THE ANALYSIS OF EQUIVALENT CIRCUITS OF THE ELECTRODE IMPEDANCE

E. A. Ukshe

UDC 541.13

The investigation of the complex impedance of the electrode-electrolyte interphase with alternating current must include the following operations: a) synthesis of the equivalent circuits, i.e., expression of the kinetic parameters of the electrochemical reactions through elements of electrical circuits (active resistances R, capacitances C, inductances L); b) experimental determination of the input impedance of the electrode, Z_e, as a function of ac frequency, ω; c) determination of the equivalent circuit for the electrode and of the values of its component elements from the experimental data, i.e., the analysis of the equivalent circuits.

In the present work, developing the ideas of Sluyters [1] and Leikis [2], we propose a technique of analyzing equivalent circuits containing three or four elements including the double-layer capacitance. Consider the equivalent circuit shown in Fig. 1a. It includes the double-layer capacitance, C_d, the transfer resistance, θ, a capacitance caused by a heterogeneous reaction or by adsorption, C_a, and a concentration impedance $Z_c = (1-j)A/\sqrt{\omega}$ where $j = \sqrt{-1}$, and the concentration constant A is determined by the well-known relation [3]

$$A = \frac{RT}{n^2F^2\sqrt{2D \cdot c_0}}. \tag{1}$$

Using the relations between series and parallel networks of equal impedance (Fig. 1b and c):

$$C_p = \frac{\beta^2}{1+\beta^2}C_s; \quad R_p = (1+\beta^2)R_s, \tag{2}$$

where

$$\beta = (\omega C_s R_s)^{-1} = \omega C_p R_p \tag{3}$$

is the tangent of the phase angle, it is easy to obtain, by elementary algebraic transformations, expressions that link the double-layer capacitance, C_d, and the quantity β with the parameters of the equivalent circuit (Fig. 1a):

$$C_d = \frac{1-(\beta\lambda)^{-1}}{1+\beta^{-2}} \cdot C_s, \quad \beta = \frac{1}{\lambda} + \frac{1+\lambda^2}{\lambda} \cdot AC_d\sqrt{\omega}, \tag{4}$$

where

$$\frac{1}{\lambda} = \frac{1+(C_aA\sqrt{\omega})^{-1}}{1+\theta\sqrt{\omega}/A}. \tag{5}$$

The quantity $1/\lambda$ is the tangent of the phase angle of the Faraday impedance Z_f that includes the active resistance $R_f = \theta + A/\sqrt{\omega}$ and the capacitative resistance $1/\omega C_f = 1/\omega C_a + A/\omega$. Obviously,

$$1/\lambda = (\omega C_f R_f)^{-1} = [\omega(C_p - C_d)R_p], \tag{6}$$

where C_p and R_p are the elements of a parallel RC network whose impedance is equal to the input impedance of the electrode, Z_e, while R_s and C_s are the elements of the corresponding series RC network. In the general case λ approaches asymptotically a straight line with increasing frequency when plotted as λ against $\sqrt{\omega}$, while with decreasing frequency a straight line is approached that can be expressed by the equation $1/\lambda = 1 + (C_aA\sqrt{\omega})^{-1}$.

Results of measurements at an arbitrary frequency contain the two parameters R_s and C_s (or C_s and β) while the circuit of Fig. 1a contains four unknown elements: C_d, θ, A, and C_a. Therefore, in order to determine each of

Institute for New Chemical Problems, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 4, No. 9, pp. 1116-1119, September, 1968. Original article submitted January 16, 1968.

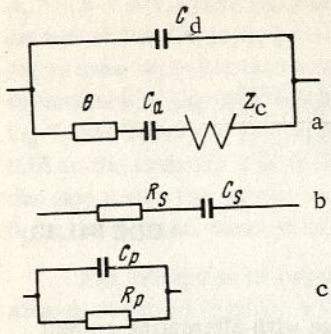


Fig. 1. Four-element equivalent circuit (a) and representation of the input impedance by series (b) and parallel (c) RC networks.

these elements one needs measurements at two fixed frequencies. A numerical solution of two pairs of equations of the type of Eq. (4) can be obtained with the aid of computers. A simpler though less reliable way consists in extrapolating the plot C_p against $1/\omega R_p$ to $1/\omega R_p = 0$ for an evaluation of the quantity C_d [4]. From this one can determine $1/\lambda$ using Eq. (6), and then from the first Eq. (5) again calculate C_d. Repeating this operation one can attain constancy of the calculated value of C_d, and then, transforming from the parallel circuit of the Faraday impedance (C_p-C_d, R_p) to the series circuit ($Z_f = R_f - j/\omega C_f$), determine the values R_f and C_f which for the circuit of Fig. 1a must satisfy the relations

$$1/C_f = 1/C_a + A\sqrt{\omega}, \quad R_f = \theta + A/\sqrt{\omega}, \tag{7}$$

i.e., in the corresponding plots one can obtain straight lines whose parameters allow θ, C_a, and A to be calculated.

The analysis is substantially simplified if the equivalent circuit for the electrode contains only three elements. With $1/\omega C_a = 0$, for example,

$$\lambda = 1 + \frac{\theta}{A}\sqrt{\omega} \tag{8}$$

and for determining C_d one can use the quadratic equation for pairs of frequencies

$$aC_d^2 + bC_d + d = 0, \tag{9}$$

where

$$a = x_1x_2 \cdot (y_1 - y_2) \cdot z_1z_2,$$
$$b = (x_1y_1z_1 - x_2y_2z_2) - x_1x_2(y_1 - y_2)(z_1 - z_2),$$
$$d = (1 - x_1)x_2y_2 - (1 - x_2)x_1y_1,$$
$$x = \beta; \quad y = \sqrt{\omega}; \quad z = 1/C_p.$$

Constancy of the calculated C_d values over a wide range of frequencies is a criterion for the correctness of the circuit selected. A less laborious way consists in selecting C_d values conforming with the results of extrapolating plots of C_p against $1/\omega R_p$ such that Eq. (8) is fulfilled. After determining C_d the values θ and A are found from the relations

$$\theta/A = \frac{\lambda - 1}{\sqrt{\omega}}, \quad A = \frac{\lambda}{1 + \lambda^2} R_p \sqrt{\omega} = \frac{1}{(1 + \lambda^2)(C_p - C_d)\sqrt{\omega}}. \tag{10}$$

In the case $\theta = 0$

$$C_d = \frac{(x_1 - 1)y_1 - (x_2 - 1)y_2}{x_1y_1z_1 - x_2y_2z_2} \tag{11}$$

with the same notations as for Eq. (9). The condition

$$1/\lambda = 1 + (C_aA\sqrt{\omega})^{-1} \tag{12}$$

must likewise be satisfied, while the parameters C_a and A can be found from the equations

$$C_aA = \frac{\lambda}{(1 - \lambda)\sqrt{\omega}}, \quad A = \frac{\lambda^2}{1 + \lambda^2} R \cdot \sqrt{\omega} = \frac{\lambda}{(1 + \lambda^2)(C_p - C_d)\sqrt{\omega}}. \tag{13}$$

Finally, for a two-element circuit consisting of C_d and Z_c

$$C_d = \frac{1 - \beta^{-1}}{1 + \beta^{-2}} C_s = \text{const}, \quad \beta = 1 + 2AC_d\sqrt{\omega}. \tag{14}$$

Carrying out the calculations for various frequencies, C_d values are obtained that, (if the selected circuit is correct), do not depend on frequency while in a plot of β against $\sqrt{\omega}$ the experimental points must fall on a straight line that has an intercept of unity with the ordinate.

TABLE 1. Impedance of an Equilibrium Platinum Electrode (C in $\mu F/cm^2$, R in $\Omega \cdot cm^2$)

$\omega \cdot 10^{-3}$	C_s	R_s	β	C_p	R_p	C_d	λ	A	θ
125,7	620	0,0161	0,792	240	0,0262		3,40	2,51	0,017
94,24	808	0,0184	0,715	273	0,0278	150	3,10	2,50	0,017
62,83	1130	0,0214	0,660	342	0,0307		2,70	2,51	0,017
31,42	1880	0,0269	0,630	535	0,0375	152	2,20	2,50	0,017
18,85	2710	0,0315	0,643	765	0,0445	148	1,935	2,49	0,017
12,57	3320	0,0360	0,637	1020	0,0520		1,760	2,50	0,017

TABLE 2. Impedance of a Polarized Platinum Electrode (C in $\mu F/cm^2$, R in $\Omega \cdot cm^2$)

$\omega \cdot 10^{-3}$	C_s	R_s	β	C_p	R_p	C_d	λ	A	C_a
314,2	53,0	0,0142	4,22	50,2	0,268		0,955	71,6	532
251,3	55,0	0,0186	3,09	51,6	0,301	38,4	0,956	72,2	596
188,5	58,0	0,0259	3,45	53,7	0,350		0,949	72,0	597
125,7	63,2	0,0400	3,41	57,4	0,435	37,2	0,936	71,9	572
94,24	67,3	0,0542	2,98	60,4	0,507		0,925	71,9	556
62,83	75,1	0,0815	2,06	65,4	0,632	37,9	0,912	71,7	573
31,42	92,4	0,1535	2,42	76,8	0,925		0,880	71,6	580
18,85	108,5	0,2380	2,05	87,3	1,240	38,2	0,855	71,8	600

In order to illustrate the methods considered for analyzing three-element circuits, results are given below for impedance measurements in molten salts. Table 1 gives data pertaining to the system $Pt/PtCl_2$, KCl-LiCl at 450°C. The equilibrium potential of the test electrode was about 0.96 V against a lead-chloride reference electrode. These were analyzed with the aid of Eqs. (9) and (10).

Table 2 gives data obtained for the system Pt/KCl-NaCl (1 : 1) at 700°C with applied cathodic polarization (potential $\varphi = +0.10$ V). In this case the calculations were carried out using Eqs. (11) and (13). We intend to publish the results of a systematic investigation into the properties of a platinum electrode under ac at a later date. For the present it was only intended to demonstrate the possibility to analyze the equivalent circuits with the methods proposed. It is interesting to note that in the case where the Faraday impedance contains a transfer resistance θ, the tangent of the phase angle assumes a value of less than unity at not too high frequencies. Conversely, for circuits that contain a capacitance C_a, it always remains substantially larger than unity. This rule allows giving a qualitative assessment of the possible equivalent circuit without carrying out calculations.

LITERATURE CITED

1. J. H. Sluyters, Rec. Trav. Chim., 79, 1092 (1960).
2. D. I. Leikis, Élektrokhimiya, 1, 472 (1965).
3. K. Vetter, Electrochemical Kinetics [Russian translation], "Mir," Moscow (1967).
4. R. de Levie, Electrochim. Acta, 10, 395 (1965).