THE SECOND HARMONIC PHASE OF A VARIABLE POTENTIAL AND THE TRANSFER COEFFICIENT OF FAST CHEMICAL REACTIONS

Corresponding Member of the Academy of Sciences, USSR,
V. G. Levich, B. M. Grafov, and B. I. Khaikin

Institute of Electrochemistry, Academy of Sciences, USSR

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It can be taken as a firmly established fact that electrochemical discharge is a retarded process [1]. The exchange current of the electrochemical reaction and the so-called transfer coefficient are used as parameters in the theoretical equation for the retarded discharge. When oxidation-reduction reactions are considered, the rate constant k_s of the chemical reaction at standard potential can be conveniently used instead of the exchange current, and the retardation of the electrochemical stage can be characterized by the length $L^{el} = D/k_s$, where D is the diffusion coefficient. The parameter L^{el} has the dimension of a length and may be called the effective length of the electrochemical reaction.

Analysis of the known methods [1-12] used in investigating electrochemical reactions reveals that, in order to obtain reliable data on the electrochemical stage of an electrode process, the effective length of the electrochemical reaction L^{el} must be larger than, or comparable to, the diffusion length L^{dif}. In fast electrochemical reactions the length L^{el} is short and this makes it necessary to reduce the diffusion length L^{dif}. Thin diffusion layers (small L^{dif}) are produced by applying sinusoidal currents. In this case

$$L^{\text{dif}} \sim \sqrt{D/\omega},$$

where ω is the frequency of the variable current. The faster the electrochemical reaction the higher must be the frequency ω. However, application of high frequencies gives rise to complications due either to the charge current of the double layer capacitance and the ohmic resistance of the solution (method of Faraday impedance), or to considerable technical difficulties (method of Faraday rectification). Consequently, it is undoubtedly of interest to work out a method by which at least one of the parameters in the theory of retarded discharge – the transfer coefficient α – can be determined at low frequencies, however fast the electrochemical reaction may be. Such a method would considerably facilitate the determination of the rate constants of fast electrochemical reactions by means of other methods in which the nonlinear properties of the cell are utilized. In fact, if α were known, the rate constant k_s might be determined fairly accurately at diffusion lengths L^{dif} in the order of L^{el}, whereas much higher frequencies must be used to determine the two parameters in the theory of retarded discharge in the event α is unknown [4].

The main aim of the present paper is to show that the coefficient α can be determined by applying a low frequency and using the relationship between the electrode potential and the phase shift of the second harmonic in the variable potential with respect to the phase of the purely sinusoidal current polarizing the electrode. In paper [13] the amplitudes and the phases of the second harmonic of a variable potential were calculated for conditions near equilibrium, and it was proposed that electrochemical processes should be studied by measuring the amplitudes (method of Faraday distortion). When allowance is made for the dependence of the concentration near the electrode on the potential, further analysis of the equation for the oxidation-reduction reaction

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

leads to the formula

$$\operatorname{ctg} \chi = YP^{\alpha} \frac{1-\alpha-\alpha P+YP^{\alpha}(^1/_2-\alpha)}{1-P^2+YP^{\alpha}(1-\alpha-\alpha P)}, \tag{1}$$

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, respectively;

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

φ denotes the potential and $\varphi_{\frac{1}{2}}$ the halfwave potential:

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

$\varphi^{(0)}$ being the standard potential. The phase χ appears as follows in the equation for the electrode potential component varying with the frequency 2ω.

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

The variable current polarizing the electrode is given by

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

The magnitude of Y is comparable to the L^{el}/L^{dif} ratio and is small at low frequencies even in fast electrochemical reactions. In Fig. 1 it is shown how in this case the phase of the second harmonic χ depends on the parameter P as found from formula (2). It will be seen that phase χ is equal either to $+\pi/2$ or to $-\pi/2$. Phase reversal takes place at the halfwave potential (P = 1, phase reversal I) and at a definite potential value ($P = P_\alpha$, phase reversal II) depending solely on the transfer coefficient: $P = (1-\alpha)/\alpha$, or

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

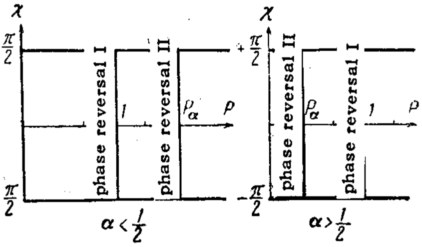

Fig. 1

Consequently, if the value of the electrode potential φ_a at which phase reversal II takes place is known, then, the transfer coefficient can be easily found from formulas (2) and (3).*

Application of methods utilizing nonlinear properties of the cell normally implies that second-order terms of the signal amplitude (voltage or current rectification, amplitudes of the second harmonic, etc.) have to be measured. Here, we need to record only the potential at which one of the parameters reverses its phase. This must, of course, lead to considerable technical simplifications. Utilization of low frequencies, i.e., of frequencies at which the electric resistance of the electrode-solution boundary is determined by the Faraday impedance, eliminates the effect of the double layer capacitance which causes the effective signal to drop at high frequencies when the method of Faraday distortion is applied [13].

It is also of definite interest to measure the electrode potential as a function of the phase shift of the second harmonic at higher frequencies where $L^{el} \sim L^{dif}$. As follows from Eq. (1), the sharp phase reversal I disappears and is replaced by a smooth transition, whereas phase reversal II is preserved. In this case the rate constant k_s can be

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* We note that the phase reversal may be used to record the halfwave potential more accurately.

determined from the χ versus P curve (the parameter α is assumed to be known from measurements at a low frequency). However, this method of determining k_s cannot be used in the most interesting case where fast chemical reactions and low concentrations of the potential-determining ions are involved, since under these conditions the resistance resulting from the double layer capacitance is lower than the Faraday impedance, and the effective signal intensity drops. This circumstance also limits the application range of the Faraday distortion methods. Nonetheless, the method of measuring the χ versus P curve at high frequencies may have some advantages over the two methods mentioned above: unlike the Faraday impedance method it eliminates the ohmic resistance of the solution, and unlike the Faraday distortion method it does not require knowledge of the potential electrode component varying at the main frequency.

Since the transfer coefficient α can be determined at low frequencies, it is particularly advantageous to combine the method of Faraday heterodynization [14] with our method of measuring the χ versus P curve at low frequencies in order to determine simultaneously the parameters which appear in the equation of the theory of retarded discharge and characterize fast chemical reactions. In this case all measurements can be performed in the stationary regime and only sinusoidal currents and voltages have to be used.

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