Effects of adaptation and self-healing of protective polymer coatings in corrosive media

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Abstract

The existence of the adaptation effect and enhancement of insulating and protective properties of protective polymer coatings in aggressive NaCl solution was studied. Two types of composite multilayer coatings (composite ML-Ct) were explored that contained the same commercialquality Zn-rich protective primer and the top layers of inert epoxy enamel or a chemically resistant epoxy coating with reactive phenol-furan (RPF) additives. The coatings were applied onto inert (platinum, Pt) or corroding (steel, St3) substrates. A combination of a primer layer and an upper layer with specific active additives (ML-Ct M-01// model epoxy-RPF) in the ML-Ct is an optimal way since it ensures an increase in both total (|Z|) and active (R_{act}) resistance of the composite coating. It was found that the effect is rather long-lasting even for model thin-layer systems and may exceed hundreds of days in accelerated tests in 3% NaCl at an elevated temperature (60°C). The forecast for the service life of industrial-thickness coatings under standard conditions of use is 10 years or more. The results obtained demonstrate that this type of composite ML-Ct with active additives can be used as a basis for the development of a new class of polymer coatings with the effect of growing protective capacity in corrosive media (adaptive coating) and self-healing coatings.

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1. Background

The most promising way for improvement anticorrosion polymer protective coatings for aggressive media is an increasing their insulating properties against molecular diffusion components of aggressive media and technological and operational defects self-sealing.

Research in this area is carried out quite actively in various directions [1-6]. Currently, it is usually suggested to make sealing materials based on nano- and microcapsules [7, 8] with glue composites that are destroyed upon mechanical impact, for example, abrasion [9].

At the same time, it should be noted that the fraction of such microcapsules in a material can hardly be significant. The glue can be cured in different ways: a) by using combined microcapsules with a film former and a hardener in the same capsule [10] or in two different

capsules [11], b) due to a reaction with air moisture [12], c) due to a catalyst distributed in the matrix, for example, one based on ruthenium [13].

It is also suggested to use the polymer base of the coating itself as a source of the material. But rearrange ability can be reached only for non-cross-linked [14, 15] or labile polymers. It was proposed to use external heating as the energy source for structural rearrangement [16], but that eliminates the idea of self-healing. The development of Scratch Guard Coat paint with self-healing of surface scratches by Nissan was reported [17].

It is apparent that the problem of self-healing is not trivial and requires some restructuring of the internal coating structure. Such a restructuring must be maintained, first, by an internal source of energy, and second, by an additional compound for creating new structural elements and blocking the defects.

Both requirements can be implemented in a natural way upon penetration of corrosive media into protective polymer coatings, since the penetrating chemically reactive corrosive medium has free energy excess to perform the structural rearrangement and is potentially capable of forming new poorly soluble products in the coating to block the defects.

In our opinion, the most promising materials for implementing the self-healing effect are those materials in which, on interaction with a corrosive medium, enhancement of insulating properties is realized. Our studies have shown [3, 4] that such properties are exhibited by materials that contain three types of additives: a) solid-phase powders of metals, for example Zn, that form sealing products in reactions with corrosive media; b) lowmolecular-weight or oligomeric chemically reactive organic additives that can migrate and form sealing polymeric products in reactions with the environment; and c) inorganic and organic micro- and nanoencapsulated inhibitors for the metal substrate to be protected, in which the inhibitor is released upon penetration of the medium.

In terms of estimating the overall prospects of this approach, it should be noted that the problem under consideration is quite complex and its implementation can lead to both desirable and undesirable effects.

If metal protector powders are used, it should be taken into account [3] that the structure may become more compacted during their oxidation and formation of solid-phase products in the bulk of the polymer matrix, *i.e.*, defects are sealed, or, conversely, the defectiveness of the coating layer may increase due to the growth of local internal stresses. The resulting changes in the composition and properties of the filler can also affect the electrical insulating properties of the protective coating and its protective characteristics in various directions.

In addition to metal particles, active organic additives are very promising, especially those that can polymerize upon penetration of the corrosive medium. For example, it has been shown in [4] that if active phenol-furan additives are used in a polymer coating, the protective properties of the polymer film (impedance modulus, active resistance, and dielectric loss angle) are enhanced on exposure to a chloride-containing corrosive medium, and the potential of the substrate under the film increases. Moreover, at the stage when disintegration of the coating begins, the behavior of the model epoxy-RPF coating observed

can be interpreted as a self-healing effect, namely, recovery (up to 100%) of the total impedance of the coating combined with recovery of a large (up to 89°) dielectric loss angle.

Thus, the available results show that both some primers and insulating polymer materials with active organic additives can exhibit adaptation to corrosive environments and provide some increase in the protective ability. However, the duration of the effects reported to date in publications is rather limited. However, it is known [18] that multilayered coatings consisting of layers with different compositions feature have significantly stronger protective properties due to the selective permeability effect. This circumstance can potentially create more favorable conditions for the enhancement and prolongation of the action of the desired adaptation and self-healing effects.

The approaches and results considered above make it possible to conclude that multilayered composite coatings with special active additives of certain types in primer and top layers provide a very promising basis for the development of coatings whose protective properties grow, *i.e.*, coatings that adapt to a corrosive environment and, in the future, self-healing protective coatings.

The goal of this study was to check the possibility to implement the adaptation effect and enhancement of insulating properties and protective capacity in multilayered composite coatings with active additives of various types.

2. Experimental

2.1. Object and techniques of the study

Electrochemical impedance spectroscopy (EIS) was used to examine the kinetics of changes in coating and potentials of metal substrate upon long-term test of a composite multilayered coating and to compare the results with those for individual layers of a metal-rich primer and an insulating coating.

Two types of composite coatings with the same primer layer consisting of METACOR-01 (M-01), TU (technical specifications) 2312-003-11490792-99, a commercial-grade Znrich protective primer, were used as the objects in this study. In the first type of composite coating, epoxy enamel ROCOR-5095 (R-5095), TU 2312-042-11490792-09, was used as the upper layer, while in the second type, a model chemically resistant epoxy coating with reactive (phenol-furan) additives (model epoxy-RPF) was employed.

In the study we explored the behavior of the coatings under long-term exposure to 3% NaCl solution on inert (platinum, Pt) and corroding (steel, St3) substrates at temperatures ranging from 20 to 60°C.

Electrochemical impedance spectroscopy (EIS) [19–22] was used in combination with the potentiometric technique. The area of the working electrode (coated sample) was 6.2 cm^2 .

Impedance was studied using an FRA-1 analyzer made by the Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences according to the ISO methodology recommended for polymer coatings [23] in the (100 kHz–0.1 Hz) frequency

range. Impedance spectra were analyzed in the characteristic ranges: high-frequency (HF = 100 kHz-1 kHz), mid-frequency (MF = HF = 1 kHz-10 Hz) and low-frequency (LF = HF = 10 Hz-0.1 Hz) ranges.

The area of the auxiliary platinum electrode was 16.9 cm²; this value is sufficient, which is confirmed by the fact that a decrease in this area did not affect the measurement results. The equivalent electrical circuit parameters were calculated using the spectra thus obtained by means of the DCS software package.

The potentials of substrates with deposited coatings were measured directly in the cell for impedance measurements with respect to a silver/silver-chloride electrode. The following circuit was used: the sample under study/working solution/saturated KCl solution/AgCl/Ag with the auxiliary platinum electrode. The values of all potentials are presented with reference to the standard hydrogen electrode.

3. Results and Discussion

3.1. Kinetic studies on the electrochemical properties of composite coatings in the reaction with the corrosive media

3.1.1. Adaptive primer M-01 + porous coating R-5095

As shown previously [24], composite multilayered materials with protective metal fillers make it principally possible to implement the protective effect through ennoblement of the potential of the substrate being protected by 600–800 mV, while preserving the capability of thermal activation of Zn oxidation and the protector properties. The formation of solid-phase oxidation products would change the structure of a metal-polymer composite material, which can result either in structure compactification or, vice versa, in the growth of defectiveness which, in turn, affects the electric insulating properties of the protective coating.

In view of this, in this study we examined the kinetics of changes in the complex resistance of a composite multilayered coating and its layers, *i.e.*, a metal-rich primer and an upper inert insulating coating, upon long-term exposure. Typical results of impedance spectroscopy studies are displayed below (Figures 1–6 and Table 1).

The plots of frequency dependence of |Z| (Figures 1 and 5), in addition to kinetics, also show asymptotic values (|Z| at $F \rightarrow 0$), which can be used to estimate the active resistance of the coating film to direct current (R_{act} at $F \rightarrow 0$).



Figure 1. Frequency dependence of the impedance modulus |Z| of R-5095 with inert filler (TiO₂) on a platinum substrate after exposure to 3% NaCl for 20 (1) and 160 (2) days.



Figure 2. Bode plot of R-5095 with inert filler (TiO₂) on a platinum substrate after exposure for 20 days to 3% NaCl. (Dots – experiment, curve – calculation based on the equivalent circuit).



Figure 3. Frequency dependence of the impedance modulus |Z| of the Zn-rich M-01 primer on a platinum substrate after exposure to 3% NaCl for 3 (1) and 100 (2) days.



Figure 4. Bode plot of Zn-rich M-01 primer on a platinum substrate after exposure for 3 days to 3% NaCl and its approximation using the two-phase Voight circuit (3) with separation into HF (1) and LF (2) components. (Dots – experiment, curve – calculation based on the equivalent circuit).



Figure 5. Frequency dependence of the impedance modulus |Z| of the composite Ct (M-01//R-5095) on a platinum substrate after exposure to 3% NaCl for 30 (1) and 160 (2) days.



Figure 6. Bode plot of the composite Ct (M-01//R-5095) on a platinum substrate after exposure for 30 days to 3% NaCl and its approximation using the three-phase Voight circuit (3) with separation into HF (1), MF (2), and LF (3) components. (Dots – experiment, curve – calculation based on the equivalent circuit).

It was shown previously [3, 4] that the EIS properties of the systems under study can be described using known equivalent circuits (EC). Table 1 below displays data on the kinetics of changes in the electrochemical properties of the systems, including the potential of the substrates under the coatings (V), active resistances of the coating layers (R_1), and impedance modulus (|Z|) in the low-frequency regions ($F \rightarrow 0$).

Table 1. Kinetic dependences of the electrochemical characteristics of the M-01 primer, R-5095 enamel, and the M-01//R-5095 composite coating on Pt and St3 at the initial stage of exposure to 3% NaCl at a temperature of 25° C.

System	Duonoutri	Exposure time, days							
	Property	1	3	7	14	28	100		
	V, mV (SHE)	-519	-523	_	_	-465	-325		
Pt/M-01	R_1 , Ohm	4.6	23.5	_	_	701.7	2871.5		
	R_2 , Ohm	605	2040			12162	_		
	$ Z $ at $F \rightarrow 0$ Hz, Ohm	>230	>1010	_	_	>7220	>19500		
	HF max, Hz	6707	6707	_	_	6707	9319		

C	Duranta	Exposure time, days							
System	Property -	1	3	7	14	28	100		
	V, mV (SHE)	-560	-482	_	_	-373	-388		
	R_1 , Ohm	12.9	21.2	_	_	3790	1777		
St3/M-01	R_2 , Ohm	_	—	_	_	_	14622		
	$ Z $ at $F \rightarrow 0$ Hz, Ohm	4700	1005	_	_	4040	>11700		
	HF max, Hz	6707	6707	_	—	1295	12494		
	V, mV (SHE)	274	_	310	340	364	589		
Pt/P-5095	R_1 , MOhm	0.53	—	0.74	0.87	0.96	0.94		
	$ Z $ at $F \rightarrow 0$ Hz, MOhm	_	_	_	—	1.0	0.95		
	HF max, Hz	4827	_	3474	3474	4827	6707		
	V, mV (SHE)	144	122	90	-50	-31	102		
	R_1 , MOhm	0.72	0.73	0.66	0.51	0.39	0.18		
St3/R- 5095	R ₂ , MOhm	_	_	_	_	_	0.06		
5075	$ Z $ at $F \rightarrow 0$ Hz, MOhm	_	_	_	_	_	0.24		
	HF max, Hz	6707	3474	4827	4827	4827	12949		
	V, mV (SHE)	248	-32	39	242	284	286		
	R_1 , MOhm	1.27	0.91	0.93	0.56	1.47	1.08		
St3/M-	R_2 , MOhm	5.36	2.69	1.72	1.18	1.30	1.47		
01//P-	R ₃ , MOhm	6.71	1.08	0.54	1.23	0.96	1.10		
5095	$R_1 + R_2 + R_3$, MOhm	13.3	4.7	3.2	3.0	3.7	3.7		
	$ Z $ at $F \rightarrow 0$ Hz, MOhm	11.3	4.5	3.1	2.8	3.7	3.8		
	HF max, Hz	671	671	932	932	4827	6707		

The table above shows that the |Z| of the systems under study are significantly different. The minimal resistance values are exhibited by the metal-filled Zn-rich protector primer. The resistance of the enamel layers is more than two orders of magnitude higher, while the composite coating features large impedance that increases after the end of impregnation, beginning from the 14th day of exposure. The latter circumstance indicates the fundamental possibility of spontaneous growth of the composite ML-Ct protective properties during aggressive environment exposure.

In addition, the following results are also of importance:

a) The modulus of the composite coating impedance exceeds the additive value of the complex resistances of the layers (Table 2);

- b) For the composite ML-Ct, beginning from the 7th day, the contributions of R_2 and R_3 are larger than that of R_1 , and it is these contributions that determine the growth of $|Z|F \rightarrow 0$ at large exposure times. As follows from the adopted EC model for ML-Ct, the total of active resistances $(R_1 + R_2 + R_3)$ virtually coincides with $|Z|F \rightarrow 0$.
- c) The growth is observed in the entire frequency range (Figure 7) and continues at large times of exposure to the medium, at least until 340 days (Table 2).
- d) It may be hypothesized that the most probable mechanism of |Z| growth involves the formation of low-permeable insulating segments consisting of the products of Zn powder corrosion both in the primer layer and the R-5095 layer.

Table 2. Modulus of the impedance $|Z|F \rightarrow 0$ of coatings on a steel substrate upon long-term exposure to 3% NaCl.

Coating	Ct material	Thickness, µm	$ Z F \rightarrow 0$, MOhm	
Zn-rich primer	M-01	100	Actual value of $ Z $ after exposure for 100 days at 25°C	0.02
Insulating coating	R-5095	100	Actual value of Z after exposure for 100 days at 25°C	0.24
Two-layer Ct (primer//upper insulating layer)	M-01//R-5095	200 (100+100)	Additive calculated value of $ Z $ after exposure for 100 days at 25°C	0.26
Two-layer Ct (primer//upper insulating layer)	M-01//R-5095	200 (100+100)	Actual value of Z after exposure for 100 days at 25°C	3.6
Two-layer Ct (primer//upper insulating layer)	M-01//R-5095	200 (100+100)	Actual value of $ Z $ after exposure for 340 days at 25°C	11.0



Figure 7. Frequency dependence of impedance modulus |Z| of the protective coatings on a steel substrate (St3) after exposure for 100 days to 3% NaCl at 25°C. 1 – individual Zn-rich protective primer M-01; 2 – individual inert insulating coating R-5095; 3 – composite coating(M-01//R-5095); 4 – composite coating (M-01//R-5095) after exposure for 340 days.

For the composite ML-Ct under study, which consists of the Zn-protective primer and an upper inert enamel layer, the most probable mechanism of |Z| growth involves the formation of low-permeable segments consisting of the products of Zn powder corrosion. This is confirmed by electron microscopy of the original and exposed coatings, which are provided below (Figures 8 and 9).

It can be seen that long-term exposure results in the formation in a primer layer of extended agglomerates (Figure 9); such agglomerates emerge and remain in the bulk of the primer layer rather than protrude from the coating surface.

It may be assumed that it is the upper layer consisting of an inert paint-and-varnish material that creates the conditions which hinder the exit of corrosion products from the primer, while a white powdery substance, which consists of loose deposits of such products, is always formed on the free surface of a Zn-protective primer (without an upper protective layer). The second possible mechanism that facilitates the formation and retention of agglomerates in the bulk of a protective primer is a change in the composition of the inner electrolyte in the polymer matrix compared with that of the outside solution [25].



Figure 8. Scanning electron microscopic image of a section of the M-01 primer layer as part of the composite coating (M-01//R-5095) in the original state.



Figure 9. Scanning electron microscopic image of a section of the M-01 primer layer as part of the composite coating (M-01//R-5095) after exposure for 340 days to 3% NaCl at 25°C.

Thus, the use of composite polymer coatings with primers that contain active protector Zn additives can yield a significant enhancement of the impedance and electric insulating properties under exposure to corrosive chloride media even if used in combination with porous coatings of R-5095 type.

It may be assumed that the discovered effect can be used in the development of a new class of protective coatings, namely, the coatings whose protective capacity grows in use (adaptive coatings), or even self-healing coatings for corrosive environments.

3.2. Adaptive M-01 primer + adaptive R-EPF coating

Below we present the electrochemical impedance spectra of a composite coating with an upper insulating layer of adaptive model epoxy-RPF coating, which contains active oligomeric additives.

Comparison of the above EIS results of the composite coating with an inert upper layer (Tables 1 and 2, and Figure 7) and a two-layer composite coating comprising adaptive M-01 primer and the upper adaptive model epoxy-RPF coating (Figures 10 and 11) shows that the second system features a much higher complex resistance, and this conclusion refers both to the real and imaginary components of |Z|.

Since the |Z| of the ML-Ct under study in the analyzed frequency range varies by 4 or more orders of magnitude (Figure 12), the graphic representation of both the frequency dependence of the impedance modulus and its plot is insufficiently informative. Below, to analyze and present the results obtained, we'll primarily consider the frequency dependences of the dielectric loss angle that reflect the relationship between the imaginary and real components of impedance (Figure 13).



Figure 10. Impedance plot of the composite Ct (M-01// model epoxy-RPF) on a platinum substrate after exposure to 3% NaCl for 3 (1), 7 (3), and 100 (5) days and on a steel substrate after exposure to 3% NaCl for 3 (2), 7 (4), and 100 (6) days. Exposure at 60° C.



Figure 11. Kinetics of impedance modulus |Z| of the composite Ct (M-01// model epoxy-RPF) on a steel substrate after exposure to 3% NaCl at frequencies of 25000 (1) and 67 (3) Hz and on a platinum substrate after exposure to 3% NaCl at frequencies of 25000 Hz (2) and 67 Hz (4). Exposure at 60°C.



Figure 12. Dependence of the impedance modulus |Z| of the composite Ct (M-01// model epoxy-RPF) on a platinum substrate after exposure to 3% NaCl for 3 (1), 7 (3), and 100 (5) days and on a steel substrate after exposure to 3% NaCl for 3 (2), 7 (4), and 100 (6) days. Exposure at 60°C.



Figure 13. Bode plot of the composite Ct (M-01// model epoxy-RPF) on a platinum substrate after exposure to 3% NaCl for 3 (1) and 100 (3) days and on a steel substrate after exposure to 3% NaCl for 3 (2) and 100 (4) days. Exposure at 60°C.

3.2.1. Comparative analysis of EIS results for ML-Ct on various substrates

Analysis of the description of EIS data using standard ECs [4] has shown that the Voight circuit for multiphase components (Figures 14–19) is more adequate for both the composite

ML-Ct (M-01//model epoxy-RPF), similarly to the composite ML-Ct (M-01//R-5095) considered above (Figure 6).



Figure 14. Bode plot of the composite ML-Ct (M-01// model epoxy-RPF) on a platinum substrate after exposure for 3 days to 3% NaCl at 60°C and its approximation using a three-phase Voight circuit (4) with separation into HF (1), MF (2), and LF (3) components. (Dots – experiment, curve – *EC*-based calculation).



Figure 15. Bode plot of the composite ML-Ct (M-01// model epoxy-RPF) on a steel substrate after exposure for 3 days to 3% NaCl at 60°C and its approximation using a three-phase Voight circuit (4) with separation into HF (1), MF (2), and LF (3) components. (Dots – experiment, curve – *EC*-based calculation).



Figure 16. Bode plot of the composite ML-Ct (M-01// model epoxy-RPF) on a platinum substrate after exposure for 30 days to 3% NaCl at 60°C and its approximation using the two-phase Voight circuit (3) with separation into HF (1) and MF (2) components. (Dots – experiment, curve – *EC*-based calculation).



Figure 17. Bode plot composite ML-Ct (M-01// model epoxy-RPF) on a steel substrate after exposure for 30 days to 3% NaCl at 60°C and its approximation using the two-phase Voight circuit (3) with separation into HF (1) and MF (2) components. (Dots – experiment, curve – EC-based calculation).



Figure 18. Bode plot of the composite ML-Ct (M-01// model epoxy-RPF) on a platinum substrate after exposure for 210 days to 3% NaCl at 60°C and its approximation using the two-phase Voight circuit (3) with separation into HF (1) and MF (2) components. (Dots – experiment, curve – EC-based calculation).



Figure 19. Bode plot of the composite ML-Ct (M-01// model epoxy-RPF) on a steel substrate after exposure for 210 days to 3% NaCl at 60°C and its approximation using the two-phase Voight circuit (3) with separation into HF (1) and MF (2) components. (Dots – experiment, curve – *EC*-based calculation).

Qualitative analysis of the data presented above shows that:

- 1. In the initial period (up to 7 days), both on the inert platinum substrate and on the corroding steel substrate, similarly to the previous system with R-5095, three relaxation processes (HF, MF, and LF) are observed with virtually identical characteristic frequencies and dielectric loss angles, *i.e.*, the ratio of the imaginary and real impedance components.
- 2. On longer exposures to the corrosive medium (after 30 days), the impedance spectrum is transformed: the relaxation spectra are shifted to the low-frequency region. However, it is noteworthy that a concurrent increase in the dielectric loss angle is observed. At this exposure stage, only two relaxation processes (HF and MF) can be distinguished in the frequency range accessible for measurements. At even longer exposures to the corrosive medium (more than 200 days), the effect of the substrate type on the frequency dependence of the dielectric loss angle is insignificant.

A summary of the quantitative results for the EC parameters, characteristic frequencies, and potentials on the platinum and steel substrates is presented below (Tables 3 and 4).

Table 3. Kinetics of electrochemical parameters of the M-01// model epoxy-RPF coating on a p	platinum
substrate under exposure to 3% NaCl at 60°C based on the results of raw EIS data processing. Measu	urements
at 60°C.	

	Exposure time, days							
Characteristics of the coating/substrate system	3	30	100	120	210			
	Pt substrate							
R_1 , Ohm	$1.18 \cdot 10^{6}$	$2.39 \cdot 10^{6}$	$1.52 \cdot 10^{7}$	$4.04 \cdot 10^{7}$	$5.57 \cdot 10^{6}$			
CPE-T1, F	$1.24 \cdot 10^{-9}$	$1.27 \cdot 10^{-9}$	$1.50 \cdot 10^{-9}$	$1.08 \cdot 10^{-9}$	$2.05 \cdot 10^{-9}$			
Z , Ohm at HF (2500 Hz)	$2.36 \cdot 10^5$	$2.64 \cdot 10^5$	$2.47 \cdot 10^5$	$2.41 \cdot 10^5$	$2.36 \cdot 10^5$			
Characteristic frequency of the HF process, Hz	2500	1799	483	671	1295			
R_2 , Ohm	$1.54 \cdot 10^{7}$	$2.10 \cdot 10^8$	$6.50 \cdot 10^8$	$7.17 \cdot 10^8$	$2.35 \cdot 10^8$			
CPE-T2, F	$7.03 \cdot 10^{-10}$	$3.25 \cdot 10^{-10}$	$4.31 \cdot 10^{-10}$	$4.53 \cdot 10^{-10}$	$3.50 \cdot 10^{-10}$			
Z , Ohm at MF (67.1 Hz)	$6.40 \cdot 10^{6}$	$7.92 \cdot 10^{6}$	$9.32 \cdot 10^{6}$	$8.21 \cdot 10^{6}$	$8.37 \cdot 10^{6}$			
Characteristic frequency of the MF process, Hz	48.3	25 Less than 9.32		Less than 9.32	9.32			
R ₃ , Ohm	$4.89 \cdot 10^7$	_	_	_	_			
CPE-T3, F	$2.28 \cdot 10^{-9}$	_	_	_	_			

		Exp	oosure time, d	lays				
Characteristics of the coating/substrate system	3	30	100	120	210			
	Pt substrate							
Characteristic frequency of the LF process, Hz	4.83	_	_	_	_			
Substrate potential (SHE), mV	-332	-307	66	110	305			

Table 4. Kinetics of electrochemical parameters of the M-01// model epoxy-RPF coating on a steel substrate under exposure to 3% NaCl at 60°C based on the results of raw EIS data processing.

	Exposure time, days								
Characteristics of the coating/substrate system	3	30	100	120	210				
	St3 substrate								
R_1 , Ohm	$1.66 \cdot 10^{6}$	$5.28 \cdot 10^{6}$	$3.44 \cdot 10^{6}$	$2.30 \cdot 10^{7}$	$3.47 \cdot 10^{6}$				
CPE-T1, F	$1.72 \cdot 10^{-9}$	$1.09 \cdot 10^{-9}$	$2.19 \cdot 10^{-9}$	$1.40 \cdot 10^{-9}$	$1.37 \cdot 10^{-9}$				
Z , Ohm at HF (2500 Hz)	$2.38 \cdot 10^5$	$2.54 \cdot 10^5$	$2.39 \cdot 10^{5}$	$2.39 \cdot 10^{5}$	$2.20 \cdot 10^{5}$				
Characteristic frequency of the HF process, Hz	2500	931	1295	932	1295				
R_2 , Ohm	$2.29 \cdot 10^{7}$	$3.67 \cdot 10^8$	$2.20 \cdot 10^{8}$	$1.14 \cdot 10^{8}$	$3.26 \cdot 10^{8}$				
CPE-T2, F	$5.94 \cdot 10^{-10}$	$3.68 \cdot 10^{-10}$	$3.50 \cdot 10^{-10}$	$8.19 \cdot 10^{-10}$	$3.83 \cdot 10^{-10}$				
Z , Ohm at MF (67.1 Hz)	$6.03 \cdot 10^{6}$	$7.95 \cdot 10^{6}$	$7.96 \cdot 10^{6}$	$6.93 \cdot 10^{6}$	$7.24 \cdot 10^{6}$				
Characteristic frequency of the MF process, Hz	48.3	Less than 9.32	18	4	12.9				
R ₃ , Ohm	$5.08 \cdot 10^{7}$	_	—	$1.23 \cdot 10^{9}$	_				
CPE-T3, F	1.73.10-9	_	_	1.15.10-9	_				
Z , Ohm at HY (2.5 Hz)	$50.4 \cdot 10^{6}$	_	_	$138 \cdot 10^{6}$	_				
Characteristic frequency of the LF process, Hz	3.47	_	_	Less than 0.93	_				
Substrate potential (SHE), mV	-361	-82	237	232	370				

The data obtained show (Tables 3 and 4) that the multilayered ML-Ct (M-01//model epoxy-RPF) on the platinum and steel substrates features patterns that are common for the changes in the substrate potentials, EIS spectra, and EC components:

1. The potentials of both Pt and St3 under the ML-Ct significantly increase during exposure to a corrosive medium. The |Z| of this increase on the platinum and steel

substrates are virtually the same and decrease as the measurement temperature decreases: more than 1000 mV at 30°C, 600-700 mV at 40°C (Figure 20), and 500-600 mV at 60°C. Since the potentials of unprotected metals (Pt and St3) at 30°C in NaCl differ significantly (+700 and -500 mV), this phenomenon can be associated with the slowdown of the penetration of aqueous salt solution components into the polymers and a change in the composition of the internal solution; it was described previously and agrees with previous results [25].

- 2. On the platinum and steel substrates in the initial exposure stage (less than 60 days), the characteristic frequencies of the HF process decrease and then stabilize. The most probable reason for the decrease in the characteristic frequencies is the reduced mobility of charge carriers.
- 3. On both substrates, the active resistance R_1 of the HF process (Figure 21) also significantly grows (by a factor of 3–7) during the first 30–60 days with a subsequent trend to stabilize, while the capacitive component on Pt and St3 varies insignificantly.
- 4. Similar changes are observed in the characteristics of the MF process and, in addition, the capacitive component CPE-T2 on St3 decreases in the entire time range. This behavior is an indication of the reduced dielectric permeability of the coatings.
- 5. It should be noted as well that both on the inert (Pt) and corroding (St3) substrates coated with M-01//model epoxy-RPF, the value of |Z| under exposure to 3% NaCl virtually does not change or increases.



Figure 20. Kinetics of the potential of steel (1) and platinum (2) substrates under composite ML-Ct (M-01// model epoxy-RPF) exposed to 3% NaCl. The measurement temperature is 40°C.

In conclusion, let us compare the impedances of each ML-Ct layer and their changes for two types of composite coatings: a) with the adaptive Zn-rich protective primer M-01 and the upper adaptive layer of model epoxy-RPF and b) with the adaptive Zn-rich protective primer M-01 and the upper adaptive layer of R-5095 that coat a steel substrate which is of practical importance.



Figure 21. Kinetics of the parameters of the HF and MF processes exposed to 3% NaCl of the composite ML-Ct (M-01// model epoxy-RPF) on various substrates: $1 - R_1$ on St3; $2 - R_1$ on Pt; $3 - R_2$ on St3; $4 - R_2$ on Pt.

The results presented above show that the individual layers and the composite ML-Ct systems under consideration differ significantly in protective capacity in 3% NaCl. In view of this, systems with higher protective capacity (St3/M-01// model epoxy-RPF) should be tested in accelerated test mode (at elevated temperature of 60°C) compared to the (St3/M-01//R-5095) system which was tested at 25°C. Moreover, it was shown above that the properties of the coatings with active additives and, hence, the EC describing them vary in the course of long-term exposure to a corrosive environment.

Hence, from the methodological perspective, it is reasonable to perform comparative analyses using the values and kinetics of |Z|, since the modulus of impedance is an experimental quantity that is in no way related to the subsequent processing of EIS spectra and/or selection of a particular EC.

The results are presented below (Table 5). In the analysis of the data displayed, the growth of the modulus of impedance can be considered as a criterion of the spontaneous enhancement of the protective capacity under exposure to a corrosive environment.

Grade	Thickness, Con	Condition	Potential (SHE),	Modulus of impedance Z , MOhm at frequencies of:				
	μπ		mV	<i>F</i> =10 kHz	0 kHz F=100 Hz	<i>F</i> =10 Hz	$F \rightarrow 0$	
St3 (exposure and measurements carried out at 25°C)								
M-01	100	Actual value after	-400	0.0009	0.009	0.013	0.02	
R-5095	100	exposure for 100 days	102	0.008	0.13	0.20	0.24	
M-01 //R-5095	100+100	Additive	_	0.009	0.14	0.21	0.26	

Table 5. Comparison of the electrochemical parameters of two ML-Ct.

Grade	Thickness,	Condition	Potential (SHE), mV	Modulus of impedance Z , MOhm at frequencies of:			
	μΠ			<i>F</i> =10 kHz	<i>F</i> =100 Hz	<i>F</i> =10 Hz	$F \rightarrow 0$
	St3//M-	01 + R-5095 (exposu	re and measu	urements carr	ried out at 25°	°C)	
		Actual value after exposure for 3 days	-32	0.05	1.6	3.6	4.5
M-01 //R-5095	100+100	Actual value after exposure for 100 days	286	0.028	1.3	2.7	3.8
		Actual value after exposure for 340 days	304	0.027	1.7	6.6	10.6
St3 (exposure and measurements carried out at 60°C)							
M-01	100	Actual value after exposure for 10 days	-519	0.0003	0.0005	0.001	0.007
model epoxy- RPF	200	Actual value after exposure for 10 days	42	0.064	4.8	13.8	15.6
M-01 // model epoxy- RPF	100+200	Additive	_	0.064	4.8	13.8	15.61
	St3//M-01 +	model epoxy-RPF (ex	posure and	measurement	s carried out	at 60°C)	
		Actual value after exposure for 3 days	-360	0.055	5.0	28.3	68.2
		Actual value after exposure for 65 days	85	0.056	5.8	51.7	495
M-01 // model epoxy-		Actual value after exposure for 100 days	237	0.055	5.9	51.7	_
RPF		Actual value after exposure for 120 days (20 days at 25°C)	232	0.064	5.6	45.4	_
		Actual value after exposure for 300 days	338	0.064	5.5	43.5	_

The data presented above show that under exposure of a multilayered composite coating consisting of individual primer layers and an upper protective layer, favorable conditions are created for the growth of the coating impedance and ennoblement of the potential of the steel substrate being protected. It should be emphasized that:

- the effect of the multilayered character of the coatings is observed for both types of composite ML-Ct;
- the increase in $|Z|F \rightarrow 0$ upon exposure to a corrosive environment for the ML-Ct with the adaptive upper layer of model epoxy-RPF (38 MOhm for 100 days) is significantly larger than in the case of the R-5095 inert material (6.5 MOhm for 330 days);
- the effect of growth during ML-Ct exposure to 3% NaCl is observed even at 60°C, *i.e.*, under the conditions where the protector effect of metallic Zn that directly contacts with St3 ceases;
- the effect of |Z| growth under exposure to a corrosive environment at 60°C even for a thin model composite ML-Ct persists for a long time, although it decreases insignificantly. The protective properties remain superior to those in the original state during the entire testing period;
- for both ML-Ct types exposed to NaCl, a growth in the steel substrate potentials is observed. The increment of the potential under exposure to the corrosive environment in the case of the ML-Ct with an adaptive model epoxy-RPF upper layer (by 700 mV in 300 days) is significantly higher than that in the case of the ML-Ct with the R-5095 inert material (340 mV in 340 days).
- Thus, the test results indicate the advantage of two-layer composite ML-Ct with active additives in both layers and better initial insulating properties of the upper layer.

The correlation between the changes in |Z| and EC parameters calculated using spectral data is also worthy of note. For example, comparison of the data from the Tables 3–5 shows that the change in the active resistance upon exposure to a corrosive environment is such a parameter for protective insulating-type polymer coatings. The system that consists of a primer and an upper layer with active additives on an inert substrate (Pt/M-01// model epoxy-RPF) under exposure to NaCl exhibits a growth in R_1 (HF) by a factor of 20 and a growth in R_2 (MF) by a factor of 30 to 35, while the growth in R_1 for the coating on the corroding substrate (St3/M-01// model epoxy-RPF) is somewhat smaller (10-fold), while in the MF range, the growth of R_2 is 10- to15-fold.

4. Conclusions

Based on the set of the results obtained, conclusions pertaining to the methodology and materials science can be drawn for electrochemical studies of the polymer protective coatings that exhibit a growth in the protective capacity in corrosive media.

From the methodological perspective, it is important to consider the whole complex of the electrochemical properties of coatings, in which the effect of changes in the protective properties during exposure to corrosive media can be manifested.

The most important parameters to be considered are the values and kinetics of |Z| variation, since the modulus of impedance is an experimental quantity that is in no way related to subsequent processing of EIS spectra and/or selection of a particular EC.

The growth in the impedance modulus in a broad frequency range can be considered as a condition sufficient for a spontaneous increase in protective capacity under exposure to a corrosive environment. It should be noted as well that a temporary decrease in the impedance modulus at the stage of impregnation of a coating with a medium is not an unambiguous indication that self-healing is not possible at later exposure stages.

The following results are apparently of interest for materials science:

- 1. The protective electrochemical properties of a composite ML-Ct consisting of materials with active additives are superior to the expected additive values for a two-layer coating that consists of a primer and an upper insulating layer.
- 2. Combining a primer layer and an upper layer in a ML-Ct, where each of the layers contains specific active additives (ML-Ct M-01// model epoxy-RPF), is an optimal solution, since it ensures the growth of both |Z| and R_{act} of the coating.
- 3. The duration of the effect even for model thin-layer systems is very large and can exceed hundreds of days in accelerated tests in 3% NaCl a tan elevated temperature (60°C). The predicted service life of industrial-thickness coatings under standard operation conditions (at temperatures below 40°C) may be estimated as 10 years or more.

To summarize, the composite ML-Ct with active additives can be used as a basis for the development of a new class of protective polymer coatings for corrosive media with the effect of protective capacity enhancement in the course of operation, adaptive coatings, and self-healing coatings.

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