Research Article

Performance Evaluation of Layered Double Hydroxides Containing Benzotriazole and Nitrogen Oxides as Autonomic Protection Particles against Corrosion

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Layered double hydroxides (LDH) are lamellar structures with positively charged laminates and charge-compensating interlayer anions. The ion-exchange capacity of LDHs makes them as promising hosts for corrosion inhibitor anions with stimulus-responsive release and self-healing anticorrosion. In the current work, LDHs loaded with two different corrosion inhibitors (nitrogen oxides and benzotriazole) were evaluated for their ion-exchange capacity and autonomic protection against corrosion on carbon steel. Studies on nitrogen oxide-loaded LDH (NO_x-LDH) showed that nitrogen oxides were successfully intercalated in LDH structure, which were released in chloride media. Open Circuit Potential (OCP) results showed that NO_x-LDH extract shifted OCP to nobler values, indicating the protection of metal. For benzotriazole-loaded LDH (BTZ-LDH), the results indicated the presence of benzotriazole in the structure, but its release was not observed. OCP results showed no significant increase of carbon steel protection, corroborating with the conclusion that benzotriazole ions did not migrate to metal surface. Considering these results, the insertion of NO_x-LDH in an automotive primer was proceeded, under three different concentrations (0.2, 1.0, and 3.0%). Electrochemical impedance spectroscopy (EIS) showed that the more effective NO_x-LDH concentration on corrosion delay was 0.2%, which better balanced protection level conferred by LDH with a possible loss on effectiveness of coating due to increase in porosity.

1. Introduction

Layered double hydroxides (LDH), also known as ‘anionic clays’, consist of positively charged hydroxide layers (having structural similarity to brucite compounds) with anions and water molecules intercalated between these layers. LDH can be represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$, where M^{II} and M^{III}

are divalent and trivalent metal cations, respectively, and Aⁿ⁻ is the anion located between the layers to balance the positive charges. Distance between hydroxide layers allows the insertion of a wide range of anions, either organic or inorganic, with different sizes and on different spatial orientations [1–3].

LDH structures have been used in anticorrosion studies for the insertion of corrosion inhibitors in their anionic form

FIGURE 1: SEM images of (a) NO_x -LDH and (b) BTZ-LDH.

between the layers [1, 4–6], so that the release of these anions is triggered by the anionic change with chloride ions of aggressive medium. Thus, LDH containing corrosion inhibitors play a double role on corrosion protection process: (a) promote controlled release of corrosion inhibitors, which may migrate to metal surface to create a passive barrier, and (b) accomplish corrosive ion trapping, decreasing the aggressiveness of medium [1, 7]. In this sense, LDH containing corrosion inhibitors may be inserted as additives on ordinary organic coatings, aiming to provide autonomic protection against extensive corrosion of metal substrates.

The current research work is aimed at evaluating and comparing the anticorrosion performance of two types of corrosion inhibitor-loaded Zn/Al-based LDH coating over carbon steel. Different from previous investigations, this research considered two different approaches to make LDH-based coating over carbon steel, LDH in extract form (acting as a kind of electrolyte ‘pretreatment’) and LDH dispersed in a coating matrix. The focus was on electrochemical discussions, which were supported by characterization data analysis.

2. Materials and Methods

Benzotriazole-loaded LDH (BTZ-LDH) and nitrogen oxide-loaded LDH (NO_x -LDH) were supplied from Smallmatek® and were analyzed by scanning electron microscopy (SEM) for structural evaluation of morphology, physical form, and agglomeration patterns. LDH powder samples were dispersed in ethanol using ultrasound bath for 1 h to destruct clusters of particles, and the morphological analysis was performed using a scanning electron microscope (TESCAN VEGA3 LMU equipment).

Chemical analysis of LDH samples was performed through fourier transform infrared spectroscopy (FTIR) technique using a Bruker OPTIK GmbH HTS-XT Vertex 70 equipment. In this procedure, KBr pastilles containing

LDH aliquots were inserted on equipment’s sample holder and spectra were acquired in an observation range of 4000 cm^{-1} to 400 cm^{-1} resolution of 4 cm^{-1} and 32 scans. As a complementary analysis to FTIR, the X-ray diffraction (XRD) technique was employed to investigate LDH’s structure and calculate interlamellar distances. Diffractograms were collected in the range of 5° to 70° , with a step amplitude of 0.02° using a Bruker-AXS D2-Phaser equipment, operating at 30 kV and 10 mA with $\text{CuK}_{\alpha 1}$ ($\lambda = 1.540\text{ \AA}$) radiation.

BTZ-LDH and NO_x -LDH were evaluated on their ability to prevent corrosion under two different approaches: after suspension in the electrolyte (LDH extracts) and dispersed on a coating matrix over the metal substrate.

For LDH extract preparation, the LDH powders were suspended in 3.5% NaCl solution under magnetic stirring for 24 h to promote ion exchange between inhibitor ions and chloride ions. After stirring, suspensions were centrifuged to obtain a clear solution containing released inhibitor ions and a precipitate composed by LDH containing entrapped chloride ions. The obtained precipitate was washed with ultrapure water and dried at 55°C to obtain a dry powder and analyzed through FTIR and XRD techniques employing the same procedures described above. The clarified solution obtained was employed as electrolyte on electrochemical tests. For OCP, PP (potentiostatic polarization) and EIS measurements, presanded and degreased carbon steel plates were employed. On each plate, three areas of 17 cm^2 were delimited to proceed measurements in triplicate and 40 mL of clarified solutions was added to each area. For electrochemical measurements, a three-electrode arrangement was employed, being the reference electrode Ag/AgCl (KCl saturated), the counter electrode a platinum wire, and the working electrode the carbon plate itself. Data was acquired using a PGSTAT302N Metrohm Autolab equipment. PP measurements were accomplished in the range of -200 mV to $+400\text{ mV}$ vs. OCP with a scanning speed of $1\text{ mV}\cdot\text{s}^{-1}$. EIS measurements were acquired in a frequency range of

FIGURE 2: Comparative spectra of pristine NO_x -LDH before and after exposure to 3.5% NaCl (a) spectrum in full and (b) zoom in the 1384 cm^{-1} region.

10 kHz to 0.01 Hz with applied 10 mV sinusoidal perturbation and collecting 10 points per decade.

For developing LDH on a coating matrix, a polyester-based automotive primer coating was used as matrix. LDH powders were dispersed in primer under mechanical stirring on mass fraction of 0.2%, 1.0%, and 3.0%. The LDH-enriched primer was applied to presanded and degreased carbon steel

1020 plates using a professional paint gun so that the dried thickness was around 40 μm . After drying, three areas were delimited on each plate surface and 3.5% NaCl solution was added to proceed electrochemical measurements. Parameters and arrangement of electrochemical measurements were the same as described above, but in this case, EIS data was collected from 100 kHz to 0.01 Hz.

TABLE 1: Characteristic bands of FTIR spectrum obtained for NO_x-LDH.

Wavenumber (cm ⁻¹)	Assignment
3436	Water molecules adsorbed and hydroxyl groups [11]
1633	Bending stretching of water molecules [11]
1383	Nitrates symmetrical stretching [11]
1269	Nitrite ion deformation [12]
551	Zn/Al-OH translation [13]
426	Al-O condensed groups [13]

3. Results and Discussion

SEM analysis was performed in order to get insight into morphology and agglomeration patterns of LDH. Figure 1 shows SEM images obtained for both NO_x- and BTZ-loaded LDH. SEM analysis indicated that both types of LDH showed agglomeration patterns and plate-like morphology as reported previously [8–10].

FTIR analysis was made to verify characteristic bands of chemical bonds present on particle structure, as hydroxide groups, water molecules, Zn-Al bonds, and specific bonds of inhibitors. FTIR spectra of NO_x-LDH after exposure to 3.5% NaCl at 0.2, 1.0, and 3.0% *w/v* were acquired and are showed in Figure 2. Characteristic bands in pristine NO_x-LDH spectrum are given in Table 1. NO_x-LDH FTIR spectrum presented some band characteristics of structural components, such as water molecules and hydroxyl groups, besides nitrate and nitrite (inhibitors) characteristic bands, indicating the presence of these anions in the structure. Figure 2(a) shows that, after chloride exposure, the noticeable changes were the absence of bands at 1384 cm⁻¹ and 1270 cm⁻¹ which are characteristic of nitrate and nitrite ions, respectively. However, while observing the 1384 cm⁻¹ region with more details (Figure 2(b)), it is possible to infer that this peak is composed by the overlap of two bands, one more defined (on the left of stretching) and a ‘shoulder’ on the right, initially of unknown nature. Figure 2(b) shows that, after chloride exposure, there is a significant decrease in the intensity of 1384 cm⁻¹ stretching (and not its complete absence), maintaining the associated ‘shoulder’. As 1384 cm⁻¹ is associated with nitrate ions, it is inferred that such significant decrease on peak intensity was related to majority release of nitrate ions from the interlayer galleries, and the associated “shoulder” would be related to some structural portion of LDH, once it remained intact on spectrum. This result indicates that the nitrate and nitrite ions were initially located at the interlayer gallery and were satisfactorily released and exchanged with chloride ions after exposure.

Figure 3 shows the FTIR spectrum obtained for BTZ-LDH before and after exposure to 3.5% NaCl. The spectrum obtained for BTZ-LDH also allowed the identification of structural characteristic bands, such as water molecules and Zn/Al hydroxides (Table 2). The 1384 cm⁻¹ stretching is marked in Table 2 with an asterisk due to the dubiety of its assignment: although it has been reported on literature that this stretching may be related to triazole ring deformation, it is also possible to relate it to the symmetrical stretching

of nitrates, or even both contributions simultaneously. The presence of nitrate groups would be related to incomplete exchange of these ions (coming from the pristine LDH) for benzotriazole ions. Likewise, the peak on the region of 778 cm⁻¹ highlighted on Table 2 with two asterisks may be interpreted in a first moment in two different ways: Al-OH (present in LDH structure) bond deformation or C-H bonds stretching from benzotriazole molecule. To settle this ambiguity, FTIR spectra of BTZ-LDH after chloride exposure were considered. The results obtained for the three investigated concentrations are shown in Figure 3. The peaks observed for the material after exposure to the medium rich in chlorides are the same as the pristine BTZ-LDH. Such as what was observed to NO_x-LDH, the exception is the stretching at 1384 cm⁻¹ which presented the same kind of significant decrease in intensity after exposition when compared to the original LDH. This behavior is better seen in Figure 4(b) (zoom in the region of 1384 cm⁻¹). This result corroborates with the previous conclusion that the peak at 1384 cm⁻¹ would be related to nitrate ions remaining in the interlayer galleries, which represents majority release and exchange of chloride ions. Despite this peak having been identified on isolated spectrum of benzotriazole (not shown), it is refused the hypothesis of this peak be related only to ring deformations which could be refused, since the other peaks attributed to benzotriazole remained in the spectrum after exposition, indicating that insertion of benzotriazole as interlayer anion was not achieved.

XRD measurements were done as a complementary technique to FTIR to characterize LDH structure to confirm the presence or absence of inhibitor anion intercalations in the interlayer gallery.

Basal space ‘*d*’ was calculated through XRD results employing Bragg’s law (Equation (1)) [17].

$$d = \frac{\lambda}{2 \sin \theta}, \quad (1)$$

where λ is the wavelength of X-ray (1.54062 Å) and θ is the angle of the most intense peak. Other lattice parameters were obtained through relations established for rhombohedral systems, as shown on Figure 4. According to Figure 4, for systems with rhombohedral symmetry, the lattice parameter ‘*c*’ is the triple of basal space ‘*d*’. The lattice parameter ‘*a*’ is related to lamella’s atom nature, and its value can be estimated through the distance obtained by the (110) plane,

FIGURE 3: Comparative spectra of BTZ-LDH before and after exposure to 3.5% NaCl (a) spectrum in full and (b) zoom in the 1384 cm⁻¹ region.

according to Equation (3).

$$a = 2d_{(110)}. \quad (2)$$

The parameter 'h', related to lamellar interstice size, was estimated by subtracting the value of hydroxide layer thick-

ness (around 47.1 Å for Zn/Al LDH [18]) from 'd' basal space value.

The analysis and comparison of pristine LDHs with LDH after exposure to chloride-rich medium were made to verify structural changes associated with the ion exchange. Figure 5 shows the diffractogram obtained for NO_x-LDH before and after exposure to 3.5 wt% NaCl. The diffractogram

TABLE 2: Characteristic bands of FTIR spectrum obtained for BTZ-LDH.

Wavenumber (cm ⁻¹)	Assignment
3437	Adsorbed water molecules and hydroxyl groups in the structure [11]
1384*	Triazolic ring (from benzotriazole) [14]/nitrate symmetrical stretching* [11]
778**	Al-OH deformation [13]/out of plane C-H stretching (from benzotriazole)** [15]
750	Aromatic ring=C-H bond (benzotriazole) [16]
550	Zn/Al-OH translation [13]
427	Al-O condensed groups [13]

FIGURE 4: Relation between rhombohedral structure parameters for LDH. Adapted from Crepaldi and Valim (1998) [19].

presents characteristics of layered materials such as thin and intense peaks at low values of 2θ and less intense peaks (usually asymmetric) at higher values of 2θ . These are characteristics of hexagonal network systems with rhombohedral symmetry (R-3m special group), which are commonly used to describe LDH [20]. The NO_x -LDH diffractogram showed defined peaks at 11.32° and 23.10° , related to diffraction by planes (003) and (006), respectively. The diffractogram of NO_x -LDH before exposure to saline medium is quite similar to that reported on literature [8, 11, 21]. The maximum space that a nitrate ion can occupy is $3.80 \text{ \AA}$ [22]. The inorganic ions may be arranged between layers at different ways: perpendicularly, horizontally, or tilted at an angle [23], which may reduce the space occupied by these ions by some extension. Hence, the interlayer space value of $3.10 \text{ \AA}$ may be associated with a more compact orientation of nitrate ions, in addition to the presence of nitrite ions which tend to present a smaller spatial diameter.

XRD analysis was also employed as a complementary technique to FTIR to determine LDH efficiency to trap chloride ions. Table 3 shows the parameters calculated for LDH before and after exposure to the NaCl medium. Figure 5 shows a comparison between obtained diffractograms in both situations, and the region of $7^\circ < 2\theta < 31^\circ$ was enlarged to evidence changes on main peaks. Comparing the diffractograms obtained for NO_x -LDH before and after exposition, it is possible to observe displacement on (003) and (006) planes to higher 2θ values, which indicates a decrease on interlayer spacing according to Bragg's law. This result corroborates

with the previous conclusion that the ion exchange was effective in this case, since chloride ions are smaller than nitrate/nitrite ions, promoting layer structure contraction. In addition to that, no displacement was observed on the (110) plane, indicating that the nature of elements which comprise the layer structure (Zn and Al) did not change [18]. Figure 6 shows a schematic drawing of the ion-exchange process of NO_x -LDH when exposed to a saline medium.

Diffractogram obtained for BTZ-LDH is showed in Figure 7. The diffractogram of BTZ-LDH showed characteristic peaks of lamellar system. Basal spaces were calculated through the same methodology employed to NO_x -LDH, and Table 4 shows the obtained results. Comparison between diffractograms before and after exposure is showed in Figure 8. In this case, ' d ' and ' h ' parameters are quite similar to the values ($7.56 \text{ \AA}$ and $2.85 \text{ \AA}$, respectively) reported by Serdechnova and coworkers for the same material [18]. According to them, it would not be possible for the benzotriazole anion to locate in an interlayer space (' h ') in the order of magnitude found in this case, due to the relatively big spatial volume of benzotriazole. Serdechnova and coworkers also investigated the insertion of benzotriazole in Mg/Al LDH and mercaptobenzotriazole in Zn/Al LDH. For both cases, the values obtained for ' d ' and ' h ' parameters were in the range of $15 \text{ \AA}$ and $11 \text{ \AA}$, respectively. These results show that benzotriazole anions and its derivatives, like mercaptobenzotriazole, demand bigger interlayer space for their intercalation to be possible. In addition to that, the diffractogram in Figure 7 shows the presence of unknown peaks (identified with asterisks). Serdechnova and coworkers attributed these peaks to reaction products between LDH hydroxide layers and benzotriazole, since it is known that there is high affinity between benzotriazole and zinc and the tendency of them to form complexes [24]. Thus, it was concluded that the attempt to insert benzotriazole in pristine nitrogen oxides containing Zn/Al LDH resulted in partial decomposition of LDH, and the portion that remained intact may be filled with hydroxyls as the interlayer ion. Moreover, the comparison between the diffractograms obtained for BTZ-LDH before and after exposure did not show displacements on main peaks, indicating that the interlayer space did not change and, consequently, ion exchange did not seem to happen. Absence of displacement on the (110) peak indicated the permanence of Zn and Al in lamellar structure.

Those results, aligned to FTIR spectra, indicate that benzotriazole insertion as interlayer ion was not effective in the

(a)

(b)

FIGURE 5: Diffractograms obtained for NO_x -LDH before (black) and after (green) exposure to 3.5% NaCl (a) region between 8 and 31° and (b) region between 54 and 77° . Peaks assigned with red risk are related to the standard ZnO added to the sample to the correction of peak position.

productive process of BTZ-LDH, resulting in the inefficiency of ion exchange when exposed to the saline medium. Figure 9 shows an illustrated scheme of proposed mechanism from the BTZ-LDH obtainment until its exposition to the saline

medium. In Figure 9, pink rectangles, which represent benzo-triazole molecules, appear anchored to the LDH structure, in an allusion to the possibility of them to be complexed with structural zinc.

TABLE 3: Structural parameters calculated for NO_x -LDH.

	d_{basal} (Å)	h (Å)	c (Å)	a (Å)
Before Cl^- exposure	7.81	3.10	23.43	3.07
After Cl^- exposure	7.71	3.00	23.13	3.07

FIGURE 6: Schematic drawing of the ion-exchange process of pristine NO_x -LDH in 3.5% NaCl medium.

FIGURE 7: Diffractogram obtained for BTZ-LDH.

TABLE 4: Structural parameters calculated for BTZ-LDH.

	d_{basal} (Å)	h (Å)	c (Å)	a (Å)
Before Cl^- exposition	7.58	2.87	22.74	3.07
After Cl^- exposition	7.58	2.87	22.74	3.07

The low solubility of LDH in the neutral medium does not make it possible to evaluate its efficiency regarding active mechanism against corrosion through its direct insertion on the electrolyte, because particle decantation would lead to the formation of a film which would act as a physical passive barrier on the metal. Thus, a 'treatment' was made by putting LDH in a 3.5% NaCl solution to perform ion exchange; then, the LDH particles were removed. This approach allowed evaluation of each system efficiency on trapping chlorides and releasing inhibitor ions by avoiding factors, which may provide wrong results. Figure 10 shows OCP profiles of carbon steel 1020 for dif-

ferent systems employing LDH on extract form. OCP migrated to values that are more negative over immersion time for all systems, and this profile is a result of progressive penetration of the electrolyte in the metal and consequent increase of oxidized species concentration. For the control system (black curve), the initial value was -0.540 V, which decreased quickly to a stabilization value of -0.750 V. This value was reached after approximately 400 min (6 hours) of immersion, and the value stayed constant until the end of analysis. For NO_x -LDH systems, it was observed that all concentrations shifted OCP to nobler values, meaning that the higher the concentration, the greater the displacement. These results indicate that NO_x -LDH addition to the electrolyte was effective to decrease the aggressiveness of the medium through chloride entrapment. In addition to that, the late stabilization and irregular profile of decay may indicate the adsorption of inhibitor ions on metal surface.

BTZ-LDH systems showed decay profiles quite similar to those observed for the control system, with a slight increment

FIGURE 8: Diffractograms obtained for BTZ-LDH before (black) and after (green) exposure to 3.5% NaCl (a) region between 8 and 31° and (b) region between 54 and 77°. Peaks assigned with a red line are related to the standard ZnO added to the sample to the correction of peak position.

of OCP values to a nobler direction as long as the concentration increased. However, such increment was too subtle to be attributed to benzotriazole inhibitor release, especially in higher concentrations in which a more pronounced inhibitive effect would be expected. Thus, these results corroborate with what was said before about nonrelease of benzotriazole from LDH to act as corrosion inhibitor on a metal surface, meaning that the observed slight effect resulted in few remaining NO_x ions on LDH structure (as shown in Figure 9).

As better results were obtained for LDH extracts at 3.0%, potentiostatic polarization analyses were performed employing extracts in this concentration. Figure 11 shows obtained potentiostatic polarization curves, and electrochemical parameters obtained after Tafel extrapolation are tabulated in Table 5. Comparing blue and red curves in Figure 11, it was observed that the BTZ-LDH extract addition did not cause significant changes on sample behavior in comparison with the control system, indicating again that in this case,

FIGURE 9: Schematic drawing of ion-exchange process from pristine NO_x -LDH until BTZ-LDH obtaintment and its posterior exposition to 3.5% NaCl medium.

FIGURE 10: OCP profiles obtained for extract form LDH systems.

FIGURE 11: Potentiostatic polarization curves obtained for different LDH extract systems (E vs. Ag/AgCl reference electrode and scanning speed of $1 \text{ mV} \cdot \text{s}^{-1}$).

TABLE 5: Electrochemical parameters obtained from polarization curves for carbon steel samples.

Extract	E_{corr} (V)	i_{corr} ($\mu\text{A} \cdot \text{cm}^{-2}$)	cr ($10^{-4} \text{ mm} \cdot \text{d}^{-1}$)	R_{pol} ($\Omega \cdot \text{cm}^2$)
Control	-0.650	3.36	1.07	330.84
BTZ-LDH	-0.626	9.01	48.77	182.51
NO_x -LDH	-0.345	3.56	1.10	533.00

there was not enough inhibitor ion concentration on electrolyte. Values reported on Table 5 show that current density (i_{corr}) suffered an increase in the presence of the BTZ-LDH extract, as well as corrosion rate (cr). Polarization resistance (R_{pol}) suffered a decrease in comparison to the control system. These results indicate that the BTZ-LDH extract system becomes more susceptible to corrosion than the control system. For the NO_x -LDH system, displacements of both

FIGURE 12: Nyquist plots (1) and Bode modulus plots (2) obtained for systems containing (a) 0.2%, (b) 1.0%, and (c) 3.0% extracts after 1 h of immersion (exposed area: 17 cm²).

portions (anodic and cathodic) of polarization curve to less negative potential values were observed. This system showed a well-defined passivation region, showing the action of inhibitor ions on the formation of a barrier on metal sites. In this case, polarization resistance suffered an increment of around 1.6 times. Corrosion current and corrosion rate remained equivalent to those of the control system.

Electrochemical impedance spectroscopy (EIS) analyses were made as an additional technique to obtain information about corrosion resistance of different systems. Figure 12 shows obtained results for extract systems at different concentrations after 1 h of immersion. Scattered points represent experimental data, and lines represent fitting. All curves of Figure 12 were fitted to an $R(RQ)$ equivalent circuit, as shown on Figure 13.

The equivalent circuit in Figure 13 is known as the Randles circuit and is commonly employed to describe uncoated metals exposed to an electrolyte [25, 26]. In this model, there is only one time constant, referring to the metal-electrolyte interface. In this way, R_s element refers to uncompensated resistance between work and reference electrodes and refers to electrolyte resistance [27]. R_{ct} element refers to charge transference resistance, and Q_{dl} element (constant phase element) refers to double-layer capacitance ('dl' subscribed index). In real systems, the change of a pure capacitive element for a constant phase element usually facilitates curve fitting, because this element describes semicircles flattening better. Constant phase elements are expressed by Equation (3) [27].

$$Q = \frac{1}{Y_0(j\omega)^N}. \quad (3)$$

Q_{dl} has two components, being Y_0 an element referred to admittance and N a dimensionless exponent, where $N = 1$ represents an ideal capacitor [25]. j is a complex number ($j^2 = -1$), and ω is the angular frequency ($\omega = 2\pi f$).

Table 6 shows obtained values for parameters after graph adjustment to equivalent circuit. R_{ct} values of the BTZ-LDH system showed slight increases in comparison to the control system on 0.2% and 1.0%, which reveals a discreet increasing on corrosion protection performance. For 3.0% concentration, the R_{ct} value of the BTZ-LDH system was slightly smaller than the control system's. These results indicated that BTZ-LDH was not efficient on promoting carbon steel protection against corrosion on extract tests.

Regarding NO_x -LDH, significant increases on R_{ct} values in comparison with control system were observed. The biggest increase was observed in the 3.0% NO_x -LDH system. This result suggests that nitrate/nitrite ions initially free in solution were efficient in adsorbing on the metal surface in sufficient amount, blocking metal sites, and decreasing corrosive processes development. Values for $N(Q_{dl})$ components showed essentially equivalents for all systems. In this case, as there is no coating applied on the substrate, this parameter may be related to metallic surface morphology. As all bodyproofs had the same composition and received the same pre-

FIGURE 13: Equivalent circuit $R(RQ)$ fitted on EIS results for extract systems.

TABLE 6: Values of parameters obtained through attribution of EIS results to equivalent circuits.

Concentration	System	OCP (V)	R_s (Ω)	R_{ct} (Ω)	$Y_0(Q_{dl})$ (mS)	$N(Q_{dl})$
0.2%	Control	-0.667	1.43	105	49.3	0.804
	BTZ-LDH	-0.660	1.50	165	33.8	0.815
	NO_x -LDH	-0.507	1.50	630	34.8	0.796
1.0%	Control	-0.662	1.23	80	15.1	0.751
	BTZ-LDH	-0.663	1.04	310	13.8	0.709
	NO_x -LDH	-0.328	1.29	1000	10.8	0.721
3.0%	Control	-0.699	1.65	120	46	0.81
	BTZ-LDH	-0.692	1.25	117	43.5	0.793
	NO_x -LDH	-0.122	1.65	1600	12.1	0.865

vious treatment (sanding and degreasing), this result is coherent.

Initially, it could be considered that the development of corrosive processes on bodyproofs over the exposure time would lead to the formation of a new interface (electrolyte-corrosion products). However, this behavior was not evidenced by EIS measurements, since all results were satisfactorily adjusted to $R(RQ)$ circuits. A reason for this behavior may be the fact that bodyproofs were uncoated metals, leading the corrosion products to leave the metal surface and migrate to the medium due to its low substrate adherence. This dynamic process would avoid the formation of a properly new interface, justifying the obtained result. Figure 14 shows a schematic drawing of the proposed mechanism.

Therefore, there are evidences that NO_x ions protected the metallic surface mainly through competitive adsorption with chloride ion mechanism and not through stabilization of formed oxides. Considering the results obtained on extract tests, incorporation of LDH in an organic coating matrix was accomplished by employing only NO_x -LDH. Figure 15 shows EIS results for carbon steel samples coated with NO_x -LDH-enriched primer in three different concentrations. The 0.2% NO_x -LDH system presented very particular behavior, with

FIGURE 14: Schematic drawing of proposed processes of formation and migration of corrosion products on metallic surface without coating.

FIGURE 15: Nyquist plots (1) and Bode modulus plots (2) for coated systems after (a) 1 h and (b) 8 h of immersion (exposed area: 17 cm^2).

total impedance values higher than other systems. In this case, a $R(RQ)(RQ)$ circuit fit all experimental data. In the carbon steel samples coated with a primer layer, there was the presence of a coating-electrolyte interface (beyond metal-electrolyte interface already identifiable due to primer porosity), characterizing two time constants of two (RQ) pairs. In this circuit, beyond R_s and R_{ct} (parameters described above),

there is the presence of a R_{coat} . Capacitive elements in this case were related to coating capacitance (Q_{coat}) and double-layer capacitance (Q_{dl}). Unlike in extract tests (where corrosion products showed low adherence on substrate and migrated to the medium), the formation of a new time constant was observed in this case, suggesting the presence of a new interface on the system. As the reference primer was

FIGURE 16: Proposed scheme for the formation and trapping processes of corrosion products at the substrate-coating interface.

FIGURE 17: $R(RQ)(RQ)(RQ)$ equivalent circuit attributed to EIS results for samples coated with NO_x -LDH-enriched primer.

TABLE 7: Electrochemical parameters obtained after fitting EIS data of coated samples to equivalent circuit $R(RQ)(RQ)(RQ)$.

	Control		0.2%		1.0%		3.0%	
Immersion time (h)	1	8	1	8	1	8	1	8
OCP (V)	-0.447	-0.482	-0.503	-0.484	-0.472	-0.560	-0.515	-0.529
R_{coat} ($\text{k}\Omega$)	60.7	11.6	1030	134	28.1	4.29	9.17	6.16
$Y_0(Q_{\text{coat}})$ (μS)	23.1	1400	1.21	25	64.1	843	315	660
$N(Q_{\text{coat}})$	0.585	0.419	0.673	0.557	0.534	0.171	0.593	0.278
R_{ct} ($\text{k}\Omega$)	31.1	3.35	150	66.8	27.5	1.09	7.31	0.697
$Y_0(Q_{\text{dl}})$ (μS)	2.14	22.3	0.0726	1.34	0.869	25.7	16.7	199
$N(Q_{\text{dl}})$	0.634	0.616	0.842	0.64	0.659	1.02	0.55	0.662
R_{ox} ($\text{k}\Omega$)	2.77	0.504	50	16.3	8.73	0.801	0.613	0.124
$Y_0(Q_{\text{ox}})$ (μS)	0.366	5.90	0.0152	0.0109	0.0236	27.3	0.217	0.091
$N(Q_{\text{ox}})$	0.762	0.568	0.894	0.913	0.862	0.766	0.766	0.915

relatively porous and the layer was not that thick, the occurrence of electrolyte penetration through the coating layer and the consequent formation of a layer of corrosion products between metal and primer were admitted. It was then considered that the primer layer was efficient on trapping corrosion products reducing its migration to medium and forming a layer identifiable by EIS technique. Figure 16 shows a representative scheme of this hypothesis.

Thus, after some time of immersion, the appropriate equivalent circuit was $R(RQ)(RQ)(RQ)$, where the new (RQ) pair (R_{ox} and Q_{ox}) refers to the corrosion product layer as shown in Figure 17. Values of electrochemical parameters obtained by fitting EIS data to equivalent circuit are shown in Table 7. OCP values were similar on all cases. Regarding R_{coat} , a decrease of values in all systems was observed as long as

the immersion time increased, with this being a result of progressive penetration of electrolyte through coating pores. The NO_x -LDH 0.2% system showed R_{coat} , R_{ct} , and R_{ox} significantly increased in comparison to other systems over the time period investigated. These results suggest that NO_x -LDH insertion in this concentration promoted an improvement on primer's barrier properties, increasing the resistance to electrolyte passage and to the development of corrosive processes on metal. R_{ox} increment of values on concentration of 0.2% may be explained by the action of inhibitors on stabilization and increase of adherence of corrosion products on coating matrix, with this being one mechanism of action of anodic inhibitors. For other systems (NO_x -LDH at 1.0% and 3.0%), a tendency of resistance values decreasing in the order control >1.0% >3.0% was observed. These results

FIGURE 18: Physical aspect of metallic surfaces coated using primer with and without NO_x -LDH during immersion time.

indicate that higher concentrations of LDH on primer may cause an increase in porosity, harming original barrier properties. In this case, the protective effect conferred by NO_x -LDH would be compromised or even canceled by the increase of electrolyte permeability, resulting on less effective protection than on the control medium. Another parameter employed to measure the influence of LDH addition on coating matrix was Y_0 (Q_{coat}) values. The increase of these values along time indicates progressive delamination of coating from the metallic surface [27]. Thus, a lower increment on Y_0 (Q_{coat}) values observed for coating containing 0.2% of NO_x -LDH indicates improvement on adhesion of primer on substrate in this case in comparison with other systems, where Y_0 (Q_{coat}) values suffered higher increments. These results indicate that LDH addition on primer was efficient only in the lower investigated concentration, which was capable of improving barrier properties conferring higher protection to metal. NO_x -LDH addition at 1.0% did not show significant differences in comparison with control system, whereas the 3.0% addition clearly made the coating more susceptible to electrolyte penetration, as since the beginning of exposure, this system showed quite lower values for total impedance.

Figure 18 shows images of the physical aspect of surfaces coated using primer with and without NO_x -LDH during immersion time. These images corroborate with EIS results, indicating the high corrosion inhibition capacity of the system containing 0.2% of NO_x -LDH in comparison with other systems. After 24 h of immersion, control, 1.0%, and 3.0% systems already showed corrosion product formation in significant amounts, whereas the 0.2% system remained intact. After 4 days of exposure, control, 1.0%, and 3.0% systems were completely recovered by corrosion products and the 0.2% system showed some isolated points of corrosion (moreover in low amount than other systems after only 24 h).

4. Conclusions

LDH containing two different corrosion inhibitors (benzotriazole and nitrogen oxides) were characterized, and their

ability to promote autonomic protection against corrosion was evaluated. Chemical analyses indicated that benzotriazole was not found as interlamellar ion in BTZ-LDH (therefore unavailable for ionic change) as it might adsorb to structural Zn. XRD results also confirmed that the identified interlamellar space would be incompatible to benzotriazole ion size. For NO_x -LDH, it was identified that nitrogen oxides were satisfactorily intercalated and available for ion change. Performance tests in extract form showed that BTZ-LDH did not show any significant protection in comparison with control system, not even at elevated concentration. For NO_x -LDH, a higher protection of metal in comparison with control system was observed and was proportional to the concentration of extract. In NO_x -LDH-incorporated organic coating, the existence of an optimum concentration of NO_x -LDH to enhance the protection against corrosion without impairing original barrier properties of coating was observed. The concentration, which better balanced the benefic action of NO_x -LDH with the deleterious effect of porosity increase of coating, was 0.2%.

It was concluded that NO_x -LDH comprised a good alternative as anticorrosive additive and self-healing action on corrosion protection. As complementary future studies, it is suggested to investigate optimal concentration around 0.2% (as 0.05%, 0.1%, and 0.15%, for example) of NO_x -LDH in the organic coating matrix, to optimize the minimum amount required to provide protection effects similar to what was observed at 0.2%.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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