THEORY OF FARADAIC RECTIFICATION

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Abstract

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THEORY OF FARADAIC RECTIFICATION

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When an alternating current passes through an electrolyte, in addition to an alternating voltage there also arises at the electrode a certain constant shift of potential ([1–3]). An attempt to give a theoretical interpretation of the phenomenon for the case of small currents was made in works ([4–6]). However, in the work of Doss and Agarwal ([4,5]) equality of the bulk concentrations of the oxidant and reductant and equality of their diffusion coefficients were assumed. Below we shall show that even a small difference in the diffusion coefficients may be of substantial significance. In Oldham' s work ([6]), in which the name adopted here—Faradaic rectification—was proposed, the general case is considered. In the calculation, however, necessary terms were omitted, and therefore the results obtained differ substantially from ours.

In the present work a theoretical investigation of the indicated effect is given. There are two possible paths for the passage of alternating current through the electrode surface. One path is associated with the charging and discharging of the double layer at the electrode surface. The phenomenon here is analogous to the passage of alternating current through a capacitor. The second path, which gives the Faradaic component of the alternating current proper, is directly connected with the electrochemical oxidation-reduction reaction at the electrode surface. At not too high frequencies and not too small a concentration of the reacting particles, one may neglect phenomena in the double layer and confine oneself to consideration of the Faradaic component of the alternating current. The dependence of the Faradaic component of the current on the alternating voltage at the electrode has been investigated in a number of works ([2,7–10]).

Let an alternating current i pass through an electrode of area A cm^2,

$$i = I \cos \omega t. \tag{1}$$

The flow of current is associated with an oxidation-reduction reaction at the electrode

$$\mathrm{Ox} + nele f tarrows \mathrm{Rd}. \tag{2}$$

I. Suppose that in the solution there are both oxidant ions with bulk concentration c, and reductant ions with bulk concentration $\bar{c}$. As an example one may

cite the system Fe^{3+}, Fe^{2+}/Pt-electrode, investigated in works ([4,5]).

If U is the electrode potential at $i = 0$, measured with respect to a reference electrode, then the equilibrium condition in such a system is written in the form:

$$i = \overleftarrow{i} - \vec{i} = nAFk_2\bar{c}'\, e^{\frac{n(1-\alpha)FU}{RT}} - nAFk_1 c\, e^{-\frac{n\alpha FU}{RT}} = 0. \tag{3}$$

Here $\overleftarrow{i}$ and $\vec{i}$ are the exchange currents. At equilibrium they are equal to one another. k_1, k_2 (cm/sec) characterize the reaction rate, and α is a coefficient having a value between zero and unity.

When an alternating current passes, the potential of the electrode changes. We shall denote this change by φ. Since the current is a periodic function of time, it is evident that the electrode potential will change with the same period. In this case

$$i = I\cos\omega t = \overleftarrow{i} - \vec{i}, \tag{4}$$

$$\overleftarrow{i} = nAFk_2c_0' \exp\left\{\frac{n(1-\alpha)}{RT}F(U+\varphi)\right\},$$

$$\vec{i} = nAFk_1c_0 \exp\left\{-\frac{n\alpha}{RT}F(U+\varphi)\right\}. \tag{5}$$

We assume that a capacitor is connected in series with the electrode in the circuit, so that a constant component cannot appear in the current. c_0 and c_0' are the concentrations of ions at the electrode surface. These quantities are found by solving the diffusion equation $\partial c/\partial t = D\,\partial^2 c/\partial x^2$ with the boundary conditions $c = \bar{c}$ as $x \to \infty$ for any t, and $(c)_t = (c)_{t+\frac{2\pi}{\omega}m}$ for integer m and any x. (Analogously also for c'.) In addition, we must relate the current to the concentration gradient at the electrode surface:

$$i = -\left[e_1 D\left(\frac{\partial c}{\partial x}\right)_0 + e_2 D'\left(\frac{\partial c'}{\partial x}\right)_0\right] FA. \tag{6}$$

Here e_1 and e_2 are the charges of the Ox and Rd ions, and D and D' are their diffusion coefficients. The fluxes of Ox and Rd ions are easily related to one another. Since each Ox ion corresponds to an Rd ion and their fluxes are directed in opposite directions, $D(\partial c/\partial x)_0 = -D'(\partial c'/\partial x)_0$. We do not take ion migration into account, assuming that there is an excess of indifferent electrolyte in the solution.

Under these conditions we obtain:

$$c_0 = \bar{c}\left[1 + q\sin\left(\frac{\pi}{4} + \omega t\right)\right] \tag{7}$$

and an analogous expression for c':

$$q = \frac{I}{nAF\bar{c}\sqrt{D\omega}}; \qquad q' = -\frac{I}{nAF\bar{c}'\sqrt{D'\omega}}. \tag{8}$$

We substitute the obtained concentration values into (5). Relation (4) gives the connection between the current and the potential φ. We eliminate from this relation the equilibrium potential U $\left(e^{\frac{nF}{RT}U} = \frac{k_1}{k_2}\frac{\bar{c}}{\bar{c}'}\right)$ from (3). Taking the current, and consequently the corresponding shift of potential, to be small and expanding the exponential functions in a series up to terms of second order of smallness, we obtain

$$\frac{I\cos\omega t}{nAFk\bar{c}}\left(\frac{\bar{c}}{\bar{c}'}\right)^{\alpha} = \frac{nF}{RT}\varphi + \frac{1-2\alpha}{2}\left(\frac{nF}{RT}\varphi\right)^2 + (q-q')\sin\left(\frac{\pi}{4} + \omega t\right) +$$

$$+ [q'(1-\alpha)\varphi + q\alpha\varphi]\frac{nF}{RT}\sin\left(\frac{\pi}{4} + \omega t\right), \tag{9}$$

where $k = k_1^{1-\alpha}k_2^{\alpha}$.

We expand the periodic function φ in a Fourier series. It is sufficient to restrict ourselves to the first harmonic, since the remaining terms give only small corrections.

$$\varphi = \psi + V_1\cos\omega t + \widetilde{V}_1\sin\omega t = \psi + V\cos(\omega t + \vartheta). \tag{10}$$

From equation (9), equating the coefficients of the different harmonics, we find the relation between the amplitude of the alternating voltage V and the current I, the phase shift of the alternating voltage ϑ, and the dependence of the constant component

shift of the potential ψ due to the alternating voltage. The latter relation is of greatest interest:

$$\psi = \left(\alpha - \frac{1}{2}\right)\frac{nF}{2RT}V^2 - \frac{nF}{2RT}\frac{V^2}{G}\left(\alpha - \frac{\tau\sqrt{\dfrac{D}{D'}}}{1+\tau\sqrt{\dfrac{D}{D'}}}\right)\left(1 + \frac{\sqrt{D\omega}\,\tau^{-\alpha}}{\sqrt{2}\,k\left(1+\tau\sqrt{\dfrac{D}{D'}}\right)}\right), \tag{11}$$

where

$$\tau = \frac{\bar{c}}{\bar{c}'}, \qquad G = \left[1 + \frac{\tau^{-\alpha}\sqrt{2D\omega}}{k\left(1+\tau\sqrt{\frac{D}{D'}}\right)} + \frac{\tau^{-2\alpha}D\omega}{k^2\left(1+\tau\sqrt{\frac{D}{D'}}\right)^2} \right]. \qquad (12)$$

The appearance of a constant shift of the potential at the electrode when an electric current passes through it is easy to understand if one takes into account that relations (5) are not symmetric with respect to the sign of φ. The quantity ψ, as it were, correspondingly equalizes the rates of the forward and reverse reactions. From these same considerations it is clear that ψ must become zero if relations (5) are symmetric, and this will occur under the condition $\bar{c} = \bar{c}'$, $D = D'$, $\alpha = 1/2$.

Indeed, under these conditions, as is seen from (11), $\psi = 0$. The corresponding formula obtained in work [6] gives the vanishing of ψ at $\bar{c} = \bar{c}'$, $D = D'$ and arbitrary α. The inaccuracy consists in the fact that, in the calculation method adopted in work [6], it is necessary to retain in the exponent terms not only with the first but also with the second harmonic of the expansion of φ. Formula (11) is somewhat simplified if the bulk concentrations of the reacting ions are equal to each other, $\bar{c} = \bar{c}'$, i.e. $\tau = 1$. In this case

$$\psi = \left(\alpha - \frac{1}{2}\right)\frac{nF}{2RT}V^2 - \frac{nF}{2RT}\frac{V^2}{G'}\left(\alpha - \frac{1}{1+\sqrt{\frac{D'}{D}}}\right)\left(1 + \frac{\sqrt{D\omega}}{\sqrt{2}\,k\left(1+\sqrt{\frac{D}{D'}}\right)}\right), \qquad (13)$$

where $G' = G$ at $\tau = 1$.

In the limiting case $k \gg \sqrt{D\omega}$

$$\psi = \frac{nF}{2RT}V^2\left(\frac{1}{1+\sqrt{\frac{D'}{D}}} - \frac{1}{2}\right) + \frac{nF}{2RT}V^2\left(\alpha - \frac{1}{1+\sqrt{\frac{D'}{D}}}\right)\frac{\sqrt{D\omega}}{\sqrt{2}\,k\left(1+\sqrt{\frac{D}{D'}}\right)}. \qquad (14)$$

For $k \ll \sqrt{D\omega}$

$$\psi = \left(\alpha - \frac{1}{2}\right)\frac{nF}{2RT}V^2 - \frac{nF}{2RT}V^2\left(\alpha - \frac{1}{\sqrt{\frac{D}{D'}}+1}\right)\frac{k\left(1+\sqrt{\frac{D}{D'}}\right)}{\sqrt{2D\omega}}. \quad (15)$$

From the expressions obtained it is seen that the quantity ψ depends on α. By measuring experimentally the quantities V and ψ, one can use the formulas obtained to find α. Doss and Agarwal [4,5] were the first to draw attention to this. The formula [5] derived by them corresponds to (13) under the condition that $D = D'$. However, if α is close to one half, even a small difference in the diffusion coefficients may prove very significant, and therefore for determining α one must use formulas (11) or (13).

II. A potential shift ψ also arises in the case when only ions of the oxidizing agent are present in the solution. An example may be a metal electrode immersed in a solution containing its ions.

In this case there is an excess of the reducing agent in the surface layer, and the oxidation rate does not depend on the concentration of the reducing agent. In equations (5) and (9) we must then put $q' = 0$. The calculation is carried out in an analogous way. Finally we obtain:

$$\psi = \left(\alpha - \frac{1}{2}\right)\frac{nF}{2RT}V^2 - \frac{\alpha}{2}\frac{nF}{RT}V^2\frac{1+\frac{\tau^\alpha\sqrt{D\omega}}{\sqrt{2}k}}{1+\frac{\sqrt{2D\omega}\,\tau^\alpha}{k}+\frac{D\omega}{k^2}\tau^{2\alpha}}. \quad (16)$$

For $k \gg \tau^\alpha\sqrt{D\omega}$

$$\psi = -\frac{1}{4}\frac{nF}{RT}V^2. \quad (17)$$

In the opposite limiting case, $k \ll \tau^\alpha\sqrt{D\omega}$,

$$\psi = \left(\alpha - \frac{1}{2}\right)\frac{nF}{2RT}V^2 - \frac{\alpha}{2}\frac{nF}{RT}V^2\frac{k}{\tau^\alpha\sqrt{2D\omega}}. \quad (18)$$

In work ([6]) the system $Hg_2^{2+} + 2eleftharpoons2Hg$ was investigated. Although the general formula for ψ, for the same reasons as we have already indicated, is incorrect, the limiting case $k \gg \tau^\alpha\sqrt{D\omega}$ coincides with (17). The experimental verification carried out in ([6]) in fact related to this limiting case, although the frequency ω was varied from 20 to 5000 rev/sec. (at high frequencies it is necessary to take into account the current associated with charging the double layer).

It was found (from measurements of V and ψ) that the quantity $\frac{2RT\psi}{FV^2}$ varied within the limits from -1.26 to -0.84, i.e., formula (17) was well confirmed ($n = 2$).

However, in order to confirm the general formula (and to determine α), it is necessary to study experimentally the case $k \ll \tau^{\alpha}\sqrt{D\omega}$.

In the calculations we did not take into account the influence of the double layer, in particular on the value of the surface concentration.

In conclusion I take this opportunity to express my gratitude to Academician A. N. Frumkin, who drew my attention to the question considered, and to Prof. V. G. Levich for a useful discussion.

Note added in proof. When the present work had already been submitted for publication, a letter ([11]) appeared in which a formula for the potential shift is given, apparently analogous to the one obtained by us.

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