SIMULATION OF ELECTROCHEMICAL SYSTEMS BY ANALYZING IMPEDANCE SPECTRA

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ABSTRACT

In this work is carried out simulation of electrochemical system: primary transducer - object by analyzing impedance spectra in different frequency ranges and for different concentrations of these objects. On the basis of modeling, the electrochemical processes occurring in the investigated system are interpreted using elements of the higher hierarchical level of construction of bipolar units.

Index Terms - primary transducer, simulation of electrochemical system, impedance spectra, non-electric nature objects

1. INTRODUCTION

Any object can be represented by an electrochemical system, the properties of which can be studied and its behavior predicted in different conditions, reflecting its corresponding substitution scheme (equivalent scheme). If impedance is the general method that characterizes the behavior of the whole studied electrochemical system, then impedance modeling is necessary for the study of electrochemical kinetics and electrochemical systems in general by constructing model structures. These structures consist of individual elements [1, 2, 3]. In addition, for different types of electrode systems (for example, different materials - platinum, stainless steel, graphite) during the study of the same object, the frequency dependences of the admittance are obtained, which differ in shape. If impedance is the general method that characterizes the behavior of the whole studied electrochemical system, then impedance modeling is necessary for the study of electrochemical kinetics and electrochemical systems in general by constructing model structures. Therefore, in order to correctly interpret the admittance spectra, as well as to understand the processes occurring at the boundary of the studied Object - Primary Converter, it is necessary to analyze the admittance spectra and model electrochemical systems. Modeling can be performed in two ways, one of which is the classical approach, based on the acceptance of hypotheses about the specifics of the object under study and the compilation of a system of differential equations [4, 5]. This approach is logically correct, but the complexity of real models, which often cannot be solved, limits the possibilities of the classical approach. Very often simplifications need to be made. This may contradict the basic conditions of the experiment, so it is necessary to look for new analytical solutions with minor changes in the original hypothesis. Therefore, the theoretically derived equation of the dependence of the impedance on the electrochemical parameters may contain more elements than practically determined elements. Structural modeling should be used to overcome these shortcomings. It is based on a systematic approach to object analysis. It is considered as a system of electrical elements connected to each other. The structural model becomes

completely adequate to the structure of the corresponding theoretical equation, but contains fewer parameters required to describe the impedance in a certain frequency range [6, 7, 8]. Structural impedance models contain quantitative information about the behavior of the object under study in the frequency range, as well as information about the physics of the processes. If the system Primary Converter - Object of control is presented in the form of a passive bipolar, then the interconnected basic elements such as resistors, capacitors, and inductors will be its parameters. It is possible to reproduce the internal structure of the bipolar according to the impedance frequency spectra, to construct an equivalent circuit. However, during the control of non-electrical nature objects (in particular in the form of solutions) there are cases when the solution-electrode system undergoes processes that cannot be described by a finite number of elements. Thus, at the electrode-solution interface, an electrode electric layer is formed, the phenomena of charge diffusion (transfer of ion charge to the electrode surface) occur, and electrochemical reactions take place on the electrode surface. Then it is necessary to move to a higher level of synthesis of bipolar. It is necessary to apply special electrochemical elements, which in their physical content correspond to the processes modeled by them [9, 10, 11]. The electrical properties [12] of the contact surface of the electrode and the test object - solution, are very important for the design of devices for determining electrochemical quality indicators, because during modeling it is possible to detect parasitic phenomena (electrode parasitic capacitance, additional impedance electrodes, additional impedance due to the formation of fractals, getting into the oxygen solution during contact of the electrochemical cell surface with air, violation of the ideal polarization of the electrodes and, consequently, the emergence of additional impedance due to electrochemical reaction on the electrodes, etc.). Identification of these features will make it possible to take appropriate corrective action to minimize the impact factors in the system Primary Converter - Object during monitoring the quality of solutions - non-electrical nature objects by electrochemical devices [13, 14].

2. THE ANALYSES OF IMPEDANCE SPECTRA

The aim of this work is to investigate the impedance spectra of low-impedance and high-impedance objects. This will allow you to correctly select the design parameters of electrochemical transducers (shape, size), electrode material depending on the characteristics of the object (different ability to conduct current, different concentration ranges, the ability of electrodes to adsorb) and test conditions, frequency ranges, temperatures, test signal level ranges).

3.1. Simulation of electrochemical systems of low-impedance objects

Based on computer simulation of the impedance spectra (obtained by experiment for a system with two electrodes made of stainless steel in the form of plates), conducted with the EIS Spectrum Analyzer soft, the values of the substitution circuit elements (Fig. 1a) were calculated (for example NaCl) of different concentrations (c = (1 ÷ 9) g / l) and in different frequency ranges. The program performs modeling based on the Levenberg-Marquardt algorithm, which is one of the optimization methods, aimed at solving least squares problems and is a modification of Newton's method (Fig. 1). The results of computer simulation of the electrode-electrolyte system are presented in table 1.

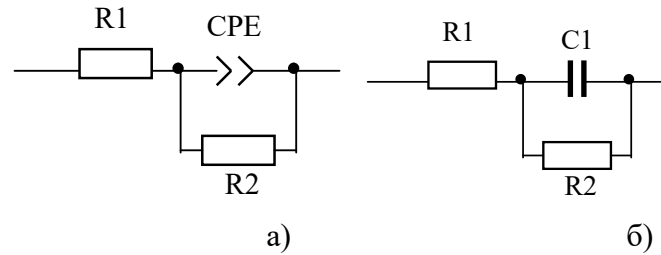a)   б)

Figure 1. Electrode-electrolyte system substitution schemes (aqueous NaCl salt solution) for frequencies not exceeding 1 kHz: C1 - double electric layer capacitance, CPE - constant phase element, R1 - electrolyte resistance, R2 - interphase transition resistance

An electric current flows through the electrode-solution interface, and there is a resistance to charge transfer R2, which characterizes the reaction between the electrode-electrolyte interface. Since the impedance is calculated from current and voltage values, it is logical to apply electrical equivalent schemes, but classical electrical quantities are not enough to accurately describe the variety of real processes and objects, so special electrochemical elements are used. One of these is the constant phase element (CPE), or the element with a constant angle of loss. The movement of ions in solution occurs due to diffusion of different concentrations ions in individual parts of the electrolyte, their convection due to the capture by the flow of moving fluid, the migration of ions under the impact of an electric field, thermal phenomena.

Analysis of the Table 1 showed that at frequencies higher than 1000 Hz, the substitution scheme (Fig. 1a) is not suitable for reproducing the saline solution properties, because the circuit element R2 is the resistance between the phase transition (or diffusion process resistance) is reproduced with errors exceeding 1000%.

Table 1 - Reproduction of the values of the substitution scheme elements (Fig. 1a) in different frequency ranges for different values of the aqueous salt solution concentration

C g/l	F, Hz	R1, Ohm	δ_{R1}, %	R2, Ohm	δ_{R2},%	P	δ_P,%	n	δ_n,%
1	50÷100000	153.01	0.47	536.06	42	0.00050498	3.57	0.55389	0.88
1	50÷1000	153.7	1.089	575.86	70	0.00050496	5.09	0.55668	1.33
1	1000÷100000	7143	33.4	49188	>1000	0.0000043	>1000	1.01	>1000
5	50÷100000	16.29	4.46	66.82	26.27	0.00047882	14.01	0.67312	2.30
5	50÷1000	17.98	7.82	75.35	54.14	0.00050495	12.67	0.69000	2.44
5	1000÷100000	16.31	2.19	2.79	>1000	0.00047334	14.95	0.65154	2.02
9	50÷100000	8.87	5.6	48.25	34.3	0.00050498	14.9	0.69617	2.27
9	50÷1000	7.58	43.22	34.05	137.7	0.00050493	29	0.67747	5.40
9	1000÷100000	8.63	4.8	5.96	>1000	0.00045809	23.8	0.67416	2.94

It should be noted that the simulation of the impedance of the electrolyte solution with the resistance R1 is valid for highly concentrated solutions in a wide range of frequencies. Only at frequencies exceeding (1 ÷ 5) MHz, it is necessary to introduce additional elements that take into account the relaxation processes in the electrolyte. As the concentration of the saline solution increases, the resistance values of the electrolyte R1 decrease. The values of the impedance components of the CPE are quite stable. The average value of the exponential index n = 0.654, which is included in the formula for calculating the impedance ZCPE of this element

$$Z_{CPE}(j\omega) = P^{-1}(j\omega)^{-n}, \qquad (1)$$

and this corresponds to the case of modeling by the CPE of the process of diffusion of electrolyte ions to the interfacial electrode-electrolyte boundary, the transfer of a substance due to the equalization of its concentration (more precisely, chemical potential) in an inhomogeneous system approaching homogeneous. The unit of measurement of the coefficient

P in this case will be equal to the unit of measurement of the Warburg coefficient λ (impedance due to diffusion processes of charge transfer) Ohm·c$^{-1/2}$. It is believed that there is a relationship between CPE and the surface roughness of the electrode, so the smoother the electrode surface, the faster n approaches the unit and becomes exclusively capacitive, the CPE is a measure of the degree of inhomogeneity of the electrode. Therefore, if we have an ideal geometry of the electrode working surface in the impedance sense, a homogeneous electric field, which is provided by the configuration of the cell, the impedance of its double layer can be represented by capacitance C1 (Fig. 1b, 2a).

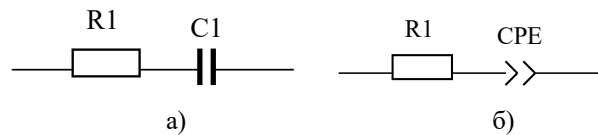a)   б)

Figure 2. Substitution scheme of the electrode - electrolyte system: a) for a perfectly polarized electrode, on which no electrochemical reaction occurs; b) in the presence of diffusion phenomena in the electrode region and the flow of Faraday current due to electrode reactions

In order to analyze the circuit (Fig. 2b) a simulation have done (the results are summarized in table 2). Analysis of table 5.5 data shows that at high frequencies (1000 ÷ 100000 Hz) the reproduction error of the elements of the substitution schem (Fig. 2b) is very small compared to the substitution scheme (Fig. 1a). The error of reproduction of the value of the resistance of the investigated electrolyte at high frequencies is several times smaller than in the low-frequency range and is almost invariant to the solution concentration change (Fig. 3).

Table 2. Reproduction of the values of the elements of substitution scheme elements (Fig. 3b) in different frequency ranges for different values of the aqueous salt solution concentration

C, g/l	F, Hz	R1, Ohm	δ_{R1}, %	P	δ_P, %	n	δ_n, %
1	50÷100000	155.38	0.79	0.00050438	5.99	0.57229	1.11
1	50÷1000	158.18	1.68	0.00050496	7.64	0.57723	1.66
1	1000÷100000	151.92	0.18	0.00049368	2.44	0.53551	0.43
5	50÷100000	18.34	5.84	0.00050497	22.2	0.73032	2.78
5	50÷1000	21.84	14.5	0.00045088	29.9	0.76204	4.20
5	1000÷100000	16.29	1.61	0.00049194	10.5	0.64697	1.43
9	50÷100000	10.01	9.43	0.00050491	33.9	0.75841	3.70
9	50÷1000	13.56	21.6	0.00045153	39.2	0.79840	4.97
9	1000÷100000	8.59	3.51	0.00050247	15.8	0.66328	2.01

However, in the low-frequency range of the resistance values reproduction error for the test object increases rapidly with increasing electrolyte concentration (Fig. 3).
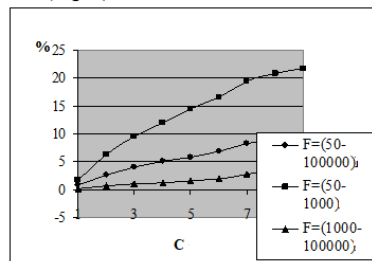

Figure 3. Dependence of relative errors of resistance values reproduction of electrolyte according to the substitution scheme in Fig. 2 on change of its concentration

Therefore, it was proposed to investigate in different frequency ranges the equivalent scheme (Fig. 4), which in comparison with the circuit in Fig. 1a is supplemented by an element C1 that simulates the capacitance of the electrode layer.
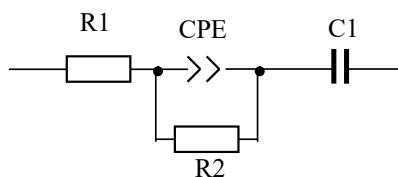

Figure 4. Substitution scheme of the electrode - electrolyte system, taking into account the electrode capacity C1

Table 3. Reproduction of the elements values of the substitution scheme (Fig. 4) in different frequency ranges for different values of the concentration of the aqueous salt solution

C g /l	F, Hz	R1, Ohm	δ_{R1} %	C1, μF	$\delta_{C1,}$ %	R2, Ohm	$\delta_{R2,}$ %	P	$\delta_{P,}$ %	n	$\delta_{n,}$ %
1	50÷100000	151.9	0.49	144	12.9	139.6	9.2	0.00050121	3.97	0.54	0.99
1	50÷1000	151.7	1.07	147	21.8	139.2	14.6	0.00048286	6.79	0.55	1.76
1	1000÷100000	151.54	0.14	27	12.9	39.76	11.9	0.00045057	3.81	0.53	0.72
5	50÷100000	16.13	1.63	251	12.9	29.48	8.47	0.00050497	6.87	0.65	1.22
5	50÷1000	16.33	4.16	257	17.8	29.99	10.50	0.00050103	9.61	0.65	1.89
5	1000÷100000	15.70	0.48	55	13.1	9.52	7.88	0.00048743	7.02	0.61	1.11
9	50÷100000	8.33	3.02	274	17.96	20.59	9.65	0.00050500	10.79	0.65	1.70
9	50÷1000	7.40	16.8	219	67.35	18.85	23.32	0.00050499	52	0.62	8.87
9	1000÷100000	8.07	0.79	75.78	9.33	7.76	5.78	0.00037555	3.39	0.65	0.48

Analyzing the data in table 3, we can conclude that in the low-frequency range it would be possible to apply a model of the type (Fig. 4), but in general there is a manifestation of the CPE as an element characterizing the diffusion of active particles to the electrode-electrolyte interface, so ions movement through the electrolyte occurs only due to the diffusion of conduction ions. Therefore, near the electrode, the charge transfer processes are determined by diffusion, charge transfer in the diffusion layer, where the diffusion capacity of the Stern electrode layer is formed. This impedance is called the Warburg diffusion impedance to reflect the impedance of an ideal linear semi-infinite diffusion (Fig. 5 a,b), the investigated frequencies are not low enough to ensure the penetration of the diffusion sinusoidal wave to the boundary of the real diffusion layer.
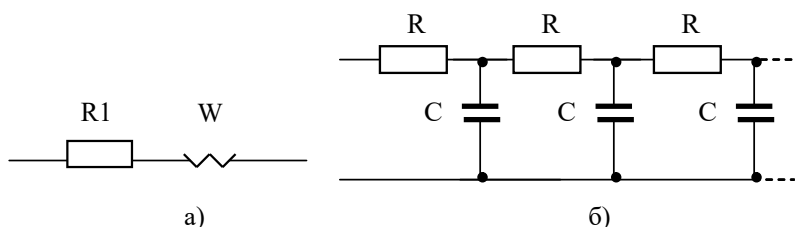

Figure 5. Warburg impedance: a) the substitution scheme of the electrode - electrolyte system, taking into account the impedance of Warburg; b) and the equivalent Warburg impedance scheme

Replacement of the CPE with the Warburg element (Fig. 5a) led to an increase in the accuracy of the results on the reproduction of the substitution scheme elements (Tab. 4).

Table 4 - Reproduction of the substitution scheme elements values (Fig. 5) in different frequency ranges for different values of the concentration of the aqueous salt solution

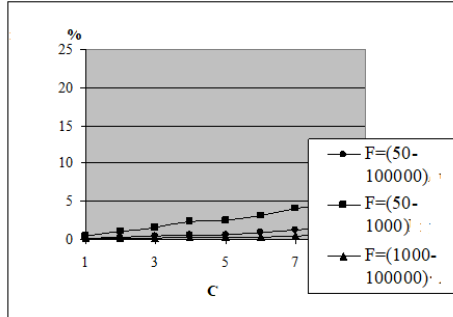| C, g/l	F, Hz	R1, Ohm	δ_{R1}, %	AW	Δ_{AW}, %
1	50÷100000	152.05	0.22	932.52	1.54
1	50÷1000	152.07	0.51	931.22	1.88
1	1000÷100000	151.32	0.11	1063.5	2.07
5	50÷100000	15.74	0.69	372.29	2.58
5	50÷1000	15.89	2.49	370.43	2.81
5	1000÷100000	15.46	0.27	414.64	1.95
9	50÷100000	8.16	1.48	302.62	4.07
9	50÷1000	8.61	4.26	296.17	3.32
9	1000÷100000	7,85	0,65	353,36	2,47

Figure 6. Dependence of the relative errors of reproduction of the resistance values of the electrolyte according to the substitution scheme in Figure 6a on the values of its concentration

Comparison of the dependences of the reproduction errors of the substitution scheme elements containing the CPE (Tab. 3) and the Warburg element (Tab. 4) allowed us to conclude that at frequencies from 50Hz to 1kHz the equivalent scheme can be represented by Figure 6a and the Warburg impedance (Fig. 5b) adequately describes the processes occurring in the test system at higher frequencies (from 1 kHz to 100 kHz), at which the electrode effects practically disappear.

3.2. Simulation of electrochemical systems of high-impedance objects

Biochemical systems based on natural materials, in particular sugar solutions, are of interest for research when it comes to non-electrical nature objects, namely high-resistance objects. Based on the experimental data of impedance measurements, their analysis was performed and the corresponding structure of the substitution scheme was obtained (Fig. 7).

a)   б)
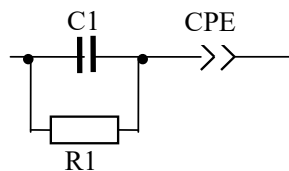
Figure 7. Modeling of the electrochemical system of aqueous sugar solution: a) the substitution scheme of the electrode - non-electrolyte system for aqueous sugar solution) b) the impedance spectrum of the sugar solution

Since these are polarized electrodes, the substitution scheme contains a link that describes the presence of the capacitance C1 in the electrode Helmholtz layer and the resistance of charge

transfer R1. The presence of the CRE in the substitution scheme is explained by the inhomogeneity of the electrode surface, which may be due to selective adsorption of sugar on the electrodes, or the presence of even a small amount of gas (air oxygen), which leads to the formation of phase boundaries (fractals). The latter leads to local changes in the electrochemical parameters of the electrode surface, which is best modeled by CPE. In order to eliminate this phenomenon, it is recommended to create closed-type electrochemical cells to minimize the area of contact of the solution with air. Elements of the substitution scheme were reproduced with sufficient accuracy from 0.2% to 4% for different concentrations of sugar solutions (Tab. 5).

Table 5 - Reproduction of the substitution scheme elements values (Fig. 7) in different frequency ranges for different values of the concentration of aqueous sugar solution

C, g/l	F, Hz	R1, Ohm	δ_{R1},%	C1, pF	δ_{C1},%	P	δ_P, %	n	δ_n, %
20	50÷100000	189170	0.24	7.6	0.7	0.0000031	11.9	0.68336	4.1
30	50÷100000	122720	0.25	7.4	0.9	0.000010	11.1	0.49843	3.2
40	50÷100000	80065	1.31	7.2	1.4	0.000004	10.7	0.67296	2.2

The error of reproduction of the test object resistance increases with increasing concentration (Tab. 5). This may indicate that equivalent scheme may also differ for different concentration ranges as in the case of different frequency subranges.

The study of impedance spectra of non-electrical nature objects have been done. Equivalent substitution schemes have been developed for low-resistance and high-resistance objects.

In particular, for low-resistance objects - salt solutions, circuits containing the capacity of the double electric layer and circuits with a constant phase element were synthesized. For high-resistance objects, it is recommended to create closed-type electrochemical cells to minimize the area of contact of the solution with air.

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