaging in (2) gives:

$$z_-\langle\tilde{\psi}^* - \tilde{\psi}^{(d)}\rangle = \left\langle\frac{\tilde{n}_-^{(d)}}{n_-^0} z_-(\tilde{\psi}^* - \tilde{\psi}^{(d)})\right\rangle$$
$$+ \frac{1}{2} z_-^2 \langle(\tilde{\psi}^* - \tilde{\psi}^{(d)})^2\rangle - \langle\tilde{\mathscr{E}}^{*2}\rangle \varkappa_-^{-2} e^{-z_-\bar{\psi}^*}. \tag{3}$$

Equations obtained by keeping only the first-order terms, i.e., equations employed in calculating the cell impedance [1], may be used for computing the average of second-order terms of the type $\langle n_-^{(d)}(\tilde{\psi}^* - \tilde{\psi}^{(d)})\rangle$. The averaging of second-order terms is carried out precisely in this way.

Computing the average potential drop in the diffusion layer is done with the transport equation

$$j_- = D_-\left(-\frac{\partial n_-}{\partial x} - z_-\mathcal{E}n_-\right).$$

This equation yields, with an accuracy up to second-order terms,

$$\langle z_-\widetilde{\mathcal{E}}\rangle = \frac{1}{n_-^0}\left\langle\frac{\widetilde{n}_-}{n_-^0}\frac{\partial\widetilde{n}_-}{\partial x}\right\rangle + \frac{1}{n_-^0 D_-}\langle\widetilde{j}_-\widetilde{n}_-/n_-^0\rangle. \tag{4}$$

The average value of the potential drop in the diffusion layer is found from (4) by direct integration. If the expression thus obtained is combined with (3), averaging of the potential drop over the entire cell gives:

$$\begin{aligned} z_-\langle\widetilde{V}\rangle &= z_-\langle\widetilde{\psi}^* - \widetilde{\psi}^{(d)}\rangle + z_-\langle\widetilde{\psi}^{(d)} - \widetilde{\psi}^{(L)}\rangle \\ &= \frac{1}{4}\left(\frac{D_+z_+}{D_+z_+ + D_-z_-}\right)^2 \frac{i_0^2}{z_-^2 e^2 n_-^{02} D_-\omega} - \frac{1}{4}e^{-z_-\overline{\psi}^*}\frac{4\pi i_0^2}{\varepsilon\theta\omega^2 n_-^0}, \end{aligned} \tag{5}$$

where i_0 is the amplitude of the sinusoidal current.

It is interesting to note that the total potential drop is determined by two terms of opposite sign which depend on the frequency in a different way. Hence, at a given frequency $\omega = \omega_{\text{crit}}$, the average value of the potential drop passes through zero. From (5) it follows that

$$\begin{gathered} \omega_{\text{crit}} = \omega_0 e^{-z_-\overline{\psi}^*}\xi^{-1}; \\ \omega_0 = \frac{4\pi e^2 n_-^0 D_-}{\varepsilon\theta} = \varkappa_-^2 D_-; \quad \xi = \frac{1}{z_-^2}\left(\frac{D_+z_+}{D_+z_+ + D_-z_-}\right)^2. \end{gathered} \tag{6}$$

The frequency at which no rectification occurs being known, $\overline{\psi}^*$, i.e., the psi-primed potential, can be determined:

$$z_-\overline{\psi}^* = \ln\frac{\omega_0}{\xi\omega_{\text{crit}}}. \tag{7}$$

If $\omega \gg \omega_{\text{crit}}$, rectification originates from the first term in (5) and, hence, the potential drop at constant current amplitude is inversely proportional to the frequency. If $\omega \ll \omega_{\text{crit}}$, rectification originates from the second term in (5) and, hence, the potential drop at constant current amplitude is inversely proportional to the square of the frequency.

If the charge in the diffusion layer is determined mainly by positive ions, Eq. (5) will be valid again, provided that the indices are changes as follows (+) → (−), (−) → (+).

In conclusion, it is noted that the results obtained are valid only on the condition that the frequency ω is much lower than the frequency of double-layer relaxation. The latter frequency is of the order of $\omega_0 = \varkappa_-^2 D_-$.

LITERATURE CITED

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