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Abstract

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THE INFLUENCE OF REACTION IRREVERSIBILITY ON FARADAY IMPEDANCE IN A BINARY ELECTROLYTE

In paper (1) a method was developed that makes it possible to take into account the influence of the double layer on the process of passage of an alternating electric current. By this method an expression was obtained for the complex conductivity of a binary electrolyte under the assumption of complete reversibility of the electrochemical reaction. Of interest is an expression for the impedance that takes into account the finite rate of the electrochemical reaction. In this case the boundary condition should be written in the form

$$i_+^* = i_0 \left(e^{\alpha z + \Delta\psi} - e^{-\beta z + \Delta\psi} n_+^* / \tilde{n}_+ \right). \tag{1}$$

Here and below the notation of paper (1) is used; i_0 is the exchange current, $i_0 = z_+ e n_+^0 v_+$; v_+ is the reaction-rate constant. If one carries out calculations analogous to those performed in (1), but taking condition (1) into account, one can obtain for the complex resistance the expression (here and below the expression for the impedance refers to an electrode of unit area):

$$R = \frac{\theta}{z_+^2 e^2 D_+ n_+^0} \frac{k_\omega^{-1}(z_- D_-)(z_+ D_+ + z_- D_-)^{-1} + L \ \ + L_\mathrm{p}}{1 + \theta i \omega C \ \ (L \ \ + L_\mathrm{p})(z_+^2 e^2 D_+ n_+^0)^{-1}}, \tag{2}$$

where $L \ \ = \chi^{-1} e^{(z_+ - z_-/2)\psi^*} \left[V^2 (z_+ - z_-/2) \right]^{-1}$ is the effective diffusion length in the double layer; $L_\mathrm{p} = D_+/v_+$ is the effective reaction length; $C \ \ = \varepsilon_r / 4\pi\delta_r$ is the double-layer capacitance;

$$k_\omega = \left(i\omega \frac{\dfrac{1}{D_+ z_+} + \dfrac{1}{D_- z_-}}{\dfrac{1}{z_+} + \dfrac{1}{z_-}} \right)^{1/2}.$$

In deriving (2) it was assumed that the frequency ω is sufficiently small, so that the electric current associated with the charging of the double layer is small in comparison with the electric current due to the electrochemical reaction. It was also assumed that

$$\frac{\varepsilon_r}{\varepsilon \delta_r \theta^*} \ll 1.$$

It was assumed that $z_+ > z_-/2$; here and below the expression for the impedance does not take into account the ohmic losses in the solution, which enter additively into the total resistance.

If the influence of the double layer is not taken into account, then for the complex resistance R_0 one can obtain the expression

$$R_0 = \frac{\theta}{z_+^2 e^2 D_+ n_+^0} \left\{ \frac{1}{k_\omega} \frac{z_-}{z_+ + z_-} + L_\mathrm{p} \right\}. \tag{3}$$

Expressions (2) and (3) coincide only in the case when $D_+ = D_-$, $L_\mathrm{p} \gg L\ $, and when the frequency is sufficiently small that the second term in the denominator of (2) can be neglected. Let the frequency ω be sufficiently small, so that (2) can be rewritten in the form

$$R = \frac{\theta}{z_+^2 e^2 D_+ n_+^0} \left\{ \frac{1}{k_\omega} \frac{z_- D_-}{z_+ D_+ + z_- D_-} + L\ + L_\mathrm{p} \right\}. \tag{4}$$

It follows from (4) that the sum of the lengths $L\ + L_\mathrm{p}$ can be found by the usual alternating-current method (2), i.e., from the formula

$$R_s - \frac{1}{\omega C_s} = \frac{\theta}{z_-^2 e^2 D_+ n_+^0} (L\ + L_\mathrm{p}), \tag{5}$$

where R_s and C_s are the parameters of the series equivalent circuit. From (5) there follows the important conclusion that the rate constant of the electrochemical reaction (or the reaction length L_p) can be determined by the alternating-current method only in the case where the reaction is sufficiently slow, so that the relation $L\ \ll L_p$ is satisfied. Otherwise, the alternating-current method will determine not the reaction length (or the rate constant), but the effective diffusion length in the double layer.

If the condition $z_+ > z_-/2$ is not fulfilled, but the opposite condition is fulfilled, then the effective diffusion length $L\ $ is, in order of magnitude, the same as the thickness of the diffusion layer, and therefore in our approximation it must be set equal to zero. In this case the reaction rate constant can be determined from (5).

The results presented referred to the case where the charge of the double layer was determined by negative ions, while positive ions participated in the electrochemical reaction. Using the method developed in ([1]), one can investigate the case where only negative ions, which determine the electric charge in the diffusion layer, participate in the electrochemical reaction.

The expression for the complex resistance, taking into account both the current of the electrochemical reaction and the charging current of the double layer, has in this case the form

$$R = \frac{\theta}{z_-^2 e^2 n_-^0 D_-} \left\{ \frac{z_+ D_+}{z_- D_- + z_+ D_+} \frac{1}{k_\omega} + \frac{L_p}{1 + i\omega C \; L_p / (z_-^2 e^2 n_-^0 D_- \theta^{-1})} \right\}. \tag{6}$$

At sufficiently low frequencies, expression (6) can be rewritten as

$$R = \frac{\theta}{z_-^2 e^2 n_-^0 D_-} \left\{ \frac{z_+ D_+}{z_- D_- + z_+ D_+} \frac{1}{k_\omega} + L_p \right\}. \tag{7}$$

If R is calculated without taking into account the influence of the double layer, then instead of (7) we obtain

$$R_0 = \frac{\theta}{z_-^2 e^2 n_-^0 D_-} \left\{ \frac{z_+}{z_+ + z_-} \frac{1}{k_\omega} + L_p \right\}. \tag{8}$$

Expression (8) coincides with (7) if the diffusion coefficients of both sorts of ions are equal to one another. It follows from (7) that the reaction rate constant can be found from a formula analogous to formula (5).

Formula (6) is somewhat unusual and differs in its structure from the formulas for impedance relating to the case where the discharging ions do not form the double layer. Let us assume that the reaction is very fast, i.e. $L_p = 0$, and let us increase the signal frequency ω. Then, in the case where the ions forming the double layer do not participate in the reaction, a moment will occur when the electric current is determined mainly by the charging and discharging current of the double layer. In the case, however, where the ions forming the double layer participate in a fast electrochemical reaction, as follows from (6), the impedance at all admissible frequencies will coincide with the Faradaic impedance.

In conclusion, let us note that the results obtained are naturally carried over to the case where the charge in the double layer is determined by positive ions.

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