ALTERNATING CURRENT IN A BINARY ELECTROLYTE

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It is of interest to investigate the distribution of the field and the electrolyte in the simplest electrochemical system – a cell with a binary electrolyte – in the case of a reversible electrode reaction. We have investigated the impedance of this system.

The distribution of the field and the concentration of the electrolyte in the cell are given by the well-known equations

$$j_+ = D_+ (-\partial n_+ / \partial x + z_+ E n_+ e / kT); \tag{1}$$

$$j_- = D_- (-\partial n_- / \partial x - z_- E n_- e / kT); \tag{2}$$

$$\partial E / \partial x = 4\pi e (z_+ n_+ - z_- n_-) / \varepsilon; \tag{3}$$

$$\partial j_+ / \partial x + \partial n_+ / \partial t = 0, \quad \partial j_- / \partial x + \partial n_- / \partial t = 0, \tag{4}$$

where j_+ and j_-, n_+ and n_-, and z_+ and z_- are the current, the concentration, and the charge of ions; E is the electric field.

We shall investigate the polarization of the cell by weak sine current by using the concept of a sharp transition between the diffusing layer and the diffusion region. To eliminate the effect of natural convection, we shall consider that the electrolysis is carried out in a capillary of length L at the open end of which the initial concentration of ions, n_+^0 and n_-^0 [1], is maintained. We can represent any value as a sum of a constant value (indicated by a straight line) and a variable value (indicated by a wavy line). In the diffusion region $x^{(d)} \leq x \leq L$ we obtain from (1), (2), and (4), using the condition of electrical neutrality,

$$z_- \tilde{n}_- = z_+ \tilde{n}_+ = z_+ \tilde{n}_+^{(d)} e^{-k_\omega (x - x^{(d)})}; \tag{5}$$

$$z_+ \tilde{n}_+^{(d)} = \frac{\tilde{j}_+^{(d)} D_+^{-1} + \tilde{j}_-^{(d)} D_-^{-1}}{k_\omega (z_+^{-1} + z_-^{-1})}; \quad k_\omega = \left[i\omega \frac{(D_+ z_+)^{-1} + (D_- z_-)^{-1}}{z_+^{-1} + z_-^{-1}} \right]^{1/2}, \tag{6}$$

where ω is the frequency of the sine curve $I = I_0 \exp(i\omega t)$. In Eqs. (5) and (6) we assume that $|k_\omega^{-1}| \ll L$ and, therefore, we seek the solution in the unbound region. The terms with the index (d) refer to the boundary between the diffusing and diffusion layers. Taking into account that $\bar{E} = 0$, $\bar{n}_+ = n_+^0$, and $\bar{n}_- = n_-^0$, we obtain from (1) and (2) the drop of potential in the diffusion region

$$\tilde{\varphi}^{(d)} - \tilde{\varphi}^{(L)} = (z_+ e \tilde{j}_+^{(d)} - z_- e \tilde{j}_-^{(d)}) \lambda^{-1} L + (D_- - D_+) \lambda^{-1} e z_+ \tilde{n}_+^{(d)}, \tag{7}$$

where λ is the conductivity of the solution. The first term in (7) represents the ohmic drop in a solution of constant concentration. We shall omit this term in what follows, assuming that the ohmic drops are included in some ohmic resistance in series with the cell. The second term in (7) refers to the variation of the concentration in the diffusion region

$$(\tilde{\varphi}^{(d)} - \tilde{\varphi}^{(L)})_{\text{conc.}} = e (D_- - D_+) \lambda^{-1} \tilde{n}_+^{(d)} z_+. \tag{8}$$

Let us now investigate the diffusing part of the double layer $0 \leq x \leq x^{(d)}$. We shall assume that the positive ions take part in the electrochemical reaction, while the electrical charge in the diffusing layer is determined by the negative ions. The Poisson equation (3) can be written in the form

$$\frac{\partial\mathscr{E}}{\partial x} = -\frac{4\pi e^2 z_-}{\varepsilon\theta} n_- \quad \left(\mathscr{E} = \frac{eE}{\theta};\ \theta = kT\right). \tag{9}$$

The concentration of negative ions increases toward the electrode. The passage of the electric current practically does not change the Boltzmann distribution of negative ions

$$n_- = n_-^{(d)} e^{z_-(\psi - \psi^{(d)})} \quad \left(\mathscr{E} = -\frac{\partial\psi}{\partial x}\right). \tag{10}$$

To obtain (10) formally one must drop the term containing the current in (2). The calculation shows that this is possible if the frequency of the alternating current ω is much less than the frequency of the relaxation of the charge in the double layer. The value of ω_0 is of the order of $D_-\varkappa_-^2$, where $\varkappa_-^2 = 4\pi e^2 n^0$ $(\varepsilon\theta)$. We shall assume that the inequality $\omega \ll \omega_0$ is satisfied.

From (10) we can obtain (9) in the form

$$\frac{1}{2}\mathscr{E}^2 = \frac{4\pi e^2}{\varepsilon\theta} n_-^{(d)} (e^{z_-(\psi - \psi^{(d)})} - 1) + \frac{1}{2}(\mathscr{E}^{(d)})^2.$$

The constant of integration is determined from the condition of contact with the diffusion region. Taking into account that the intensity of the electric field in the diffusion region is low, and that the exponential function varies rapidly, one can assume that for the larger part of the diffusion layer, the following condition

$$\frac{1}{2}\mathscr{E}^2 = \varkappa_-^2 \frac{n_-}{n_-^0} = \varkappa_-^2 \frac{n_-^{(d)}}{n_-^0} e^{z_-(\psi - \psi^{(d)})} \tag{11}$$

is fulfilled at least when $\psi - \psi^{(d)} \gg 1$.

The displacement current in the Helmholtz part of the double layer is due to the oscillation of the density of negative ions in the diffusing part of the double layer. The displacement current is increasingly transformed into an electric current of negative ions as the distance from the electrode increases. Therefore, the current of negative ions at the boundary of the diffusion layer is equal to the displacement current in the plane closest to the boundary. The values for this plane will be indicated by a star

$$\tilde{j}_-^{(d)} = -\frac{\varepsilon\theta}{4\pi e^2 z_-} i\omega\tilde{\mathscr{E}}^*. \tag{12}$$

Since the positive ions do not intervene in the formation of the charge of the double layer and a displacement current is not created by the oscillation of their density, the current of positive ions will not change within the limits of the double layer

$$\tilde{j}_+^{(d)} = \tilde{j}_+^*. \tag{13}$$

Using (11) and (13) we can write solution (2) in the form

$$n_+ = n_+^{(d)} e^{-z_+(\psi - \psi^{(d)})} + \tilde{j}_+^{(d)} e^{-\frac{z_-}{2}(\psi - \psi^{(d)})} \left[\varkappa_- D_+ (z_+ - z_-/2) \sqrt{2\frac{n_-^{(d)}}{n_-^0}}\right]^{-1}. \tag{14}$$

We have considered that $z_+ > z_-/2$, and used large values of $\psi - \psi^{(d)}$ (we shall not treat the case of $z_+ < z_-/2$). The relationships between small variable magnitudes can be found from (10), (11), and (14) by direct differentiation. Thus, we have

$$\begin{gathered} \tilde{\psi}^* - \tilde{\psi}^{(d)} = \frac{1}{z_-}\frac{\tilde{n}_-^*}{n_-^0} e^{-z_-\bar{\psi}^*} - \frac{1}{z_-}\frac{\tilde{n}_-^{(d)}}{n_-^0}; \\ \bar{\mathscr{E}}^*\tilde{\mathscr{E}}^* = \frac{\varkappa_-^2 \tilde{n}_-^*}{n_-^0}; \end{gathered} \tag{15}$$

$$\tilde{n}_+^* = (z_+^{-1} + z_-^{-1}) z_+ \tilde{n}_+^{(d)} e^{-z_+\bar{\psi}^*} - \frac{z_+}{z_-}\bar{n}_+^* e^{-z_-\bar{\psi}^*}\frac{\tilde{n}_-^*}{n_-^0} + \frac{\tilde{j}_+^{(d)} e^{-\frac{z_-}{2}\bar{\psi}^*}}{D_+\varkappa_-(z_+ - z_-/2)\sqrt{2}}. \tag{16}$$

In the case of reversible reaction, we can write for the concentration of discharging ions,

$$n_+^* = \bar{n}_+^* e^{z_+\Delta\psi}; \quad \Delta\psi = \varepsilon\delta_H(\mathcal{E}^* - \bar{\mathcal{E}}^*)/\varepsilon_H,$$

where δ_H and ε_H are the thickness and the dielectric constant of the Helmholtz layer. From here we find for the variable magnitudes

$$\tilde{n}_+^* = \bar{n}_+^* z_+ \Delta\tilde{\psi}; \quad \Delta\tilde{\psi} = \varepsilon\delta_H \tilde{\mathcal{E}}^*/\varepsilon_H. \tag{17}$$

Using (6), (12), (13), (15), (16), and (17) we find for the complex conductivity of the cell

$$\sigma = \frac{i\omega C_{dbl} + \dfrac{[z_+\bar{n}_+^* + k_\omega^{-1} D_-^{-1} e^{-z_+\bar{\psi}^*} \theta i\omega C_{dbl}(e^2 z_-)^{-1}]\, z_+ e^2 \theta^{-1}}{k_\omega^{-1} D_+^{-1} e^{-z_+\bar{\psi}^*} + e^{-z_-\bar{\psi}^*/2}\,[D_+\varkappa_- \sqrt{2}(z_+ - z_-/2)]^{-1}}}{1 - \dfrac{D_+ k_\omega^{-1}}{n_+^0 (z_+D_+ + z_-D_-)} \dfrac{z_+\bar{n}_+^* - i\omega\theta C_{dbl} e^{-z_-\bar{\psi}^*/2}\,[e^2 z_- D_- \varkappa_- \sqrt{2}(z_+ - z_-/2)]^{-1}}{k_\omega^{-1} e^{-z_-\bar{\psi}^*/2}\,[\varkappa_- \sqrt{2}(z_+ - z_-/2)]^{-1}}}, \tag{18}$$

where $C_{dbl} = \varepsilon_H/(4\pi\delta_H)$.

In (18) we have omitted the value $\varepsilon_H(\varepsilon\delta_H\bar{\mathcal{E}}^*)^{-1}$, which is small with respect to unity. When ω is small and the condition

$$L_\omega = |k_\omega^{-1}| \gg L_{dbl} = \varkappa_-^{-1}\,[\sqrt{2}(z_+ - z_-/2)]^{-1} e^{(z_+ - z_-/2)\bar{\psi}^*}, \tag{19}$$

is satisfied, one can obtain from (18)

$$\sigma = \left(\frac{z_+D_+ + z_-D_-}{z_-D_-}\right)^2 i\omega C_{dbl} + \frac{z_+D_+ + z_-D_-}{z_-D_-} \frac{z_+^2 e^2}{\theta} n_+^0 k_\omega. \tag{20}$$

In the derivation of (20) we have assumed that $|\varepsilon_H k_\omega^2 L_{dbl}[\varepsilon\delta_H \varkappa_-^2]^{-1}|$ is small with respect to unity. If the inequality reciprocal to (19) is satisfied and the frequency is not too high, so that $|k_\omega^2 L_{dbl} \varkappa_-^{-1}| \ll 1$, we find from (18)

$$\sigma = i\omega C_{dbl} - \frac{z_-D_-}{z_+D_+ + z_-D_-} \frac{e^2 z_+^2 n_+^0 D_+}{\theta L_{dbl} k_\omega L_{dbl}} + \frac{e^2 z_+^2 n_+^0 D_+}{\theta L_{dbl}}. \tag{21}$$

Finally, in the case of higher frequencies, when not only an inequality reciprocal to (19), but also $|k_\omega^2 L_{dbl} \varkappa_-^{-1}| \gg 1$ is satisfied, we obtain from (18)

$$\sigma = i\omega C_{dbl} + e^2 z_+^2 n_+^0 D_+ \theta^{-1} L_{dbl}^{-1}. \tag{22}$$

Let us note that the expression of L_{dbl} in (19), obtained for the case of alternating current, coincides with the expression of the effective length of diffusion in the double layer in the case of direct current obtained in [2]. The oscillations of negative ions due to the displacement current in the diffusion region induce oscillations of the discharging (positive) ions because of the electrical neutrality of the solution. If (19) is satisfied, these oscillations can reach the electrode and induce a current whose order of magnitude is the same as that of the displacement current. The first term in (20) refers to this current and to the displacement current. If the value of $[(z_+D_+ + z_-D_-)/z_-D_-]^2$ is large with respect to unity, then the capacitance, which is independent of the frequency, is anomalously high. If (19) is satisfied, the oscillations of the density of positive ions satisfying condition (17) penetrate easily through the region of the double layer into the diffusion region and there induce oscillations responsible for the second term in (20). The form of this term is identical to the form of ordinary Faraday impedance, whose properties are well known [3].

If the inequality reciprocal to (19) is satisfied, then the relationship between the oscillations of the positive ions in the Helmholtz plane, and the oscillations in the diffusion region no longer holds. In this case, as can be shown by (22), the capacitance of the cell is determined by the charge capacitance, while the resistance is independent of the frequency and is determined by the oscillations of positive ions within the limits of the double layer.

To conclude, let us note that the theory presented here can easily be extended to the case where the charge in the double layer is determined by the positive ions, while the discharge is due to negative ions.

LITERATURE CITED

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