ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA
VOL. LIV/LV, 13 SECTIO AA 1999/2000

Electrical equivalent circuits and electrochemical impedance spectroscopy

K. Darowicki, S. Krakowiak and J. Orlikowski
Politechnika Gdańska, Wydział Chemii
ul. Narutowicza 11/12, 80-952 Gdańsk, Poland

The role of electrical equivalent circuits used in the frequency analysis of impedance results has been discussed. In the case of simple electrochemical processes the physical sense of component elements of electrical equivalent circuits is simple and does not require additional explanation. The electrical equivalent circuit is used directly in that case. The electrical equivalent circuit fulfils another function when the physical sense cannot be unequivocally determined of each electrical element of a complex process. In this case the electrical equivalent circuit fulfils an intermediate function and is only a tool in the complex analysis of the investigated process.

1. INTRODUCTION

There are many analogies between electrochemical and electrotechnical investigations. Also there are many differences resulting from the dynamic character of electrochemical processes, the ionic nature of conductance, the structure of the phase interface, the kinetics of processes, etc., therefore there is no direct link between electrotechnical and electrochemical systems.

The theory of electrical circuits, being the basis of electrotechnology, was adapted to impedance investigations already in the fifties of this century [1,2]. In the initial stage of development of electrochemical impedance spectroscopy the description of the investigated process was inseparably connected with determination of the electrical equivalent circuit [3-5]. As relatively simple electrode reactions were the investigated electrochemical processes, not many ambiguities were stated in such procedures.

Many elements used in electrical equivalent circuits have no equivalents in electrotechnology. Elements such as the Warburg impedance [6], Gerischer impedance [7], constant phase elements are not constant [8,9], they depend on the frequency. The structure or more accurately the physicochemical state of the electrode surface can have an effect on results of impedance measurements of electrochemical reactions [10]. More strictly, the physical and chemical nonhomogeneity of the electrode surface have an effect on experimental results. These factors are reflected in the observed frequency dispersion of electrical elements.

From this short introduction one can see that electrochemical systems differ from electrotechnical systems. Also, the role of the electrical equivalent circuit differs from the role that it fulfils in electrochemistry. This problem was discussed by Novoseleskii et al., [11]. In spite of the wide application of equivalent circuits in impedance measurements, at present there are a number of ambiguities and controversies concerning their role in impedance investigations. These complex problems are the subject of this work.

2. GRAPHICAL RECORD OF AN IMPEDANCE SPECTRUM

The electrical equivalent circuit in impedance measurements plays a significant role, however its significance and use in recent times has evolved. Two main opinions have become outlined on the use and importance of electrical equivalent circuits and their application in impedance investigations. These two views will be presented in this chapter. Let us analyse the impedance spectrum presented in Figure 1. On the basis of a preliminary, simple analysis one may determine the properties of the investigated process:

1. The investigated electrochemical process is connected with the DC flow because the impedance value determined for infinitely low frequencies is real in character and assumes finite values.
2. The process exhibits two time constants, two semicircles are present.
3. The electrode process is activation controlled because in the area of limiting low frequencies the impedance spectrum does not exhibit a characteristic course for diffusion control or another connected, for example, with the course of a preceding or consecutive chemical reaction.

The mentioned conclusions refer to the spectrum presented in Figure 1. All other conclusions at this stage of analysis are only far reaching assumptions, not confirmed on the basis of the carried out impedance experiment.

The analysed impedance spectrum can be represented by four electrical equivalent circuits presented in Figure 2. By using on of the non-linear regression methods one can, in a simple way, determine the values of each element of the electrical equivalent circuits. The values of these elements are given in Table 1. Fitting of the presented electrical equivalent circuits to measurement data is ideal. All four electric diagrams equally well represent the analysed impedance spectrum presented in Figure 1. Determination of values of each capacitance and resistance at this stage does not bring anything new into the analysis. The presented electrical diagrams with the determined resistance and capacitance values are only a graphical, short notation of experimental measurement results, usually presented in the form of a three column matrix [f_i, Z'(f_i), Z''(f_i)].

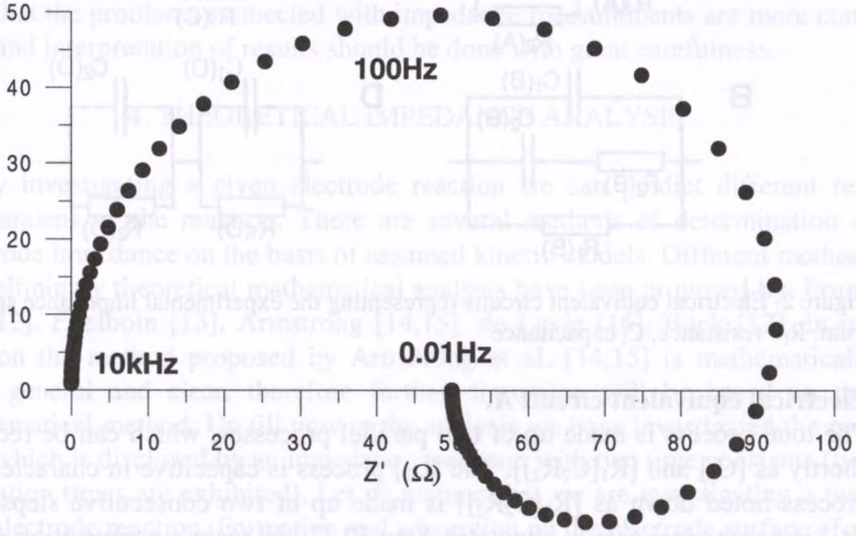


Figure 1. The experimental impedance spectrum of an electrochemical process with two time constants

3. PHYSICAL SENSE OF THE ELECTRICAL EQUIVALENT CIRCUIT

The full analysis of impedance results requires assignment of a physical sense to each element of the analysed electrical equivalent circuit. In the case of the Randles electrical equivalent circuit it is extremely simple, but in the case of a more complex diagram it is a more complicated problem. It cannot be determined which of these diagrams is correct on the basis of simple fitting of the electrical equivalent circuit to measurement results. The electrical diagram is not only the number and type of electric elements and their values but also their mutual connections. The method of connection of each electrical element should reflect the course of the investigated process. This problem will be discussed on the basis of electrical equivalent circuits presented in Figure 2.

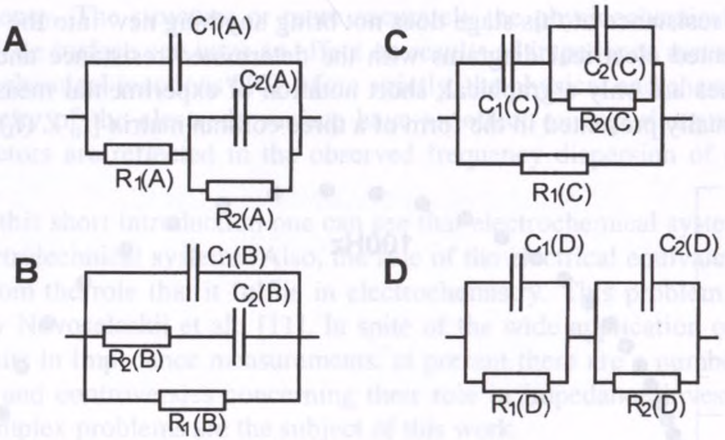


Figure 2. Electrical equivalent circuits representing the experimental impedance spectrum: R_i - resistance, C_i capacitance

Electrical equivalent circuit A.

The total process is made up of two parallel processes, which can be recorded shortly as [C_1] and [R_1[C_2R_2]]. The [C_1] process is capacitive in character. The process noted down as [R_1[C_2R_2]] is made up of two consecutive steps. Step [R_1] is a stage resistive in character. Step [R_2C_2] is again a composition of two parallel subprocesses: capacitive [C_2] and resistive [R_2].

Electrical equivalent circuit B.

The investigated process is a composition of three parallel processes [C_1], [R_1] and [R_2C_2]. Process [C_1] is capacitive in nature. Process [R_1] is resistive in nature. Process [R_2C_2] is a composition of two consecutive subprocesses: capacitive [C_2] and resistive [R_2].

Electrical equivalent circuit C.

The global process is made up of two parallel processes [R_1] and [C_1[R_2C_2]]. Process [R_1] is a resistive process, while process [C_1[R_2C_2]] is made up of two consecutive processes: capacitive [C_1] and the [R_2C_2] process being again a composition of parallel processes [C_2] and [R_2].

Electrical equivalent circuit D.

The course of this process is determined by two consecutive processes [R_1C_1] and [R_2C_2]. Process [R_1C_1] is a composition of two parallel subprocesses, resistive R_1 and capacitive [C_1]. The course of process [R_2C_2] is similar.

Analysis of a single spectrum is ambiguous. One cannot choose a single electrical equivalent circuit and base on it the further physicochemical analysis of the investigated process. To make an unequivocal choice it is essential to carry out impedance measurements for different variable experimental conditions such as: the electrode potential, concentration of reagents, concentration of basic electrolyte, hydrodynamic conditions, etc. Obtained characteristics of each electric diagram element in the function of independent variable ensure the correct choice of the equivalent circuit. After choosing such a circuit a problem always remains of the physical sense of electric elements making up the chosen electrical equivalent circuit. One can see from the presented discussion that the problems connected with impedance measurements are more complex and interpretation of results should be done with great carefulness.

4. THEORETICAL IMPEDANCE ANALYSIS

By investigating a given electrode reaction we can predict different real mechanisms of the reaction. There are several methods of determination of electrode impedance on the basis of assumed kinetic models. Different methods of preliminary theoretical mathematical analysis have been proposed by: Frumkin [12], Epelboin [13], Armstrong [14,15], de Levie [16], Buck [17]. In my opinion the method proposed by Armstrong et al. [14,15] is mathematically most general and clear, therefore further discussion will be based on this mathematical method. Up till now in the analysis we have investigated the process which is disclosed by an impedance spectrum with two time constants (two relaxation times are exhibited). Let us assume that we are investigating a two-step electrode reaction. Formation and adsorption on the electrode surface of an intermediate product is one of the steps of the reaction. The reaction proceeds in activation control conditions. Detailed derivation of impedance for such a defined process will not be carried out here. The method leading to determination of mathematical dependencies is simple and is defined in many papers.

The theoretical impedance of a two-step electrode reaction proceeding in activation control conditions and in the presence of an adsorbing intermediate product is equal to:

$$\frac{1}{Z(j\omega)} = j\omega C_{\infty} + \frac{1}{R_{\infty}} + \frac{1}{R_{o}(1+j\omega\tau)} \tag{1}$$

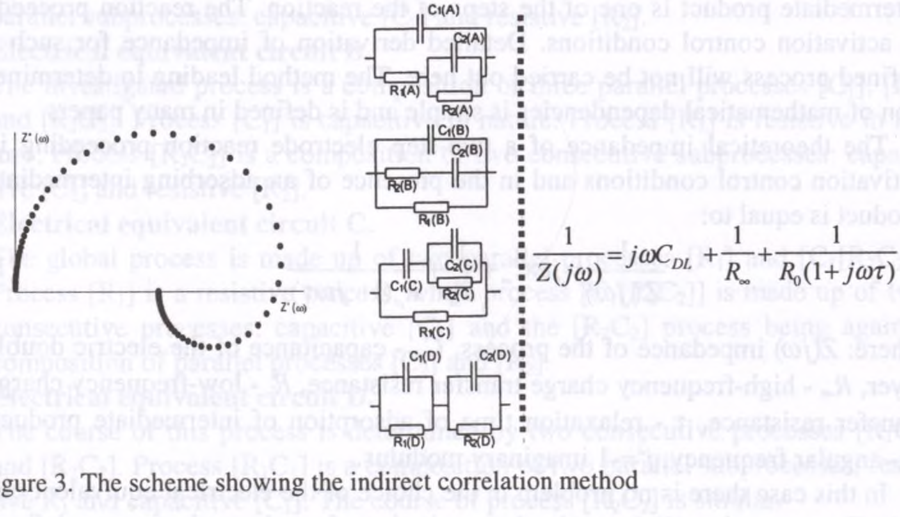
where: $Z(j\omega)$ impedance of the process, C_{∞} - capacitance of the electric double layer, R_{∞} - high-frequency charge transfer resistance, R. - low-frequency charge transfer resistance, τ - relaxation time of adsorption of intermediate product, ω - angular frequency, $j^2=-1$ imaginary modulus.

In this case there is no problem in the choice of the electrical equivalent circuit. From equation (1) it results that excitation of an electrode process defined above with a low-amplitude sinusoid signal causes a parallel flow of three currents. The first current is an imaginary quantity and it is a charge and discharge current of the electric double layer capacitance. The second current is real in character and is characterised by the high-frequency charge transfer resistance.

The third current is a complex current and it characterises the intermediate product adsorption process. In equation (1) parameters are found of a clearly defined physicochemical nature. Obviously, the same process can be described by other mathematical methods and the determined parameters can have another mathematical form.

Determination of equation (1) parameter values can be reduced to carrying out of the correlation of the derived theoretical formula with the experimental spectrum. In the discussed case equation (1) is correlated with the impedance spectrum presented in Figure 1. If another mathematical method of analysis was applied then correlation would be carried out of parameters in a different mathematical form. In each case a differently noted objective function would have to be determined. Such an approach is irrational. A new correlation procedure would have to be formed for analysis of each process described by a different equation.

There is a different approach. Correlation procedures such as the procedure proposed by Boukamp [18] or MacDonalds [19] procedure are based on the symbolic notation of the electrical equivalent circuit and are thus very general. Their value is based on the fact that in reality the electrical equivalent circuit is only an intermediate stage binding the form of the experimental spectrum with the derived theoretical equation [11,20,21]. The scheme of the analysis is presented in Figure 3.



$$\frac{1}{Z(j\omega)} = j\omega C_{DL} + \frac{1}{R_\infty} + \frac{1}{R_0(1+j\omega\tau)}$$

Figure 3. The scheme showing the indirect correlation method

In the procedure presented here it makes no difference if we use the electric circuit 2A, 2B, 2C or 2D.The form of this schematic diagram has no significant effect on the result, because the problem is reduced to fitting of equation (1) to the experimental spectrum. The electric equivalent circuit, its form, method of connection is of no significance. The electric equivalent circuit is used in the analysis of impedance spectra only in an intermediate way. This fact is illustrated by numerical values of equation (1) determined on the basis of fitting of numerical values to the given electric schematic diagrams 2A, 2B, 2C and 2D. The numerical values of these parameters have been given in Table 1. Depending on the choice of electric equivalent circuit the quantities R_∞, R_0, C_∞ and τ are defined in different ways but their numerical values are always independent of the choice made.

Table 1. The values of electrical R_i and C_i elements of four equivalent electrical circuits

	Electrical equivalent circuit			
Determined values	A	B	C	D
R_1 / W	100,0	50,0	50,0	138,2
C_1 / mF	20,0	20,0	-1800,0	16,6
R_2 / W	-50,0	-100,0	-123,0	-88,2
C_2 / mF	-200,0	-200,0	18,0	-98,6

Electric equivalent circuit 2A

$$R_\infty = R_1(A) = 100\Omega, \qquad R_0 = \frac{R_1(A)[R_1(A)+R_2(A)]}{R_2(A)} = 100\Omega$$

$$\tau = \frac{C_2(A)R_1(A)R_2(A)}{[R_1(A)+R_2(A)]} = 0.02s, \qquad C_\infty = C_1(A) = 20\mu F$$

Electric equivalent circuit 2B

$$R_\infty = \frac{R_1(B)R_2(B)}{R_1(B)+R_2(B)} = 100\Omega, \qquad R_0 = -R_2(B) = 100\Omega$$

$$\tau = C_2(B)R_2(B) = 0.02s, \qquad C_\infty = C_1(B) = 20\mu F$$

Electric equivalent circuit 2C

$$R_\infty = \frac{R_1(C)R_2(C)[C_1(C)+C_2(C)]^2}{R_1(C)C_1^2(C)+R_2(C)[C_1(C)+C_2(C)]^2} = 100\Omega,$$

$$R_0=-\frac{R_2(C)[C_1(C)+C_2(C)]^2}{C_1^2(C)}=100\Omega$$

$$\tau=R_2(C)[C_1(C)+C_2(C)]=0.02s,\qquad C_\infty=\frac{C_1(C)C_2(C)}{[C_1(C)+C_2(C)]}=20\mu F$$

Electric equivalent circuit 2D

$$R_\infty=\frac{[C_1(D)+C_2(D)]^2R_1(D)R_2(D)]}{C_1^2(D)R_1(D)+C_2^2(D)R_2(D)}=100\Omega,$$

$$R_o=\frac{[R_1(D)+R_2(D)][C_1(D)+C_2(D)]^2R_1(D)R_2(D)}{2C_1(D)C_2(D)R_1(D)R_2(D)-R_1^2(D)C_1^2(D)-R_2^2(D)C_2^2(D)}=100\Omega$$

$$\tau=\frac{[C_1(D)+C_2(D)]R_1(D)R_2(D)}{R_1(D)+R_2(D)}=0.02s,\qquad C_\infty=\frac{C_1(D)C_2(D)}{C_1(D)+C_2(D)}=20\mu F$$

From the presented analysis it results that the values of the high-frequency charge transfer resistance, low-frequency charge transfer resistance, electric double layer capacitance and the relaxation time of adsorption of intermediate product do not depend on the assumed electric circuit. Independently of the choice of electric equivalent circuit the values of these parameters are always identical. This is understandable as in the proposed procedure the experimental result which was the impedance spectrum presented in Figure 1 was correlated with equation (1) and not a given electric circuit.

4. SUMMARY

Impedance investigations of complex electrochemical processes are based on a preliminary creation of the largest possible number of theoretical models. These models are connected with hypothetical (but real) courses of the analysed process and allow determination of corresponding impedance expressions. In the second stage experimental results (experimental spectrum) are recorded in the graphical form called the electric equivalent circuit. It doesn't matter what kind of structure exists of connections of each element. It is essential in the whole investigated range of frequencies for the experimental impedance spectrum to be reliably represented by numerical values of electric elements of the chosen electric circuit. In the next stage the derived theoretical equations are correlated with the electric circuit. In this way the electric circuit only plays an intermediate role, it is a translator in the experimental spectrum notation and the derived equations.

In this way the electrical parameters of hypothetical equations are given specific numerical values. The reality of these values, especially the direction of their change with temperature, concentration and other quantities characterising experimental conditions are a verification of preliminary hypotheses concerning the mechanism of the reaction. In other words, on the basis of impedance measurements we are able to state which mechanism is most probable and which mechanisms cannot be realised in given experimental conditions.

Acknowledgement. This work has been financed by grant DS/010

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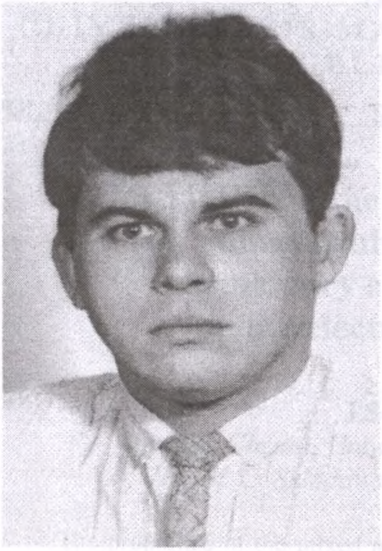
CURRICULA VITAE

Prof. Kazimierz Darowicki was born in Gdańsk in 1955. He graduated from the Technical University of Gdansk in 1981 and received his M.S. degree in chemical technology (Department of Anticorrosion Technology). In 1991, Darowicki received his Ph.D. degree in technical science from the Technical University of Gdansk, Faculty of Chemistry. Kazimierz Darowicki has employed in Technical University of Gdańsk since 1981. He has been Head of Department of Anticorrosion Technology since 1996. He is President of Polish Corrosion Society. His main interest is modern electrochemistry, corrosion and corrosion protection, materials science. He published over 70 papers in international journals and 120 papers in conference proceedings on corrosion and electrochemistry. He is member of International Society of Electrochemistry, National Association of Corrosion Engineering.



Dr. Stefan Krakowiak was born in Gdańsk in 1964. He graduated from the Technical University of Gdansk in 1988 and received his M.S. degree in chemical technology (Department of Anticorrosion Technology). In 1999, Krakowiak received his Ph.D. degree in technical science from the Technical University of Gdansk, Faculty of Chemistry. Stefan Krakowiak has employed in Technical University of Gdańsk since 1988. He published over 40 papers in international journals and conference proceedings on corrosion and electrochemistry. His main interest is corrosion and corrosion control, stainless steels for aggressive environments, coatings, corrosion monitoring.

Dr. Juliusz Orlikowski was born in Gdynia in 1969. He graduated from the Technical University of Gdansk in 1993 and received his M.S. degree in chemical technology (Department of Anticorrosion Technology). In 1998, Orlikowski received his Ph.D. degree in technical science from the Technical University of Gdansk, Faculty of Chemistry. Juliusz Orlikowski has been employed in Technical University of Gdańsk since 1998 as assistant. He published 7 papers in international journals and conference proceedings on corrosion and electrochemistry. His main interests are corrosion and corrosion monitoring and digital measurements.