STUDY OF THE PRIMARY CONVERTER-OBJECT SYSTEM FOR ELECTROCHEMICAL DEVICES

Tetiana Bubela, *Dr. Sc., Prof.,* ***Vasyl Yatsuk,*** *Dr. Sc., Prof.,* ***Tetiana Fedyshyn,*** *Ph. D. Student,*
Roman Ivakh*, Ph.D., As.-Prof.,*
Lviv Polytechnic National University, Ukraine; e-mail: tetiana.z.bubela@lpnu.ua
Hristo Krachunov, *Dr. Sc., As. Prof.,*
Technical University of Varna, Bulgaria; e-mail: euro_expert@abv.bg

Abstract. The problem of creating electrochemical devices and the issues that arise in the system of the primary converter-object of control are considered. Low-resistance (salt solutions) and high-resistance (sugar solutions) objects were selected as the subject of study. To solve the problem, we have applied the method of impedance spectrum analysis with EIS Spectrum Analyzer software, which performs modeling on the Levenberg–Marquardt algorithm. Substitution schemes in different frequency and concentration ranges of studied objects were synthesized. This enables appropriate corrective action to minimize the impact of adverse events in the system while monitoring the quality of solutions – non-electrical nature objects – by electrochemical devices.

Key words: Electrochemical devices; Impedance spectra; Non-electrical nature object; Substitution scheme; Computer simulation; Primary converter.

1. Introduction

Since the basic concept of the work is the evaluation of objects as a system and the development of methods for quality indicators assessment aimed at the application of advanced methods. The properties of this system can be studied. Its behavior can be predicted in different conditions, reflecting its corresponding substitution scheme (equivalent scheme). If the impedance is the general method that characterizes the behavior of the whole studied electrochemical system, then impedance modeling becomes necessary for the study of electrochemical kinetics and electrochemical systems in general by constructing model structures. These structures consist of individual elements [1–3].

For different types of electrode systems (for example, different materials – platinum, stainless steel, graphite) while studying the same object, the frequency dependences of the admittance are obtained, that differ in shape. 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 approach. 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 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 objective analysis. It is considered a system of electrical elements connected. The structural model becomes completely adequate to the structure of the corresponding equation but contains fewer parameters required to describe the impedance in a certain frequency range [6–8]. Structural impedance models contain quantitative information about the behavior of the object understudy 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 inner structure of the bipolar according to the impedance frequency spectra and construct an equivalent circuit. While monitoring the non-electrical nature objects (in particular the solutions) it happened that 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 becomes necessary to pass to a higher level of synthesis of bipolar. It is necessary to apply special electrochemical elements, which physically correspond to the processes modeled by them [9–11].

The electrical properties 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 parameters (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 makes it possible to take appropriate corrective action minimizing the impacts in the system Primary Converter – Object during monitoring the quality of non-electrical nature objects by electrochemical devices.

2. Disadvantages

The known substitution schemes for objects do not contain information about the frequency range and features of the application of different nature electrochemical systems.

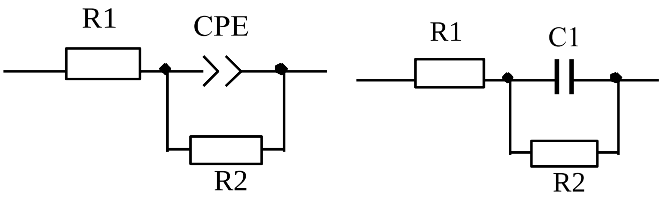
3. Goal

Investigation of the impedance spectra of low-impedance and high-impedance objects aiming correct selection of 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).

4. Impedance spectra investigation

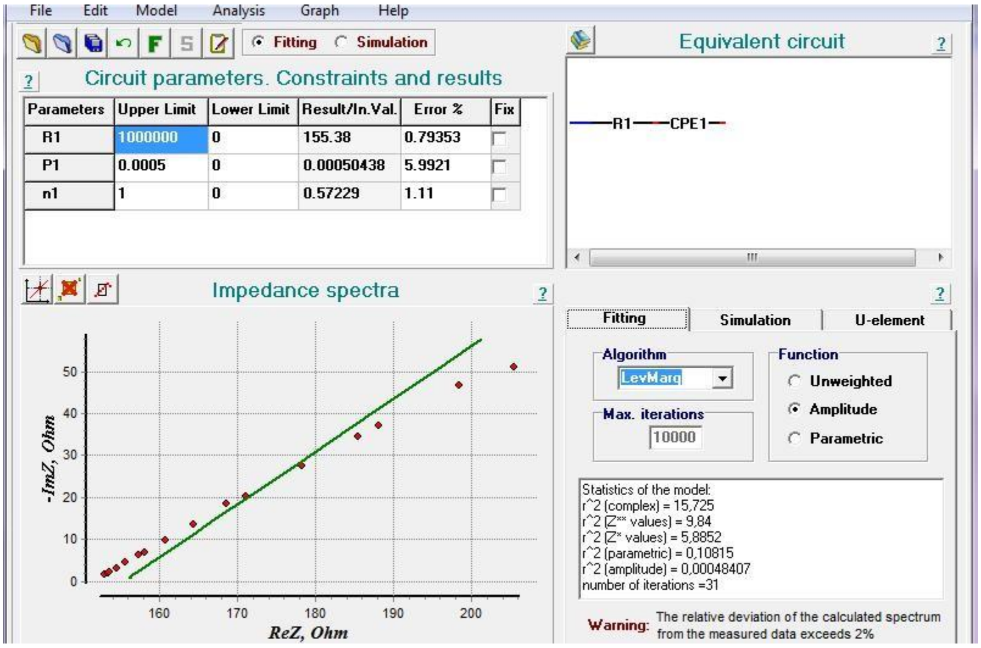
4.1. Equivalent low-impedance substitution schemes

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. 1, *a*) were calculated (for example NaCl) of different concentrations (c = (1÷9) g/l) and at different frequency ranges. The program performs modeling based on the Levenberg–Marquardt algorithm, which is one of the optimization methods and is a modification of Newton's method (Fig. 1). The results of the computer simulation of the electrode-electrolyte system are presented in Table 1.



a *b*

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



Parameters	Upper Limit	Lower Limit	Result/In.Val.	Error %	Fix
R1	1000000	0	155.38	0.79353	☐
P1	0.0005	0	0.00050438	5.9921	☐
n1	1	0	0.57229	1.11	☐

Algorithm: LevMarq

Max. iterations: 10000

Function: ○ Unweighted ● Amplitude ○ Parametric

```
Statistics of the model:
r^2 (complex) = 15,725
r^2 (Z** values) = 9,84
r^2 (Z* values) = 5,8852
r^2 (parametric) = 0,10815
r^2 (amplitude) = 0,00048407
number of iterations =31
```

Warning: The relative deviation of the calculated spectrum from the measured data exceeds 2%

Fig. 2. EIS Spectrum Analyzer interface of salt solution impedance spectrum analysis

Table 1

Reproduction of the values of the substitution scheme elements (Fig. 1, *a*) within 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
2	50÷100000	51.56	1.34	138.28	32.34	0.00050494	6.84	0.6292	1.38
2	50÷1000	52.66	1.16	143.91	53.52	0.00050495	9.45	0.6365	2.07
2	1000÷100000	50.31	0.35	85.21	67.56	0.00050494	3.22	0.5859	0.55
3	50÷100000	30.03	2.06	93.24	30.48	0.00050497	8.54	0.6552	1.58
3	50÷1000	32.65	16.15	41.11	45.83	0.00005376	70.27	0.9916	6.99
3	1000÷100000	29.03	0.52	53.56	52.05	0.00050497	3.88	0.6078	0.63
4	50÷100000	21.88	2.6	88.19	29	0.00050494	8.93	0.65728	1.59
4	50÷1000	23.28	6.21	94.19	48.5	0.00050495	11.5	0.67074	2.29
4	1000÷100000	21.4	1.59	5.83	>1000	0.00050135	11.6	0.62845	1.66
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
6	50÷100000	13.36	6.77	53.56	35.71	0.00050493	15.09	0.66605	2.55
6	50÷1000	1.60	414	30.78	35.69	0.00004022	229.3	0.78856	16.8
6	1000÷100000	13.72	2.74	9.345	>1000	0.00046512	17.63	0.65988	2.32
7	50÷100000	10.12	11.1	49.71	27.45	0.00050491	19.25	0.6678	2.88
7	50÷1000	12.42	11.2	52.24	49.13	0.00050495	15.39	0.70792	2.76
7	1000÷100000	10.65	3.75	7.86	>1000	0.00047876	20.25	0.66123	2.61
8	50÷100000	9.52	5.34	48.95	32.49	0.00050495	14.02	0.69252	2.16
8	50÷1000	10.90	13.06	48.04	66.44	0.00050499	15.65	0.71364	2.89
8	1000÷100000	9.25	4.30	7.36	>1000	0.00049293	21.38	0.66301	2.72
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

An electric current passes through the electrode-solution interface. There arises a resistance $R2$ caused by charge transmission, 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; nevertheless, the classical electrical quantities are not enough to describe exactly the variety of real processes and objects. So special electrochemical elements are applied. 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 the diffusion of different concentrations of 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.

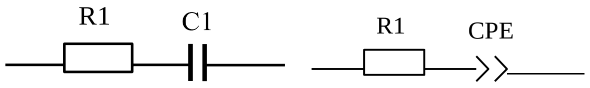
Analysis of the Table 1 showed that at frequencies higher than 1000 Hz, the substitution scheme (Fig. 1, *a*) is not suitable for reproducing the saline solution properties since the circuit element $R2$ is the interphase resistance (or diffusion process resistance). The latter is reproduced with an error of ~1000 %.

It should be noted that the simulation of the impedance of the electrolyte solution with the resistance $R1$ is valid for highly concentrated solutions within a wide range of frequencies. Only at frequencies exceeding (1÷5) MHz, it is necessary to introduce additional elements that describe the relaxation in the electrolyte. As the concentration of the saline solution increases, the resistance values of the electrolyte $R1$ fall. 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 Z_{CPE} of this element:

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

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 is equal to the unit of measurement of the Warburg coefficient λ (impedance due to diffusion processes of charge transfer) $\text{Ohm}\cdot c^{-1/2}$. It is believed that there exists 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, for 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 *C*1 (Fig. 1, *b*; 3, *a*).

To analyze the circuit (Fig. 3, *b*) a simulation has been performed (the results are summarized in Table 2). Analysis of Table 1 data shows that at high frequencies (1000÷100000 Hz) the reproduction error of the elements of the substitution scheme (Fig. 3, *b*) is quite small compared to the substitution scheme (Fig. 1, *a*). The error of reproduction of the resistance of the studied electrolyte at high frequencies is several times smaller compared to the low-frequency range and is almost invariant to the solution concentration (Fig. 4).



a *b*

Fig. 3. 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

However, in the low-frequency range of the resistance values reproduction error for the test object increases rapidly with the electrolyte concentration (Fig. 4).

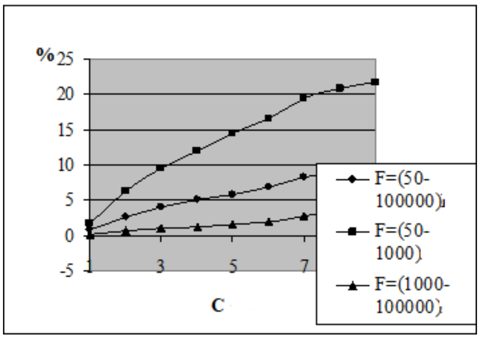


Fig. 4. Dependence of relative errors of resistance values reproduction of electrolyte according to the substitution scheme in Fig. 3 on concentration changes

Therefore, it was proposed to investigate in different frequency ranges the equivalent scheme (Fig. 5), which in comparison with the circuit of Fig. 1, *a* is supplemented by an element *C*1 simulating the capacitance of the electrode layer.

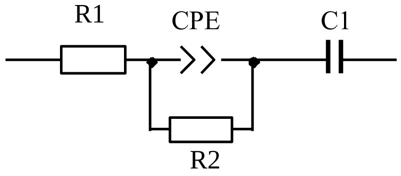


Fig. 5. Substitution scheme of the electrode-electrolyte system, taking into account the electrode capacity C1

Table 2

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

C, g/l	*F*, Hz	*R*1, Ohm	δ_{R1}, %	*P*	δ_P, %	*n*	δ_n, %
1	2	3	4	5	6	7	8
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
2	50÷100000	54.26	2.67	0.00047582	16.5	0.67971	2.35
2	50÷1000	58.29	6.31	0.00044873	19.5	0.70323	3.21
2	1000÷100000	50.82	0.60	0.00047418	6.82	0.60586	1.02
3	50÷100000	32.29	3.93	0.00050500	18.50	0.70704	2.51
3	50÷1000	35.97	9.45	0.00046501	23.97	0.73309	3.66
3	1000÷100000	29.50	1.01	0.00047961	9.09	0.62965	1.29
4	50÷100000	23.81	4.98	0.00048867	22.14	0.71123	2.82
4	50÷1000	27.40	11.94	0.00047394	26.21	0.73077	3.92
4	1000÷100000	21.42	1.24	0.00048898	8.87	0.63141	1.25
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
6	50÷100000	15.59	6.75	0.00050498	26.4	0.74110	3.14
6	50÷1000	19.14	16.5	0.00045494	33.3	0.77474	4.51
6	1000÷100000	13.68	1.97	0.00050330	11.86	0.65062	1.59

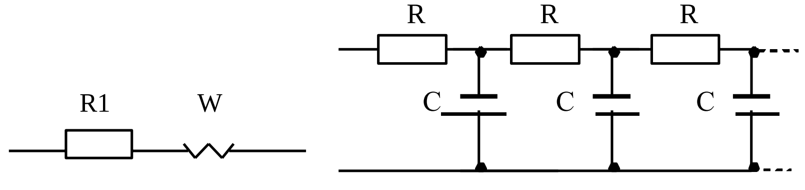
Continuation of Table 2

1	2	3	4	5	6	7	8
7	50÷100000	12.26	8.23	0.00050496	32.06	0.74755	3.60
7	50÷1000	15.92	19.4	0.00045885	37.17	0.78453	4.85
7	1000÷100000	10.62	2.78	0.00050470	13.99	0.65502	1.82
8	50÷100000	10.75	9.02	0.00050490	34.41	0.75516	3.77
8	50÷1000	14.33	20.8	0.00045771	39.9	0.79273	5.08
8	1000÷100000	9.25	3.27	0.00049790	15.4	0.66183	1.96
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

Table 3

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

C g/l	*F*, Hz	*R*1, Ohm	δ_{R1}, %	*C*1, μF	δ_{C1}, %	*R*2, Ohm	δ_{R2}, %	*P*	δ_{P}, %	*n*	δ_{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
1	50÷100000	50.47	0.95	177	13.05	46.94	7.23	0.0004654	6.76	0.61	1.37
2	50÷1000	53.12	3.7	145	51	39.31	31.4	0.00050177	31.7	0.61	6.63
2	1000÷100000	52.11	2.66	505	>1000	0.00002	>1000	0.00011223	63	0.78	6.12
3	50÷100000	29.37	1.22	216	14.2	35.34	7.99	0.00045062	7.48	0.64	1.39
3	50÷1000	30.41	2.76	251	21.7	39.65	12.29	0.00004823	9.6	0.65	1.97
3	1000÷100000	28.15	3.55	357	>1000	15.42	69.97	0.00019113	109	0.64	11.34
4	50÷100000	21.27	1.37	237	12.56	36.22	8.49	0.00050491	6.06	0.63	1.15
4	50÷1000	21.71	3.43	238	19.74	36.43	11.32	0.00050373	9.39	0.64	1.96
4	1000÷100000	20.94	0.28	53	5.5	11.19	4.35	0.00032127	2.12	0.65	0.31
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
6	50÷100000	13.49	1.87	269	14.1	26.58	8.68	0.00050493	7.65	0.65	1.31
6	50÷1000	13.83	4.67	278	18.9	27.04	10.43	0.00049735	10.2	0.66	1.96
6	1000÷100000	15.39	13.8	329	>1000	0.00004	>1000	0.00019376	>1000	0.66	>1000
7	50÷100000	10.40	2.38	278	15.8	23.72	9.07	0.00050491	8.84	0.65	1.45
7	50÷1000	11.43	4.88	301	19.55	24.49	10.95	0.00050083	9.80	0.68	1.87
7	1000÷100000	11.04	7.38	504	>1000	6.55	>1000	0.00022155	68.76	0.76	6.58
8	50÷100000	8.94	2.91	273	18.3	21.38	9.08	0.00050496	10.72	0.65	1.71
8	50÷1000	9.86	5.53	317	18.29	22.97	10.63	0.0005049	9.99	0.68	1.86
8	1000÷100000	9.86	10.5	234	>1000	4.33	496	0.00022497	>1000	0.65	>1000
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



a *b*

Fig. 6. 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

Analyzing the data in Table 3, it can be concluded that in the low-frequency range it would be possible to apply a model of the type (Fig. 5); 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 move through the electrolyte occurs only due to the diffusion of conduction ions. Near the electrode, the charge transfer processes are determined by diffusion and 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. 6, *a*, *b*). Notice, the investigated frequencies are not low enough to ensure the penetration of the diffusion sinusoidal wave to the boundary of the real diffusion layer.

Replacement of the CPE with the Warburg element (Fig. 6, *a*) led to an enhancement in the accuracy of the reproduction of the substitution scheme elements (Table 4).

Table 4

Reproduction of the substitution scheme elements values (Fig. 6) in particular frequency ranges for different values of the concentration of the aqueous salt solution

C, g/l	*F*, Hz	*R*1, 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
2	50÷100000	50.40	0.38	534.74	2.14
2	50÷1000	50.56	1.11	532.81	2.46
2	1000÷100000	49.80	0.18	617.79	1.82
3	50÷100000	29.02	0.51	435.19	2.48
3	50÷1000	29.21	1.62	433.09	2.70
3	1000÷100000	28.57	0.19	498.02	1.70
4	50÷100000	20.93	0.65	422.83	2.77
4	50÷1000	21.14	2.30	420.46	2.95
4	1000÷100000	20.54	0.24	478.06	1.87
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
6	50÷100000	13.21	0.90	345.61	3.41
6	50÷1000	13.51	3.12	342.07	3.24
6	1000÷100000	12.88	0.29	392.97	2.03
7	50÷100000	10.21	1.33	323.85	4.31
7	50÷1000	10.67	4.16	317.86	3.63
7	1000÷100000	9.84	0.48	378.34	2.18
8	50÷100000	8.83	1.51	307.98	4.54
8	50÷1000	9.31	4.52	301.4	3.69
8	1000÷100000	8.48	0.58	361.51	2.35
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

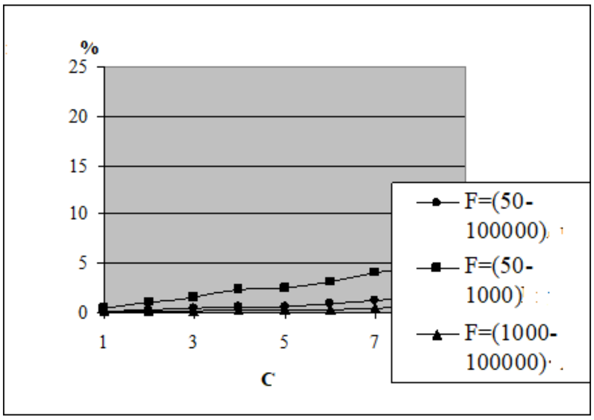


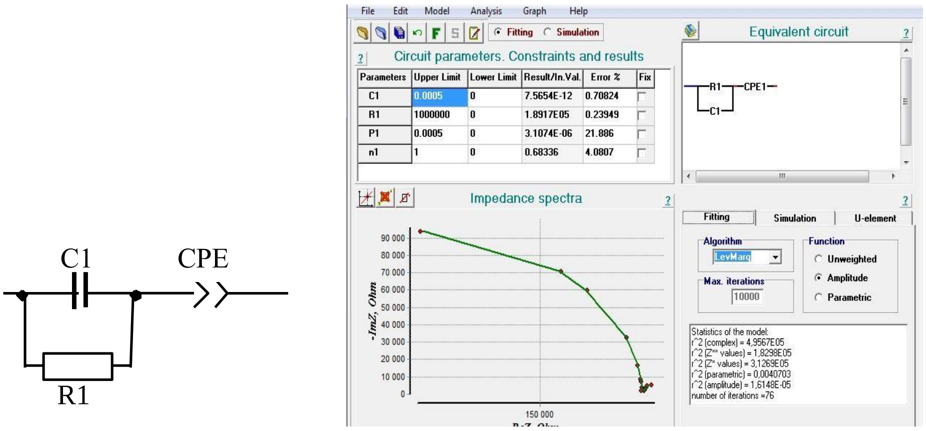
Fig. 7. Dependence of the relative errors of reproduction of the resistance values of the electrolyte according to the substitution scheme in Fig. 6 a on the values of its concentration

Comparison of the dependences of the reproduction errors of the substitution scheme elements containing the CPE (Table 3) and the Warburg element (Table 4) allowed us to conclude that at frequency band 50–1000 Hz the equivalent scheme can be represented by Fig. 6, *a* and the Warburg impedance (Fig. 6, *b*) adequately describes the processes occurring in the test system at higher frequencies (from 1–100 kHz), at which the electrode effects practically disappear.

4.2. Equivalent substitution schemes for high-impedance objects

Biochemical systems based on natural materials, in particular sugar solutions, are of interest for research of high-resistance objects. Based on the data of impedance measurements, their analysis was performed and the corresponding structure of the substitution scheme was obtained (Fig. 8).

Since these are polarized electrodes, the substitution scheme contains a link that describes the presence of the capacitance *C*1 in the electrode Helmholtz layer and the resistance of charge transfer *R*1. The presence of the CRE in the substitution scheme is explained by the inhomogeneity of the electrode surface, which may be caused by the selective adsorption of sugar on the electrodes, or even by the presence of a small amount of gas (air oxygen), which leads to the formation of phase boundaries (fractals). The latter produces the local alteration in the electrochemical parameters of the electrode surface, which is best modeled by CPE. To eliminate this phenomenon, it is recommended to create closed-type electrochemical cells for minimization 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 (Table 5).



Circuit parameters. Constraints and results

Parameters	Upper Limit	Lower Limit	Result/In.Val.	Error %	Fix
C1	0.0005	0	7.5654E-12	0.70824	☐
R1	1000000	0	1.8917E05	0.23949	☐
P1	0.0005	0	3.1074E-06	21.886	☐
n1	1	0	0.68336	4.0807	☐

Algorithm: LevMarq

Max. iterations: 10000

Function: ○ Unweighted ● Amplitude ○ Parametric

```
Statistics of the model:
r^2 (complex) = 4,9567E05
r^2 (Z** values) = 1,8298E05
r^2 (Z* values) = 3,1269E05
r^2 (parametric) = 0,0040703
r^2 (amplitude) = 1,6148E-05
number of iterations =76
```

a *b*

Fig. 8. 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

Table 5

Reproduction of the substitution scheme elements values (Fig. 8) in particular frequency ranges for different values of the concentration of aqueous sugar solution

C, g/l	*F*, Hz	R1, Ohm	δ_{R1},%	*C*1, 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

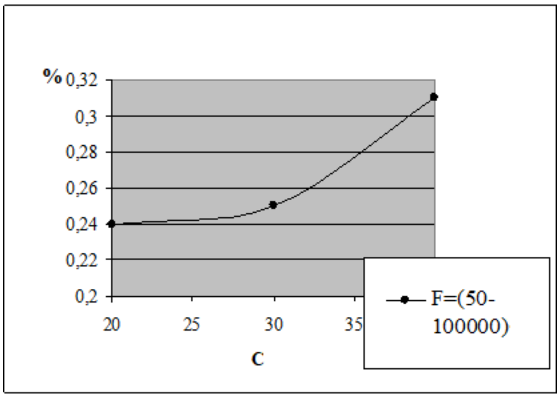


Fig. 9. Dependence of the relative errors of the resistance values reproduction of the solution according to the substitution scheme in Fig. 8, a on the values of its concentration

The error of reproduction of the test object resistance increases with concentration (Fig. 9). This may indicate that the equivalent scheme may also differ for appropriate concentration ranges as in the case of different frequency subranges.

5. Conclusions

The study of impedance spectra of non-electrical nature objects has been fulfilled. Equivalent substitution schemes have been developed for objects independent of their resistance.

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. Data analysis showed that at frequencies higher than 1000 Hz, the substitution scheme, the capacity of the double electric layer, is not suitable for reproducing the properties of saline solution because the resistance between the phase transition (or the resistance of the diffusion process) is reproduced with errors exceeding 1000 %. It is proved that the resistance simulation of the impedance of the electrolyte solution 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 considering the relaxation in the electrolyte.

There were studied the diffusion phenomena in the electrode. Comparison of the dependences of reproduction errors of substitution scheme elements containing a constant phase element and a Warburg element is available at frequencies range 50–1000 Hz.

The equivalent circuit of a low-impedance object can be represented by a constant phase element and the Warburg impedance that adequately describes the system at high frequencies (1–100 kHz). Furthermore, the electrode effects almost fall.

For high-resistance objects, it is recommended to create closed-type electrochemical cells that minimize the contact area “solution – air”.

6. Gratitude

The authors express their gratitude to the Staff of the Department of Information and Measuring Technologies of Lviv Polytechnic National University.

7. Conflict of interest

The authors state that there are no financial or other potential conflicts regarding this work.

References

[1] V. Yatsuk, T. Bubela, Y. Pokhodylo, Y. Yatsuk, R. Kochan, “Improvement of data acquisition systems for the measurement of physical-chemical environmental properties”, in *Proc. 2017 IEEE 9th International Conference on Intelligent Data Acquisition and Advanced Computing Systems: Technology and Applications, IDAACS 2017, no. 1,* Bucharest, Romania, 2017, pp. 41–46. doi:10.1109/idaacs.2017.8095046

[2] M. Grossi, B. Riccò, “Electrical impedance spectroscopy (EIS) for biological analysis and food characterization: a review”, J. Sens. Sens. Syst., 6, pp. 303-325, 2017. doi:10.5194/jsss-6-303-2017

[3] M.Orazem, B.Tribollet, *Electrochemical Impedance Spectroscopy,* Wiley, 2017. https://www.wiley.com/en-us/Electrochemical+Impedance+Spectroscopy,+2nd+Edition-p-9781118527399

[4] I. Deleebeeck, S.Veltze, “Electrochemical impedance spectroscopy study of commercial Li-ion phosphate batteries: a metrology perspective”, Int. J. Energy Res., no. 44, p. 7158–7182, 2020. doi.org/10.1002/er.5350

[5] A. Bandarenka, “Exploring the interfaces between metal electrodes and aqueous electrolytes with electrochemical impedance spectroscopy”, Analyst, no. 138, p. 5540–5554, 2013. doi:10.1039/c3an00791j

[6] M. Grossia, C. Parolin, B. Vitali, B. Riccòa, “Electrical Impedance Spectroscopy (EIS) characterization of saline solutions with a low-cost portable measurement system”, Engineering Science and Technology, an International Journal, no. 22, issue 1, p.102-108, 2019. doi.org/10.1016/j.jestch.2018.08.012

[7] C. Gabrielli, “Once upon a time there was EIS”, Electrochim. Acta 331, 135324, 2020. doi:10.1016/j.electacta.2019.135324

[8] A. Lasia, “Electrochemical Impedance Spectroscopy and its Applications”, Springer, p. 1–367, 2014. doi.org/10.1007/0-306-46916-2_2

[9] W.Watson, M. Orazem, Measurement model program, 2020. [Online]. Available: doi.org/10.1149/osf.io/kze9x

[10] A. llagui, T. Freeborn, A. Elwakil, B. Maundy, “Reevaluation of performance of electric double-layer capacitors from constant-current charge/discharge and cyclic voltammetry”, Sci. Rep., no. 6, 38568, 2016. doi: 10.1038/srep38568

[11] M. Orazem, et al. “Dielectric properties of materials showing constant-phase-element (CPE) impedance response”, J. Electrochem. Soc., no.160, C215–C225, 2013. doi.org/10.1149/2.033306jes