

THE FARADAY RECTIFICATION FOR AN ELECTROLYTE-SEMICONDUCTOR CONTACT

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When an alternating current passes through an electrochemical cell, there is produced at the electrode, in addition to an alternating voltage, a certain constant potential displacement. This effect, which is called Faraday rectification, now provides a fundamental method for studying electrochemical reactions [1-6]. Theoretical papers, however, deal only with the case of an electrolyte-metal boundary. In the present paper we have calculated the magnitude of the Faraday rectification for an electrolyte-semiconductor contact and established its relationship to the electrochemical properties of the semiconductor.

Let us assume that the passage of current is associated with a redox reaction at the electrode $Ox + me \rightleftharpoons Red$. As a result of the characteristic features of the electronic structure of the semiconductor, the reaction can take place with the participation of electrons from two zones. Thus, the electrons from the ions in the solution may move into the valence zone or into the conductivity zone, so that the system is characterized by two exchange currents $i_0^{(p)}$ and $i_0^{(e)}$. The total current $i = i^+ - i^-$, where i^+ and i^- represent 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 reagents taking part, we obtain, in accordance with [7], the following expression for the current at the contact:

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

Here and subsequently the symbols adopted in [7] are used.

Let us assume that the periodic signal of an alternating current $\tilde{i}$ passes through an electrolyte-semiconductor boundary (in order to be specific we shall consider a semiconductor of the n-type) and that its amplitude is so small that the corresponding potential $\tilde{\varphi}$ satisfies the condition $|e\tilde{\varphi}_s/kT| \ll 1$. As is usually done in an examination of the Faraday rectification effect, we shall assume that the system is close to the equilibrium position [3]. From the Boltzmann distribution we obtain, for the varying concentration of holes at the contact, with an accuracy up to quantities of the second order of smallness,

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

As a result of the quasineutrality of the diffusion region in the semiconductor, $\tilde{n}_d = \tilde{p}_d$, from which we can readily obtain for $\tilde{n}_s$ a formula analogous to (2), expressing $\tilde{n}_s$ in terms of $\tilde{p}_d$, $\tilde{\varphi}_s$, and n_∞ . From the above and (1) and (2) we obtain

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

$$\frac{1}{me} \tilde{i}_s^- = k_2 \tilde{C}_s' - k_1 e^{U/kT} \left[\tilde{C}_s + C_\infty \left(\frac{\tilde{p}_d}{n_\infty} + \frac{e\tilde{\varphi}_s}{kT} + \frac{1}{2} \left(\frac{e\tilde{\varphi}_s}{kT} \right)^2 + \frac{\tilde{p}_d}{n_\infty} \frac{e\tilde{\varphi}_s}{kT} \right) + \frac{\tilde{p}_d}{n_\infty} \tilde{C}_s + \tilde{C}_s \frac{e\tilde{\varphi}_s}{kT} \right].$$

The constant component of the potential, which is equal to the average value of the potential in the period

$$\langle \tilde{\varphi}_s \rangle = \frac{1}{T} \int_0^T \tilde{\varphi}_s(t) dt, \quad \text{can be found by averaging Eq. (3). Since } \tilde{C}_s \text{ and } \tilde{C}_s' \text{ are proportional to the current } \tilde{i}_s,$$

which according to the given condition is strictly periodic, $\langle \tilde{C}_s' \rangle = \langle \tilde{C}_s \rangle = 0$. In exactly the same way, from the equation $\tilde{i} = \tilde{i}^+ - \tilde{i}^-$, it follows that $\langle \tilde{i}_s^+ \rangle = \langle \tilde{i}_s^- \rangle$. From the above and (3) we obtain

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

where

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

Since $\langle \Phi_1 \rangle$ and $\langle \Phi_2 \rangle$ are the average values of quantities of the second order of smallness, they can be calculated using expressions obtained retaining only quantities of the second 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 volume 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 appearing in (4), we average the continuity equation $1/e \operatorname{div}(\tilde{i}^+) + \frac{\partial \tilde{p}}{\partial t} + \frac{\tilde{p}}{\tau} = 0$. Here τ is the life-time of the holes. The function $\tilde{p}(t)$ is periodic, so that $\langle \partial \tilde{p} / \partial t \rangle = 0$. In order of magnitudes, therefore, $\langle \tilde{i}^+ \rangle \sim eD_+ \langle \tilde{p} \rangle / L$ (L is the diffusion length). From this the term $i_0^{(p)} \langle \tilde{p}_d \rangle / p_\infty$, appearing in (4) in order of magnitude is equal to $i_0^{(p)} \langle \tilde{i}_d^+ \rangle L / ep_\infty D_+$. Since the exchange currents $i_0^{(p)}$ and $i_0^{(e)}$ are small compared with the limiting diffusion current of the holes $i_p \equiv e \frac{D_+}{L} p_\infty$, the term $i_0^{(p)} \langle \tilde{p}_d \rangle / p_\infty$ is small compared with $\langle \tilde{i}_s^+ \rangle$ in the ratio $i_0^{(p)} / i_p$. In analogous fashion, $i_0^{(e)} \langle \tilde{p}_d \rangle / n_\infty \ll \langle \tilde{i}_s^- \rangle$. From the above we obtain from (4)

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

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

Relationships (6) take account of the average displacement of the potential only in the volume charge region.

Estimation of the average potential displacement $\langle \tilde{\Phi}_L \rangle$ in the diffusion range gives

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

On the other hand, from (6) we obtain in order of magnitude $\langle e\tilde{\varphi}_s \rangle / kT \sim \langle \tilde{i}_s^+ \rangle / i_0$. Comparison of $\langle \tilde{\varphi}_s \rangle$ and $\langle \tilde{\varphi}_L \rangle$ and use of (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 $p_\infty \ll n_\infty$, we find that $\langle \tilde{\varphi}_L \rangle$ is much less than $\langle \tilde{\varphi}_s \rangle$, and the rectifying action of the diffusion region in the semiconductor can be neglected.

In the Helmholtz layer the potential drop $\tilde{\varphi}_r \sim d_0 \tilde{E}_s$, where d_0 is the thickness of the layer and $\tilde{E}_s \sim C_0 \tilde{\varphi}_s$, where C_0 is the static capacity of the semiconductor. From this 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 can also be neglected, since $C_0 d_0 \ll 1$. There is no rectification in the diffusion region in the electrolyte, since the solution contains an excess of indifferent electrolyte. It may thus be assumed that the total Faraday rectification of the contact is described by formula (6).

The quantities appearing in Φ_1 and Φ_2 for the case of a sinusoidal signal ($\tilde{i} \sim e^{i\omega t}$) in the first order of smallness, were found in [7]. Estimation of the terms appearing in Φ_1 and Φ_2 shows 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 estimation shows that usually $i_D \gg i_p$. From this and the condition $i_0 \ll i_p$ we obtain

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

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

It is known that the quantity $\tilde{i}_\infty \equiv \tilde{i} + \frac{e}{4\pi} \frac{\partial \tilde{E}}{\partial t}$ is independent of the coordinates. At a distance from the contact $\partial \tilde{E} / \partial t \ll \tilde{i}$ and $\tilde{i}_\infty$ is the current of the carriers in the depth of the semiconductor. Since $\frac{e}{4\pi} \frac{\partial \tilde{E}_s}{\partial t} = i\omega C_0 \tilde{\varphi}_s$, where C_0 is the capacity of the volume charge, we obtain for the current of the carriers at the contact $\tilde{i}_s = \tilde{i}_\infty - i\omega C_0 \tilde{\varphi}_s$. In accordance with [7], $\tilde{p}_d = \gamma \tilde{i}_s \{ e \sqrt{D_+ (\tilde{i}_\infty + \tau^{-1})} \}^{-1}$, $\tilde{i}_s = (1/R + i\omega C_D) \tilde{\varphi}_s$, where R is the resistance of the electrode, C_D the diffusion capacity, and γ the ratio of the hole current to the total current of the charges at the contact. From this we have

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

Using (8) and (9) and calculating the average values by means of the relationship $\langle a(t) b(t) \rangle = \frac{1}{2} \text{Re} [a(t) \cdot b^*(t)]$, we obtain:

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

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

Relationship (10) gives the overall expression for the magnitude of the Faraday rectification.

The first term in (10) is due entirely to the kinetics of the electrochemical reaction at the contact and can be either positive or negative. Since the alternating signal has no definite direction in the system, we shall consider the physical effect leading to the appearance of a particular sign for the magnitude of the potential displacement. Let us assume, for example, that $i_0^{(p)} > i_0^{(e)}$, i.e., that the reaction taking place through the valence zone predominates. When current is passed in a positive direction, it follows from (1) that the potential φ_s is displaced towards more positive values by a quantity $\Delta\varphi_1$. In the next half-period, when the current is negative, the change in potential takes place in the opposite direction by a quantity $\Delta\varphi_2$. In accordance with the given condition, the current is the same in both directions. Since the changes in the current are proportional to the change in the exponent of $\Delta\tilde{i} \sim -\Delta e^{-e\tilde{\varphi}/kT}$, however, and increases in the exponent by the same quantity in the positive and negative directions

correspond to different changes in the argument, we find that $|\Delta\varphi_1| > |\Delta\varphi_2|$ 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 related to diffusion effects and is always negative.

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

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

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

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

It follows from (11) and (12) that the quantity $\langle \tilde{\varphi}_s \rangle$ becomes markedly dependent on the frequency ($\sim \omega^{-2}$) at frequencies greater than a certain characteristic frequency ω_0 defined by the equation $\omega_0 = ei_0/C_0kT$. Assuming that $i_0 \sim 10^{-5}$ and $C_0 \sim 10^{-4} \text{ cm}^{-1}$, we obtain $\omega_0 \sim 3 \cdot 10^4 \text{ sec}^{-1}$.

It is of interest to compare the magnitude of the Faraday rectification (11) with the analogous value in other systems. On metals [6], when a chemical reaction is taking place, in order of magnitude where $i_0^{(m)}$ is the exchange current at the metallic electrode. Comparison with (11) shows that on semiconductors we can expect a greater effect for the same current amplitude, since i_0 is usually less than $i_0^{(m)}$ [8]. Preliminary calculations for n-p-junctions show that $\langle e\tilde{\varphi}_s/kT \rangle_{\text{lim}} \sim (|\tilde{i}_\infty|/i_{\text{lim}})^2$, where i_{lim} is the greater of the two limiting currents of the n-p-junction, which generally speaking is much greater than i_0 . From this $\langle \tilde{\varphi}_s \rangle_{\text{lim}} \ll \langle \tilde{\varphi}_s \rangle$. From the above estimates it can be seen that an electrochemical cell with a semiconducting electrode is a system in which the Faraday rectification effect may be most clearly defined.

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