Physical Chemistry

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Abstract

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Faradaic Heterodyning

The application of methods using alternating current began more than 20 years ago and made it possible to solve a number of fundamental questions in the theory of electrode processes ([1]). At present, for the study of the kinetics of fast electrochemical reactions, the impedance-measurement method ([2]), corresponding to the Faradaic component of the current, i.e., that part of the alternating current which is associated with the occurrence of the electrochemical reaction at the electrode, has become widespread. The application of methods using alternating current to the study of fast electrochemical reactions is based on the reduction of diffusion limitations with increasing frequency of the alternating current. However, a significant increase in frequency leads to an increase in the non-Faradaic component of the current (through the capacitance of the double layer) in comparison with the Faradaic component, and also to a decrease in the electrical resistance of the electrode–solution boundary in comparison with the ohmic resistance of the cell. These two causes limit the possibilities of the Faradaic-impedance method.

Recently, for the study of the kinetics of fast electrochemical reactions, methods have been used that exploit the nonlinear properties of the electrochemical cell ([3–7]). The advantage of these methods over the Faradaic-impedance method consists in the fact that, under certain conditions, the nonlinearity of the cell is mainly due to the occurrence of the electrochemical reaction, and, consequently, the effects associated with nonlinearity provide information concerning the electrochemical reaction (provided, of course, that the diffusion limitations are removed).

At present, in the study of electrochemical reactions, two methods are used that exploit the nonlinear properties of the electrochemical cell: the method of Faradaic rectification with the use of a high-frequency signal amplitude-modulated by rectangular pulses ([4], [6], [7]), and the method of Faradaic distortion ([5]). The first method has two varieties, associated with the use of high-frequency current or voltage generators. The aim of the present work is to develop yet another analogous method, which may offer certain advantages (including advantages of an instrumental nature) in comparison with the existing methods. The corresponding calculations (see below) can be carried out in a very general form, since the results of the calculations can be expressed through quantities that had previously been calculated (or can be calculated) for a number of specific electrochemical systems.

Let the electrode be polarized by an alternating current, the density of the Faradaic component of which we denote by j^*. If the magnitude j is sufficiently small that the change in the electrode potential caused by the passage of the alternating current satisfies the condition $\Delta\varphi \ll RT/nF$ (notation as usual), then, in the first approximation, a linear relation between the quantities $\Delta\varphi$ and j is valid:

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

where $\hat{L}_\varphi$ is a linear operator.

* It is assumed that the Faradaic and non-Faradaic components of the current pass independently. This is valid in the presence of an excess of indifferent electrolyte.

If the current j has a purely sinusoidal character

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

($j^{(0)}$ is the amplitude, ω the frequency, t the time), then operation (1) in the steady state reduces to a change in the amplitude and phase of the sinusoidal quantity:

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

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

Similarly, the change of any other quantity Δa, caused by the passage of alternating current through the cell (for example, a change in the concentrations of substances near the electrode surface or a change in surface coverage during adsorption, etc.), may, to a first approximation, be expressed by means of the linear relation

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

where $\hat{L}_a$ is the linear operator corresponding to the quantity a. In the steady state, analogously to (3), we have

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

The values of the quantities $Z_a(\omega)$ and $\theta_a(\omega)$ are determined by the properties of the operator $\hat{L}_a$. The linear relation (1) is valid only to first order in the signal magnitude. In the next approximation, quadratic terms are added to the right-hand side of (1), i.e., terms of the type $\Delta\varphi \cdot \Delta a$, $(\Delta\varphi)^2$, etc. As the factors in the quadratic terms one should take quantities calculated in the first approximation. Therefore, accurate to quantities of the second order of smallness, instead of (1) one may write

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

where the summation is carried out over all quadratic terms. The coefficients γ_{ab} are parameters characterizing the nonlinear stage of the process. In the case considered by us, such a stage is the electrochemical reaction, and the coefficients γ_{ab} depend on the exchange current and on the so-called transfer coefficients in accordance with the known equation of the theory of slow discharge. Substituting expressions (3) and (5) into relation (6), we find that in the steady state, taking into account terms of the second order of smallness, a constant shift of the potential ψ_0 arises at the electrode (Faradaic rectification), as well as a potential varying with twice the frequency, $\psi_{2\omega}$ (Faradaic distortion):

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

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

Quadratic detection and frequency doubling are particular cases of nonlinear transformations carried out in radio engineering with the aid of nonlinear elements ([8]). In addition to the nonlinear operations indicated, frequency mixing —heterodyning—can also be performed. Suppose that, instead of current (1), a current flows

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

representing the sum of two sinusoidal currents of frequencies ω_1 and ω_2 of one and, for simplicity, amplitudes of amplitude $j^{(0)}$. Then, in the steady-state regime, the electrode potential is the sum of sinusoidal quantities varying with the frequencies ω_1, ω_2, $2\omega_1$, $2\omega_2$, $\omega_1+\omega_2$, $\omega_1-\omega_2$, and a constant shift. We shall be interested in the component of the potential that varies with the difference frequency $\Delta\omega = \omega_1 - \omega_2$. For it, from (6) using (9), one obtains the expression

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

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

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

then from (10) and (7) it follows that

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

where ψ_0 is the magnitude of the faradaic rectification calculated earlier for a number of specific electrochemical systems [3,4,6,7]. Formula (12) (in contrast to the usual radio-engineering relation [8]) is valid only in the case of sufficiently small values of $\Delta\omega$. This is connected with the fact that an electrochemical cell, in terms of the theory of electrical circuits, is a system with distributed parameters and nonlinearity.

In a number of cases it may prove expedient to polarize the electrode not with alternating currents, but with alternating potentials (from voltage generators). In these cases a current begins to flow through the cell, the density of whose faradaic component in the first approximation is equal to

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

where $\hat{L}_\varphi^{-1}$ is the operator inverse to $\hat{L}_\varphi$. In the steady-state regime, the operation (13) reduces to division of the potential amplitude by $Z_\varphi(\omega)$ and a change of phase by the angle $-\theta_\varphi(\omega)$ (cf. (1)–(3)). In the second approximation, the current flowing through the cell will have a complex spectrum. From (6) it follows that, for the current components in the second approximation, the formula is valid

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

For the current of the difference frequency in the steady-state regime, to within an inessential phase factor, it follows from (14) that

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

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

To clarify the possibilities of the faradaic heterodyning method (measurement of the potential or current of the difference frequency), let us compare it with other methods that use the nonlinear properties of an electrochemical cell. The method of faradaic rectification with polarization by an alternating current and the method of faradaic distortion cannot be used in the case of high frequencies and low concentrations of the potential-determining ions (the former because of transient processes in the circuit containing the double-layer capacitance [(4)], the latter because of the shunting action of the double-layer capacitance [(5)]). The method of faradaic rectification with polarization of the electrode by an alternating potential can be applied in this most

in a more important case, but it is associated with measurements under non-stationary conditions ([6], [7]) and requires complex apparatus. The method of Faradaic heterodyning considered here makes it possible to carry out measurements only of sinusoidal quantities that have become steady in time (which leads to considerable simplifications in the apparatus) and can be used in the case of high frequencies and small concentrations of the potential-determining ions. For this it is only necessary to choose the difference frequency $\Delta\omega$ sufficiently small that the resistance of the double-layer capacitance at this frequency is much greater than the Faradaic impedance (at the fundamental frequencies ω_1 and ω_2 the resistance of the double-layer capacitance may be much smaller than the Faradaic impedance). The smallness of the difference frequency in the indicated sense also ensures the smallness of the distortions introduced by the nonlinearity of the double-layer capacitance.

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REFERENCES

1. M. A. Proskurnin, A. N. Frumkin, Trans. Farad. Soc., **31**, 110 (1935); M. A. Proskurnin, M. A. Vorsina, DAN, **24**, 915 (1939); M. A. Vorsina, A. N. Frumkin, DAN, **24**, 918 (1939); A. Frumkin, Trans. Farad. Soc., **36**, 117 (1940); P. I. Dolin, B. V. Ershler, ZhFKh, **14**, 886 (1940); P. I. Dolin, B. V. Ershler, A. N. Frumkin, ZhFKh, **84**, 907 (1940); P. I. Dolin, A. N. Frumkin, B. V. Ershler, ZhFKh, **14**, 916 (1940).

2. J. E. B. Randles, Disc. Farad. Soc., **1**, 11 (1947); B. Ershler, Disc. Farad. Soc., **1**, 269 (1947); B. V. Ershler, ZhFKh, **22**, 683 (1948); D. C. Grahame, J. Electrochem. Soc., **99**, C370 (1952); P. Delahay, *New Instruments and Methods in Electrochemistry*, Moscow, 1957.

3. K. S. G. Doss, H. P. Agarwal, Proc. Ind. Acad. Sci., **34**, sec. A, 263 (1951); **35**, sec. A, 45 (1952); Yu. A. Vdovin, DAN, **120**, 554 (1958); G. C. Barker, R. L. Faircloth, A. W. Gardner, Nature, **181**, 247 (1958).

4. G. C. Barker, Trans. Symp. Electrode Proc., Philadelphia, 1959.

5. K. B. Oldham, J. Electrochem. Soc., **107**, 766 (1960).

6. H. Matsuda, P. Delahay, J. Am. Chem. Soc., **82**, 1547 (1960).

7. P. Delahay, M. Senda, C. Weis, J. Am. Chem. Soc., **83**, 312 (1961); M. Senda, P. Delahay, J. Phys. Chem., **65**, 1580 (1961); J. Am. Chem. Soc., **83**, 3763 (1961); M. Senda, H. Imai, P. Delahay, J. Phys. Chem., **65**, 1253 (1961).

8. B. P. Aseev, *Fundamentals of Radio Engineering*, Moscow, 1947; A. A. Kharkevich, *Fundamentals of Radio Engineering*, Moscow, 1963.

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