
Equivalent circuit of electrochemical processes involving two consecutive charge transfer steps

Arvydas Survila and
Vilma Baliukienė

*Institute of Chemistry,
A. Goštauto 9,
LT-2600, Vilnius, Lithuania*

The structure of equivalent circuit is deduced from analytical equations describing the faradaic impedance of electrochemical processes involving two consecutive one-electron transfers. It consists of two parallel subcircuits, each containing charge transfer resistance and Warburg impedance in series. The modified equivalent circuit accounting for the effects arising from the roughness of the electrode surface and limited space of diffusion is proposed. This circuit makes it possible to describe impedance data obtained for a Cu|Cu(II) system with an accuracy of $\pm 2\%$. Exchange current densities in 0.01 M CuSO₄ solution are found to be equal 0.02 mA cm⁻² and 0.8 mA cm⁻² for the processes of Cu²⁺ + e → Cu⁺ and Cu⁺ + e → Cu, respectively.

Key words: consecutive charge transfer, equivalent circuit, faradaic impedance

INTRODUCTION

At present, electrochemical impedance spectroscopy (EIS) is acknowledged to be among the most powerful methods used for investigation of electrode processes. A significant progress in this field is associated not only with advancements in the EIS theory (see, *e.g.*, [1]), but with improvements in measurement devices as well. Modern equipment makes it possible to obtain impedance data in a wide region of frequencies (ω) covering 7–8 orders of magnitude. However, certain problems arise with the analysis of such data, especially when the electrode process is not simple and involves some chemical or electrochemical steps.

Such problems can be obviated to some extent by using special computer programs designed for analyzing impedance spectra. An example of this type of service may be the program elaborated by Boukamp [2]. It is based on the determination and analysis of equivalent circuits reflecting electrical properties of an electrochemical system.

In specific cases, only analytical relationships have been obtained for real (Z') and imaginary (Z'') parts of faradaic impedance, but no consideration has been given to the structure of equivalent circuit. In particular, such a situation is specific for processes involving consecutive charge transfer steps [3–7]. We failed to find in available references the data concerning the equivalent circuit which could rigorously follow from the analytical solutions of differential equations [3, 4]. Only simplified cases have

been reported in [5–7]. In this connection, the problem mentioned above seems to be worth of a more detailed consideration.

EXPERIMENTAL

Impedance measurements were carried out within the frequency range from 10⁻¹ to 5 × 10⁴ Hz, using a Zahner Elektrik (Germany) IM6 Impedance Spectrum Analyzer. Solutions under investigation contained 0.01 M of CuSO₄ and 0.3 M of K₂SO₄ as a supporting electrolyte. Analytical grade salts were purified additionally by means of recrystallization and heating. Solutions were deaerated by argon stream over 0.5 h. Thrice-distilled water was used for preparation of solutions.

A Pt wire of 0.3 cm² surface area was used as a substrate for preparation of the working electrode. It was coated by a copper layer 5–7 μm thick in an acid sulphate solution at a current density of 10 mA cm⁻². A saturated Ag|AgCl, KCl electrode served as a reference electrode. Potentials of the electrode were converted to the standard hydrogen scale. All experiments were carried out at room temperature.

THEORETICAL

When the electrochemical process proceeds by two one-electron transfers:





the following equations are valid for the real and the imaginary parts of faradaic impedance at equilibrium potential [3, 4]:

$$Z' = Z_{\infty} \frac{1 + \frac{\sqrt{2}}{2} y [(a_1 + a_2 + 1) + \sqrt{2} y (a_1 + a_2) + a_1 a_2 y^2]}{1 + \sqrt{2} y + y^2}, \quad (3)$$

$$-Z'' = Z_{\infty} \frac{\frac{\sqrt{2}}{2} y (a_1 + a_2 - 1) + a_1 a_2 y (\sqrt{2} + y)}{1 + \sqrt{2} y + y^2}, \quad (4)$$

where $Z_{\infty} = \lim_{\omega \rightarrow \infty} Z'$, $y = p\sqrt{\omega}$. Parameters p , a_1 and

a_2 depend on exchange current densities (i_{01} and i_{02}), diffusion coefficients (D_O , D_Y , D_R) and bulk concentrations (c_O , c_Y , c_R) of species O, Y and R, respectively. Specific expressions for those parameters given in [3, 4] are different and depend on whether a soluble [3] or insoluble (metallic phase) [4] product R is formed.

Now, let us consider the circuit shown in Fig. 1 in the dotted frame. There resistances and Warburg impedances are symbolized as R_1 , R_2 and Z_{W1} , Z_{W2} , respectively. The Warburg impedances (electric analogues of diffusive mass transport) can be given by

$$Z_{W_i} = \frac{W_i(1-j)}{\sqrt{\omega}}, \quad (5)$$

where W_i are Warburg coefficients ($i = 1, 2$) and $j = \sqrt{-1}$.

An analysis of given equivalent circuit yields:

$$Z' = R c_1 c_2 \frac{1 + \frac{\sqrt{2}}{2} y \left[\frac{c_1^2 d_2 + 2c_1 c_2 + c_2^2 d_1}{c_1 c_2} + \sqrt{2} y \frac{c_1 d_2 + c_2 d_1}{c_1 c_2} + \frac{d_1 d_2}{c_1 c_2} y^2 \right]}{1 + \sqrt{2} y + y^2}, \quad (3a)$$

$$-Z'' = R c_1 c_2 \frac{\frac{\sqrt{2}}{2} y \frac{c_1^2 d_2 + c_2^2 d_1 + d_1 d_2 (\sqrt{2} + y)}{c_1 c_2}}{1 + \sqrt{2} y + y^2}, \quad (4a)$$

where $y = \sqrt{\frac{2}{\omega}} \frac{W}{R}$ and new parameters are determined by relationships:

$$\begin{cases} R_1 = c_1 R, \\ R_2 = c_2 R, \\ W_1 = d_1 W, \\ W_2 = d_2 W, \\ R = R_1 + R_2, \\ W = W_1 + W_2. \end{cases} \quad (6)$$

It follows from the identity of Eqns. (3), (3a) and (4), (4a) that

$$\begin{cases} p = \sqrt{2} \frac{W}{R}, \\ Z_{\infty} = R c_1 c_2, \\ a_1 = \frac{d_1}{c_1}, \\ a_2 = \frac{d_2}{c_2}. \end{cases} \quad (7)$$

Equations (7) give the relations between kinetic parameters of the processes (1) and (2) and electric elements of the equivalent circuit when metallic phase is deposited. When $D_O = D_Y = D$, then

$$i_{01} + i_{02} = \frac{RT}{F} \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \quad (8)$$

$$\frac{1}{i_{01}} + \frac{1}{i_{02}} = \frac{R_1 + R_2}{W_1 + W_2} \frac{1}{F \sqrt{D}} \left(\frac{1}{c_O} + \frac{4}{c_Y} \right). \quad (9)$$

The derived equations are valid in the case of one-dimensional semi-infinite diffusion. The total electrode impedance is obtained when such extra parameters as the ohmic resistance of solution R_{Ω} and the capacitance of double electric layer C_{dl} are added. Such an equivalent circuit is shown in Fig. 1. According to [2], its description code is $R_{\Omega}([R_1 W_1][R_2 W_2]C_{dl})$: elements in series are given in square brackets and elements in parallel are in parentheses. This circuit is applicable for a somewhat idealized system and does not account for the effects arising from the roughness of the electrode, limited space of diffusion, etc.

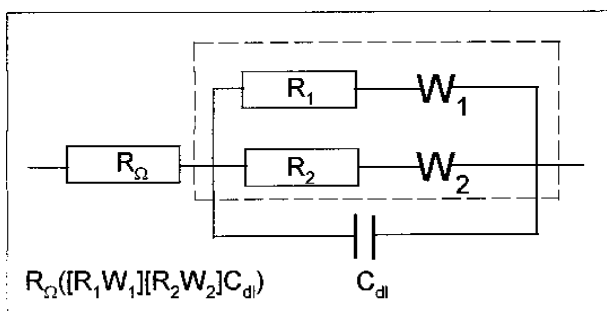


Fig. 1. Idealized equivalent circuit representing consecutive charge transfer process. Faradaic elements are given in the dotted frame.

RESULTS AND DISCUSSION

As may be seen from the above, all the elements of faradaic impedance depend on the kinetic characteristics of both steps (1) and (2). Therefore, the ki-

netic parameters can be determined only by a certain analytical procedure. It is of interest to compare the values of the electric elements under discussion with those describing separate simple charge transfer processes:



and that given by Eqn. (2). The following set of parameters was used for simulations: $i_{02} = 1 \text{ mA cm}^{-2}$, $c_o = 10^{-5} \text{ mol cm}^{-3}$, $c_y = 10^{-7} \text{ mol cm}^{-3}$, $D_o = D_y = 5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and i_{01} was taken as a variable. Taking into account the logarithmic scale of Fig. 2, it is possible to state a significant difference between the two cases under discussion.

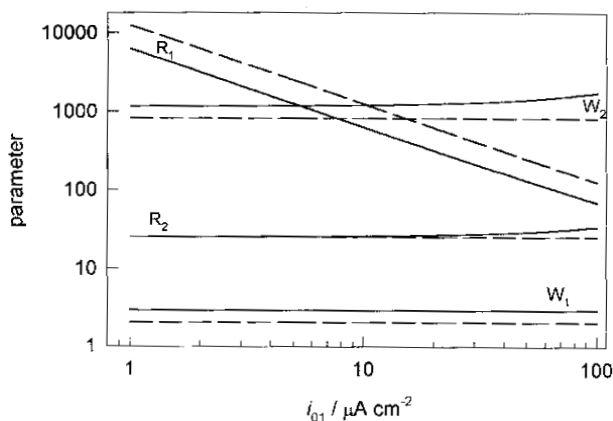


Fig. 2. Charge transfer resistances ($R / \Omega \text{ cm}^2$) and Warburg coefficients ($W / \Omega \text{ cm}^2 \text{ s}^{0.5}$) as functions of i_{01} . Simulated data for consecutive charge transfer (full lines) and for two independent processes given by Eqns. (1a) and (2) (dotted lines)

The typical example of the process proceeding by (1) and (2) is the electroreduction of Cu^{2+} aquations. The Nyquist plots obtained under open-circuit conditions contain arcs centered below abscissa axis (Fig. 3). An analysis of experimental data shows that the element W_1 (see Fig. 1) cannot be reliably defined. Moreover, it can be deleted from the equivalent circuit due to its significantly lower value as compared with W_2 (see Fig. 2). The element O accounting for the finite thickness of Nernst-type diffusion layer [1, 2] is more preferable than W_2 . Finally, the double layer capacitance C_{dl} needs to be changed for the constant phase element Q which can better reflect the properties of rough electrodes [1]. Thus, the reasonable equivalent circuit takes a form of $R_\Omega(R_1[R_2O]Q)$.

The parameters of the circuit elements obtained by fitting procedure [2] are listed in Fig. 4. The value of $B = 3.5 \text{ s}^{0.5}$ coincides quite well with that ($3.37 \text{ s}^{0.5}$) obtained for acetate solutions of Cu(II) [8]. The modified equivalent circuit makes it possib-

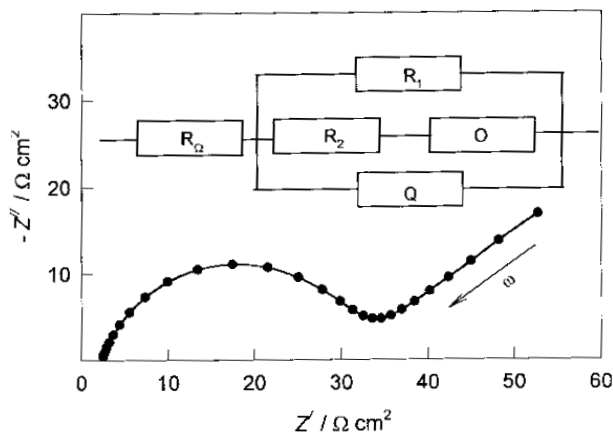


Fig. 3. Comparison of Nyquist plots simulated for given equivalent circuit (line) and obtained experimentally for the solution containing 0.01 M Cu(II) , 0.3 M K_2SO_4 at pH 5 and $T = 290 \text{ K}$ (points). Open circuit conditions ($E = 0.24 \text{ V}$)

le to describe the experimental data with a rather high ($\pm 2\%$) accuracy (Figs. 3–5).

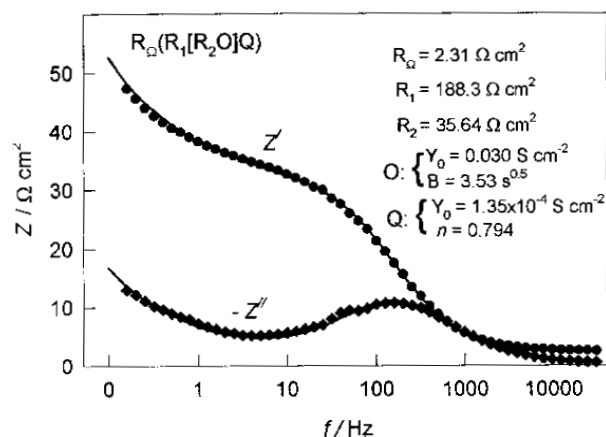


Fig. 4. Experimental (points) and simulated (lines) spectra of real (Z') and imaginary (Z'') parts of Cu electrode impedance

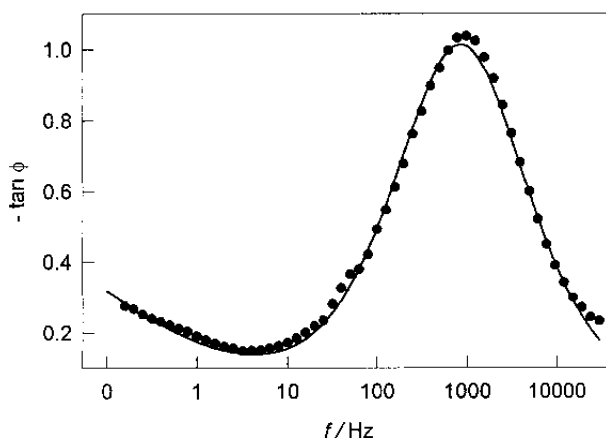


Fig. 5. Experimental (points) and simulated (lines) spectra of phase angle between real (Z') and imaginary (Z'') parts of Cu electrode impedance

It follows from the experimental data and Eqn. (8) that $i_{01} + i_{02} = 0.83 \text{ mA cm}^{-2}$. According to the impedance data obtained in [9], $i_{01} = 0.02 \text{ mA cm}^{-2}$. Then $i_{02} \approx 0.8 \text{ mA cm}^{-2}$. To our knowledge, the latter parameter has not been estimated to a sufficient accuracy up to now. As a rule, only the least exchange current density is available from voltammetric data in the case of consecutive charge transfer.

CONCLUSIONS

1. The structure of equivalent circuit is deduced from the analytical equations describing the faradaic impedance of electrochemical processes involving two consecutive one-electron transfers. It consists of two parallel subcircuits, each containing charge transfer resistance and Warburg impedance in series.

2. A modified equivalent circuit accounting for the effects arising from the roughness of the electrode surface and limited space of diffusion is proposed. This circuit makes it possible to describe impedance data obtained for Cu|Cu(II) system with an accuracy of $\pm 2\%$.

3. Exchange current densities in 0.01 M CuSO₄ solution are found to be equal to 0.02 mA cm⁻² and 0.8 mA cm⁻² for the processes of Cu²⁺ + e → Cu⁺ and Cu⁺ + e → Cu, respectively.

ACKNOWLEDGMENTS

The authors sincerely thank Dr. M. Samulevičienė for assistance in recording impedance spectra.

Received 25 January 2001
Accepted 12 February 2001

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A. Survila, V. Baliukienė

ELEKTROCHEMINIŲ PROCESŲ SU DVIEM NUOSEKLAUS KRŪVIO PERNEŠIMO STADIJOMIS EKVIVALENTINĖ SCHEMA

S a n t r a u k a

Iš analitinių lygčių, aprašančių elektrocheminių procesų su dviem nuosekliai krūvio pernešimo stadijomis faradėjinį impedansą, nustatyta ekvivalentinės grandinės struktūra. Ji susideda iš dviejų lygiagrečių grandinių, kurios savo ruožtu yra sudarytos iš nuosekliai sujungtos krūvio pernešimo varžos ir Varburgo impedanso. Pasiūlyta modifikuota ekvivalentinė grandinė, įvertinanti efektus, atsirandančius dėl elektrodo paviršiaus šiurkštumo ir ribotos difuzijos erdvės. Ši grandinė leidžia aprašyti Cu|Cu(II) sistemos impedansą $\pm 2\%$ tiksumu. Nustatyta, kad procesų Cu²⁺ + e → Cu⁺ ir Cu⁺ + e → Cu mainų srovių tankiai yra lygūs atitinkamai 0,02 mA cm⁻² ir 0,8 mA cm⁻².

A. Сурвила, В. Балукеене

ЭКВИВАЛЕНТНАЯ СХЕМА ЭЛЕКТРОХИМИЧЕСКИХ ПРОЦЕССОВ, ВКЛЮЧАЮЩИХ ДВЕ ПОСЛЕДОВАТЕЛЬНЫЕ СТАДИИ ПЕРЕНОСА ЗАРЯДА

Р е з ю м е

На основании аналитических уравнений, описывающих фарадеевский импеданс электрохимических процессов, включающих две последовательные стадии переноса заряда, определена структура эквивалентной цепи. Она состоит из двух параллельных цепей, которые, в свою очередь, образованы из последовательно соединенных сопротивлений переноса заряда и импеданса Варбурга. Предложена модификация эквивалентной цепи, учитывающая эффекты, возникающие из-за шероховатости поверхности электрода и ограниченности диффузионной области. Эта цепь позволяет описать импеданс системы Cu|Cu(II) с точностью $\pm 2\%$. Определено, что плотности токов обмена процессов Cu²⁺ + e → Cu⁺ и Cu⁺ + e → Cu равны 0,02 mA cm⁻² и 0,8 mA cm⁻² соответственно.