FARADAY RECTIFICATION IN A BINARY ELECTROLYTE SOLUTION

V. G. Levich and B. M. Grafov

Corresponding Member, Academy of Sciences, USSR
Institute of Electrochemistry, Academy of Sciences, USSR

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Recently, the Faraday rectification effect [1] has begun to be used to investigate the kinetics of electrochemical reactions. When a cell is polarized by an applied sinusoidal current, in addition to the alternating voltage, some constant potential shift occurs, due to nonlinearity of the electrochemical cell. Definite conclusions may be drawn from this potential shift with regard to the rate constant and the so-called transference coefficients of the electrochemical reaction. The existing theory of Faraday rectification [1, 2] applies to a cell in which there is an excess of indifferent electrolyte. Along with this there is unquestionably interest in the rectification effect in a cell without any extraneous electrolyte, i.e., in a cell containing a binary electrolyte. We shall consider polarization of a cell containing an immobile binary electrolyte solution using relatively low frequency current, so that it will be possible to neglect the double layer capacity and the retardation effects in the diffusion part of the double layer. Further, the notation employed will be everywhere that used in [3, 4].

We shall consider the case of a quite large equilibrium potential in the plane of greatest approximation $|\bar{\psi}^{*}| \gg 1$. Then it may be assumed that the electric charge in the diffusion part of the double layer is determined principally by the charge on just one sort of ions, for example the charge on the negative ions.

Consider first the case where the negative ions participate in the electrode reaction. For the electric current density flowing through the electrode, we may write, in accordance with the theory of delayed charge [5],

$$i_{-} = z_{-} e n_{-}^{0} v_{-} \left[e^{\alpha \Delta\psi z_{-}} n_{-}^{*} / \bar{n}^{*} - e^{-\beta \Delta\psi z_{-}} \right], \tag{1}$$

where the quantity $z_{-} e n^{0}_{-} v_{-}$ is equal to the exchange current in the electrochemical reaction, and v_{-} is the reaction rate constant. We shall assume, as is usually done in discussing the Faraday rectification effect [1, 2], that the polarization of the cell is produced close to the equilibrium state by a sinusoidal current of quite small amplitude. Then, keeping only terms of first and second order of smallness in the current amplitude, Eq. (1) may be rewritten in the form

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

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

$$\langle \Delta\tilde{\psi} \rangle = \frac{\omega}{2\pi} \int_{0}^{2\pi/\omega} \Delta\tilde{\psi} \, dt. \tag{3}$$

Averaging Eq. (2) over the time, we obtain

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

In calculating the mean values from quantities of the second order of smallness of the type $\langle \Delta\widetilde{\psi}^2 \rangle$, and $\langle \Delta\widetilde{\psi}\widetilde{n}_-^* \rangle$ we can use the expressions obtained by keeping only terms of the first order of smallness, i.e., the expressions which were used to find the cell impedance [3, 4]. In what follows, the calculation of the mean values of the quantities representing the product of two alternating quantities will be carried out in this way alone.

In calculating the mean potential shifts in the diffusion part of the double layer $\langle \widetilde{\psi}^* - \widetilde{\psi}^{(d)} \rangle$ we can use the expression [3]

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

from which with an accuracy to quantities of the second order of smallness it follows that

$$\overline{\mathscr{E}}^*\widetilde{\mathscr{E}}^* + \frac{1}{2}\widetilde{\mathscr{E}}^{*2} = \varkappa_-^2 e^{z_-\overline{\psi}^*} \{\widetilde{n}_-^{(d)}/n_-^0 + z_-(\widetilde{\psi}^* - \widetilde{\psi}^{(d)}) + \\ + \frac{1}{2} z_-^2 (\widetilde{\psi}^* - \widetilde{\psi}^{(d)})^2 + z_-(\widetilde{\psi}^* - \widetilde{\psi}^{(d)})\, \widetilde{n}^{(d)}/n_-^0\}.$$

Averaging over the time gives

$$\langle \widetilde{\psi}^* - \widetilde{\psi}^{(d)} \rangle = \frac{e^{-z_-\overline{\psi}^*}}{2\varkappa_-^2 z_-} \langle \widetilde{\mathscr{E}}^{*2} \rangle + \overline{\mathscr{E}}^* \frac{\varepsilon_g}{\varepsilon\delta_g} e^{-z_-\overline{\psi}^*} \langle \Delta\widetilde{\psi} \rangle - \\ - \frac{1}{2} z_- \langle (\widetilde{\psi}^* - \widetilde{\psi}^{(d)})^2 \rangle - \langle (\widetilde{\psi}^* - \widetilde{\psi}^{(d)})\, \widetilde{n}_-^{(d)}/n_-^0 \rangle. \tag{5}$$

In calculating the mean potential shift in the diffusion region, we shall use the transference equation

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

from which, with an accuracy to terms quadratic in the current amplitude, it follows that

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

If we integrate (6) over the coordinate, and in averaging we use quantities calculated with an accuracy to the first order of smallness, it may be found that

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

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

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

Having a mean potential shift in the region adjacent to the diffusion layer (the region is electrically neutral) comes physically from a change in the fraction of the current carried by ions of a given sort. In the immediate vicinity of the diffusion layer, the current is carried mainly by ions taking part in the electrode reaction. Far from the electrode, the fraction of the current carried by ions of any given sort is determined by Ohm's law. If the diffusion coefficients of the ions are all equal, there is no potential shift in the diffusion region.

In the region where Ohm's law is obeyed, the mean potential shift is equal to zero, since there is a linear relation between the field strength and the electric current.

By using (7), (4), (5) and the results of [4], the following expression may be obtained for the mean shift in the total voltage drop:

$$\langle\widetilde{V}\rangle = \langle\Delta\widetilde{\psi}\rangle + \langle\psi^{*} - \widetilde{\psi}^{(d)}\rangle + \langle\widetilde{\psi}^{(d)} - \widetilde{\psi}^{(L)}\rangle = \\ = \frac{1}{4z_{-}}\left(\frac{i^{(0)}}{z_{-}en_{-}^{0}}\right)^{2}\left\{\frac{\beta-\alpha}{v_{-}^{2}} + \frac{1}{D_{-}\omega}\left(\frac{z_{+}D_{+}}{z_{+}D_{+}+z_{-}D_{-}}\right)^{2}\right\}. \tag{8}$$

In writing (8), we left out the quantity $\varepsilon_g(\varepsilon\delta_g\overline{\delta}^{*})^{-1}$ as being small in comparison with the difference $(\beta-\alpha)$.

The expression for the potential in a binary electrolyte is more conveniently written in terms of the amplitude of the sinusoidal current $i^{(0)}$ than in terms of the amplitude of the sinusoidal voltage $V^{(0)}$, which is equal to the voltage drop at the cell less purely Ohmic losses. This comes from the fact that the Ohmic losses in a cell with a binary electrolyte are very large, and separating out from the background of the losses the part coming from the nonlinearity of the cell (double layer, etc.) can be difficult. However there is some point in rewriting Eq. (8) in terms of the voltage amplitude $V^{(0)}$ so as to be able to compare the rectification effect in a binary electrolyte with the Faraday rectification when an indifferent electrolyte is present.

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

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

Equation (9) differs from the corresponding expression for the voltage shift when an extraneous electrolyte is present [1, 2] only in the factor $(z_{+}D_{+} + z_{-}D_{-})/[D_{+}(z_{+} + z_{-})]$. If the diffusion coefficients are equal, the difference drops out.

At high frequencies, where $\omega \gg v_{-}^{2}/D_{-}$, Eq. (8) takes the form

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

which is exactly the same as the corresponding formula for high frequencies when an indifferent electrolyte is present. This is a perfectly natural result, since the finite value of the discharge rate has an effect at high frequencies. On this basis, the voltage drop comes on the Helmholtz layer, and there is no difference between a binary electrolyte and an electrolyte with an indifferent electrolyte added.

By using the same method of calculation and the results of [3, 4], an expression may be obtained for the Faraday rectification in the case where the (positive) ions being discharged are repelled from the electrode. It has the form:

$$\langle\widetilde{V}\rangle = \langle\Delta\widetilde{\psi}\rangle + \langle\widetilde{\psi}^{*} - \widetilde{\psi}^{(d)}\rangle + \langle\widetilde{\psi}^{(d)} - \widetilde{\psi}^{(L)}\rangle = \\ = \frac{1}{4}\frac{i^{(0)2}}{z_{+}^{3}e^{2}n_{+}^{02}D_{+}^{2}}\left\{-\frac{z_{-}^{2}D_{-}^{2}D_{+}}{(z_{+}D_{+}+z_{-}D_{-})^{2}\omega} + \sqrt{2}\,\frac{-L_{\text{дв}}+L_{p}(\beta-1)}{k_{\omega}'} + \right. \\ \left. + (L_{p}+L_{\text{db}})\,[L_{\text{db}} + (2\beta-1)\,L_{p}]\right\}, \tag{11}$$

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

$$L_{p} = \frac{D_{+}}{v_{+}},\quad L_{\text{db}} = e^{(z_{+}-z_{-}/2)\overline{\psi}^{*}}\,[\varkappa_{-}\sqrt{2}\,(z_{+}-z_{-}/2)]^{-1},$$

and v_{+} is the reaction rate constant. The quantity $z_{+}en_{+}^{0}v_{+}$ is the exchange current in the electrode reaction.

Equation (11) only holds for the case where twice the charge on the positive ions is greater than the charge on the negative ions, which determine the charge in the diffusion layer, i.e., if the following inequality is satisfied:

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

If, instead of the inequality (12), the opposite inequality is satisfied, the expression obtained for the Faraday rectification is

$$\langle\widetilde{V}\rangle = \langle\Delta\widetilde{\psi}\rangle + \langle\widetilde{\psi}^{*} - \widetilde{\psi}^{(d)}\rangle + \langle\widetilde{\psi}^{(d)} - \widetilde{\psi}^{(L)}\rangle =$$
$$= \frac{1}{4}\,\frac{\tilde{i}^{(0)2}}{z_{+}^{3}e^{2}n_{+}^{(0)2}D_{+}^{2}}\left\{-\frac{z_{-}^{2}D_{-}^{2}D_{+}}{(z_{+}D_{+}+z_{-}D_{-})^{2}\omega} + \sqrt{2}\,\frac{L_{p}(\beta-1)}{k'_{\omega}} + (2\beta-1)L_{p}^{2}\right\}. \qquad (13)$$

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

Note in conclusion that the results obtained are easily generalized to the case where the charge on the diffusion layer is determined mainly by the charge on the positive ions.

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