Temperature dependences of the electrochemical parameters of adaptive composite polymer coatings during long-term exposure in corrosive media

V.A. Golovin* and S.A. Dobriyan

A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky pr. 31, 119071 Moscow, Russian Federation
**E-mail: golovin@rocor.ru*

Abstract

The effect of temperature variation on the electrochemical characteristics of individual adaptive epoxy polymer coatings (PCs) and composite systems consisting of two adaptive layers with different active additives was studied. It was shown that the mechanism of spontaneous impedance growth under natural conditions of exposure in a corrosive environment without any additional external impact can be operative in adaptive composite PCs. A correlation between the kinetic dependences of changes in the impedance modulus and in the potential of the substrate under the coating was identified. It was found that at the stages of growth and stabilization of the potential and impedance modulus (up to 500 days of exposure in 3% NaCl), a strong dependence of the substrate potential on the measurement temperature exists. It was shown that the electrochemical characteristics of a composite coating with two adaptive layers of different materials are significantly higher than those of an individual adaptive PC. The effect of growth in activation energy of ion transfer through the coating was found for the composite PC both on inert platinum (Pt) and on corroding steel (St3) substrates. It was shown that an adaptive composite bilayer coating on corroding St3 substrate can have more stable electrochemical characteristics than a similar coating on inert Pt substrate.

Received: October 2, 2024. Published: November 5, 2024 doi: 10.17675/2305-6894-2024-13-4-17

Keywords: *electrochemical impedance spectroscopy, EIS, polymer coatings, "smart" adaptive coatings, self-healing coatings, corrosive environments.*

1. Introduction

Since the temperature significantly affects the thermodynamics and rates of the main physicochemical and corrosion processes, it is one of the most important factors determining the performance of polymer protective coatings (PC) in corrosive liquid media.

The protective properties of coatings in corrosive environments during prolonged exposure in a wide temperature range and on the effect of temperature on the main physical and chemical processes in coatings were studied in a considerable number of works [1–3]. However, even short-term temperature effects can be used to clarify the specific features of the protective effect of coatings at different stages of exposure in a corrosive environment.

This methodological approach is of particular interest for so-called "smart" adaptive coatings, in which the mechanisms of growth in protective properties are realized upon their interaction with a corrosive environment. Adaptive properties can be imparted to such systems by incorporating various types of oligomeric, solid-phase and microencapsulated additives into the functional layers of the coating [4–6]. Upon penetration of the corrosive medium, such additives can provide additional cross-linking of the polymer base, formation of insoluble compounds in defect zones and release of corrosion inhibitors, which significantly changes the electrochemical and operational protective properties of the coatings.

It should also be noted that studies on the regularities of the evolution of electrochemical properties is a necessary basis for the creation of digital models in the development of new-generation anticorrosion coatings [7], which are usually composite materials that have a layered gradient structure [8–10].

2. Purpose

The purpose of this work was to identify the temperature dependences of the electrochemical characteristics of individual adaptive PC sand composite systems consisting of several adaptive layers with different active additives under natural exposure conditions in corrosive media.

3. Objects and Methods

3.1. Objects

The following objects were studied: a chemically resistant epoxy coating with reactive (phenol-furan) functional additives (R-EFF) with adaptive properties and a composite coating consisting of industrial protective primer METAKOR-01 (M-01), TU 2312-003-11490792-99, containing solid-phase active metal additives, and an R-EFF coatings.

In this work, the behavior of coatings during long-term exposure in 3% NaCl solution on inert platinum (Pt) and on corroding steel (St3) substrates at temperatures from 23 to 60°C was studied.

3.2. Research methods and choice of digital models

The variation of electrochemical properties of coatings in 3% NaCl solution at temperatures from 23 to 60°C were studied until the coatings lost protective properties. The studies on steel substrate (St3) lasted up to 1240 days.

Electrochemical methods were used in this work, namely, electrochemical impedance spectroscopy (EIS) [11–14] combined with the potentiometry method. The area of the working electrode (sample with a coating) was 6.2 cm^2.

The EIS method is known to provide a comprehensive estimate of the electrochemical properties of substrate/coating systems, based on which numerical models can be suggested, including those for single-layer adaptive coatings [7].

Impedance studies were carried out using an FRA-2 analyzer manufactured by IPCE RAS according to the ISO method recommended for polymer coatings [15] in the frequency range of 25 kHz–0.25 Hz. The area of the auxiliary platinum electrode was 16.9 cm^2, which is sufficient, as confirmed by the fact that its reduction does not affect the measurement results.

The potential of coated substrates was measured directly in the impedance measurement cell versus a silver chloride electrode connected to the cell through a salt bridge. All the potentials are given with respect to the normal hydrogen electrode.

The EIS spectra obtained were processed using the DCS (Dummy Circuit Solver) program by selecting the optimal equivalent circuit (EC).

The ECs are formed by connecting groups of R/CPE elements, each of which has its own time constant and can be regarded as a characteristics of a certain structural element of the coating that is noticeably different from the neighboring phases or sublayers. The presence of a few time constants (or characteristic resonance frequencies) is observable in the Bode phase plots [16].

4. Results

From the physicochemical point of view, the systems of adaptive polymer coatings considered in this work are typical layered composite structures in which each of the layers has its own regularities of interaction with the corrosive medium.

Systems of adaptive insulating coating alone (P-EFF) and 2-layer coatings comprising a bottom layer (Zn-filled adaptive composite primer) and a top adaptive layer (R-EFF) were studied for each of the substrates.

In accordance with the general approach used to analyze EIS data, we initially analyze the original experimental data as Bode plots, then the results of their processing and simulation of equivalent electrical circuits.

To identify the regularities of evolution of the electrochemical properties of such coatings, it is expedient to systematize them by the key structural parameters. It is best to begin with isolating the effect of the metal substrate type. At first, we will consider coatings on an inert platinum substrate (Pt), then on a corroding steel substrate (St3).

The results of recording the frequency dependences of impedance in Bode coordinates on an inert Pt substrate are presented below (Figure 1, Figure 2).

As it can be seen from the presented data, both coatings, namely the R-EFF insulating PC with an adaptation effect (Figure 1) and the composite PC with two different layers and adaptation mechanisms (Figure 2), applied on Pt substrate, upon exposure for 100–125 days in a corrosive environment (3% NaCl at 60°C) show a growth in both the absolute impedance values (Figure 1A and Figure 2A) and dielectric properties (Figure 1B and Figure 2B).

It should be noted here that the impedance modulus growth in the initial period of exposure is higher in the system without a Zn-containing primer layer, *i.e.*, where there is no principal possibility for water-soluble corrosion products of the metal filler to be formed.

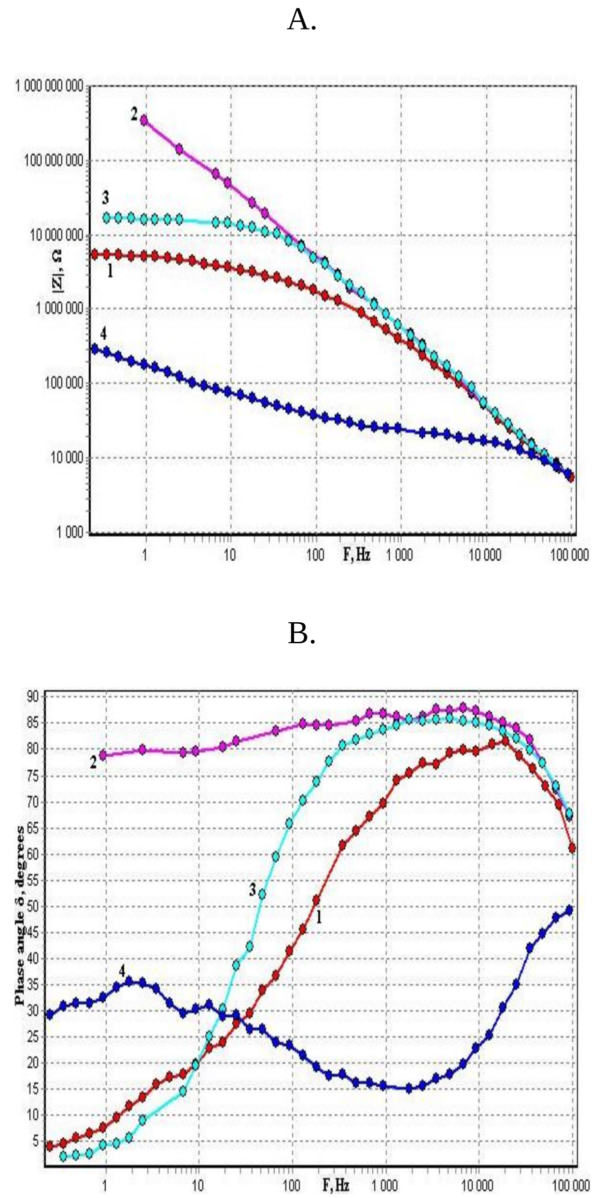


Figure 1. Bode plots. Impedance modulus |*Z*| (A) and phase angle δ (B) of R-EFF PC on platinum substrate after exposure in 3% NaCl at 60°C for: 1 – 30 minutes; 2 – 125 days; 3 – 210 days; 4 – 240 days. The measurement temperature was 60°C.

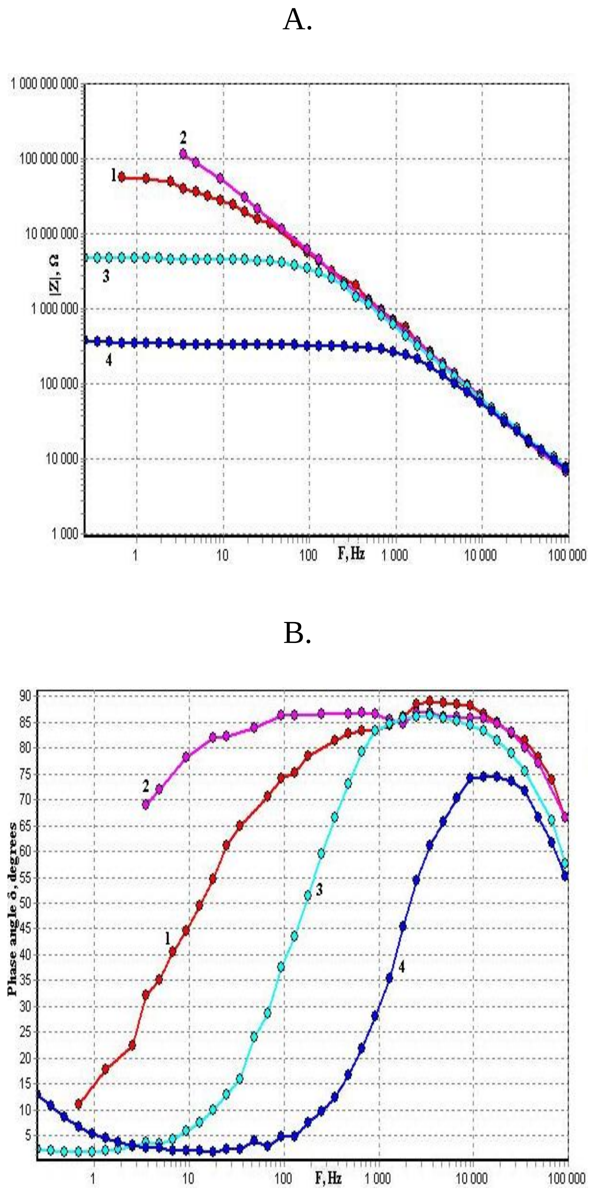


Figure 2. Bode plots. Impedance modulus |*Z*| (A) and phase angle δ (B) of composite M-01//R-EFF PC on platinum substrate after exposure in 3% NaCl at 60°C for: 1 – 30 minutes; 2 – 100 days; 3 – 660 days; 4 – 1040 days. The measurement temperature was 60°C.

However, on further exposure (240 days or more), the coating made of the R-EFF insulating material only shows a significant drop in impedance modulus on Pt (|*Z*| at 1 Hz=0.2 MOhm, 240 days, 60°C), while the composite coating with the active primer retains rather high values up to 660 days (|*Z*| at 1 Hz=4.6 MOhm, 660 days, 60°C), *i.e.*, almost 3 times longer.

Certainly, the anticorrosion coatings for the protection of steels are of the main interest from the practical point of view. The frequency dependences of impedance modulus |*Z*| and phase angle δ for the R-EFF coating and M-01//R-EFF composite coating are given below (Figures 3, 4).

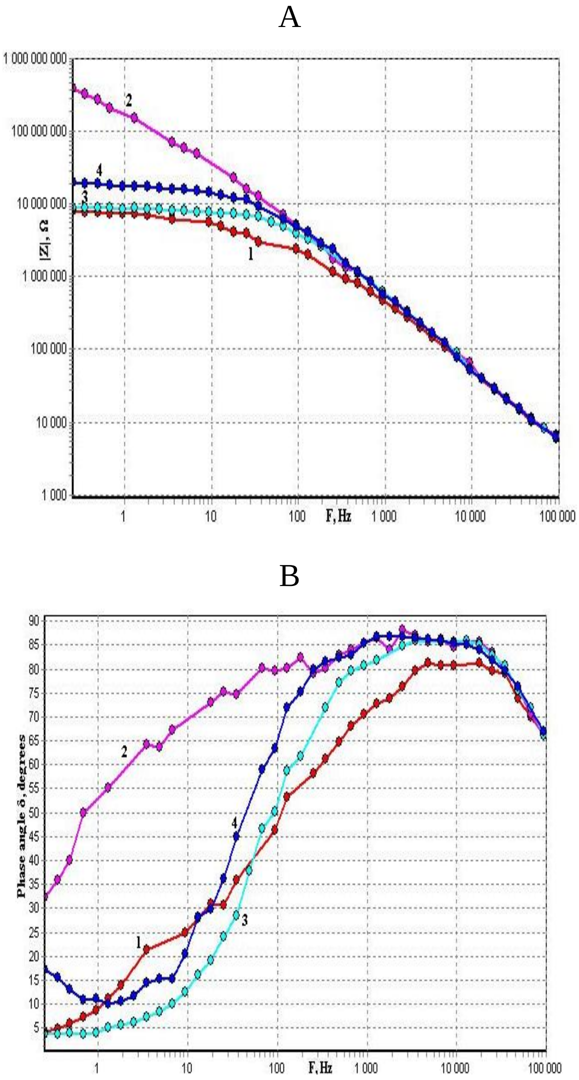


Figure 3. Bode plots. Impedance modulus |*Z*| (A) and phase angle δ (B) of the R-EFF PC on steel (St3) substrate after exposure in 3% NaCl at 60°C for: 1 – 30 minutes; 2 – 30 days; 3 – 45 days; 4 – 530 days. The measurement temperature was 60°C.

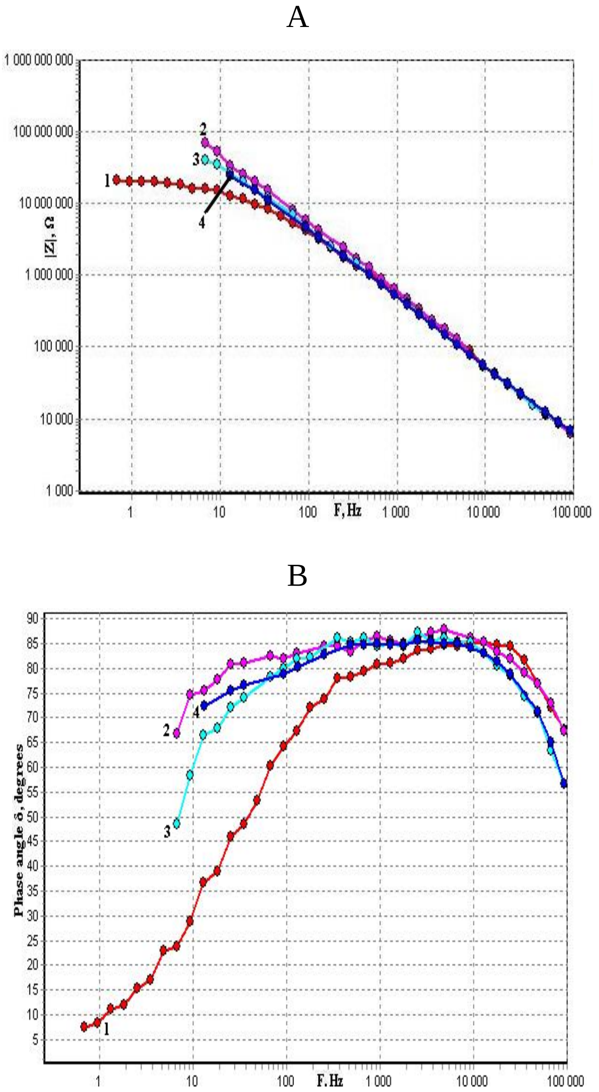


Figure 4. Bode plots. Impedance modulus |*Z*| (A) and phase angle δ (B) of M-01//R-EFF composite PC on steel (St3) substrate after exposure in 3% NaCl at 60°C for: 1 – 30 minutes; 2 – 100 days; 3 – 1040 days; 4 – 1240 days. The measurement temperature was 60°C.

Comparison of the dependences on St3 and Pt shows that there is no qualitative difference in the impedance kinetics in the course of exposure in 3% NaCl on inert Pt substrate (Figure 1 and Figure 2) and on corroding St3 substrate (Figure 3 and Figure 4).

At the initial stage, an impedance and phase angle growth are observed for the coatings on St3 substrate during the exposure process, like on Pt. However, on the corroding St3 substrate, the values of the maximum impedance modulus growth for the individual R-EFF insulating coating and for the composite coating differ insignificantly.

Moreover, as noted above, the stability period of both the impedance modulus value |*Z*| and phase angle δ is significantly longer for composite coatings on a corroding steel substrate (up to 1240 days of exposure in 3% NaCl) than on inert platinum (Pt) substrate.

To clarify the mechanism of protective action, it is of interest to reveal the correlation between the electrochemical parameters of the coating and the change in the potential of different substrates: inert (Pt) and corroding one (St3), since the measurement of the potential of substrates under polymer coatings during exposure in a corrosive environment is a classical estimation method [17].

The possibility of development of the subfilm corrosion process is determined by the permeability of the coating film, selectivity of transfer, and hydrolytic stability of adhesive bonds of the coating with the metal substrate [18].

For coatings with a Zn-protector primer, the potential of the substrate will be largely determined by the potential and corrosion kinetics of the reactive metal filler. In case of adaptive coatings, the effect of increasing the insulating properties of the coating film should also be estimated.

Since all of the processes listed above significantly depend on temperature, complex temperature dependences of the substrate potential under complex adaptive coatings can be expected.

Comparison of the kinetic dependences of the insulating properties of the coating film, namely, the impedance modulus |*Z*| and the potentials of St3 and Pt substrates under the composite (M-01//R-EFF) PC on varying the measurement temperature from 30 to 60°C, is shown below (Figures 5–8).

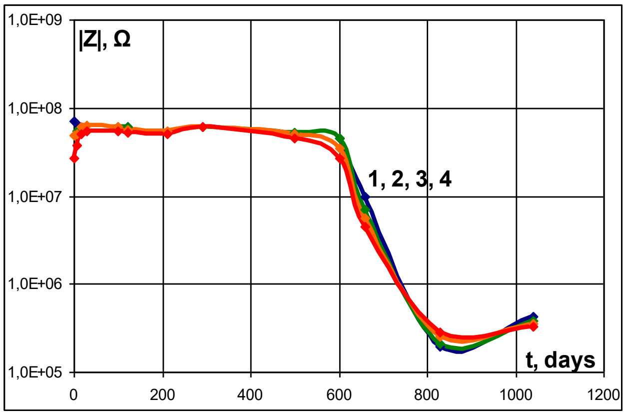


Figure 5. Kinetics of impedance |*Z*| at 25 Hz of composite PC (M-01//R-EFF) on platinum substrate during 1040 days of exposure in 3% NaCl at various measurement temperatures: 1 – 30°C; 2 – 40°C; 3 – 50°C; 4 – 60°C.

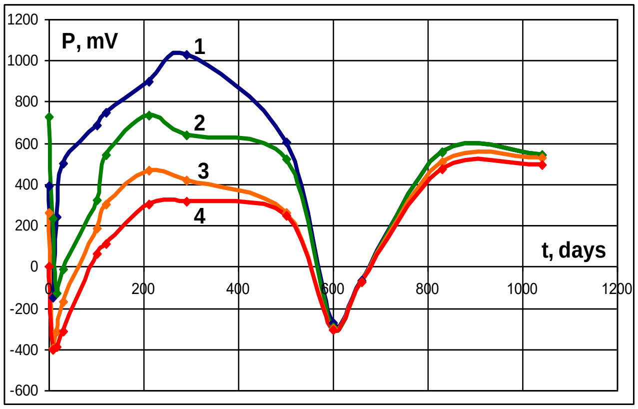


Figure 6. Kinetics of potential (NHE) of platinum substrate under composite PC (M-01//R-EFF) during 1040 days of exposure in 3% NaCl at various measurement temperatures: 1 – 30°C; 2 – 40°C; 3 – 50°C; 4 – 60°C.

Comparative analysis of the kinetics of the properties of coatings on inert Pt substrate allows us to draw the following conclusions:

1. The stage of initial coating impregnation with the electrolyte during the initial exposure period (up to 125 days) is accompanied by a fast growth in the substrate potential with transition to the positive region, followed by a period of stabilization. This effect qualitatively correlates with the above-mentioned growth in electrical insulating properties of the adaptive coatings under consideration.
2. The lower the measurement temperature, the more positive the potential of the Pt substrate becomes. For example, at a measurement temperature of +30°C, the potential reaches +1000 mV after 300 days of exposure in 3% NaCl.
3. At the stages of growth and stabilization of the potential and impedance modulus (up to 500 days of exposure), a strong dependence of the substrate potential on the temperature is observed: the higher the measurement temperature, the less positive the substrate potential. The authors believe that this can be explained by a growth in the coating permeability with increasing temperature.
4. In the period of 500–600 days, a symbate drop of both the impedance modulus ($|Z|$ at 25 Hz) and substrate potential (P) with transition to the negative region is observed. The temperature dependence of P degenerates completely.
5. For the Pt substrate, the shift to the negative region can only be a consequence of the activation of Zn-protector particles in the primer due to direct access of the electrolyte through defects in the top coating layer.

The results of a similar comparative analysis for the same complex coating applied to a St3 substrate make it possible to reveal both common and characteristic features introduced by the presence of a potentially corrosive substrate in the system being modified.

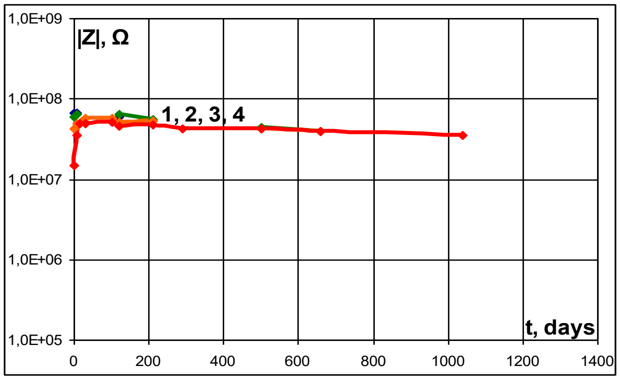


Figure 7. Kinetics of impedance |*Z*| at 25 Hz of (M-01//R-EFF) composite PC on steel substrate during 1240 days of exposure in 3% NaCl at various measurement temperatures: 1 – 30°C; 2 – 40°C; 3 – 50°C; 4 – 60°C.

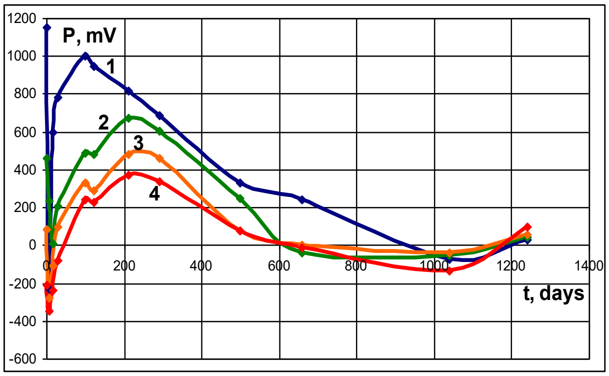


Figure 8. Kinetics of potential (NHE) of steel (St3) substrate under (M-01//R-EFF) composite PC during 1240 days of exposure in 3% NaCl at various measurement temperatures: 1 – 30°C; 2 – 40°C; 3 – 50°C; 4 – 60°C.

As it can be seen from the results obtained:

1. Like on the inert Pt substrate, a fast increase in both |*Z*| and *P* is observed in the initial period.
2. Similarly to the Pt substrate, the lower the measurement temperature, a more positive potential of St3 substrate is recorded: at +30°C, the potential reaches +1000 mV after 300 days of exposure in 3% NaCl.
3. Up to 1000 days, a significant dependence of the substrate potential on the measurement temperature is observed: the higher the temperature, the less positive the potential. This is similar to the effect observed on the Pt substrate and may also be due to accelerated transfer of the corrosive medium through the upper insulating layer to the primer with an increase in temperature.
4. On St3 substrate, unlike the Pt substrate, no sharp drop in impedance modulus is observed at exposure times up to 1000 days (Figure 7), but a slight decrease in |*Z*| at 25 Hz and the corresponding smooth drop in *P* are recorded.

The results under consideration concerning the temperature-kinetic dependences of electrochemical properties indicate the presence of both general regularities and individual features determined by both the type of metal substrate and the coating type.

The results presented above can serve as a basis for building digital models of adaptive polymer coatings, including composite ones, obtained on metal substrates featuring different corrosion activity when operated in corrosive environments. In the case of coatings providing protection against electrochemical corrosion, this primarily implies a justified choice of equivalent electrical circuits.

It has been shown for standard polymer coatings containing no adaptive additives that in the course of long-term exposure in corrosive media, an evolution of the EC is observed, involving a sequential transition from multiphase Voigt circuits describing low-defect composites to circuits with local defects [19].

As it can be seen from the data presented in Figures 9 and 10, in the initial period of exposure in a corrosive environment, the frequency dependences of impedance modulus |*Z*| at the same temperature are quite similar for coatings on Pt and St3 substrates.

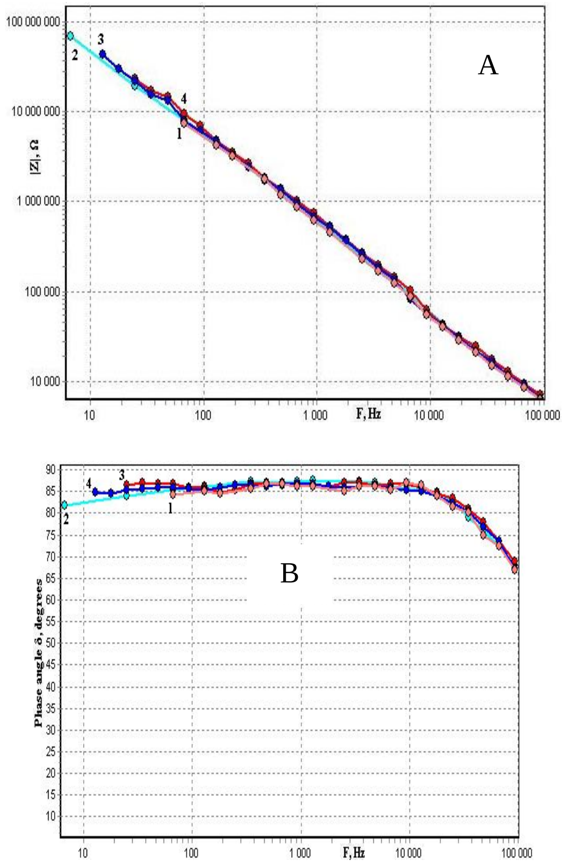


Figure 9. Bode plots. Impedance modulus |*Z*| (A) and phase angle δ (B) after exposure of coatings in 3% NaCl at 60°C for 30 days: 1 – R-EFF on Pt; 2 – R-EFF on St3; 3 – M-01//R-EFF on Pt; 4 – M-01//R-EFF on St3. The measurement temperature is 40°C.

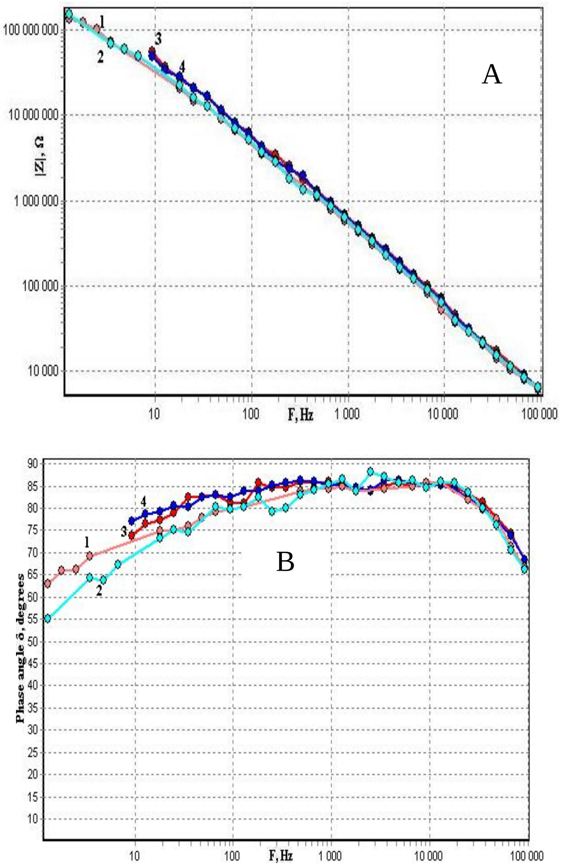


Figure 10. Bode plots. Impedance modulus |*Z*| (A) and phase angle δ (B) after exposure of coatings in 3% NaCl at 60°C for 30 days: 1 – R-EFF on Pt; 2 – R-EFF on St3; 3 – M-01//R-EFF on Pt; 4 – M-01//R-EFF on St3. The measurement temperature is 60°C.

In this case, as the measurement temperature is increased, the dielectric properties of the coatings go down and differences between coatings made of a single material and composite coatings made of two adaptive materials become apparent. Coatings of the second type show higher dielectric properties on both Pt and steel (St3) substrates.

Figure 11 below is an example of approximation of the frequency dependence of the phase angle using a 2-phase Voight circuit.

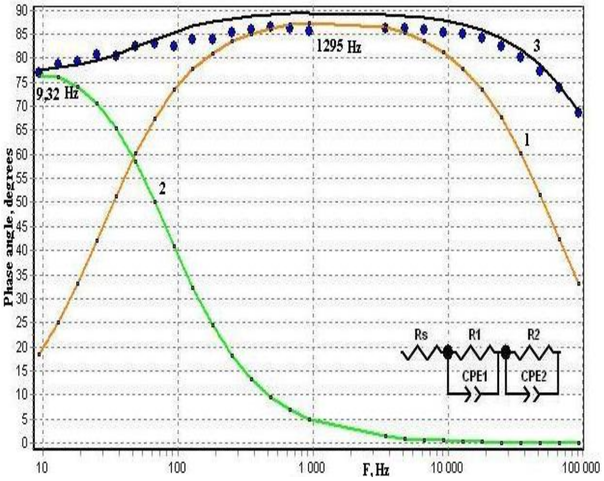


Figure 11. Bode plot. Phase angle for (M-01//R-EFF) composite PC on steel substrate after 30 days of exposure in 3% NaCl at 60°C and its approximation by a 2-phase Voigt circuit (3) with decomposition into HF (1) and MF (2) components. (Dots – experiment; lines – calculation according to the EC) [17]. The measurement temperature is 60°C.

It is fundamentally important to note that for all adaptive coatings studied, this EC is also applicable for coatings on steel substrate at various temperatures.

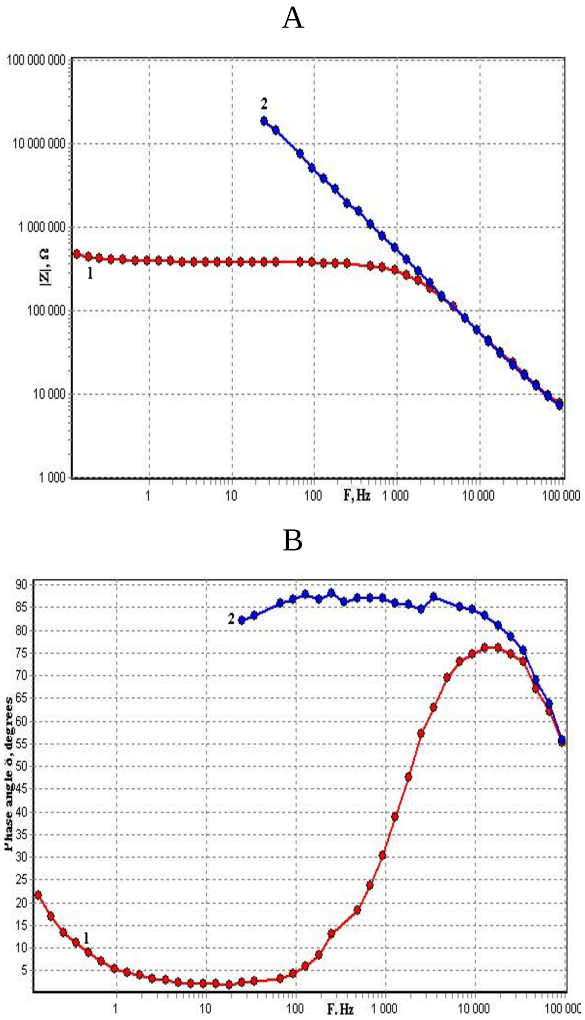
As noted above, at long exposure times in 3% NaCl (more than 1000 days), only composite adaptive PCs on St3 retain protective properties.

Figures 12 and 13 below demonstrate the Bode plots of composite coatings on Pt and steel (St3) substrates recorded at 40 and 60°C.

It can be seen that the composite coating on St3 retains high dielectric properties after prolonged exposure, which is manifested in the pronounced frequency dependence of the impedance modulus $|Z|$ and a high phase angle δ.

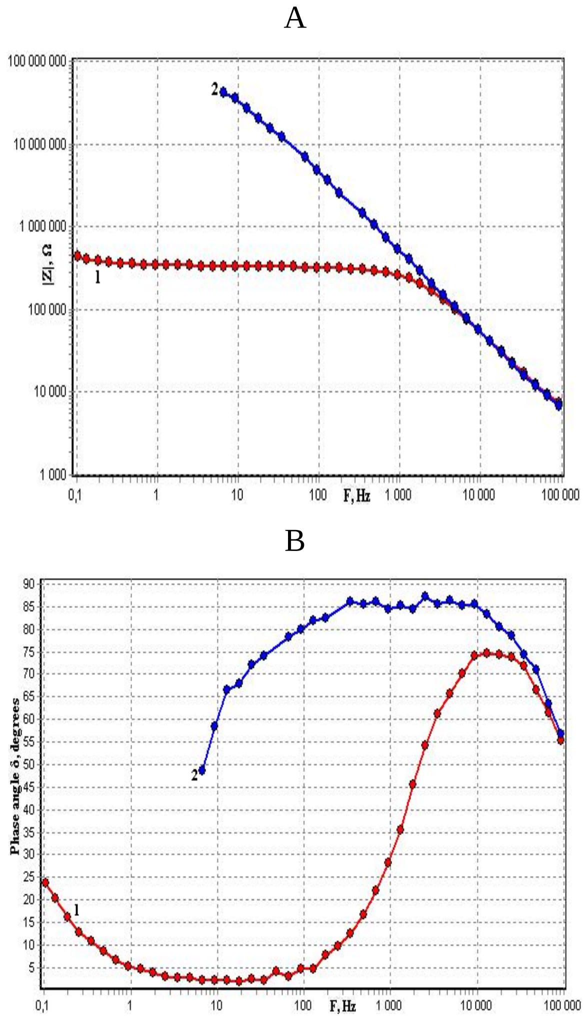
At the same time, a similar coating on Pt substrate shows a significant drop of the electrochemical parameters in the high-frequency (HF) and medium-frequency (MF) regions (1–10 kHz), while in the low-frequency (LF) region (less than 100 Hz) an almost complete degeneration of the capacitive impedance component is observed.

However, despite the significantly different Bode frequency dependences on St3 and Pt, processing of the experimental data obtained at longer times allows describing them within a single Mansfeld equivalent circuit (Figures 14 and 15).


A

B

Figure 12. Bode plots. Impedance modulus |*Z*| (A) and phase angle δ (B) of coatings after exposure in 3% NaCl at 60°C for 1040 days: 1 – M-01//R-EFF on Pt; 2 – M-01//R-EFF on St3. The measurement temperature is 40°C.


A

B

Figure 13. Bode plots. Impedance modulus |*Z*| (A) and phase angle δ (B) of coatings after exposure in 3% NaCl at 60°C for 1040 days: 1 – M-01//R-EFF on Pt; 2 – M-01//R-EFF on St3. The measurement temperature is 60°C.

As it is known, the Mansfeld EC was suggested for simulation of the local subfilm corrosion of a substrate in the zone of through pores [20]. The fact that this scheme is suitable for describing the behavior of a composite coating on an inert Pt substrate indicates that the LF process in the composite adaptive coatings studied is caused by the corrosion of the Zn filler in the primer layer.

It can also be noted that this process in composite coatings is realized on both Pt and St3 substrates. Moreover, the process on St3 substrate occurs with preservation of high dielectric properties in the HF region, which, together with a high level of impedance modulus, indicates a hindered ion transport through the complex coating.

The dependences of the active resistance values on the inverse temperature in the HF region (Figures 16–19) allowed us to estimate the activation energy (E_{act}) of the ion transport process [21, 22] for all the coatings studied on both substrates (Tables 1 and 2).

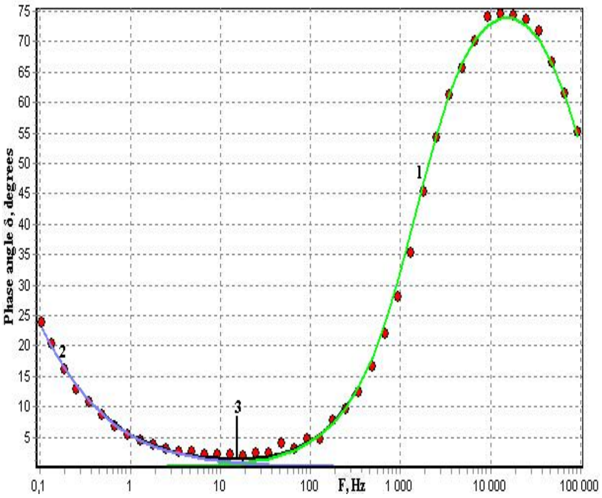


Figure 14. Bode plots. Phase angle δ for (M-01//R-EFF) composite PC on platinum substrate after 1040 days of exposure in 3% NaCl at 60°C and its approximation by Mansfeld circuit (3) with decomposition into HF (1) and LF (2) components. (Dots – experiment; lines – calculation according to the EC).

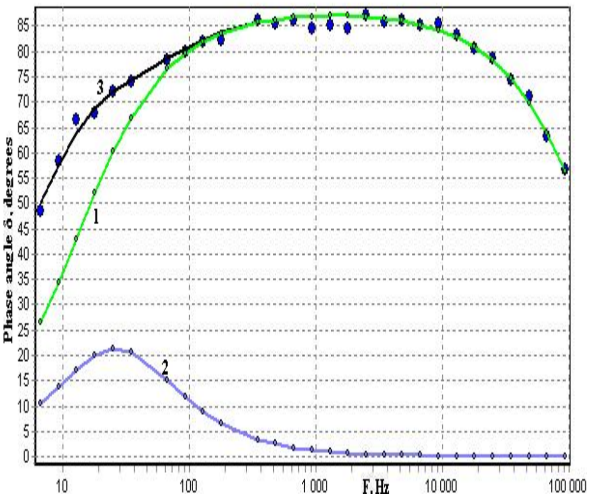


Figure 15. Bode plots. Phase angle δ for (M-01//R-EFF) composite PC on steel substrate after 1040 days of exposure in 3% NaCl at 60°C and its approximation by Mansfeld circuit (3) with decomposition into HF (1) and LF (2) components. (Dots – experiment; lines – calculation according to the EC).

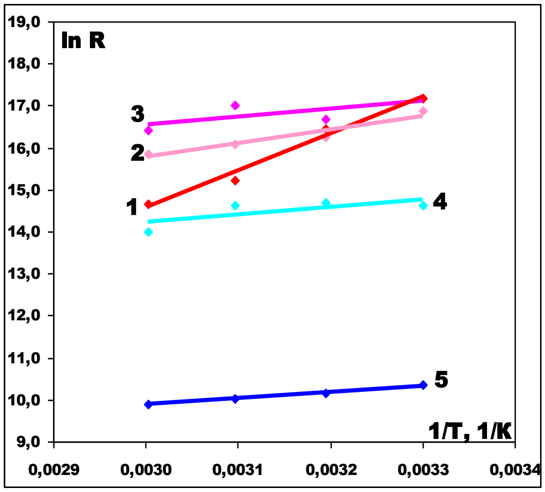


Figure 16. Dependences of the natural logarithm of the resistance of (R-EFF) PC deposited on Pt substrate on inverse temperature after exposure in 3% NaCl for: 1 – 30 minutes; 2 – 1 day; 3 – 125 days; 4 – 210 days; 5 – 240 days.

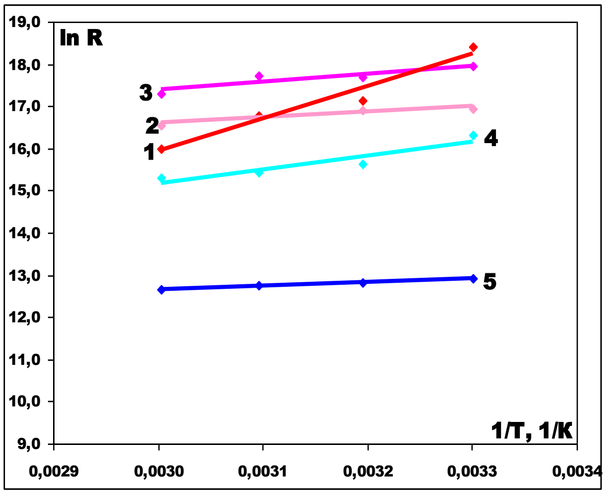


Figure 17. Dependences of the natural logarithm of the resistance of (M-01//R-EFF) composite PC deposited on Pt substrate on the inverse temperature after exposure in 3% NaCl for: 1 – 30 minutes; 2 – 30 days; 3 – 100 days; 4 – 660 days; 5 – 1040 days.

Table 1. Activation energy of the HF transfer process (based on active resistance value) through (R-EFF) adaptive PC and (M-01//R-EFF) composite PC on platinum substrate (Pt) during exposure in 3% NaCl for 1040 days.

Time, days	**Exposure temperature, °C**	**E_{act}, kJ/mol**	
		R-EFF	**M-01//R-EFF**
30 min	60	73.0	64.2
7	60	33.7	24.4
30	60	18.5	11.0
100	60	19.6	16.8
125	23	15.8	15.1
290	60	7.3	19.8
500	23	–	11.7
600	23	–	34.0
660	23	–	27.2
1040	23	–	6.8

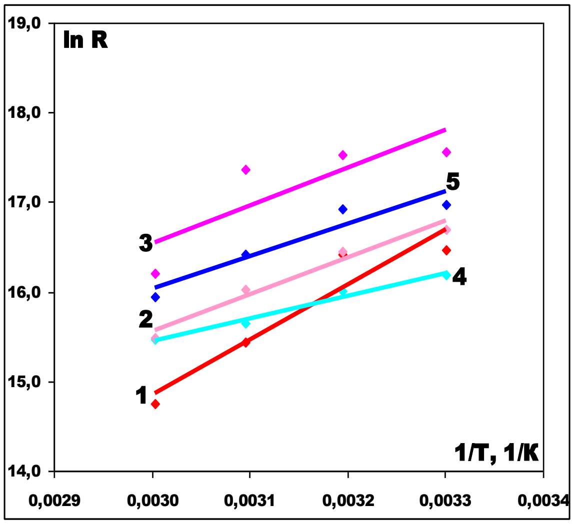


Figure 18. Dependences of the natural logarithm of the resistance of (R-EFF) PC deposited on St3 substrate on inverse temperature after exposure in 3% NaCl for: 1 – 30 minutes; 2 – 1 day; 3 – 30 days; 4 – 45 days; 5 – 526 days.

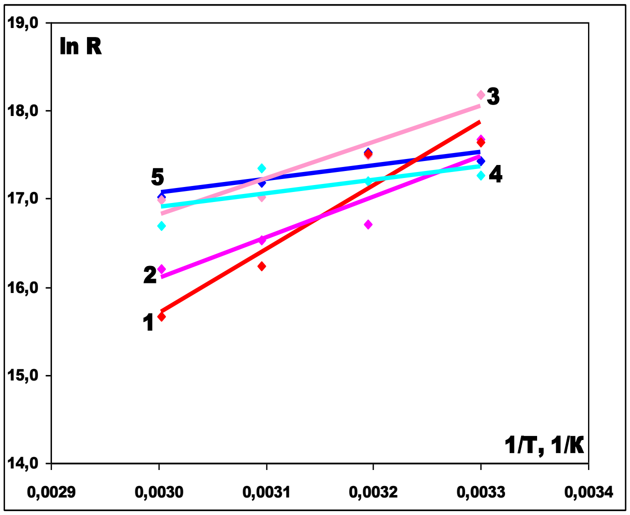


Figure 19. Dependences of the natural logarithm of the resistance of (M-01//R-EFF) composite PC deposited on St3 substrate on inverse temperature after exposure in 3% NaCl for: 1 – 30 minutes; 2 – 100 days; 3 – 600 days; 4 – 830 days; 5 – 1040 days.

Table 2. Activation energy of the HF transfer process (based on the active resistance value) through (R-EFF) adaptive PC and (M-01//R-EFF) composite PC on steel substrate (St3) during exposure in 3% NaCl for 1040 days.

Time, days	Exposure temperature, °C	E_{act}, kJ/mol	
		R-EFF	M-01//R-EFF
30 min	60	51.2	60.1
7	60	30.9	56.9
30	60	31.6	20.1
100	60	29.6	38.7
290	23	28.2	18.6
500−526	60	30.0	31.6
660	23	–	22.9
830	23	–	12.9
1040	23	–	12.8

The results of estimating the activation energy of transport processes based on the active resistance value in the HF region allow us to draw the following conclusions:

1. The process of ion transfer in the composite PC is hindered, as indicated by the higher values of activation energy compared to the individual adaptive PC.
2. For the composite PC, an effect of E_{act} growth was found for the ion transfer process through the coating on both Pt and St3 substrates (after its decrease around the 30thday at the impregnation completion stage).
3. The composite bilayer coating on St3 has higher and more stable electrochemical characteristics compared to the similar coating on Pt substrate, including a significantly higher hindrance of the ion transport mobility in the HF region (Table 3).

Table 3. Characteristic frequencies of the HF process in the composite coatings on different metal substrates during exposure in 3% NaCl.

Exposure time, days	Frequency, Hz	
	M-01//R-EFF on Pt	M-01//R-EFF on St3
0	2500	2500
100	932	1295
500	1295	1295
660	3474	1295
1040	12949	1295
1240	–	2500

5. Conclusion

1. The effect of temperature variation on the electrochemical characteristics of individual adaptive polymer epoxy coatings and composite systems consisting of two adaptive layers with different active additives has been studied.
2. It has been shown that the mechanism of spontaneous growth in impedance modulus $|Z|$ under natural conditions of exposure in a corrosive environment without any additional external impact is realized in adaptive composite PCs.
3. A correlation between the kinetic dependences of variation in the impedance modulus and potential of the substrate under the coating has been found. It has been found that at the stages of growth and stabilization of the potential and impedance modulus (up to 500 days of exposure in 3% NaCl), a strong dependence of the substrate potential on the measurement temperature is observed: the lower the measurement temperature, the more positive the substrate potential.
4. It has been shown that a stable description based on a numerical model of a low-defect composite is possible for composite polymer coatings containing adaptive additives upon long-term exposure in corrosive media.
5. It has been shown that the electrochemical characteristics of the composite coating with two adaptive layers of different materials are significantly higher than those of the individual adaptive PC. An effect of the increase in the activation energy of ion transfer through the coating on both inert platinum (Pt) and corroding steel (St3) substrates has been found for the composite PC.
6. It has been shown that a composite bilayer adaptive coating on a corroding St3 substrate can have higher and more stable electrochemical characteristics than a similar coating on an inert Pt substrate.

The work was carried out with the financial support of the Ministry of Science and Higher Education of the Russian Federation.

References

1. J.H.W. de Wit, D.H. van der Weijde and G. Ferrari, *Organic coatings of corrosion mechanisms in theory and practice*, Second edition, Marcel Dekker, 2002, p. 19.
2. G.P. Bierwagen, D. Tallman, J. Li, L. He and C. Jeffcoate, EIS studies of coated metals in accelerated exposure, *Prog. Org. Coat.*, 2003, **46**, 148–157. doi: 10.1016/S0300-9440(02)00222-9
3. G.P. Bierwagen, J. Li, L. He, L. Ellingson and D.E. Tallman, Consideration of a new accelerated evaluation method for coating corrosion resistance thermal cycling testing, *Prog. Org. Coat.*, 2000, **39**, 67–78.
4. V.A. Golovin and S.A. Tyurina, Microencapsulation of corrosion inhibitors and active additives for anticorrosive protective polymer coatings, *Int. J. Corros. Scale Inhib.*, 2019, **8**, no. 2, 179–198. doi: 10.17675/2305-6894-2019-8-2-2

5. Y. Jinglei, M.W. Keller, J.S. Moore, S.R. White and N.R. Sottos, Microencapsulation of isocyanates for self-healing polymers, *Macromolecules*, 2008, **41**, no. 24, 9650–9655. doi: 10.1021/ma801718v
6. H. Wei, Y. Wang, J. Guo, N.Z. Shen, D. Jiang, X. Zhang, X. Yan, J. Zhu, Q. Wang, L. Shao, H. Lin, S. Wei and Z. Guo, Advanced micro/nanocapsules for self-healing smart anticorrosion coatings, *J. Mater. Chem. A*, 2015, **3**, no. 2, 469–480. doi: 10.1039/c4ta04791e
7. A. Cohades, C. Branfoot, S. Rae, I. Bond and V. Michaud, Progress in self-healing fiber-reinforced polymer Composites, *Adv. Mater. Interfaces*, 2018, **5**, no. 17. doi: 10.1002/admi.201800177
8. M.Yu. Kvasnikov, A.V. Makarov, A.A. Silaeva, N.V. Fedyakova and T.M. Kvasnikov, Self-healing paint polymer coatings, *Zh. Prikl. Khim.* (*J. Appl. Chem.*), 2019, **92**, no. 5, 656–667 (in Russian).
9. V.A. Golovin, S.A. Dobriyan and V.A. Shchelkov, Processes of adaptation and protective characteristics growth in multilayer polymer coatings modified with carbon nanotubes, *Int. J. Corros. Scale Inhib*., 2023, **12**, no. 4, 1849–1862. doi: 10.17675/2305-6894-2023-12-4-23
10. K. Naresh, W.J. Cantwell, K.A. Khan and R. Umer, Single and multilayer core designs for Pseudo-Ductile failure in honeycomb sandwich structures, *Compos. Struct*., 2021, **256**, 113059. doi: 10.1016/j.compstruct.2020.113059
11. C. Gabrielli, *Use and application of electrochemical impedance techniques*, Technical Report, Schlumberger Technologies, Farnborough, 1990, 78 pp.
12. F. Brambilla, E. Campazzi, D. Sinolli and P.-J. Lathiere, *Accelerated corrosion testing: a predictive tool*, Theses of The Annual Congress of the European Federation of Corrosion (EUROCORR 2018), Cracow, Poland, September 9–13, 2018, 120935.
13. N.A. Poklonskii and N.I. Gorbachuk, *Fundamentals of the impedance spectroscopy of composites*, Minsk, BGU, 2005, 130 pp. (in Russian).
14. D. Ramesh and T. Vasudevan, Evaluation of corrosion stability of water soluble epoxy-ester primer through electrochemical studies, *Mater. Sci. Appl*., 2012, **3**, no. 6, 333–347. doi: 10.4236/msa.2012.36049
15. ISO 16773-1, 2, 3, 4, Electrochemical impedance spectroscopy (EIS) on high-impedance coated specimens.
16. V.A. Golovin, S.A. Dobriyan and V.E. Kasatkin, Electrochemical properties and processes of self-healing of multilayer metal-filled coatings during exposure in a corrosive environment, *Int. J. Corros. Scale Inhib*., 2024, **13**, no. 2, 1337–1354. doi: 10.17675/2305-6894-2024-13-2-37
17. I.L. Rozenfeld, F.I. Rubinshtein and K.A. Zhigalova, *Protection of metals from corrosion by paint coatings*, Moscow, Khimiya, 1987, 224 pp. (in Russian).
18. L.S. Saakiyan, A.P. Efremov and I.A. Soboleva, *Improving the corrosion resistance of oil and gas field equipment*, Moscow, Nedra, 1988, 211 pp. (in Russian).

---

19. V.A. Golovin, S.A. Dobriyan and A.K. Buryak, Polymer coatings long-term adaptation and self-healing effects in corrosive media, *Int. J. Corros. Scale Inhib.*, 2022, **11**, no. 3, 1172–1190. doi: 10.17675/2305-6894-2022-11-3-16
20. F. Mansfeld, Use of electrochemical impedance spectroscopy for the study of corrosion protection by polymer coating, *J. Appl. Electrochem.*, 1995, **25**, 187–202.
21. Z. Sharer and J. Sykes, Electrochemical impedance spectroscopy on thermal aging of epoxy coating containing zinc rich primer, *Int. Res. Eng. Technol.*, 2013, **2**, no. 10, 134–139.
22. V.A. Golovin and S.A. Dobriyan, Evolution of EIS properties of composite polymer protective coatings in aggressive environments, *Int. J. Corros. Scale Inhib.*, 2021, **10**, no. 4, 1493–1515. doi: 10.17675/2305-6894-2021-10-4-8

◆ ◆ ◆