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

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A method has been developed in [1] which makes it possible to take account of the effect which a double layer has on the passage of an alternating electric current. This method has been used to find an expression for the complex conductivity of a binary electrolyte under the assumption that the electrochemical reaction is completely reversible. There is some interest in an expression for the impedance which allows for the finite rate of the electrochemical reaction. In this case, the boundary condition must be written in the form

$$\overset{*}{i}_+ = i_0\left(e^{\alpha z_+\Delta\psi} - e^{-\beta z_+\Delta\psi}\overset{*}{n}_+/\overline{\overset{*}{n}}_+\right). \tag{1}$$

Here, and in what follows, the nomenclature of [1] is used: i_0 is the exchange current $i_0 = z_+ e n_+^0 v_+$, and v_+ is the rate constant of the reaction. If we make calculations similar to those made in [1], but taking account of condition (1), we can obtain for the complex resistance the expression (here, and in what follows the expression for the impedance is referred to an electrode of unit area):

$$R = \frac{\theta}{z_+^2 e^2 D_+ n_+^0} \frac{k_\omega^{-1}(z_- D_-)(z_+ D_+ + z_- D_-)^{-1} + L_{db} + L_r}{1 + \theta i\omega C_{db}(L_{db} + L_r)(z_+^2 e^2 D_+ n_+^0)^{-1}}, \tag{2}$$

where $L_{db} = \varkappa_-^{-1} e^{(z_+ - z_-/2)\overline{\psi}^*}[\sqrt{2}(z_+ - z_-/2]^{-1}$ is the effective diffusion length in the double layer, $L_r = D_+/v_+$ is the effective reaction length, $C_{db} = \varepsilon_g/4\pi\delta_g$ is the double layer capacity, and $k_\omega = \left(i\omega\frac{\frac{1}{D_+z_+} + \frac{1}{D_-z_-}}{1/z_+ + 1/z_-}\right)^{1/2}$

It was assumed in deriving (2) that the frequency ω is small enough so that the electric current associated with charging the double layer is small in comparison with the electric current due to the electrochemical reaction. It was also assumed that $\varepsilon_g/\varepsilon\delta_g\overline{\mathcal{E}}^* \ll 1$. It was assumed that $z_+ > z_-/2$, and here and in what follows the expression for the impedance neglects the ohmic losses in the solution, which enter additively into the total resistance.

If we do not take account of the effect of the double layer, we get for the complex resistance R_0 the expression

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

Equations (2) and (3) are the same only in the case where $D_+ = D_-$, $L_r \gg L_{db}$, and the frequency is small enough so that the second term in the denominator of (2) may be neglected. Let the frequency ω be small enough for (2) to be rewritten in the form

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

It follows from (4) that the sum of the lengths $L_{db} + L_r$ may be found by the usual alternating current method [2], i.e., from the formula

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

where R_s and C_s are the constants of the equivalent series circuit. The important conclusion follows from (5) that the rate constant of the electrochemical reaction (or the reaction length L_r) may be found by the alternating current method only in case the reaction is slow enough to satisfy the relation $L_{db} \ll L_r$. In the opposite case, the alternating current method will not give the reaction length (or the rate constant), but the effective diffusion length in the double layer.

If the condition $z_+ > z_-/2$ is not satisfied, but the opposite condition is satisfied, the effective diffusion length L_{db} will be of the same order of magnitude as the thickness of the diffuse layer, and so, in our approximation should be set equal to zero. In this case, (5) may be used to find the reaction rate constant.

The results given were for the case where the charge on the double layer was determined by negative ions, and positive ions took part in the electrochemical reaction. Using the method developed in [1], we can investigate the case where only the negative ions which determine the electric charge in the diffuse layer take part in the electrochemical reaction.

The expression for the complex resistance including both the electrochemical reaction current and the double layer charging current in this case has the form.

$$R = \frac{\theta}{z_-^2 e^2 n_-^0 D}\left\{\frac{z_+ D_+}{z_- D_- + z_+ D_+}\,\frac{1}{k_\omega} + \frac{L_r}{1 + i\omega C_{db} L_r / (z_-^2 e^2 n_-^0 D_- \theta^{-1})}\right\}. \tag{6}$$

If the frequencies are low enough, Eq. (6) may be rewritten in the form

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

If we calculate R neglecting the effect of the double layer, instead of (7) we obtain

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

Equation (8) is the same as (7) if the diffusion coefficients of both kinds of ions are equal. It follows from (7) that the reaction rate constant may be found from a formula similar to formula (5).

Formula (6) is somewhat unusual and differs in structure from the formulas for the impedance which apply to the case where the discharging ions do not form a double layer. We shall assume that the reaction is very fast, i.e., $L_r = 0$, and we shall increase the signal frequency ω. Then, in the case where the ions forming the double layer take no part in the reaction a time will come when the electric current will be determined mainly by the charge and discharge current of the double layer. However, in the case where the ions forming the double layer take part in a rapid electrochemical reaction, as follows from (6), the impedance at all permissible frequencies will be the same as the Faraday impedance.

We note in conclusion that the results obtained can be extended in a natural way to the case where the charge in the double layer is determined by positive ions.

LITERATURE CITED

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