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## Abstract

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# Faradaic Rectification of an Electrolyte-Semiconductor Contact

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When an alternating current passes through an electrochemical cell, in addition to the alternating voltage, a certain constant potential shift is also produced at the electrode. This effect, called Faradaic rectification, is at present one of the fundamental methods for studying electrochemical reactions (1-6). In theoretical work, however, only the case of an electrolyte-metal boundary has been considered. In the present article the magnitude of Faradaic rectification is calculated for an electrolyte-semiconductor contact, and its connection with the electrochemical properties of the semiconductor is established.

Let the passage of current be associated with the oxidation-reduction reaction at the electrode $\mathrm{Ox} + me \rightleftarrows \mathrm{Rd}$. The special features of the electronic structure of the semiconductor are manifested in the fact that the reaction can proceed with the participation of electrons from two bands. Namely, electrons from solution ions can pass both into the valence band and into the conduction band; accordingly, the system is characterized by two exchange currents $i_0^{(p)}$ and $i_0^{(e)}$. The total current $i$ is equal to $i = i^+ - i^-$, where $i^+$ and $i^-$ are the hole and electron currents. Neglecting the potential drop in the Helmholtz layer and assuming that the rate of the electrochemical reaction is proportional to the concentration of the participating reactants, we obtain, in accordance with (7), the following expression for the currents at the contact:

$$\begin{aligned} i_s^+ &= me\left[k_1' C_s - k_2' C_s' \frac{p_s}{p_\infty}\right] = i_0^{(p)}\left[\frac{C_s}{C_\infty} - \frac{C_s'}{C_\infty'}\frac{p_s}{p_\infty}e^{eU/kT}\right], \\ i_s^- &= me\left[k_2 C_s' - k_1 C_s \frac{n_s}{n_\infty}\right] = i_0^{(e)}\left[\frac{C_s'}{C_\infty'} - \frac{C_s}{C_\infty}\frac{n_s}{n_\infty}e^{-eU/kT}\right]. \end{aligned} \tag{1}$$

Here and below the notation of work (7) is used.

Let a periodic alternating-current signal $\tilde{i}$ be passed through the electrolyte-semiconductor boundary (for definiteness, we shall consider an $n$-type semiconductor), its amplitude being so small that the corresponding potential $\tilde{\varphi}$ satisfies the condition $|e\tilde{\varphi}_s/kT| \ll 1$. As is usually done in considering the Faradaic rectification effect, we assume that the system is close to equilibrium (3). Starting from the Boltzmann distribution, we obtain for the alternating concentration of holes at the contact, accurate to quantities of second order of smallness,

$$\tilde{p}_s = e^{-eU/kT}\left\{\tilde{p}_d - p_\infty\left[e\tilde{\varphi}_s/kT - \frac{1}{2}\left(e\tilde{\varphi}_s/kT\right)^2\right] - \tilde{p}_d e\tilde{\varphi}_s/kT\right\}. \tag{2}$$

By virtue of the quasineutrality of the diffusion region in the semiconductor, $\tilde{n}_d = \tilde{p}_d$; hence it is easy to write for $\tilde{n}_s$ a formula analogous to (2), expressing $\tilde{n}_s$ in terms of $\tilde{p}_d$, $\tilde{\varphi}_s$, and $n_\infty$. Taking account of what has been said above, from (1) and (2) we obtain

$$\begin{gathered}\frac{1}{me}\tilde{i}_s^{+} = k_1'\tilde{C}_s - k_2' e^{-eU/kT}\left[\tilde{C}_s' + C_\infty'\left(\frac{\tilde{p}_d}{p_\infty} - \frac{e\tilde{\varphi}_s}{kT} + \frac{1}{2}\left(\frac{e\tilde{\varphi}_s}{kT}\right)^2 - \frac{\tilde{p}_d}{p_\infty}\frac{e\tilde{\varphi}_s}{kT}\right) + \frac{\tilde{p}_d}{p_\infty}\tilde{C}_s' - \tilde{C}_s'\frac{e\tilde{\varphi}_s}{kT}\right], \\ \frac{1}{me}\tilde{i}_s^{-} = k_2\tilde{C}_s' - k_1 e^{eU/kT}\left[\tilde{C}_s + C_\infty\left(\frac{\tilde{p}_d}{n_\infty} + \frac{e\tilde{\varphi}_s}{kT} + \frac{1}{2}\left(\frac{e\tilde{\varphi}_s}{kT}\right)^2 + \frac{\tilde{p}_d}{n_\infty}\frac{e\tilde{\varphi}_s}{kT}\right) + \frac{\tilde{p}_d}{n_\infty}\tilde{C}_s + \tilde{C}_s\frac{e\tilde{\varphi}_s}{kT}\right].\end{gathered} \tag{3}$$

We shall find the constant component of the potential, equal to the mean value of the potential over a period,

$$\langle\tilde{\varphi}_s\rangle \equiv \frac{1}{T}\int_0^T \tilde{\varphi}_s(t)\,dt,$$

by averaging equations (3). Since $\tilde{C}_s$ and $\tilde{C}_s'$ are proportional to the current $\tilde{i}_s$, which, by assumption, is strictly periodic, $\langle\tilde{C}_s'\rangle = \langle\tilde{C}_s\rangle = 0$. In exactly the same way, from the equality $\tilde{i} = \tilde{i}^{+} - \tilde{i}^{-}$ it follows that $\langle\tilde{i}_s^{+}\rangle = \langle\tilde{i}_s^{-}\rangle$. Taking the above into account, from (3) we obtain

$$\begin{gathered}\langle\tilde{i}_s^{+}\rangle = -\,i_0^{(p)}\left[\frac{\langle\tilde{p}_d\rangle}{p_\infty} - \left\langle\frac{e\tilde{\varphi}_s}{kT}\right\rangle + \langle\Phi_1\rangle\right], \\ \langle\tilde{i}_s^{-}\rangle = -\,i_0^{(e)}\left[\frac{\langle\tilde{p}_d\rangle}{n_\infty} + \frac{\langle e\tilde{\varphi}_s\rangle}{kT} + \langle\Phi_2\rangle\right],\end{gathered} \tag{4}$$

where

$$\begin{gathered}\Phi_1 = \frac{1}{2}\left(\frac{e\tilde{\varphi}_s}{kT}\right)^2 - \frac{\tilde{p}_d}{p_\infty}\frac{e\tilde{\varphi}_s}{kT} + \frac{\tilde{p}_d}{p_\infty}\frac{\tilde{C}_s'}{C_\infty'} - \frac{e\tilde{\varphi}_s}{kT}\frac{\tilde{C}_s'}{C_\infty'}, \\ \Phi_2 = \frac{1}{2}\left(\frac{e\tilde{\varphi}_s}{kT}\right)^2 + \frac{\tilde{p}_d}{n_\infty}\frac{e\tilde{\varphi}_s}{kT} + \frac{\tilde{p}_d}{n_\infty}\frac{\tilde{C}_s}{C_\infty} + \frac{e\tilde{\varphi}_s}{kT}\frac{\tilde{C}_s}{C_\infty}.\end{gathered} \tag{5}$$

Since $\langle \Phi_1 \rangle$ and $\langle \Phi_2 \rangle$ are mean values of quantities of second order of smallness, in calculating them one may use the expressions obtained when retaining only quantities of first order of smallness.

Assuming, in accordance with (7), that the value of the hole current at the contact $\tilde{i}_s^+$ coincides with its value $\tilde{i}_d^+$ at the boundary of the space-charge region and the diffusion region, we obtain $\langle \tilde{i}_s^+ \rangle = \langle \tilde{i}_d^+ \rangle$.

For a comparative estimate of the terms entering into (4), we average the continuity equation

$$\frac{1}{e}\,\mathrm{div}(\tilde{i}^+) + \frac{\partial \tilde{p}}{\partial t} + \frac{\tilde{p}}{\tau} = 0.$$

Here $\tau$ is the lifetime of holes. The function $\tilde{p}(t)$ is periodic; therefore $\langle \partial\tilde{p}/\partial t \rangle = 0$. Then, in order of magnitude, we obtain

$$\langle \tilde{i}^+ \rangle \sim eD_+ \frac{\langle \tilde{p} \rangle}{L},$$

where $L$ is the diffusion length. Hence the term $i_0^{(p)} \langle \tilde{p}_d \rangle / p_\infty$, entering into (4), is, in order of magnitude, equal to

$$i_0^{(p)} \langle \tilde{i}_d^+ \rangle \frac{L}{ep_\infty D_+}.$$

Since the exchange currents $i_0^{(p)}$ and $i_0^{(e)}$ are small in comparison with the limiting diffusion current of holes

$$i_p \equiv e\frac{D_+}{L} p_\infty,$$

the term $i_0^{(p)} \langle \tilde{p}_d \rangle / p_\infty$ is small in comparison with $\langle \tilde{i}_s^+ \rangle$ in the ratio $i_0^{(p)}/i_p$. Similarly,

$$i_0^{(e)} \langle \tilde{p}_d \rangle / n_\infty \ll \langle \tilde{i}_s^- \rangle.$$

Taking these remarks into account, from (4) we find:

$$\left\langle \frac{e\tilde{\varphi}_s}{kT} \right\rangle = \frac{1}{i_0}\left( i_0^{(p)} \langle \Phi_1 \rangle - i_0^{(e)} \langle \Phi_2 \rangle \right), \qquad \langle \tilde{i}_s^+ \rangle = -\frac{i_0^{(p)} i_0^{(e)}}{i_0} \left( \langle \Phi_1 \rangle + \langle \Phi_2 \rangle \right). \tag{6}$$

Here $i_0 \equiv i_0^{(p)} + i_0^{(e)}$.

Relations (6) take into account the mean shift of the potential only in the space-charge region.

An estimate of the mean shift of the potential $\langle\tilde{\varphi}_L\rangle$ in the diffusion region gives

$$\left\langle \frac{e\tilde{\varphi}_L}{kT} \right\rangle \sim \frac{\langle \tilde{i}^- \rangle}{i_p} \frac{p_\infty}{n_\infty}. \tag{7}$$

On the other hand, from (6) we obtain, to order of magnitude,

$$\langle e\varphi_s \rangle / kT \sim \langle \tilde{i}_s^+ \rangle / i_0.$$

Comparison of $\langle\tilde{\varphi}_s\rangle$ and $\langle\tilde{\varphi}_L\rangle$ using (7) gives

$$\frac{\langle\tilde{\varphi}_L\rangle}{\langle\tilde{\varphi}_s\rangle} \sim \frac{\langle \tilde{i}_s \rangle}{\langle \tilde{i}_s^+ \rangle} \times \frac{i_0}{i_p} \frac{p_\infty}{n_\infty}.$$

Since $\langle \tilde{i}_s^- \rangle = \langle \tilde{i}_s^+ \rangle$, $i_0 \ll i_p$, and also $p_\infty \ll n_\infty$, we obtain that $\langle\tilde{\varphi}_L\rangle$ is much smaller than $\langle\tilde{\varphi}_s\rangle$, and the rectifying action of the diffusion region in the semiconductor may be neglected.

In the Helmholtz layer the potential drop is $\tilde{\varphi}_r \sim d_0 \tilde{E}_s$, where $d_0$ is the thickness of the layer; $\tilde{E}_s \sim C_0 \tilde{\varphi}_s$, where $C_0$ is the static capacitance of the semiconductor. Hence we have $\langle\tilde{\varphi}_r\rangle \sim C_0 d_0 \langle\tilde{\varphi}_s\rangle$, and the rectifying action of the Helmholtz layer may also be neglected, since $C_0 d_0 \ll 1$. In the diffusion part in the electrolyte there is no rectification, since the solution contains an excess of indifferent electrolyte. Thus, the total Faradaic rectification of the contact may be considered to be described by formula (6).

The quantities entering into $\Phi_1$ and $\Phi_2$, for the case of a sinusoidal signal ($\tilde{i} \sim e^{i\omega t}$), were found to first order of smallness in (7). Estimates of the terms entering into $\Phi_1$ and $\Phi_2$ show that

$$\left\langle \left( \frac{e\tilde{\varphi}_s}{kT} \right)^2 \right\rangle \sim \left( \frac{\tilde{i}_s}{i_0} \right)^2, \quad \left\langle \frac{\tilde{p}_d}{p_\infty} \frac{e\tilde{\varphi}_s}{kT} \right\rangle \sim \frac{\tilde{i}_s^2}{i_p i_0}, \quad \left\langle \frac{e\tilde{\varphi}_s}{kT} \frac{\tilde{C}_s'}{C_\infty'} \right\rangle \sim \frac{\tilde{i}_s^2}{i_D i_0}, \quad \left\langle \frac{\tilde{p}_d}{p_\infty} \frac{\tilde{C}_s'}{C_\infty'} \right\rangle \sim \frac{\tilde{i}_s^2}{i_p i_D},$$

where $i_D \equiv eC_\infty' \sqrt{D'\omega}$. Numerical estimates show that usually $i_D \gg i_p$. Taking this into account, as well as the condition $i_0 \ll i_p$, we obtain:

$$\langle \Phi_1 \rangle = \frac{1}{2} \left\langle \left( \frac{e\tilde{\varphi}_s}{kT} \right)^2 \right\rangle - \left\langle \frac{\tilde{p}_d}{p_\infty} \frac{e\tilde{\varphi}_s}{kT} \right\rangle, \qquad \langle \Phi_2 \rangle = \frac{1}{2} \left\langle \left( \frac{e\tilde{\varphi}_s}{kT} \right)^2 \right\rangle. \tag{8}$$

Here only terms not smaller than of order $\tilde{i}_s^2/i_0 i_p$ have been retained.

As is known, the quantity

$$\tilde{i}_\infty \equiv \tilde{i} + \frac{\varepsilon}{4\pi}\frac{\partial \tilde{E}}{\partial t}$$

does not depend on the coordinates. Far from the contact, $\partial \tilde{E}/\partial t \ll \tilde{i}$, and $\tilde{i}_\infty$ has the meaning of the carrier current in the bulk of the semiconductor. Since

$$\frac{\varepsilon}{4\pi}\frac{\partial \tilde{E}_s}{\partial t} = i\omega C_0 \tilde{\varphi}_s,$$

where $C_0$ is the space-charge capacitance, for the carrier current at the contact we obtain

$$\tilde{i}_s = \tilde{i}_\infty - i\omega C_0 \tilde{\varphi}_s.$$

In accordance with (7),

$$\tilde{p}_d = \gamma \tilde{i}_s \left\{ e\sqrt{D_+(i\omega + \tau^{-1})} \right\}^{-1}, \qquad \tilde{i}_s = (1/R + i\omega C_D)\tilde{\varphi}_s,$$

where $R$ is the electrode resistance, $C_D$ is the diffusion capacitance, and $\gamma$ is the ratio of the hole current to the total charge current at the contact. Hence

$$\tilde{\varphi}_s = \frac{\tilde{i}_\infty}{1/R + i\omega(C_D + C_0)}, \qquad \tilde{p}_d = \tilde{i}_\infty \frac{1/R + i\omega C_D}{1/R + i\omega(C_D + C_0)} \frac{\gamma}{e\sqrt{D_+(i\omega + \tau^{-1})}}. \tag{9}$$

Using (8) and (9) and calculating the mean values by means of the relation

$$\langle a(t) b(t) \rangle = \frac{1}{2} \operatorname{Re}[a(t) b^*(t)],$$

we find:

$$\langle \tilde{\varphi}_s \rangle = \frac{i_0^{(p)} - i_0^{(e)}}{i_0} \frac{e}{kT} \frac{1}{4} \frac{|\tilde{i}_\infty|^2}{(1/R)^2 + \omega^2 (C_0 + C_D)^2} - \frac{i_0^{(p)}}{i_0} \frac{\gamma}{2} \frac{\sqrt{1/R^2 + (\omega C_D)^2}}{e p_\infty \sqrt[4]{D_+^2(\tau^{-2} + \omega^2)}} \frac{|\tilde{i}_\infty|^2}{1/R^2 + \omega^2 (C_0 + C_D)^2}. \tag{10}$$

Here $|\tilde{i}_\infty|$ denotes the amplitude of the current $\tilde{i}_\infty$.

Relation (10) gives the general expression for the magnitude of the Faradaic rectification.

The first term in (10) is entirely due to the kinetics of the electrochemical reaction at the contact and may be either positive or negative. Since the alternating signal does not explicitly distinguish a definite direction in the system, let us consider the physical effect that leads to the appearance of one or another sign of the potential-displacement quantity. Suppose, for example, $i_0^{(p)} > i_0^{(e)}$, i.e., the reaction proceeding through the valence band predominates. Then, when current is passed in the positive direction, as follows from (1), the potential $\widetilde{\varphi}_s$ will shift in the positive direction by an amount $\Delta\varphi_1$. In the following half-period, when the current is negative, the change in potential occurs in the opposite direction by an amount $\Delta\varphi_2$. By condition, the current in both directions is the same. But since the changes in current are proportional to the change of the exponential $\Delta\tilde{i} \sim -\Delta e^{-e\varphi/kT}$, and equal increments of the exponential in the positive and negative directions correspond to different changes of the argument, $|\Delta\varphi_1| > |\Delta\varphi_2|$, and the constant displacement is positive in accordance with (10). If, however, $i_0^{(e)} > i_0^{(p)}$, analogous considerations lead to the conclusion that the first term is negative. The second term in (10) is associated with diffusion effects and is always negative.

If $i_0^{(p)}$ is not too close to $i_0^{(e)}$, then, as follows from the estimates given earlier, the second term in (10) is small compared with the first in the ratio $i_0/i_p$, and it may be neglected. Substituting into (10) the value of $R$ from (7) and taking into account that $1/R \gg \omega C_D$, we obtain, in the case under consideration,

$$\langle\widetilde{\varphi}_s\rangle = \frac{i_0^{(p)} - i_0^{(e)}}{i_0} \frac{1}{4} \frac{kT}{e} \frac{|\tilde{i}_\infty|^2}{i_0^2} \frac{1}{1 + \left(\dfrac{kTC_0}{ei_0}\omega\right)^2}. \tag{11}$$

If $(i_0^{(p)} - i_0^{(e)})/i_0 \ll i_0/i_p$, diffusion effects predominate. Then

$$\langle\widetilde{\varphi}_s\rangle = \frac{1}{8} \frac{kT}{e} \frac{|\tilde{i}_\infty|^2}{i_0^2} \frac{1}{1 + \left(\dfrac{kTC_0}{ei_0}\omega\right)^2} \cdot \frac{i_0}{i_p \sqrt[4]{1 + (\tau\omega)^2}}. \tag{12}$$

As follows from (11) and (12), a strong dependence of the quantity $\langle\widetilde{\varphi}_s\rangle$ on frequency ($\sim \omega^{-2}$) begins at frequencies exceeding a certain characteristic frequency $\omega_0$, determined by the equality $\omega_0 = ei_0/C_0kT$. Taking $i_0 \sim 10^{-5}$ and $C_0 \sim 10^{-4}$ cm$^{-1}$, we obtain $\omega_0 \sim 3 \cdot 10^4$ sec$^{-1}$.

It is of interest to compare the magnitude of the Faradaic rectification (11) with the analogous quantity in other systems. On metals[6], in the presence of a chemical reaction, in order of magnitude $\langle e\widetilde{\varphi}_s/kT\rangle_M \sim |\tilde{i}_\infty|^2/(i_0^{(M)})^2$, where

$i_0^{(M)}$ is the exchange current at the metallic electrode. Comparison with (11) shows that a larger effect may be expected on semiconductors at the same current amplitude, since $i_0$ is usually smaller than $i_0^{(M)}$ [8]. Estimates for $n$–$p$ junctions show that $\langle e\widetilde{\varphi}_s/kT\rangle_{\text{pr}} \sim (|\widetilde{i}_\infty|/i_{\text{pr}})^2$, where $i_{\text{pr}}$ is the larger of the two limiting currents of the $n$–$p$ junction, which, generally speaking, considerably exceeds $i_0$. Hence $\langle\widetilde{\varphi}_s\rangle_{\text{pr}} \ll \langle\widetilde{\varphi}_s\rangle$. From the estimates given it is clear that an electrochemical cell with a semiconductor electrode is a system in which the effect of Faradaic rectification can be manifested most distinctly.

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## CITED LITERATURE

1. K. S. G. Doss, H. P. Agarwall, Proc. Ind. Acad. Sci., **34**, Sec. A, 229 (1951).
2. K. B. Oldham, Trans. Farad. Soc., **53**, 80 (1957).
3. Yu. A. Vdovin, DAN, **120**, 554 (1958).
4. G. C. Barker, Trans. Simposium on Electrode Processes, Philadelphia, 1959.
5. V. G. Levich, B. M. Grafov, DAN, **146**, 1372 (1962).
6. V. G. Levich, B. M. Grafov, DAN, **147**, 1402 (1962).
7. V. A. Myamlin, Yu. A. Pureshevich, DAN, **155**, No. 1 (1964).
8. R. R. Dogonadze, Yu. A. Chizmadzhev, DAN, **150**, 333 (1963).

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