Evolution of EIS properties of composite polymer protective coatings in corrosive media

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Abstract

Electrochemical impedance spectroscopy (EIS) was used for a comparative study of the evolution of the electrochemical characteristics of protective primers, inert insulating coatings, and multilayered polymer composite coatings in chloride media. It was shown that the layers of coating with inert fillers on an inert substrate could be described as the simplest equivalent circuit (EC) with a single characteristic relaxation process in the entire range of exposure times. The same EC describes coatings on a potentially corroding substrate at the initial exposure stage. Later, as underfilm corrosion develops, the EC evolves into a system with two relaxation processes. In thin-layer systems with an active filler (Zn), the two relaxation processes are manifested starting from the initial exposure period. In thick multilayered composite coatings that contain spatially separated layers with reactive and inert fillers on a corroding steel substrate, three characteristic relaxation times are observed. These findings agree with the model of multiphase laminated volume-filled polymer composite materials and provide a justification to the usage of Voigt's additive ECs. Using this approximation, we performed a description of all EIS data for all the systems we considered at various temperatures, including inert layers based on steel and platinum, thin and multilayered Zn-rich primer layers, and multilayered coatings made of these materials. The results obtained allowed us to suggest a technique of nondestructive EIS monitoring of the physicochemical and corrosion processes in composite polymer protective coatings. The technique is based on performing comparative electrochemical impedance spectroscopy on various metal (corroding and inert) substrates at various temperatures and identification of the processes using characteristic frequencies, effective activation energies, and corrosion rate during exposure.

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1. Introduction

Multilayered composite coatings that contain a layer of a Zn-rich primer and upper layers made of an insulating polymer paint are efficient means for protection against corrosion [1]. The use of such coatings, which significantly simplifies the technology for the protection of carbon steels, is an alternative to conventional zinc plating.

However, the mechanism of the protective effect of multilayered composite coatings with active metal anticorrosion additives has not been studied yet in sufficient detail. One of the reasons is that Zn particles in composite coatings with upper insulating layers are located in an internal corrosive medium that differs from the external NaCl solution. This changes both the thermodynamics and kinetics of electrochemical processes. Due to this, the scientific basis for the efficient protection by multilayered composite materials containing metal additives has been formulated in only fragmentary form to date [2–6].

This situation is essentially due to the lack of nondestructive techniques that would allow a comprehensive study of electrochemical processes on both the protected substrate, the primer layer, and the upper insulating paint layer on long-term exposures in corrosive media.

The purpose of this study was to clarify the mechanism of the protective effect of composite coatings and estimate the electrochemical and insulating properties of both individual layers and the entire multilayered composite coatings by means of electrochemical impedance spectroscopy (EIS).

2. Objects and Methods

The objects under study included individual coatings made of commercial Zn-rich protective primer METACOR-01 (M-01) TU (Technical requirements) 2312-003-11490792-99, epoxy coating ROCOR-5095 (R-5095) TU 2312-042-11490792-09, and composite coatings on their basis.

We have studied the behavior of these coatings under long-term exposure in 3% NaCl solution on an inert (platinum, Pt) and corroding (St3 steel) substrate at temperatures ranging from 20°C to 80°C.

Electrochemical impedance spectroscopy (EIS) [7–9] combined with the potentiometry method were the main tools of the study. The area of the working electrode (coated sample) was 6.2 cm².

Impedance was studied using a FRA-1 analyzer developed by the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences, by the ISO methodology recommended for polymer coatings [10] in a frequency range of (100 kHz–0.1 Hz). The area of the auxiliary platinum electrode was 16.9 cm²; this value is sufficient for our purposes, as confirmed by the fact that a reduction in this area did not affect the measured results. The equivalent electric circuit parameters were calculated in the DCS program based on the spectra obtained.

The potential of the substrates with coatings was determined directly in the cell for impedance measurement with respect to the silver-chloride electrode using the following circuit: sample under study / working solution / saturated KCl / AgCl / Ag with an auxiliary platinum electrode. All potentials are reported against the standard hydrogen electrode.

3. Results and Discussion

3.1. Individual coatings

Multilayered composite coatings are known to contain several layers differing in composition, including metal-rich primers and upper layers made of inert formulations. The system approach prompts that in studying the properties of composite systems, it is reasonable to consider first the EIS results of estimating the electrochemical properties of individual layers of composite coatings; namely, the insulating inert paint layer and the Zn-protective polymer primer. It is also reasonable [11] to estimate the behavior of these coatings on both inert (Pt) and corroding (St3) substrates.

3.1.1. Inert coating R-5095 on platinum and steel

The Figures below display the hodographs and frequency plots of the dielectric loss tangent (Bode plots) for the electrochemical impedance of epoxy enamel R-5095 with an inert filler (TiO_2) on a platinum (Figures 1 and 2) and steel (Figures 3 and 4) substrates in the course of exposure in 3% NaCl solution. Table 1 contains the results of calculations using the equivalent circuits.

Figure 1. Impedance hodograph of coating R-5095 with an inert filler (TiO_2) on a platinum substrate after exposure in 3% NaCl solution for 30 days (1) and 160 days (2). Dots – experimental data; lines – EC-based calculation.

The shape of the impedance hodograph for inert insulating enamel R-5095 on an inert Pt substrate, which was the same for all times of exposure in 3% NaCl solution in a range of frequencies from 25 kHz to 6 Hz, can be represented as a semicircle with a displaced center.

As the exposure time increases, the quantitative characteristics of the impedance hodograph (Figure 1) and frequency plot of the dielectric loss tangent on the Bode plot (Figure 2) do not change much. This behavior corresponds to the existence, in the frequency range down to 6 Hz, of a single relaxation process with a characteristic frequency of about 5 kHz.

Figure 2. Bode plot for coating R-5095 with an inert filler (TiO_2) on a platinum substrate after exposure in 3% NaCl solution for 30 days (1) and 160 days (2). Dots – experimental data; lines – EC-based calculation.

The description of the EIS of the same coating on steel (St3 GOST mark) is more complex. In particular, primary data (Figure 3) for the frequency range under consideration show that the EIS characteristics at the initial stage of exposure are qualitatively similar to the dependences for the inert Pt substrate, although the absolute values of the impedance on St3 are somewhat smaller. However, the frequency dependence of the dielectric loss tangent on the Bode plot for St3 and Pt have virtually the same magnitude. This can be considered as an indication that no active underfilm corrosion process occurs under coating R-5095 on St3 at the initial stage of exposure (up to 30 days).

Figure 3. Impedance hodograph of coating R-5095 with an inert filler (TiO_2) on a platinum substrate after exposure in 3% NaCl solution for 14 days (1) and 30 days (2). Dots – experimental data; lines – EC-based calculation.

At longer exposure times, the shape of the hodograph on St3 becomes more complex (Figure 5). EIS analysis allows the identification (apart from Warburg impedance) of two relaxation processes (Figure 6) with high frequency (HF) and medium frequency (MF) in the frequency range under consideration.

Figure 4. Bode plot for coating R-5095 with an inert filler (TiO_2) on a platinum substrate after exposure in 3% NaCl solution for 14 days (1) and 30 days (2). (Dots – experimental data; lines – EC-based calculation).

Figure 5. Impedance hodograph of coating R-5095 with the inert filler (TiO_2) on a steel (St3) substrate after exposure in 3% NaCl solution for 160 days. Big dots – experiment; lines – EC-based calculation: 1 – HF process, 2 – LF process, 3 – Warburg impedance, 4 – integral plot.

Figure 6. Bode plot for the impedance of coating R-5095 with the inert filler (TiO_2) on a steel (St3) substrate after exposure in 3% NaCl solution for 160 days. Big dots – experiment; lines – EC-based calculation: 1 – HF process, 2 – LF process, 3 – Warburg impedance, 4 – integral plot.

The parameters of relaxation processes and the values of EC elements for R-5095 coating on Pt and St3 are presented below.

Table 1. Evolution of electrochemical parameters of coating R-5095 on Pt and St3 upon exposure in 3% NaCl solution at 25°C for the ECs (Figures 3 and 5) in a frequency range of 25000–2 Hz based on processing primary EIS data.

Characteristics of the coating/substrate system	Exposure, days				
	7	30	60	130	160
Pt substrate					
<i>R</i> 1, Ohm	$8.21 \cdot 10^5$	$7.71 \cdot 10^5$	$9.35 \cdot 10^5$	$8.54 \cdot 10^5$	$6.87 \cdot 10^5$
CPE-T1, F	$4.58 \cdot 10^{-9}$	$5.23 \cdot 10^{-9}$	$4.88 \cdot 10^{-9}$	$6.14 \cdot 10^{-9}$	$5.56 \cdot 10^{-9}$
Characteristic frequency of the HF process, Hz	3474	4827	3474	4827	4827
Substrate potential (SHE), mV	313	364	418	589	563
St3 substrate					
<i>R</i> 1, Ohm	$7.36 \cdot 10^5$	$4.12 \cdot 10^5$	$1.17 \cdot 10^5$	$8.32 \cdot 10^4$	$2.87 \cdot 10^4$
CPE-T1, F	$4.99 \cdot 10^{-9}$	$6.11 \cdot 10^{-9}$	$6.83 \cdot 10^{-9}$	$9.29 \cdot 10^{-9}$	$1.25 \cdot 10^{-8}$
Characteristic frequency of the HF process, Hz	4827	4827	9319	9319	9319
<i>R</i> 2, Ohm	–	–	$2.73 \cdot 10^5$	$1.46 \cdot 10^5$	$1.16 \cdot 10^5$
CPE-T2, F	–	–	$1.72 \cdot 10^{-7}$	$1.42 \cdot 10^{-7}$	$1.87 \cdot 10^{-7}$
Characteristic frequency of the MF process, Hz	–	–	18	67	180
Substrate potential (SHE), mV	91	–35	–93	–	–100

The primary EIS data and processing of these data show that:

- The hodographs and frequency dependences for inert coating R-5095 on Pt virtually do not change during exposition. The calculated values of the active and capacitive EC components and the characteristic frequency of the relaxation process do not change, either. It should be noted that the potential of the Pt substrate expectedly increased by 250 mV.
- However, in the case of the same coating R-5095 on the steel (St3) substrate, both primary and calculated characteristics change. It should be noted first of all that an

additional MF relaxation process emerges in the system concurrently with changes in the quantitative characteristics of the HF process.

- The main changes in the HF region are as follows: a) active resistance R_1 decreases; b) the loss tangent and, as a consequence, the capacitive component of the coating (CPE-T1) significantly increase; c) the characteristic frequency of the HF process at the initial exposure stage is 4.8 kHz but increases after 60 days of exposure.
- A characteristic feature of the MF process is that it manifests itself at exposure times of 60 days or more. The active resistance R_2 shows a decreasing trend. Similarly to the HF process, an increase in the capacitive component of the coating (CPE-T2) is observed, and the characteristic frequency increases tenfold in the course of the MF process development (from 18 to 180 Hz).
- The potential of the steel substrate under the coating during exposure in 3% NaCl solution diminishes unlike that of the Pt substrate, but even at the longest exposure time it exceeds the corrosion potential of unprotected St3, *i.e.*, -500 mV.

Thus, the data obtained demonstrate the effect of the substrate type (inert or corroding) and products of steel substrate corrosion on the entire set of electrochemical characteristics of the substrate/inert coating system.

3.1.2. Zn-rich primers on steel and platinum

The corroding dispersed filler (Zn) is distributed in Zn-rich primers throughout the volume. Some Zn particles are easily accessible for the corrosive medium while others are temporarily blocked since they are located in deep layers. As a result, the corrosion process develops with a varying rate, which should be reflected in EIS characteristics, and complicates the choice of the EC.

It also follows from the above that the electrochemical behavior of Zn-rich primer layers is controlled by a number of factors, including the thickness of the layers, content of the active metal, and type and properties of the polymer matrix.

Let us consider the effect of the primer layer thickness from the perspective of possible existence of through porosity. Thin single-layer coatings with a high degree of filling (usual for Zn-rich protective coatings) always have through defects and pores [12].

Similarly to the inert coating, let us first consider a thin single-layer primer M-01 on an inert non-corroding Pt substrate (Figures 7 and 8).

The figures show that even at the initial stage, the thin Zn-rich primer layer on a Pt substrate exposed in 3% NaCl solution exhibits two relaxation maxima: HF (5–10 kHz) and LF (0.8–5 Hz).

The results of processing the EIS data show that a satisfactory approximation is provided for small exposure times (up to 30 days) by the Mansfeld EC [13] for porous coatings, while its modified version (Table 3) ensures approximation in the entire time range (Table 2).

Figure 7. Hodographs of the impedance of thin (30 μm) Zn-rich primer M-01 on a platinum (Pt) substrate after exposure in 3% NaCl solution for: 1 – 3 days, 2 – 30 days, 3 – 100 days.

Figure 8. Bode plot for thin (30 μm) Zn-rich primer M-01 on a platinum (Pt) substrate after exposure in 3% NaCl solution for: 1 – 3 days, 2 – 30 days, 3 – 100 days.

Table 2. Parameters of the EC components for 30- μm -thick primer M-01 after exposure in 3% NaCl solution for 100 days.

EC parameters	Voigt–Mansfeld equivalent circuit			
	3 days	30 days	65 days	100 days
R_1 , Ohm	7.7	272.0	313.0	1025.0
CPE-T1, F	$3.46 \cdot 10^{-5}$	$7.94 \cdot 10^{-6}$	$1.60 \cdot 10^{-6}$	$1.17 \cdot 10^{-6}$
Characteristic frequency of the process, Hz	4827	6707	12494	9319
R_2 , Ohm	38.4	554.3	749.6	2572
CPE-T2, F	$3.77 \cdot 10^{-4}$	$1.78 \cdot 10^{-5}$	$7.32 \cdot 10^{-6}$	$8.49 \cdot 10^{-7}$
Characteristic frequency of the process, Hz	1295	180	670	670
R_3 , Ohm	2157	11773	18996	28130
CPE-T3, F	$4.13 \cdot 10^{-4}$	$9.92 \cdot 10^{-5}$	$4.76 \cdot 10^{-5}$	$2.16 \cdot 10^{-5}$
Characteristic frequency of the process, Hz	2.5	0.93	1.8	6.7
Error, %	1.33	1.40	2.08	1.40

Table 3. Equivalent circuits for the description of electrochemical properties of thin protective primers on a steel substrate at large time of exposure in 3% NaCl solution at 25°C.

Description of EC	Circuit
Mansfeld circuit [13] for porous coatings
Voigt circuit for bulk low-porosity composite materials [9]
Voigt–Mansfeld hybrid circuit [11]

The results of approximation of hodographs and frequency plots using various circuits are shown below (Figures 9–14 and Table 4).

Figure 9. Impedance hodograph of thin (30 μm) Zn-rich primer M-01 on a steel (St3) substrate in 3% NaCl solution for 100 days. Dots – experiment; lines – approximations using Mansfeld (1), Voigt–Mansfeld (2), and Voigt (3) ECs. **Figure 10.** Bode plot of the impedance of thin (30 μm) Zn-rich M-01 primer on a steel (St3) substrate in 3% NaCl solution for 100 days. Dots – experiment; lines – approximations using Mansfeld (1), Voigt–Mansfeld (2), and Voigt (3) ECs.

More complex evolution can be expected for the same Zn-rich primer M-01 layer on a corroding St3 substrate since such a coating/substrate system should be considered as a two-anode system. However, most likely, the activation and fading of the oxidation processes in the filler and substrate would not be observed concurrently. Namely, at the initial state of exposure in a corrosive medium, primarily corrosion of the protector Zn additive should occur, while development of corrosion of the steel substrate is not likely. At the final stage, as Zn is exhausted, its contribution to the galvanic protection of the substrate should diminish which potentially creates conditions for the manifestation of underfilm corrosion of the steel substrate.

Due to these circumstances, the selection of a versatile EC is a complex task. So, we considered two approximations of EIS data based on different ECs (Table 3).

The impedance of EC components of thin Zn-protective layer on St3 calculated using various circuits is displayed below (Table 4).

Table 4. Parameters of EC components for 30- μm -thick primer M-01 on a steel substrate after exposure in 3% NaCl solution for 100 days calculated using various circuits.

EC parameters	Equivalent circuit		
	Mansfeld	Voigt	Voigt–Mansfeld
R_1 , Ohm	$2.26 \cdot 10^3$	$1.90 \cdot 10^3$	$1.36 \cdot 10^2$
CPE-T1, F	$2.21 \cdot 10^{-6}$	$2.40 \cdot 10^{-6}$	$6.11 \cdot 10^{-7}$
Characteristic frequency of the process, Hz	9319	9319	9319
R_2 , Ohm	$1.37 \cdot 10^4$	$1.40 \cdot 10^4$	$2.02 \cdot 10^3$
CPE-T2, F	$2.38 \cdot 10^{-5}$	$2.54 \cdot 10^{-5}$	$1.61 \cdot 10^{-6}$
Characteristic frequency of the process, Hz	3.47	3.47	1799
R_3 , Ohm			$1.38 \cdot 10^4$
CPE-T3, F			$2.44 \cdot 10^{-5}$
Characteristic frequency of the process, Hz			3.47
Error, %	1.88	1.98	1.45

The most easily comprehensible and sensitive to the quality of EIS data approximation are the frequency plots of the loss tangent (Bode plots) (Figures 11–13).

The data displayed in the table and figures (Figures 11–13) show that the approximation errors in the three circuits are similar (1.45–1.98%), but the smallest error (1.45%) is obtained if the Voigt–Mansfeld hybrid circuit is used. However, this result is quite expected since this circuit contains a larger (+2) number of elements. Additional

arguments in favor of a preferable choice can be obtained by analyzing Zn protector primer layers of various thickness.

Figure 11. Bode plot for thin (30 μm) Zn-rich primer M-01 on a steel (St3) substrate after exposure in 3% NaCl solution for 100 days and its approximation using the Mansfeld circuit (3) with separation into HF (1) and LF (2) components.

Figure 12. Bode plot for thin (30 μm) Zn-rich primer M-01 on a steel (St3) substrate after exposure in 3% NaCl solution for 100 days and its approximation using the Voigt circuit (3) with separation into HF (1) and LF (2) components.

Figure 13. Bode plot for thin (30 μm) Zn-rich primer M-01 on a steel (St3) substrate after exposure in 3% NaCl solution for 100 days and its approximation using Voigt–Mansfeld circuit (4) with separation into HF (1), MF (2), and LF (3) components.

3.1.3. Estimation of the correctness of the models for porous and low-porosity layers

Since the primer layer is applied in more than one stage, as a result of which through defects are covered, it is reasonable to check the quality of approximation for layers with an increased thickness using models of porous and low-porosity primers.

Examples of such models are the Voigt–Mansfeld hybrid model considered above, which yielded the lowest approximation error for thin layers, and the model of a volume-filled composite material, which may be referred to as a “3-phase Voigt model”.

Figure 14. Hodograph of impedance and the Bode plot of multilayered (100 μm) Zn-rich primer M-01 on a steel (St3) substrate after exposure in 3% NaCl solution for 100 days and their approximation using the Voigt–Mansfeld circuit for porous coatings (4) with separation of the HF (1), MF (2), and LF (3) components.

Figure 15. Hodograph of impedance and the Bode plot of multilayered (100 μm) Zn-rich primer M-01 on a steel (St3) substrate after exposure in 3% NaCl solution for 100 days and their approximation using the 3-phase Voigt circuit for low-porosity coatings (4) with separation of the HF (1), MF (2), and LF (3) components.

The latter model represents a Zn protective primer layer as a 3-phase system with bulk or alternating laminar phases with different dielectric properties. Examples of such phases are: a) a polymer matrix; b) Zn powder particles initially incorporated into the matrix; c) particles of hydrated Zn oxides, which are produced as a result of Zn oxidation under the

effect of a corrosive medium. This model is very flexible since it does not *ab initio* strictly relate relaxation phenomena with certain processes, for example, capillary transport that can change considerably if multilayer coatings are applied.

The results of approximation using the two circuits under consideration are displayed below (Figures 14 and 15, Table 5).

Table 5. EC components calculated for primer M-01 with enhanced thickness (100 μm) applied in several layers after exposure in 3% NaCl solution for 100 days.

EC parameters	Equivalent circuit	
	Voigt–Mansfeld	3-phase Voigt model
$R1$, Ohm	$1.97 \cdot 10^3$	$1.16 \cdot 10^3$
CPE-T1, F	$2.65 \cdot 10^{-7}$	$1.70 \cdot 10^{-7}$
CPE-Ph1	0.83	0.92
Characteristic frequency of the process, Hz	9319	6707
$R2$, Ohm	$1.11 \cdot 10^4$	$1.33 \cdot 10^4$
CPE-T2, F	$9.68 \cdot 10^{-7}$	$1.31 \cdot 10^{-6}$
CPE-Ph2	0.70	0.64
Characteristic frequency of the process, Hz	483	670
$R3$, Ohm	$1.62 \cdot 10^{10}$	$3.34 \cdot 10^4$
CPE-T3, F	$0.20 \cdot 10^{-3}$	$0.24 \cdot 10^{-3}$
CPE-Ph3	0.25	0.44
Characteristic frequency of the process, Hz	0.25	0.25
Error, %	2.39	1.13

It can be seen that both the hodographs and frequency plots can be approximated using either of the two circuits and the root-mean-square deviations between the calculated and experimental dependences for both ECs are not very different (2.39 and 1.13). However, if the Voigt–Mansfeld hybrid circuit is employed, apparent disagreement is observed at low frequencies, and the calculated values of some EC components lose physical meaning (Table 5).

This finding allows us to make the conclusion that the best approximation for thick-layer primer coatings applied in more than one stage, which also preserves physically justified values of EC components, is provided by the 3-phase Voigt model with well-separated characteristic frequencies.

It should be noted that the use of the Voigt model does not involve any formal restrictions on the disposition of composite material components. It can be applied to both a volume-filled and laminated inhomogeneous composite material. It is for this reason that the model under consideration provides a fairly correct description for multilayered coatings made of volume-filled polymer materials.

It is believed that this approach can be applied to other types of multilayered anticorrosion composite polymer coatings.

3.2. Composite coatings

As noted above, of special interest for highly-efficient anticorrosion protection are multilayered coatings that consist of specialized layers with various composition and properties.

Based on the EIS results considered above and estimation of the ECs optimal for individual layers of the composite coating, it may be expected that the EC which may be adequate to describe the multilayered coating is an additive one. The total impedance of the coating, which is also an additive quantity ($Z = \Sigma(Z_i)$), is determined by the number (i), thickness, and composition of the coating layers.

However, the hypothesis regarding the full additivity of the composite coating impedance requires a verification, since the composition of the inner solution in polymers can differ from that of the outside solution [14], and hence, the Zn protective primer layer would be subject to different conditions.

Displayed below are the primary data of EIS kinetics (Figures 16 and 17) and results of processing these data for a composite coating M-01 (60 μm) + R-5095 (100 μm) on a steel substrate upon exposure in 3% NaCl solution for 344 days at a temperature of 20 °C and for 7 days at 60 °C.

3.2.1. EIS data for composite coatings

Figure 16. Impedance hodographs of a composite coating (M-01 (60 μm) + R-5095 (100 μm)) on a steel (St3) substrate upon exposure in 3% NaCl solution for: 1 – 30 days, 2 – 100 days, 3 – 200 days, 4 – 344 days, and 5 – 351 days.

Figure 17. Bode plots for a composite coating (M-01 (60 μm) + R-5095 (100 μm)) on a steel (St3) substrate upon exposure in 3% NaCl solution for: 1 – 30 days, 2 – 100 days, 3 – 200 days, 4 – 344 days, and 5 – 351 days.

The presented results show that both the hodograph shape and the Bode frequency plots feature a complex structure at all exposure times. This is especially well pronounced at large times of exposure in the corrosive medium.

Figure 18. Impedance hodograph of a composite coating (Zn-rich protective primer M-01 + inert upper coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20°C) and its approximation using the Voigt–Mansfeld hybrid circuit (4) with separation of the HF (1), MF (2), and LF (3) components.

Figure 19. Bode plot a composite coating (Zn-rich protective primer M-01 + inert upper coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20°C) and its approximation using the Voigt–Mansfeld hybrid circuit (4) with separation of the HF (1), MF (2), and LF (3) components.

Figure 20. Impedance hodograph of a composite coating (Zn-rich protective primer M-01 + inert upper coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20°C) and its approximation using the 3-phase Voigt circuit (4) with separation of the HF (1), MF (2), and LF (3) components.

Figure 21. Bode plot for a composite coating (Zn-rich protective primer M-01 + inert upper coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20°C) and its approximation using the 3-phase Voigt circuit (4) with separation of the HF (1), MF (2), and LF (3) components.

It should be noted that at large exposure time, an LF process is detected with a characteristic frequency in the range of 1-5 Hz, which can be related to the development of the electrochemical process of Zn oxidation.

Experimental data for a composite coating consisting of M-01 (60 μm) + R-5095 (100 μm) and their approximation using various ECs presented in Table 3, including the Voigt–Mansfeld hybrid circuit and 3-phase Voigt circuit, are displayed below (Figures 18–21 and Table 6).

As the data displayed in Figures 18 and 19 shows, the Voigt–Mansfeld hybrid EC, like in the case of a multilayered primer (Table 5), fails to provide an adequate description of the experimental data.

At the same time, the Voigt EC for 3-phase composites, similarly to multilayered primers, provides a correct description in the entire time range including large exposure

times and, which is also of importance, for various temperatures in the range of 20–60°C (Figures 22–27 and Table 7).

Table 6. Calculated EC components for a composite coating (Zn-rich protective primer M-01 + inert upper coating R-5095) with a thickness of 60 μm and 100 μm , respectively, after exposure in 3% NaCl solution for 344 days at a temperature of 20–25°C.

EC parameters	Equivalent circuit	
	Voigt–Mansfeld	3-phase Voigt model
R_1 , Ohm	$2.82 \cdot 10^3$	$6.82 \cdot 10^5$
CPE-T1, F	$5.97 \cdot 10^{-9}$	$2.65 \cdot 10^{-9}$
CPE-Ph1	1.42	0.94
Characteristic frequency of the process, Hz	17992	3474
R_2 , Ohm	$1.41 \cdot 10^6$	$5.34 \cdot 10^6$
CPE-T2, F	$9.29 \cdot 10^{-10}$	$2.03 \cdot 10^{-9}$
CPE-Ph2	0.96	0.96
Characteristic frequency of the process, Hz	3474	48.3
R_3 , Ohm	$9.73 \cdot 10^6$	$4.34 \cdot 10^6$
CPE-T3, F	$7.33 \cdot 10^{-9}$	$1.40 \cdot 10^{-8}$
CPE-Ph3	0.58	0.94
Characteristic frequency of the process, Hz	93.2	3.47
DCS program error, %	3.92	1.77

Figure 22. Impedance hodograph of a composite coating (Zn-protective primer M-01 + upper inert coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20–25°C) and next at 7 days (at 60°C) and its approximation (4) with separation of the HF (1), MF (2), and LF (3) components. Data obtained at 20°C.

Figure 23. Bode plot for a composite coating (Zn-protective primer M-01 + upper inert coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20–25°C) and next at 7 days (at 60°C) and its approximation (4) with separation of the HF (1), MF (2), and LF (3) components. Data obtained at 20°C.

Figure 24. Impedance hodograph of a composite coating (Zn-protective primer M-01 + upper inert coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20–25°C) and next at 7 days (at 60°C) and its approximation (4) with separation of the HF (1), MF (2), and LF (3) components. Data obtained at 40°C.

Figure 25. Bode plot for a composite coating (Zn-protective primer M-01 + upper inert coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20–25°C) and next at 7 days (at 60°C) and its approximation (4) with separation of the HF (1), MF (2), and LF (3) components. Data obtained at 40°C.

Figure 24. Impedance hodograph of a composite coating (Zn-protective primer M-01 + upper inert coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20–25°C) and next at 7 days (at 60°C) and its approximation (4) with separation of the HF (1), MF (2), and LF (3) components. Data obtained at 60°C.

Figure 25. Bode plot for a composite coating (Zn-protective primer M-01 + upper inert coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20–25°C) and next at 7 days (at 60°C) and its approximation (4) with separation of the HF (1), MF (2), and LF (3) components. Data obtained at 60°C.

Thus, the use of the Voigt EC for 3-phase composite materials provides a correct description of EIS data and identification of relaxation processes in the entire range of exposure times and temperatures.

To summarize, the conclusion can be drawn that the most universal description of protective thick polymer coatings should be based on the presentation of such coatings as multiphase layered volume-filled composite materials. This approach enables an adequate processing of EIS data at various temperatures for all the systems we studied, including inert layers on St3 and Pt, thin and multilayered Zn-rich primer layers, and multilayered coatings consisting of such layers.

The EC evolution in the course of exposure in a corrosive medium is also logical. The key physicochemical parameter in forecasting the evolution of circuits is the change in the phase composition of the layers of polymer protective coatings under the effect of a corrosive

medium. The second factor in the transition from model systems to actual coatings is that a layered composite material with low porosity is produced upon applying the coating.

Thus, the EC based on a combination of Voigt elements provides a correct approximation of EIS results in the entire range of exposure times and for the transition from thin coatings to multilayered structures.

Table 7. EC parameters calculated using the 3-phase Voigt circuit for a composite coating (Zn-protective primer M-01 + upper inert coating R-5095) on a steel (St3) substrate after exposure in 3% NaCl solution for 344 days (at 20–25°C) and 7 days (at 60°C)

EC parameters	Temperature of measurement, °C		
	20	40	60
R1, Ohm	$3.59 \cdot 10^5$	$1.04 \cdot 10^5$	$2.08 \cdot 10^4$
CPE-T1, F	$3.00 \cdot 10^{-9}$	$2.42 \cdot 10^{-9}$	$5.74 \cdot 10^{-9}$
Characteristic frequency of the process, Hz	3474	10000	25000
R2, Ohm	$7.17 \cdot 10^6$	$2.69 \cdot 10^5$	$1.65 \cdot 10^4$
CPE-T2, F	$1.82 \cdot 10^{-9}$	$7.27 \cdot 10^{-9}$	$1.46 \cdot 10^{-7}$
Characteristic frequency of the process, Hz	67	347	671
R3, Ohm	$1.01 \cdot 10^7$	$4.66 \cdot 10^5$	$8.58 \cdot 10^4$
CPE-T3, F	$6.29 \cdot 10^{-9}$	$9.50 \cdot 10^{-7}$	$2.65 \cdot 10^{-6}$
Characteristic frequency of the process, Hz	4.83	1.29	4.83

A significant advantage of the Voigt circuits is that identification of frequencies characteristic of relaxation processes is simplified. Three groups of processes have been found:

1. HF processes are observed in all the systems under study on both Pt and St3 substrates with both inert and corroding (Zn) filler. The frequency range is from 3.5 kHz to 9.3 kHz. With an increase in temperature, the frequency of the HF process increases to 25 kHz.
2. MF processes are only observed in the systems that contain a corroding anode (Zn or St3). The frequency range is from 48 to 670 Hz. The frequency of the MF process increases with an increase in temperature.
3. LF processes emerge in multilayered systems at large times of exposure in a corrosive medium. The frequency range is from 0.25 Hz to 93 Hz. The LF frequency does not change with an increase in temperature.

However, the issue of additional criteria required to associate the absorption maxima with specific physicochemical processes, which occur in such a complex system as a composite coating, is still unresolved.

In our opinion, to identify these processes, tests should be conducted with additional factors as a result of which the contributions of processes to EIS will change. One of such factors can be the variation of temperature that affects diffusion and corrosion in different ways.

In principle, the temperature modes of exposure and measurement can differ. Measurements of EIS at various temperatures after exposure under the same conditions are more informative. Effective activation energies can be used as indicators of the process nature.

3.3. Effective activation energy upon exposure at the same temperature–time cycles of exposure

As noted above, three main relaxation processes have been identified for the composite coatings that consist of a primer layer with an active Zn filler and an upper inert layer on a steel substrate. The characteristics of the effective activation energy for these processes calculated using the 3-phase Voigt circuit are displayed below (Table 8).

Table 8. Activation energies and frequencies of characteristic processes calculated using the 3-phase Voigt circuit for a composite polymer coating (Zn-protective primer M-01 + upper inert coating R-5095) on a steel substrate after exposure in 3% NaCl solution for 344 days (at 20–25°C) and 7 days (at 60°C).

Process parameters	Frequency range of characteristic relaxation processes, Hz		
	1–10	100–1000	5000–100000
Effective activation energy, kJ/mol	67	112	75
Characteristic frequency of the process, Hz	2.5	480	25000

It should be noted that increasing the EC complexity does not provide qualitatively new information. For example, if a 4-phase circuit is used, the parameters of the HF и LF processes do not change and only the MF process splits into two processes with close values of activation energies (116–118 kJ/mol) and close characteristic frequencies. Based on this observation and applying Occam's razor principle [15], we limit our consideration with a simple 3-phase Voigt circuit.

Calculations show that the activation energies of the LF (1–5 Hz) and HF (25–5 kHz) processes are close to each other (~65–75 kJ/mol) and are characteristic of the diffusion of low-molecular weight substances, including water (40–70 kJ/mol), in polymers. At the same time, the process observed in the MF region (67–670 Hz) features a significantly higher activation energy (112 kJ/mol) characteristic of chemical reactions [16, Table 36.3].

Taking into account that if Zn protector primers and composite coatings are used, underfilm corrosion of the steel substrate is not observed after removal of the coating, it was proposed that the medium-frequency (MF) process corresponds to the corrosion of the active solid-phase Zn additive. The activation energy of the detected LF diffusion process, which is not observed in the case of inert coatings, is characteristic of diffusion, owing to which the process may be classified as diffusion of Zn corrosion products or water they contain.

4. Conclusions

A technique for nondestructive monitoring of physicochemical and corrosion processes in composite polymer protective coatings have been developed. It is based on comparative electrochemical impedance spectroscopy (EIS) on various metal substrates (corroding and inert) at various temperatures and identification of the corrosion processes using characteristic frequencies, their evolution at various stages of the corrosion process, and estimates of effective activation energies.

It appears that the suggested development of electrochemical impedance spectrometry of composite coatings may be used as a basis for the development of nondestructive diagnostics and may encourage the improvement of anticorrosion materials with active solid-phase additives.

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