FARADAY HETERODYNING

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The application of methods using alternating current was introduced more than 20 years ago and has made it possible to solve a number of fundamental problems in the theory of electrode processes [1]. At the present time, in the study of the kinetics of rapid electrochemical reactions, extensive use is made of a method involving measurement of the impedance [2] corresponding to the Faraday component of the current, i.e., that fraction of the alternating current associated with the electrochemical reaction taking place at the electrode. The application of methods using alternating current for the study of rapid electrochemical reactions is based on the decrease in diffusion limitations with increase in the frequency of the alternating current. A marked increase in frequency, however, leads to an increase in the non-Faraday component of the current (via the capacity of the double layer) compared with the Faraday component, and also to a decrease in the electrical resistance of the electrode - solution boundary compared with the ohmic resistance of the cell. These two factors limit the possibilities of the Faraday impedance method.

Recently the kinetics of rapid electrochemical reactions have been studied by methods making use of the nonlinear properties of the electrochemical cell [3-7]. The advantage of these methods over the Faraday impedance method is that when certain conditions are observed, the nonlinearity of the cell is determined chiefly by the electrochemical reaction taking place, so that the effects associated with the nonlinearity give information on the electrochemical reaction (with the condition, of course, that the diffusion limitations are eliminated).

At the present time, electrochemical reactions are studied by two methods making use of the nonlinear properties of the electrochemical cell: the Faraday rectification method using a high-frequency signal with amplitude modulated by rectangular pulses [4, 6, 7] and the Faraday distortion method [5]. There are two versions of the first method, involving the use of high-frequency current or voltage generators. The aim of the present work was tc develop a further analogous method which might have certain advantages (including advantages associated with the nature of the apparatus used) over existing methods. The appropriate calculations (see below) can be carried out in an extremely general form and the results of the calculations can be expressed in terms of quantities which have previously been calculated (or which can be calculated) for a number of specific electrochemical systems.

Let us assume that an electrode is polarized by an alternating current and that the density of the Faraday component of this current is j.* If the value of j is so small that the change in the electrode potential produced by the passage of the alternating current, satisfies the conditions $\Delta\varphi \ll RT/nF$ (where the symbols have their usual significance), we find that as a first approximation a linear relationship exists between the quantities $\Delta\varphi$ and j:

$$\Delta\varphi^{(1)} = \hat{L}_{\varphi} j, \tag{1}$$

where L_{φ} is a linear operator.

If the current j is purely sinusoidal,

$$j = j^{(0)} \cos \omega t \tag{2}$$

($j^{(0)}$ represents amplitude, ω frequency, and t time), operation (1) under established conditions reduces to a change in the amplitude and phase of the sinusoidal quantity

*It is assumed that the passage of the Faraday and non-Faraday components of the current takes place independently. This is the case when excess of an indifferent electrolyte is present.

$$\Delta\varphi^{(1)}|_{t\to\infty} = \hat{L}_\varphi\{j^{(0)}\cos\omega t\} = Z_\varphi(\omega)\, j^{(0)}\cos[\omega t + \theta_\varphi(\omega)], \tag{3}$$

where $Z_\varphi(\omega)$ is the modulus of the Faraday impedance and $\theta_\varphi(\omega)$ is the phase angle between the potential and the current. The set of quantities $Z_\varphi(\omega)$ and $\theta_\varphi(\omega)$ determine the Faraday impedance.

In analogous fashion, a change in any other quantity Δa, produced by the passage of alternating current through the cell (for example, change in the concentration of substances close to the electrode surface or change in the degree of covering of the surface during adsorption, etc.) can as a first approximation be expressed by means of the linear relationship

$$\Delta a^{(1)} = \hat{L}_a j, \tag{4}$$

where $\hat{L}_a$ is a linear operator corresponding to the quantity a. Under established conditions, by analogy with (3), we have

$$\Delta a^{(1)}|_{t\to\infty} = Z_a(\omega)\, j^{(0)}\cos[\omega t + \theta_a(\omega)]. \tag{5}$$

The values of the quantities $Z_a(\omega)$ and $\theta_a(\omega)$ are determined by the properties of the operator L_a. The linear relationship (1) is applicable only as a first approximation with respect to the magnitude of the signal. In the next approximation, quadratic terms, i.e., terms of the type $\Delta\varphi\cdot\Delta a$, $(\Delta\varphi)^2$, etc. are added to the right hand side of (1). The quantities taken as cofactors in the quadratic terms should be the quantities calculated in the first approximation. We can therefore replace (1), with an accuracy down to the second order of smallness, by

$$\Delta\varphi = \hat{L}_\varphi j + \sum\gamma_{ab}\hat{L}_a j\cdot\hat{L}_b j, \tag{6}$$

where the summation is carried out over all the quadratic terms. The coefficients γ_{ab} are parameters characterizing the nonlinear stage of the process. In the case under consideration, this stage is the electrochemical reaction and the coefficients $\gamma_a l$ depend on the exchange current and the so-called transfer coefficients, in accordance with the familiar equations of the theory of retarded discharge. Substituting expressions (3) and (5) in (6), we find that under established conditions, with account taken of terms of the second order of smallness, there is produced at the electrode a constant potential displacement ψ_0 (Faraday rectification) and a potential which changes with the doubled frequency ψ_{2w} (Faraday distortion):

$$\psi_0 = \frac{1}{2}(j^{(0)})^2\sum\gamma_{ab}Z_a(\omega)\, Z_b(\omega)\cos[\theta_a(\omega) - \theta_b(\omega)], \tag{7}$$

$$\psi_{2\omega} = \frac{1}{2}(j^{(0)})^2\sum\gamma_{ab}Z_a(\omega)\, Z_b(\omega)\cos[2\omega t + \theta_a(\omega) + \theta_b(\omega)]. \tag{8}$$

The square-law rectification and the doubling of the frequency are particular examples of nonlinear transformations brought about in radio engineering by means of nonlinear elements [8]. In addition to these nonlinear operations, it is also possible to bring about displacement of the frequencies, heterodyning. Let us assume that instead of the current in (1), the current flowing is

$$j = j^{(0)}[\cos\omega_1 t + \cos\omega_2 t], \tag{9}$$

which is the sum of two sinusoidal currents with frequencies ω_1 and ω_2 and, for the sake of simplicity, the same amplitude $j^{(0)}$. Under established conditions, the electrode potential is then the sum of sinusoidal quantities changing with the frequencies ω_1, ω_2, $2\omega_1$, $2\omega_2\omega_1 + \omega_2$, and $\omega_1 - \omega_2$ and a constant displacement. We are interested in the component of the potential changing with the difference frequency $\Delta\omega = \omega_1 - \omega_2$. For this quantity we obtain from (6) and (9) the expression

$$\psi_{\Delta\omega} = \frac{1}{2}(j^{(0)})^2\sum\{Z_a(\omega_1)\, Z_b(\omega_2)\cos[\Delta\omega t + \theta_a(\omega_1) - \theta_b(\omega_2)] + Z_a(\omega_2)\, Z_b(\omega_1)\cos[\Delta\omega t + \theta_b(\omega_1) - \theta_a(\omega_2)]\}. \tag{10}$$

If it is assumed that the frequencies ω_1 and ω_2 are very close to one another,

$$\omega_1 \approx \omega_2 \approx \omega, \quad \frac{\Delta\omega}{\omega} = \frac{\omega_1 - \omega_2}{\omega} \ll 1, \tag{11}$$

we have, from (10) and (7),

$$\psi_{\Delta\omega} = 2\psi_0 \cos \Delta\omega t, \tag{12}$$

where ψ_0 is the magnitude of the Faraday rectification, previously calculated for a number of specific electrochemical systems [3, 4, 6, 7]. Formula (12) (unlike the usual radio engineering relationships [8]) is applicable only for the case of sufficiently small values of $\Delta\omega$. This is due to the fact that the electrochemical cell, in the terminology of electrical circuit theory, is a system with distributed parameters and nonlinearity.

In a number of cases it may prove convenient to polarize the electrode not by alternating currents but by alternating potentials (from a voltage generator). In these cases a current begins to flow in the cell, the density of the Faraday component of this current, as a first approximation, being equal to

$$j^{(1)} = \hat{L}_\varphi^{-1} \Delta\varphi, \tag{13}$$

where $\hat{L}_\varphi^{-1}$ is an operator which is the inverse of $\hat{L}_\varphi$. Under established conditions, operation (13) reduces to division of the amplitude of the potential by $Z_\varphi(\omega)$ and a change in phase by an angle $-\theta_\varphi(\omega)$ [compare (1)-(3)]. In the second approximation, the current flowing through the cell will have a complex spectrum. From (6) we find that for the components of the current, as a second approximation, the formula

$$j^{(2)} = -\hat{L}_\varphi^{-1} \left\{ \sum \gamma_{ab} \hat{L}_a j^{(1)} \cdot \hat{L}_b j^{(1)} \right\}. \tag{14}$$

is applicable.

For the difference frequency current under established conditions, with an accuracy down to the insignificant phase factor from (14), it follows that

$$j_{\Delta\omega} = \frac{\psi_{\Delta\omega}}{Z_\varphi(\Delta\omega)}, \tag{15}$$

where $\psi_{\Delta\omega}$ is determined by formulae (10) or (12) and $Z_\varphi(\Delta\omega)$ is the Faraday impedance at a frequency $\Delta\omega$, i.e., a quantity which is known for many electrochemical systems.

In order to determine the possibilities of the Faraday heterodyning method (measurement of the potential or current of the difference frequency), we can compare it with other methods which make use of the nonlinear properties of the electrochemical cell. The method of Faraday rectification with polarization by alternating current and the method of Faraday distortion cannot be used in the case of high frequencies and low concentrations of potential-determining ions (the first because of intermediate processes in the circuit containing the capacity of the double layer [4] and the second because of the shunting action of the capacity of the double layer [5]). The method of Faraday rectification with polarization of the electrode by an alternating potential can be used in this most important case, but it involves measurements under nonstationary conditions [6, 7] and requires complicated apparatus. The Faraday heterodyning method examined here makes it possible to carry out measurements of only sinusoidal quantities, established with time (which leads to considerable simplication of the apparatus), and can be used for the case of high frequencies and low concentrations of potential-determining ions. For this purpose it is necessary only to choose a difference frequency $\Delta\omega$ which is so small that the resistance of the capacity of the double layer at this frequency is much greater than the Faraday impedance (at the main frequencies ω_1 and ω_2 the resistance of the capacity of the double layer may be much less than the Faraday impedance). A small value for the difference frequency in this sense also ensures a small value for the distortions introduced by the nonlinearity of the capacity of the double layer.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
