Physical Chemistry

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1964

SovietRxiv

Abstract

Full Text

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The Phase of the Second Harmonic of an Alternating Potential and the Transfer Coefficients of Fast Electrochemical Reactions

At the present time, the concept of the slow character of electrochemical discharge may be considered firmly established ([1]). The equations of the theory of slow discharge contain, as parameters, the exchange current of the electrochemical reaction and the so-called transfer coefficients. In considering oxidation–reduction reactions, instead of the exchange current it is convenient to use the rate constant of the electrochemical reaction at the standard potential k_s, and to characterize the slowness of the electrochemical stage by the quantity $L^{\mathrm{el}} = D/k_s$, where D is the diffusion coefficient. The quantity L^{el} has the dimension of length and may be called the effective length of the electrochemical reaction.

An analysis of the existing methods for investigating electrochemical reactions ([1–12]) shows that, in order to obtain reliable information on the electrochemical stage of the electrode process, electrolysis must be carried out in such a way that the effective length of the electrochemical reaction L^{el} is much greater than, or comparable with, the diffusion length L^{diff}. For fast electrochemical reactions the length L^{el} is small and, consequently, it becomes necessary to reduce the diffusion length L^{diff}. Small thicknesses of the diffusion layer L^{diff} are achieved by using sinusoidal currents. In this case

$$L^{\mathrm{diff}} \sim \sqrt{D/\omega},$$

where ω is the frequency of the alternating current. The faster the electrochemical reaction, the higher the frequency ω must be. However, the use of high frequencies causes complications associated either with the charging current of the double-layer capacitance and the ohmic resistance of the solution (the method of Faradaic impedance), or with considerable technical difficulties (the method of Faradaic rectification). Therefore, a method would be of undoubted interest that would make it possible, at low frequencies, for arbitrarily fast electrochemical reactions, to determine at least one of the parameters of the theory of slow discharge, namely the transfer coefficient α. The creation of such a method would, at the same time, significantly facilitate the determination of the rate constant of a fast electrochemical reaction by means of other methods that make use of the nonlinear properties of the cell. Indeed, the determination of k_s, when the value of α is known, can be reliably carried out at L^{diff} of the order of L^{el}, whereas, when this value is unknown, higher frequencies must be used to determine both parameters of the theory of slow discharge (4).

The principal aim of the present work is to show that the coefficient α can be determined at low frequency by recording, as a function of electrode potential, the phase shift of the second harmonic of the alternating potential relative to the phase of the purely sinusoidal current polarizing the electrode. In (13), values were calculated for the amplitude and phase of the second harmonic of the alternating potential near the equilibrium position, and it was proposed that, for the investigation of electrode processes, the amplitude be measured (the method of Faradaic distortion). Further analysis of the expression

for the phase, taking into account the dependence of the concentrations near the electrode on the potential, leads, for the oxidation-reduction reaction

$$\mathrm{Ox} + ne^- = \mathrm{Rd}$$

to the result

$$\operatorname{ctg}\chi = YP^\alpha \frac{1-\alpha-\alpha P + YP^\alpha(1/2-\alpha)}{1-P^2+YP^\alpha(1-\alpha-\alpha P)}, \tag{1}$$

where

$$Y = \frac{\sqrt{2\omega D_1}}{k_s}\left(\frac{D_2}{D_1}\right)^{\alpha/2};$$

D_1 and D_2 are the diffusion coefficients of the substances Ox and Rd;

$$P = \exp\left\{\frac{nF}{RT}(\varphi-\varphi_{1/2})\right\}; \tag{2}$$

φ is the potential; $\varphi_{1/2}$ is the half-wave potential:

$$\varphi_{1/2} = \varphi^{(0)} + \frac{1}{2}\frac{RT}{nF}\ln\frac{D_2}{D_1};$$

$\varphi^{(0)}$ is the standard potential. The phase χ enters into the expression for the component of the electrode potential that varies with doubled frequency, in the form

$$\varphi_{2\omega} = \varphi_{2\omega}^{(0)}\cos(2\omega t-\chi).$$

Fig. 1. Schematic dependence of χ on P, with rotations of phase I and II shown for $\alpha < 1/2$ and $\alpha > 1/2$.

Figure 1: Fig. 1. Schematic dependence of χ on P, with rotations of phase I and II shown for $\alpha < 1/2$ and $\alpha > 1/2$.

In this case the alternating current polarizing the electrode is equal to

$$I = I^{(0)} \cos \omega t.$$

The value of Y is, in order of magnitude, the same as the ratio $L^{\mathrm{el}}/L^{\mathrm{diff}}$ and, for fast electrochemical reactions at low frequencies, is small. In Fig. 1, for this case, the dependence of the phase of the second harmonic χ on the quantity P, defined by relation (2), is presented. As can be seen, the phase χ assumes the constant values $+\pi/2$ and $-\pi/2$. Phase rotation occurs at the half-wave potential ($P = 1$, phase rotation I) and at a certain value of the potential ($P = P_\alpha$, phase rotation II), depending only on the transfer coefficient α: $P_\alpha = (1-\alpha)/\alpha$, or

$$\alpha = \frac{1}{1 + P_\alpha}. \tag{3}$$

Fig. 1

Thus, if the value of the electrode potential φ_α at which phase rotation II occurs is known, then by formula (3), using (2), the transfer coefficient can easily be found*.

The application of methods that use the nonlinear properties of the cell usually presupposes measurements of quantities of second order of smallness with respect to the signal amplitude (measurement of the rectified voltage or current, the amplitude of the second harmonic, etc.). Here, however, it is necessary only to register the potential at which the phase rotation of one of the

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* Let us note that phase rotation I can be used for more accurate registration of the half-wave potential.

of such quantities. This, of course, should lead to considerable technical simplifications. The use of low frequencies, i.e., frequencies at which the electrical resistance of the electrode-solution boundary is determined by the faradaic impedance, eliminates the shunting action of the double-layer capacitance, which at high frequencies causes a decrease in the magnitude of the useful signal in the method of faradaic distortion (^{13}).

Of definite interest is also the recording of the curve of the dependence on the electrode potential of the phase shift of the second harmonic at higher frequencies, when $L^{\mathrm{el}} \sim L^{\mathrm{diff}}$. As is seen from (1), the first sharp phase rotation disappears and is replaced by a smooth transition, while the second phase rotation remains. In this case, from the χ—P curve one can determine the value k_s (the value of α is assumed known from measurements at low frequency). However, such a method of determining k_s cannot be used in the most interesting case of fast electrochemical reactions and small concentrations of the potential-determining ions, since in this case the resistance of the double-layer capacitance is less than the faradaic impedance and the level of the useful signal falls. This same circumstance also limits the possibilities of the methods of faradaic impedance and faradaic distortion. Nevertheless, the method of recording the χ—P curve at high frequencies may have certain advantages over the two indicated methods: unlike the faradaic-impedance method, it excludes the influence of the ohmic resistance of the solution, and unlike the faradaic-distortion method it does not require knowledge of the magnitude of the component of the electrode potential varying at the fundamental frequency.

In view of the possibility of determining the transfer coefficient α at low frequencies, the combined use of the method of faradaic heterodyning ([14]) and the method of recording the χ—P curve at low frequencies appears especially promising for the simultaneous determination of the parameters of the slow-discharge theory equation that characterize a fast electrochemical reaction. In this case all measurements are carried out under steady-state conditions, using only sinusoidal currents and voltages.

The authors express their gratitude to Academician A. N. Frumkin, R. Sh. Nigmatullin, and S. B. Tsfasman for useful discussions.

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Received
14 IX 1963

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