Translated from *Uspekhi Khimii*, **44**, 1979-1986 (1975) U. D. C. 541.138 : 537.311.6

Electrochemical Processes in an Alternating Current

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The theory of electrochemical impedance is reviewed. Alternating current circuits equivalent to an electrochemical reaction proceeding via an adsorption state are examined for reversible and irreversible systems. The dynamic adsorption equation for a non-equilibrium electrode is discussed. The theoretical circuits are compared with experimental data for the iodine-iodide system.
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I. INTRODUCTION

The use of alternating current in electrochemistry has a long history. The first studies of these lines were begun as early as the 19th century and were associated with the measurement of the conductivities of electrolytes[1]. However, at that time it was already noted that the overall resistance of the electrochemical cell to the alternating current includes the resistance of the electrode–electrolyte boundary. Warburg[2] and Kruger[3] obtained equations for electrode impedance in the special case of diffusion-controlled electrode processes and attempted to measure it. However, the lack of a sufficiently deep understanding of the mechanism of electrochemical reactions and of a reliable experimental technique resulted in comparatively little development in this field — the alternating current was used for a long time exclusively for conductimetric studies.

A decisive breakthrough occurred only after studies by Frumkin and coworkers[4,5], in which the capacitance of the electrical double layer of an ideally polarised mercury electrode was determined for the first time by direct measurements in an alternating current and a capacitance minimum was observed in dilute aqueous solutions at the zero-charge potential, which constituted experimental confirmation of the diffuse double layer theory. Somewhat later Dolin, Ershler, and Frumkin[6–8] used alternating current to investigate the kinetics of the evolution of hydrogen on a platinum electrode. These studies began the wide-scale employment of alternating current in electrochemical kinetics[9–21]. Quantitative measurements of the impedance of readily polarisable electrodes have recently undergone a fresh development and have been discussed in detail in a number of reviews[22–27].

II. IMPEDANCE OF SLOW ELECTROCHEMICAL REACTIONS

The main property of cells with ideally polarisable electrodes is that their impedance corresponds to the simplest a.c. circuit comprising the series-connected electrolyte resistance R_e and the double-layer capacitance C_d (Fig. 1*a*):

$$Z = R_e + (j\omega C_d)^{-1}. \quad (1)$$

The rate of relaxation of the double layer in solutions is fairly high, so that, even at frequencies of the order of several Megahert, C_d (as well as R_e) is independent of the a.c. frequency[28,29]. For comparatively slow electrode processes, it is possible to isolate three classical mechanisms under these conditions.

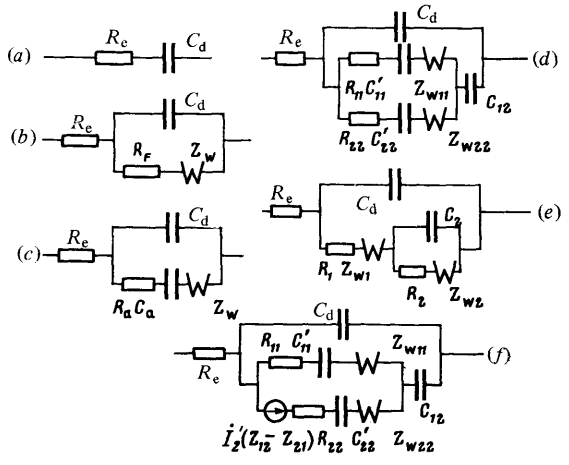


Figure 1. Equivalent a.c. circuits.

1. An electrochemical reaction not accompanied by the adsorption of the reactants: the Ershler–Randles impedance[30–32]. The process is illustrated graphically in Fig. 2*a* and the equivalent a.c. circuit is shown in Fig. 1*b*. The corresponding analytical expression for the impedance is

$$Z = R_e + \{j\omega C_d + [R_F + \tilde{W}/\sqrt{j\omega}]^{-1}\}^{-1}, \quad (2)$$

where

$$R_F = RT/(nF)^2 V_0 \quad (3)$$

is the resistance to charge transfer,

$$\tilde{W} = RT/(nF)^2 c_0 \sqrt{D} \quad (4)$$

the Warburg constant, i_0 the exchange flux for the charge-transfer reaction, c_0 the concentration of electrochemically active species in the bulk of the electrolyte, D their diffusion coefficient, F the Faraday, and n the number of charges transported in an electrochemical reaction of the type

$$Ox + ne \rightleftharpoons Red. \qquad (5)$$

The expression in square brackets in Eqn. (2) is called the Faraday impedance (Z_F).

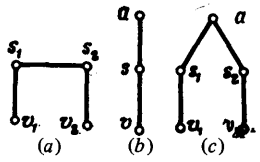


Figure 2. Schematic graphical representation of electrode processes.

2. An adsorption process without electrochemical reaction: the Frumkin–Melik–Gaikazyan impedance[33,34]. The process is illustrated by a graphical scheme in Fig. 2 and the equivalent a.c. circuit is shown in Fig. 1*c*:

$$Z = R_e + \{j\omega C_d + [R_a + \tilde{W}_a/\sqrt{j\omega} + (j\omega C_a)^{-1}]^{-1}\}^{-1}, \qquad (6)$$

where

$$\left.\begin{aligned} R_a &= RT/q_A^2 V_0;\ C_a = q_A^2/\tilde{\mu}_A, \\ \tilde{W}_a &= RT/q_{Ac_0}^2 \sqrt{D}, \end{aligned}\right\} \qquad (7)$$

q is the electrode charge, A the amount of substance in the adsorbed state, $\tilde{\mu}$ the electrochemical potential of the adsorbed substance, $q_A = (\partial q/\partial A)\varphi$, and $\tilde{\mu}_A = (\partial\tilde{\mu}/\partial A)\varphi$. Here both C_d and C_a make up the double layer capacitance; although the charging of the C_d capacitance is rapid, the C_a capacitance charges slowly and the kinetics of its charging process are determined by the rates of adsorption (R_a) and diffusion ($\tilde{W}_a$) of the species undergoing adsorption, for example dipolar organic molecules.

3. An electrochemical reaction complicated by a chemical reaction: the Gerischer impedance[35–37]. In contrast to the Ershler–Randels impedance, in this case the electrochemically active species appear near the electrode both as a result of diffusion and as a result of a chemical reaction, for example the decomposition of a complex. For this reason the Warburg impedance in the usual circuit (Fig. 1*b*) is replaced by a complex resistance, which depends on the frequency in a more complicated manner (see, for example, Vetter[13]).

III. IMPEDANCE OF ELECTROCHEMICAL REACTIONS COMPLICATED BY ADSORPTION

The theory of the impedance of electrochemical reactions complicated by adsorption has been developed since 1961.[21,38–47] Fig. 2*c* illustrates a schematic graphical representation of a reaction proceeding via an adsorbed state. A characteristic feature of such processes is that charge transfer from the reacting species to the metal can in general take place in two stages. In the first stage (line s_1a) the oxidised form passes from the state near the surface of the electrode (point s_1) to the adsorbed state (point a). This entails the transfer of a charge n_1. In the second stage (line as_2) the substance passes from the adsorbed state in the reduced form to the state near the electrode surface (point s_2). This entails the transfer of a charge n_2. The overall number of electrons supplied to the electrode via the external circuit on transition of the reactant from point s_1 to point s_2 is n under the conditions of a constant potential, so that

$$n_1 + n_2 = n; \qquad (8)$$

here n_1 and n_2 need not be integral numbers. Only their sum n is an integar. The quantities n_1 and n_2 are macroscopic characteristics— they define the amount of electricity which is supplied on average to the electrode via the external circuit when an ion or molecule of the surface-active substance passed from one state to another.

Following Lorenz and Salie[39], we put

$$n_1 = ln;\ n_2 = (1-l)n\ . \qquad (9)$$

The coefficients l and $1-l$ characterise the fraction of the charge transferred in each of the two adsorption stages. The charge transfer in the individual stages of the electrochemical reaction can be related to the adsorption characteristics of the system[21,48]:

$$l = \frac{\Gamma_{1\mu_1} + \Gamma_{1\mu_2}}{\Gamma_{1\mu_1} + \Gamma_{2\mu_2} + \Gamma_{1\mu_2} + \Gamma_{2\mu_1}}, \qquad (10)$$

where Γ_1 and Γ_2 are respectively the Gibbs adsorptions of the oxidised and reduced forms μ_1 and μ_2 are their chemical potentials, and $\Gamma_1\mu_2 = \Gamma_2\mu_1$. This relation makes it possible to calculate the charge transferred from thermodynamic data for the overall charges of the reversible electrode. Such calculations have been made, for example, for charge transfer in the adsorption of H^+ ions and hydrogen atoms on a platinum electrode[48]. It was found that in this system the parameter l varies markedly with the potential and also depends on the composition and pH of the solution. In many cases l is greater than unity. In other words, in the adsorption of H^+ ions, excess negative charge can be transferred to them.

The impedance of an electrochemical reaction proceeding via two adsorption stages can be calculated using the method of equivalent multiterminal networks and Onsager's reciprocal relations[21,43,44]. Although from the standpoint of the theory of electric circuits the electrochemical cell always consists of a two-terminal network (diode), in the presence of a two-stage process an individual current corresponds to each stage (I_1 and I_2). However, since adsorption processes do not tkae place independently because we are dealing with reactions of the same substance, the currents I_1 and I_2 are related. This can be expressed with the aid of relations between the current and polarisation analogous to the equations for a four-terminal network:

$$\left.\begin{aligned} \Delta\varphi &= Z_{11}I_1 + Z_{12}I_2, \\ \Delta\varphi &= Z_{21}I_1 + Z_{22}I_2, \end{aligned}\right\} \qquad (11)$$

where Z_{11} and Z_{22} are the input impedances for two adsorption processes (s_1a and s_2a) and Z_{12} and Z_{21} describe the interaction of these processes.

Eqns. (11) characterise a four-terminal network, which is the electrical equivalent of the given process. A characteristic feature of such a four-terminal network is that the potentials at the two pairs of its terminals are the same

and equal to $\Delta\varphi$. Eqns. (11) express in essence the phenomenological law of non-equilibrium thermodynamics as applied to electrochemical reactions. Since in the absence of an alternating current the system is at equilibrium, the Onsager relation $Z_{12} = Z_{21}$ (the equality of the kinetic cross-coefficients) should hold. Direct calculations for this process, illustrated schematically in Fig. 2*c*, show that the frequency dependences of the coefficients Z_{12} and Z_{21} are in fact the same and their equality can be confirmed independently by analysing the Gibbs adsorption equation (or more precisely the equality of the cross-derivatives of the Gibbs adsorptions of the two forms with respect to the chemical potentials $\Gamma_1\mu_2 = \Gamma_2\mu_1$).[21,46]

The Faraday impedance, calculated by Eqns. (11), can be formulated as follows:

$$Z_F = \frac{Z_{11}Z_{22} - Z_{12}^2}{Z_{11} + Z_{22} - 2Z_{12}}, \qquad (12)$$

where

$$Z_{11} = R_{11} + \widetilde{W}_{11}/\sqrt{j\omega} + (j\omega C_{11})^{-1}, \qquad (13)$$

$$Z_{22} = R_{22} + \widetilde{W}_{22}/\sqrt{j\omega} + (j\omega C_{22})^{-1}, \qquad (14)$$

$$Z_{12} = -(j\omega C_{12})^{-1}, \qquad (15)$$

and the coefficients R_{11}, C_{11}, $\widetilde{W}_{11}$, etc. are expressed in terms of parameters characterising the electrochemical reaction:

$$R_{ii} = RT/(n_iF)^2V_{i0};\ \widetilde{W}_{ii} = RT/(n_iF)^2c_{i0}\sqrt{D_i};\ C_{ik} = n_in_kF^2/\widetilde{\mu}_A, \qquad (16)$$

where $i, k = 1$ or 2. The equivalent a.c. circuit for the given process can be constructed, for example, in the way shown in Fig. 1*d*. In this case we have

$$(C_{ii}')^{-1} = C_{ii}^{-1} + C_{ik}^{-1}\ (i \neq k). \qquad (17)$$

In order to represent the Faraday impedance in a fairly compact analytical form, we introduce the following notation:

$$l/(1-l) = \xi, \qquad (18)$$

$$c_{10}\sqrt{D_1}/c_{20}\sqrt{D_2} = r;\ V_{10}/V_{20} = p\ . \qquad (19)$$

Then Eqn. (12) can be reduced to the form

$$Z_F = \frac{\widetilde{W}_{11}C_{11}^{-1}(1+r)\xi^2x^3 + [R_{11}C_{11}^{-1}(1+p) + \widetilde{W}_{11}^2r]\xi^2x^2 + R_{11}\widetilde{W}_{11}(p+r)\xi^2x + pR_{11}\xi^2}{C_{11}^{-1}(1+\xi)^2x^2 + \widetilde{W}_{11}(1+r\xi^2)x + R_{11}(1+p\xi^2)}, \qquad (20)$$

where $x = (j\omega)^{-1/2}$.

The case where the effective charge transfer in one of the stages is insignificant is of considerable interest. When the adsorption of the oxidised form is not accompanied by an appreciable charge transfer, i.e. when

$$\xi \ll 1;\ n_2 \simeq n\ , \qquad (21)$$

we have

$$Z_F = R_{22} + \frac{\widetilde{W}_{22}}{\sqrt{j\omega}} + \frac{1}{j\omega C_{22} + [R_{11}\xi^2 + \widetilde{W}_{11}\xi^2/\sqrt{j\omega}]^{-1}}, \qquad (22)$$

where $R_{11}\xi^2 = RT/(nF)^2V_{10}$ and $\widetilde{W}_{11}\xi^2 = RT/(nF)^2c_{10}\sqrt{D_1}$. Similarly, when charge transfer occurs predominantly in the stage involving the adsorption of the oxidised form, then

$$\xi \gg 1;\ n_1 \simeq n, \qquad (23)$$

and

$$Z_F = R_{11} + \frac{\widetilde{W}_{11}}{\sqrt{j\omega}} + \frac{1}{j\omega C_{11} + [pR_{11} + r\widetilde{W}_{11}/\sqrt{j\omega}]^{-1}}, \qquad (24)$$

where $pR_{11} = RT/(nF)^2V_{20}$ and $r\widetilde{W}_{11} = RT/(nF)^2c_{20}\sqrt{D_2}$. Eqns. (22) and (24) both correspond to the same equivalent circuit (Fig. 1*e*).

The results can be used to analyse the electrode reaction on platinum in the iodine–iodide system. The impedance of this system has been investigated[49–52]. Vetter[49] and Tyagai et al.[52] concluded that the electrode reaction proceeds via the discharge–recombination mechanism, the discharge stage being slow. Llopis et al.[50] showed that the experimental data correspond to the equivalent circuit in Fig. 1*e*. The hodograph of the input impedance of the cell is of the form shown in Fig. 3. Dane et al.[51] found the exchange current of the electrochemical reaction from the impedance data assuming that the resistance R_D is equal to the diameter of the half-circle shown in Fig. 3 by a dashed line and that $i_0 = RT/FR_D$. The study of the variation of i_0 with the concentration of I^- ions and of dissolved iodine led the authors[51] to the conclusion that the reaction proceeds via the discharge–electrochemical desorption mechanism. This view was confirmed by other methods and it was shown that the exchange currents are comparable for both stages[53].

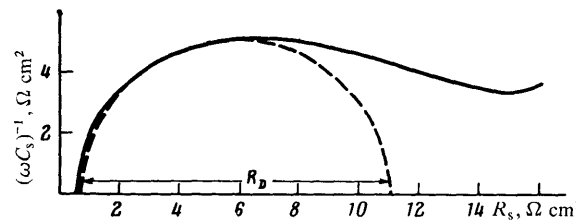


Figure 3. The hodograph of the impedance of the Pt/(1 *N* H_2SO_4 + 3.5 × 10^{-5} mole cm^{-3} KI + 0.46 × 10^{-6} mole cm^{-3} I_2) boundary at 25 °C (data of Llopis et al.[50]); impedance parameters: $R_e = 0.7\ \Omega\,cm^2$, $R_1 = 9.8\ \Omega\,cm^2$, $R_2 = 3.5\ \Omega\,cm^2$, $W_1 = 0$, $W_2 = 95.5\ \Omega\,cm^2s^{-1/2}$, $C_d = 3\ \mu F$ cm^{-2}, $C_2 = 31\ \mu F\ cm^{-2}$. The diameter of the dashed half-circle is approximately 10.2 Ω cm^2.

Parameters of the electrode impedance of the I_2/AgI system[54].

t, °C	C_d, μF cm^{-2}	C_2, μF cm^{-2}	R_1, Ω cm^2	R_2, Ω cm^2	W_1, Ω $cm^2s^{-1/2}$	W_2, Ω $cm^2s^{-1/2}$
197	46.3	15.9	0.10	0	98	2160
363	58.0	17.6	0.19	0	210	1180
498	64.5	20.8	0.20	0	130	590
549	79.6	21.5	0.20	0	92	325
618 (melt)	102	—	0.045	0	63	—

As shown previously[21], the discharge–recombination and discharge–electrochemical desorption mechanisms lead to the same a.c. current (Fig. 1*d*). If the diffusion of I^- ions does not make an appreciable contribution to the impedance (a fairly concentrated solution) and the discharge is transferred preferentially in the first stage so that $n_2 \simeq 0$ and $n_1 \simeq 2$, then the circuit in Fig. 1*d* transforms into that in Fig. 1*e*, for which $ZW_1 = 0$. The rates of the two adsorption stages, characterised by the resistance R_1 and R_2, are comparable (Fig. 3), which agrees with the results

of Povarov et al.[53]. Thus the experimental data of different workers for the impedance of the Pt/I_2, KI, H_2SO_4 boundary can be explained from the same standpoint using Eqn. (24). The C, I_2/α-AgI boundary with a solid electrolyte behaves similarly[54]. The equivalent circuit of the Faraday process in such a system is the same as in Fig. 1*d*. The impedance parameters are listed in the Table. In this case both the diffusion of I^- ions proceeding via the lattice defects and the diffusion of molecular iodine are significant. The impedance ZW_2 corresponds to the former and ZW_1 corresponds to the latter. This follows from the fact that, when the crystal melts, the impedance ZW_2 falls to zero, since all the I^- ions begin to participate in the transport.

IV. IMPEDANCE OF NON-EQUILIBRIUM ELECTROCHEMICAL SYSTEMS

The study of the properties of the electrochemical impedance of complex systems showed that it is necessary to use the principles of non-equilibrium thermodynamics and particularly the Onsager reciprocal relations. It was found that the dynamic adsorption equation for an irreversible electrode can be obtained from the Onsager relations and the adsorption equation for a reversible electrode[53]. In fact, for an ideally reversible electrode one can write the Gibbs adsorption equation:

$$-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2. \qquad (25)$$

The chemical potentials of the oxidised and reduced forms can be expressed in terms of the electrochemical ($\tilde{\mu}$) and the electrical (φ) potentials, i.e.

$$-d\gamma = \Gamma_1 d(\tilde{\mu}_1 + z_1 F\varphi) + \Gamma_2 d(\tilde{\mu}_2 + z_2 F\varphi). \qquad (26)$$

If the adsorbed species are in equilibrium with the adsorption layer, then we have for the reaction mechanism corresponding to Fig. 2*e*

$$-d\gamma = \Gamma_1 d(\tilde{\mu}_a + z_1 F\varphi) + \Gamma_2 d(\tilde{\mu}_a + z_2 F\varphi), \qquad (27)$$

$\tilde{\mu}_a$ being the electrochemical potential of the adsorbed species and z_1 and z_2 their charges. It follows directly from Eqn. (27) that[21]

$$-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + Q' d\eta_1 + Q' d\eta_2, \qquad (28)$$

where Q' and Q'' are the total thermodynamic charges on the electrode[56] and η_1 and η_2 are the overvoltages in the first and second adsorption stages.

The equation was obtained in relation to equilibrium conditions, but it is valid also for non-equilibrium electrodes (i.e. when a direct current is imposed), provided that the following two conditions are fulfilled: (a) when a direct current flows, the mechanism of the electrode process does not change; (b) the processes in the surface layer are fairly rapid, so that the thermodynamic properties of this layer are determined unambiguously by the electrode potential and the electrochemical potentials of the adsorbed species. In other words it is assumed that, regardless of whether there is an equilibrium between the surface and bulk-phase states, the state of the surface layer remains the same function of its surface variables.

If the electrochemical system in the absence of an alternating current does not correspond to equilibrium, for example when a direct current is imposed, the Onsager relations cease to hold although the Faraday process can still be represented by the equivalent multiterminal network. The overall impedance of the electrochemical reaction proceeding via the adsorbed state is in this case given by

$$Z_F = \frac{Z_{11}Z_{22} - Z_{12}Z_{21}}{(Z_{11} + Z_{22}) - (Z_{12} + Z_{21})}, \qquad (29)$$

where $Z_{12} \neq Z_{21}$. Formally the impedance Z_F can also be represented by a rational-fractional function of $(j\omega)^{-1/2}$ in which the numerator is a third-degree polynominal and the denominator is a second-degree polynomial. Thus the frequency variation of the impedance does not depend on the degree of reversibility of the system in terms of a direct current, but is determined exclusively by the mechanism of the electrochemical process. The coefficients of the rational-fractional function can vary with the degree of polarisation under a direct current. This relation can be determined on the basis of a specific reaction model.

In view of the inequality of Z_{12} and Z_{21}, the equivalent a.c. circuit of the type shown in Fig. 1*d* should include a dependent current source (see, for example, Atabekov[57]). Thus aperiodic equivalent circuits, analogous to those proposed by Barker[58,59] for reversible systems, can be constructed for irreversible systems.

The development of the theory of electrochemical impedance leads to great possibilities for the application of alternating currents in electrochemical kinetics to the study of complex reactions accompanied by adsorption both near equilibrium and following the imposition of a direct current.

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