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**Synergistic Barrier–Inhibitor Protection of Aluminum Alloy via Vanadate-Loaded
MgZnAl-LDH/Epoxy Coatings in Simulated Seawater**

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Abstract

Layered double hydroxides (LDHs) are efficient nanocontainers for corrosion protection achieved through the release of inhibitors and capturing aggressive ions, but they have limited efficiencies of active species loading using conventional methods. This work proposes a novel dual-step intercalation approach that includes co-precipitation, followed by ion exchange to maximize the amount of vanadate incorporated into ternary MgZnAl-LDH. The LDH prepared was functionalized using 3-aminopropyltriethoxysilane (APTES) to improve the compatibility with the epoxy matrix. Morphological, chemical, structural, and thermal characterizations were carried out using FESEM, EDS, FTIR, XRD, and TGA for LDH. The functionalized LDH was incorporated into epoxy at different loadings (1, 2, 3, 4 and 5 wt. %) and applied as a protective coating on AA2024 aluminum alloy to enhance corrosion resistance in 3.5 wt.% NaCl solution. The MgZnAl-vanadate LDH/epoxy coatings were completely characterized for hardness, adhesion,

contact angle, and surface morphology. Potentiodynamic polarization tests showed a significant enhancement in the corrosion resistance. The coating containing 2 wt.% LDH showed the best performance, with a protection efficiency of 99.97%, E_{corr} value of -0.521 V, and an extremely low i_{corr} of $1 \times 10^{-8} \text{ A}\cdot\text{cm}^{-2}$. The unique improvement in performance is related to the synergistic effect of enhanced inhibitor loading, controlled release and improved dispersion in the epoxy matrix.

Keywords: MgZnAl-LDH; vanadate incorporated; ion exchange; APTES functionalization; corrosion resistance.

1. Introduction

Aluminum and its alloys are considered essential industrial materials, particularly in the aerospace, automotive and marine sectors, due to their high strength-to-weight ratio and good resistance to damage. In practice, exposure to harsh environmental conditions will accelerate its deterioration and threaten its integrity, highlighting the urgent need for effective methods of corrosion protection [1]. The most widespread option for such protection is coating systems, which have been effective in reducing corrosion rates and preserving the material [2]. Due to their high adhesion and density, epoxy coatings are a cost-effective method of metal protection [3]. However, due to their application or curing process, organic coatings usually have pores and internal defects, which lead to higher permeability towards water and chloride ions [4].

The corrosion process initiates and propagates at the interface of the coating and substrate with the presence of chloride ions and water molecules if sufficient inhibitors are not

applied. In order to address this phenomenon, a variety of strategies have been developed specifically to inhibit the initiation and propagation of corrosion [5]. This was achieved using high-aspect-ratio 2D materials, including that of graphene, basalt and layered double hydroxide (LDH), which were integrated into the polymer, thereby strengthening it against water and chloride ion penetration [5].

An effective anti-corrosion coating must fulfill two essential functions: physical protection and active chemical repair [6]. LDH is a multifunctional 2D nanomaterial consisting of a main layer interspersed with anions and water molecules. LDH is characterized by its ease of synthesis and the availability of its raw materials; its surface contains numerous hydroxyl groups that promote interaction with organic resins, whilst the anions between the layers are bound to the main layer by an exchangeable electrostatic force, making it an ideal nanocontainer for anti-corrosion applications [7].

The LDH layers have unique properties of ion exchange that offer protection to the substrate through two ways: adsorbing adverse ions such as chloride and the creation of a barrier [8]. The spaces between the LDH layers offer protection by facilitating the ion exchange, which enables easier adsorption of corrosion inhibitors such as vanadates and molybdates and their subsequent release upon need, thus imparting self-healing properties and protection to the substrate. In case of any adverse ions, they get adsorbed in the spaces between the LDH layers. This leads to the release of inhibitor anions, which are also present in the spaces between the LDH layers and are released to the area where corrosion is occurring [5, 9].

Recent studies have evaluated the performance of LDH/epoxy systems, and thus smart epoxy coatings incorporating inhibitor-loaded LDHs have attracted increasing interest.

Yanning Chen and colleagues prepared vanadate-loaded, graphene oxide (GO)-doped ternary double-layered hydroxides (Mg–Al–La LDH). The outstanding catalytic performance of this coating is attributed to the controlled release of vanadate ions and the formation of the $\text{Mg}_4(\text{V}_2\text{O}_7)_2$ compound in the anodic regions. The system further shows a synergistic effect of La cations and vanadate anions, endowing the dual self-healing property [10]. Tatsiana Shulha et al. incorporated two types of inhibitors, vanadates and oxalates, into MgAl-LDH. The results showed that vanadate loading confers significantly higher efficiency on LDH in the active protection of magnesium compared to oxalate [11]. Mohammad Tabish et al. prepared 2-mercaptobenzothiazole (MBT) loading CaAl-LDH and subsequently added it to an epoxy coating in varying proportions, leading to self-healing ability and enhanced protection of the carbon steel [4]. Zuokai Wang et al. prepared an MgAl-LDH protective film on anodized 1060 aluminum through in-situ growth, which followed the treatment of stearic acid (SA) and thiourea (TU) to improve the corrosion resistance. The synergistic effect between TU and SA forms an effective LDH-TU-SA composite layer on the surface with high-density coverage, endowing the surface with efficient corrosion protection performance [12].

While double-layered hydroxides (LDHs) have been widely investigated as corrosion-protective films for metals, most of the available literature has concentrated on binary LDH systems with emphasis on MgAl-LDH and ZnAl-LDH. Ternary LDH systems, like MgZnAl-LDH, have drawn notably less interest in the scientific literature, and few studies describe their synthesis and use as protective coatings on aluminum substrates. A careful analysis of the existing literature shows that previous studies on MgZnAl-LDH ternary coatings have been limited and have mostly relied on in situ hydrothermal growth

processes. In contrast, the simpler, more adaptable, and scalable co-precipitation method for preparing MgZnAl-LDH ternary coatings for corrosion protection applications has rarely been explored. In addition to the synthesis approach, active corrosion protection using binary hydroxide systems has received more attention. Most studies using this approach have focused exclusively on binary LDH systems, and the use of inhibitor-loaded ternary MgZnAl-LDH as an active coating has not been explored. Additionally, although LDH particles incorporated into epoxy based coatings have been studied to improve barrier and active protection properties, the combination of (1) ternary hydroxide system MgZnAl-LDH, (2) a novel dual-step intercalation strategy of inhibitor ions, involving co-precipitation followed by ion-exchange loading with a corrosion-inhibiting anion (vanadate), and (3) deposition on an aluminum substrate for further assessment in a 3.5 wt. % NaCl solution similar to seawater-like environments has not been reported so far. This is a multi-layered research gap and forms the key motivation for this work, which aims to develop an innovative epoxy coating based on inhibitor-loaded ternary MgZnAl-LDH, capable of providing both passive barrier protection and active corrosion protection under simulated marine conditions.

2. Experimental

2.1. Materials

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (pro analysis, Scharlau, Spain, Art.1063), nitric acid (68%, AR grade), sodium metavanadate (NaVO_3 , 99.5%) (Sigma-Aldrich, Germany), sodium hydroxide (NaOH , analytical grade, Merck, Germany) and sodium chloride (NaCl , 99.9%, AR grade, RCI Labscan Limited, Thailand) were used

without additional purification. Epoxy resin (E44) and curing agent polyamide (Shandong Tianmao New Material Technology Co., China), n-butanol (Shanghai, China), Xylene (analytical grade, Sigma-Aldrich, Germany), deionized water, acetone (Thomas Baker, India), ethanol 99.9% (Thomas Baker, India), and AA2024-T3 aluminum alloy (Altek metal, Turkey) were purchased from the Iraqi local market. The AA2024-T3 aluminum alloy was used as the substrate. Its chemical composition was analyzed using a spectrometer type ARL3460 (USA), as shown in Table 1. Specimens with dimensions of 30 mm × 25 mm × 10 mm were prepared. The substrate surfaces were ground using silicon carbide paper in 800, 1000, 1200, 1500, and #2000 grades. The surfaces of substrates were degreased with acetone and ethanol and rinsed with deionized water. The samples were then etched for 2 min in 1 M NaOH and rinsed with deionized water. Specimens were then immersed in a 5% by volume nitric acid solution for 1 min to eliminate the alkaline residues and activate the specimen surface prior to LDH/EP coating deposition. Finally, all the samples were rinsed with deionized water before drying them with a hot air stream.

Table 1: Chemical Composition of the AA 2024-T3 aluminum alloy.

Element	Al	Cu	Mg	Mn	Si	Fe	Zn	Cr	Ti
Weight%	93.06	4.45	1.51	0.47	0.19	0.12	0.09	0.06	0.05

2.2. Synthesis of MgZnAl-LDH intercalated with vanadate

The vanadate ions were loaded between the MgZnAl-LDH layers in two stages. The first stage enabled the initial incorporation of vanadate into the LDH during co-precipitation, whereas the second stage was carried out to further increase the vanadate loading through ion exchange with the remaining exchangeable interlayer anions. In the first stage, the co-

precipitation method was used by dissolving the metal nitrates in an alkaline medium using 11.25 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 8.9 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 15.8 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 300 ml of deionized water with continuous stirring by a magnetic stirrer for 30 minutes. The molar ratio of the metal precursors (Mg:Zn:Al) was maintained at 2:1:1 ($\text{M}^{2+}/\text{M}^{3+} = 3:1$), as this ratio falls within the recommended $\text{M}^{2+}/\text{M}^{3+}$ range (2:1–4:1) for LDH synthesis, favoring the formation of pure LDH phases while minimizing the precipitation of secondary hydroxide phases [13, 14]. The 4 g of NaVO_3 was dissolved in 80 ml of deionized water and added dropwise to the metal nitrate solution for 15 min. The molar ratio of vanadate to the total metal cations ($\text{VO}_3^-/(\text{Mg} + \text{Zn} + \text{Al})$) was 0.27:1 corresponding to 0.0328 mol of vanadate (derived from 4.0 g of NaVO_3) and 0.1215 mol of total metal cations used for the LDH synthesis.

Then, pH was adjusted with 2M NaOH to 10 ± 0.2 and held at this value. After stirring for one hour at room temperature, a soft yellow gelatinous precipitate formed and was left at room temperature to age for 24 hours. The precipitate was collected by filtration and washed five times with deionized water. In each washing cycle, the precipitate was manually resuspended in deionized water for approximately 5 min, followed by filtration. This procedure was repeated until the filtrate reached approximately pH 7. It was then dried in an electric oven at 90°C for 8 hours, after which the powder was ground with a mortar and pestle to obtain a fine powder for use in the second stage. In the second stage, 10 g of as-prepared LDH powder was spread in 250 mL of a 0.1 M NaVO_3 solution. A solution-to-mass ratio of 250 mL per 10 g of LDH was chosen in order to fully disperse the LDH particles and provide an excess of vanadate ions to allow for efficient ion exchange. The pH was adjusted to 10 ± 0.2 using 2 M NaOH, and the suspension was

continuously stirred at room temperature for 24 h. This post-synthesis treatment was performed to promote ion exchange, thereby increasing the vanadate loading by replacing the remaining exchangeable interlayer anions. The resulting precipitate was washed according to the procedure described above until the filtrate reached approximately pH 7 and then dried at 90 °C for 8 h. This yielded MgZnAl-Vanadate-LDH powder, as shown in Fig. 1, which will be used later in the preparation of the coating. The MgZnAl-LDH intercalated with vanadate ions using the co-precipitation method was designated as LDH-V1, whereas the powder obtained after ion-exchange with vanadate solution was designated as LDH-V2.

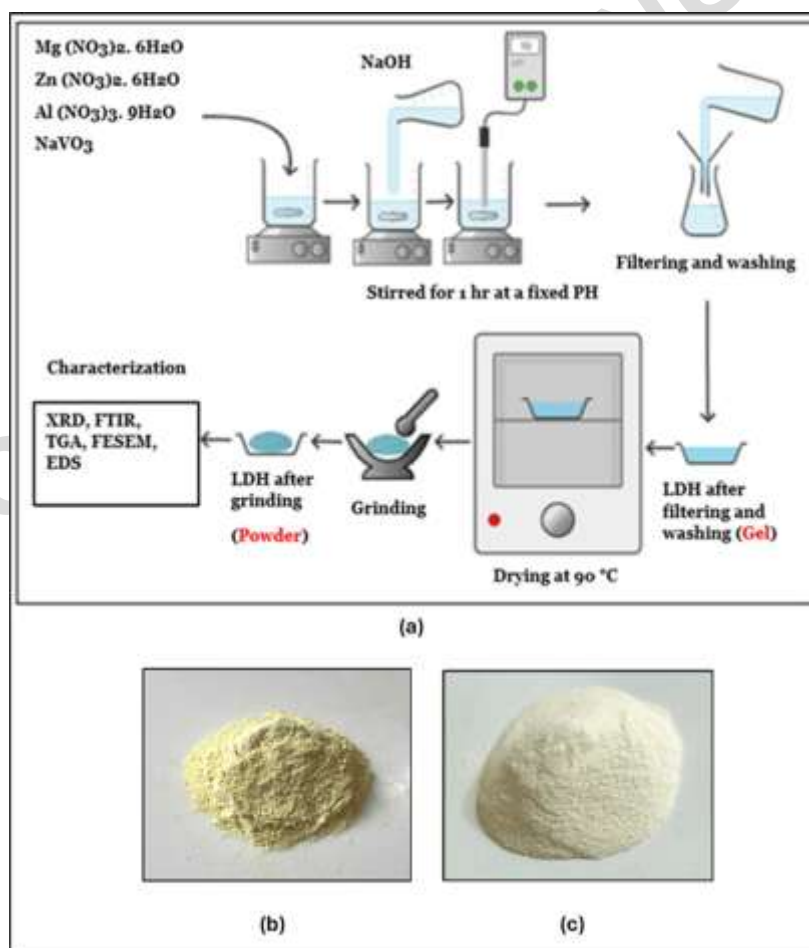


Figure 1: Co-precipitation method for preparing LDH: (a) schematic diagram showing the synthesis process of MgZnAl-vanadate LDH; (b) and (c) the appearance of the LDH-V1 and LDH-V2 powders, respectively.

2.3. Preparation of APTES-surface-modified LDH-vanadate

In order to improve the dispersion and compatibility of LDH-V with epoxy, the powder surface was first modified using 3-aminopropyltriethoxy silane (APTES). Two solutions were used for surface modification of the powder. The first solution was 150 ml of ethanol (99%) with 6 mL of deionized water. 40 g of LDH-V powder was gradually introduced into the solution with continuous stirring for 30 min. The second solution was 80 ml of ethanol with 3 mL of water. APTES is added in the amount of 1 g to this solution, and its pH is adjusted with acetic acid, where it remains at a stable value of pH = 5, followed by continuous stirring for one hour. This solution was subsequently added drop-wise to the first one while stirring and kept at pH 5. Stirring was continued for 24 hours in a closed container, after which the solution was filtered and washed three times with ethanol and a fourth time with deionized water to remove unreacted APTES. It was then dried in an electric oven at 80°C for 8 hours. The modified powder with APTES was designated as LDH-V-A.

2.4 Preparation of LDH-V-A/ Epoxy coating

The LDH-V-A powder was ground using a mortar and pestle and sieved to around a 53 μm particle size. A mixture of xylene and n-butanol was prepared (7:3 wt./wt.), which was applied to dissolve epoxy resin. For a homogeneous solution, 10 g epoxy resin and the solvent mixture (4.5 g) were mixed by magnetic stirring for 15 min. Subsequently, the select amount (1-5 wt.% to epoxy resin) of LDH powder was gradually added to the stirred resin solution. The suspension was then stirred for 15 minutes after the complete addition to achieve good dispersion homogeneity. Further, in order to break possible

agglomerates and enhance dispersion, the mixture was sonicated in an ultrasonic bath (60 kHz, 60 W) for 80 min divided into ten cycles of 8 min each. The suspension was magnetically stirred for 5 min between the sonication cycles to avoid temperature rise and increase dispersion efficiency. The system was then resumed to magnetic stirring after sonication, and the remaining epoxy resin was gradually added to modify the formulation before complete incorporation of every component. The resulting mixture was further stirred for 30 min to obtain complete homogenization. The total solvent content in the epoxy system was set to 15 wt.% of the epoxy resin (30 g epoxy resin, epoxy: hardener = 3:1). Subsequently, the mixture was continuously stirred for an additional 10 min after the addition of 10 g of curing agent to obtain the final coating formulation. As a last step, dip-coating was performed on the substrate using the prepared coating solution with an immersion/withdrawal rate of 6 mm/s and a dwell time of 30 s, followed by a drying process at room temperature for 72 hours and heat curing in an electric oven using two stages: 40°C for two hours and then held at 75°C for two hours. The average dry coating thickness (measured using a coating thickness gauge) was around $50 \pm 3 \mu\text{m}$.

2.5 Characterization methods

The surface morphology of the LDH-V-A/epoxy composite layers and the particle morphology of the LDH powder were analyzed by a field emission scanning electron microscope (Inspect F50, FEI, USA). The prepared powder was also characterized using energy-dispersive spectroscopy (EDS) (Thermo Fisher Scientific, USA) to determine its chemical composition. Both FTIR (IR Prestige-1800, Shimadzu, Japan) and

thermogravimetric analysis (TGA) (Perkin Elmer, USA) tests were used to investigate the functional groups and thermal stability of the powder, respectively. TGA was performed under the N₂ flow from 50 to 800°C at a heating rate of 10°C/min. In addition, X-ray diffraction patterns were collected to analyze the crystal structure of the samples using a diffractometer type Shimadzu (model: XRD-6000, Japan) using the Bragg–Brentano technique with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 15 mA, with a scan step of 0.02° and a scan rate of 1°/min, within a 2θ range of 5° to 80°. The X-ray diffraction data were processed using HighScore Plus software. The vanadium content of the vanadate-loaded MgZnAl-LDH (LDH-V2) was quantitatively determined using an X-ray fluorescence (XRF) spectrometer (Spectro/Ametek, XEPOS, Germany). The release of vanadate ions from the LDH powder was monitored using a UV–Vis spectrophotometer (UV-1800, Shimadzu, Japan) by measuring the absorbance at 260 nm [15]. For the release experiments, 0.05 g of LDH-V-A powder was immersed in 100 mL of 3.5 wt.% NaCl solution in sealed 100 mL amber glass bottles. The suspension was stirred for 10 min at room temperature and then allowed to stand until the predetermined immersion time. A separate bottle was used for each immersion period. After each immersion time, a 4 mL sample was withdrawn, filtered through a 0.45 μm syringe filter, and analyzed in a 10 mm quartz cuvette using a blank of a 3.5 wt.% NaCl solution. The vanadate ion released was quantified by making a calibration curve from standard solutions of sodium metavanadate (NaVO₃). For the coated samples, the coating thickness was determined using a MiniTest 3000 coating thickness gauge (ElektroPhysik, Germany) operating on the principle of electromagnetic induction.

Contact angle measurements were carried out using an optical tensiometer (Theta Lite,

model Tl100/Tl101, Biolin Scientific, Sweden). In order to evaluate the mechanical properties of the coating, a Shore D hardness tester (Model HS-D, Laryee Technology Co., Ltd., China) was used to determine the hardness of the coating material. The adhesion strength of the coatings was measured using a universal testing machine (Tinius Olsen H50KT, USA). For corrosion resistance, all samples were evaluated in an aqueous solution containing 3.5 wt.% of NaCl via dynamic polarization using a DY2321 dual-potentiometer (Digi-Ivy Inc., USA) with a conventional three-electrode cell, where a high-purity graphite plate served as the counter electrode (CE), the coated aluminum samples served as the working electrode (WE), and an Ag/AgCl electrode served as the reference electrode (RE). The corrosion rate, corrosion potential (E_{corr}), and corrosion current density (i_{corr}) were calculated using Tafel extrapolation of the dynamic electrochemical polarization curves. Electrochemical impedance spectroscopy (EIS) measurements were performed using a CorrTest electrochemical workstation (CorrTest, China) with a conventional three-electrode cell consisting of the coated sample as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a graphite rod as the counter electrode. The inhibitory efficiency ($\eta\%$) was calculated from Eq. 1 [16]:

$$\text{Protection efficiency (PE) } (\eta) = [(i_{\text{corr}} - i_{\text{corr}}^*) / i_{\text{corr}}] \times 100 \quad (1)$$

i_{corr}^* and i_{corr} are the corrosion current densities (A/cm^2) which were obtained for coated and uncoated substrates, respectively.

3. Results and Discussion

3.1. Characterization of LDH-V1, LDH-V2, and LDH-V-A

3.1.1. XRD

The powder X-ray diffraction patterns for LDH-V1, LDH-V2, and LDH-V-A in the 2θ range of 5° – 80° are shown in Fig. 2. The pristine LDH-V1 presents the expected features for layered double hydroxides-type compounds, namely, sharp and intense diffraction peaks at low angles that decrease in intensity with increasing 2θ . It can be seen from the figure that the main peaks appeared at $2\theta = 11.35^\circ$, 22.75° , and 34.65° , which agree well with JCPDS No. 014-0191 for (003), (006) and (009) crystal planes of the lamellar LDH-V1 structure, indicating that the LDH had been successfully synthesized, consistent with previous research by Abdel-Hady et al. [13]. Additional diffraction peaks at $2\theta = 38.65^\circ$, 45.35° , 60.35° , 61.4° , and 65.6° can be indexed to the (015), (018), (110), (113), and (116) planes, respectively, consistent with typical hydrotalcite reflections (JCPDS No. 014-0191 and No. 038-0486). After the ion-exchange intercalation of vanadate anions, the (003) diffraction peak of this structure moved toward a lower 2θ value ($2\theta = 11.15^\circ$), which indicated that vanadate ions were successfully introduced into the LDH interlayer space. This finding is further supported by XRF analysis, which showed a vanadium content of 7 wt% in the vanadate-intercalated LDH (LDH-V2). The corresponding interlayer spacings were calculated according to Bragg's equation, while the heights of the interlayer channels were measured after subtracting the layer thickness of 0.48 nm [17], as detailed in Table 2. The layered double hydroxide structure was kept in the XRD pattern of LDH-V-A with all characteristic peaks of the LDH-V structure. The grafting of silane also did not result in a change of interlayer spacing, implying that surface hydroxyl groups on the LDH reacted with the silane but without changing the lamellar framework [18].

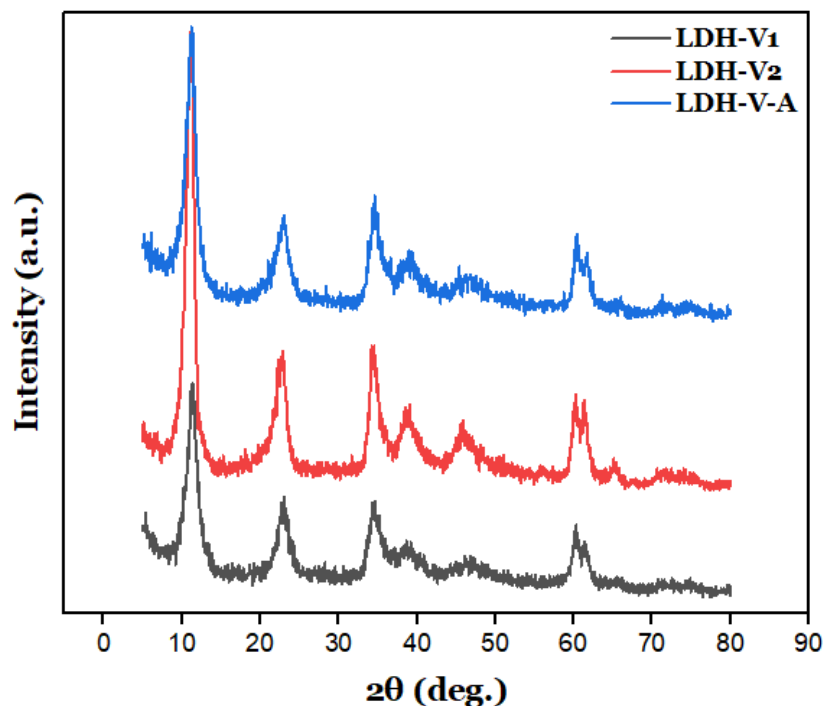


Figure 2: XRD spectra of LDH-V1, LDH-V2 and LDH-V-A powders.

Table 2: XRD analysis results for LDH-V1, LDH-V2, and LDH-V-A samples

Sample	2θ (°)	Interlayer distance (003)/nm	Gallery height (nm)
LDH-V1	11.35	0.77	0.29
LDH-V2	11.15	0.79	0.31
LDH-V-A	11.2	0.79	0.31

3.1.2. FTIR

As displayed in Figure 3, the FTIR spectra of LDH-V1, LDH-V2 and LDH-V-A powders show characteristic absorption bands that can be assigned to the vibrations of hydroxyl groups as well as intercalated anions. The strong and wide absorption band in the range of 3487-3562 cm^{-1} is attributed to the stretching vibrations of surface-adsorbed and interlayer water molecules, together with OH groups inside LDH layers [19]. The band at 3032 cm^{-1} is related to the hydrogen bond between water molecules and vibration from carbonate (CO_3^{2-}) ions [8]. The band observed at 1645 cm^{-1} can be assigned to the bending vibrations of water molecules [20], whereas the strong band at 1377 cm^{-1} is

related to asymmetric stretching vibrations of carbonate ions [21]. The band at 1487 cm^{-1} is related to the interaction of carbonate anions with hydroxyl groups situated in the octahedral sites of the cationic LDH layers [22]. On the other hand, the FTIR spectrum of LDH-V-A revealed significant differences compared with those of LDH-V1 and LDH-V2. The peak at 1556 cm^{-1} corresponds to the NH_2 scissoring vibration of APTES grafted on the surface, which suggests that surface functionalization was successfully achieved [18]. Moreover, the emergence of a new absorption band at 941 cm^{-1} is attributed to vanadate ions stretching vibrations, which confirms that the intercalation of vanadate ions has been successful. The bands recorded in the region of $500\text{--}800\text{ cm}^{-1}$ are assigned to the M–O and M–OH vibration modes characteristic of layered double hydroxides [17].

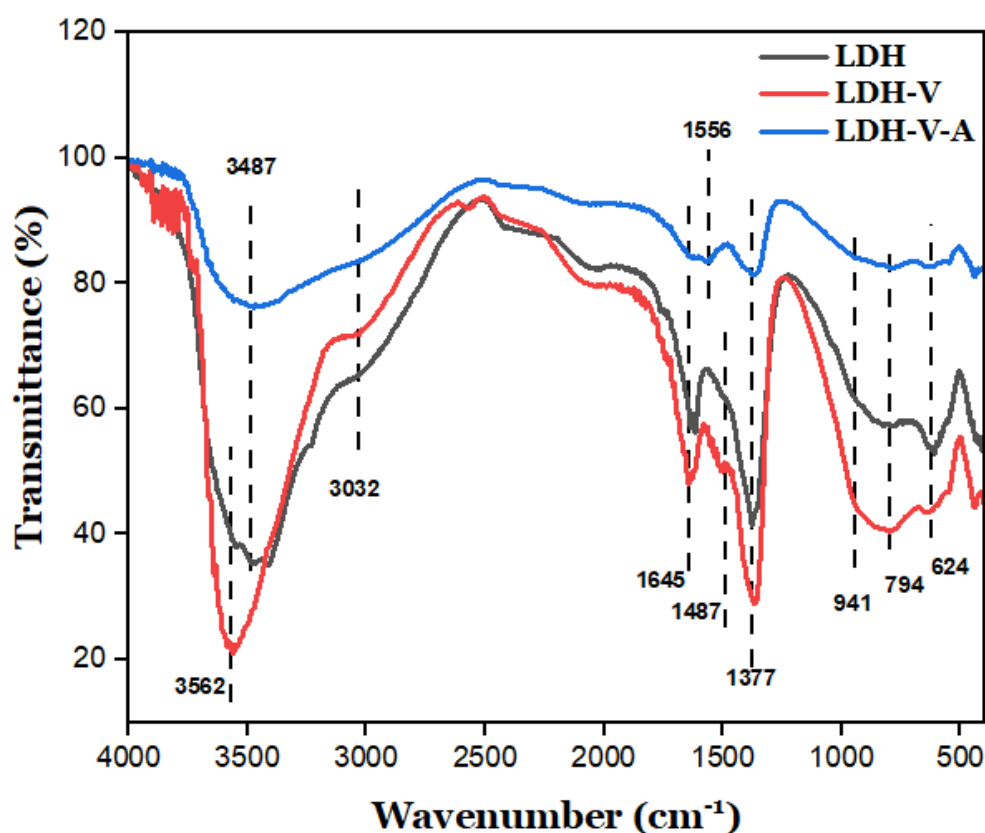


Figure 3: The FT-IR spectra of LDH-V1, LDH-V2 and LDH-V-A powders.

3.1.3. SEM and EDS

The morphology of the final vanadate-loaded LDH (LDH-V2) was examined by FESEM, whereas EDS analysis was performed for both the as-synthesized LDH (LDH-V1) and the final vanadate-loaded LDH (LDH-V2). The corresponding FESEM images and EDS spectra are presented in Figure 4. The FESEM images indicate an agglomerated structure of nanosheets, which is characteristic of the morphology observed in LDH synthesized by this method (co-precipitation), which has also been mentioned by Abdel-Hady et al. [14]. The LDH-V2 exhibits a characteristic plate-like morphology with a relatively rough surface, where the nanosheets are stacked in an ordered manner. EDS analysis confirms the elemental composition of the LDH-V. The spectra clearly showed the presence of the major LDH constituents (Mg, Zn and Al) along with vanadium. The synthesized LDH-V1 powder exhibited a vanadium content of 6.2%. The content of vanadium is increased up to 11.7% after the ion-exchange, indicating an extensive incorporation of vanadate species. The higher vanadium content determined by EDS compared with the XRF value (7 wt.% V) can be attributed to the localized and semiquantitative nature of EDS analysis, while XRF provides a bulk quantitative determination of total vanadium loading. The distinct vanadium peaks are evident as additional confirmation that the vanadate species have been successfully loading within this LDH framework.

3.1.4. Thermogravimetric analysis (TGA)

The prepared LDH powders were characterized in terms of their thermal decomposition behavior using thermogravimetric analysis (TGA), as presented in Figure 5. Two samples were studied: the LDH-V2 and LDH-V-A. TGA revealed two main stages of mass loss.

The first stage, occurring in the temperature range of 50–250°C, corresponds to the removal of physically adsorbed and interlayer water [23]. The second stage, extending from 250 to 650°C, corresponds to the decomposition of hydroxyl groups of the host layers and the intercalated anions [24]. In these stages, the DTG peaks correspond to the maximum rates of mass loss during thermal decomposition. The differences in the DTG peak intensities between LDH-V2 and LDH-V-A reflect differences in their decomposition rates. Consistent with the TGA results, LDH-V-A exhibited a lower total mass loss than LDH-V2. This suggests that, in addition to the removal of physically adsorbed/interlayer water and hydroxyl groups, part of the observed mass loss may be attributed to the thermal degradation of the APTES grafted onto the LDH surface [25]. The mass losses of the LDH-V2 and the LDH-V-A at the first stage were around 14% and 13%, respectively, while in the second stage, they reached approximately 24% and 22%, leading to total mass losses of about 38% and 35%, respectively. These results show that the thermal stability of LDH-V2 was improved after surface functionalization with APTES (LDH-V-A). The weight becomes constant at 650°C, indicating the formation of thermally stable mixed metal oxides due to the complete collapse of the LDH layered structure.

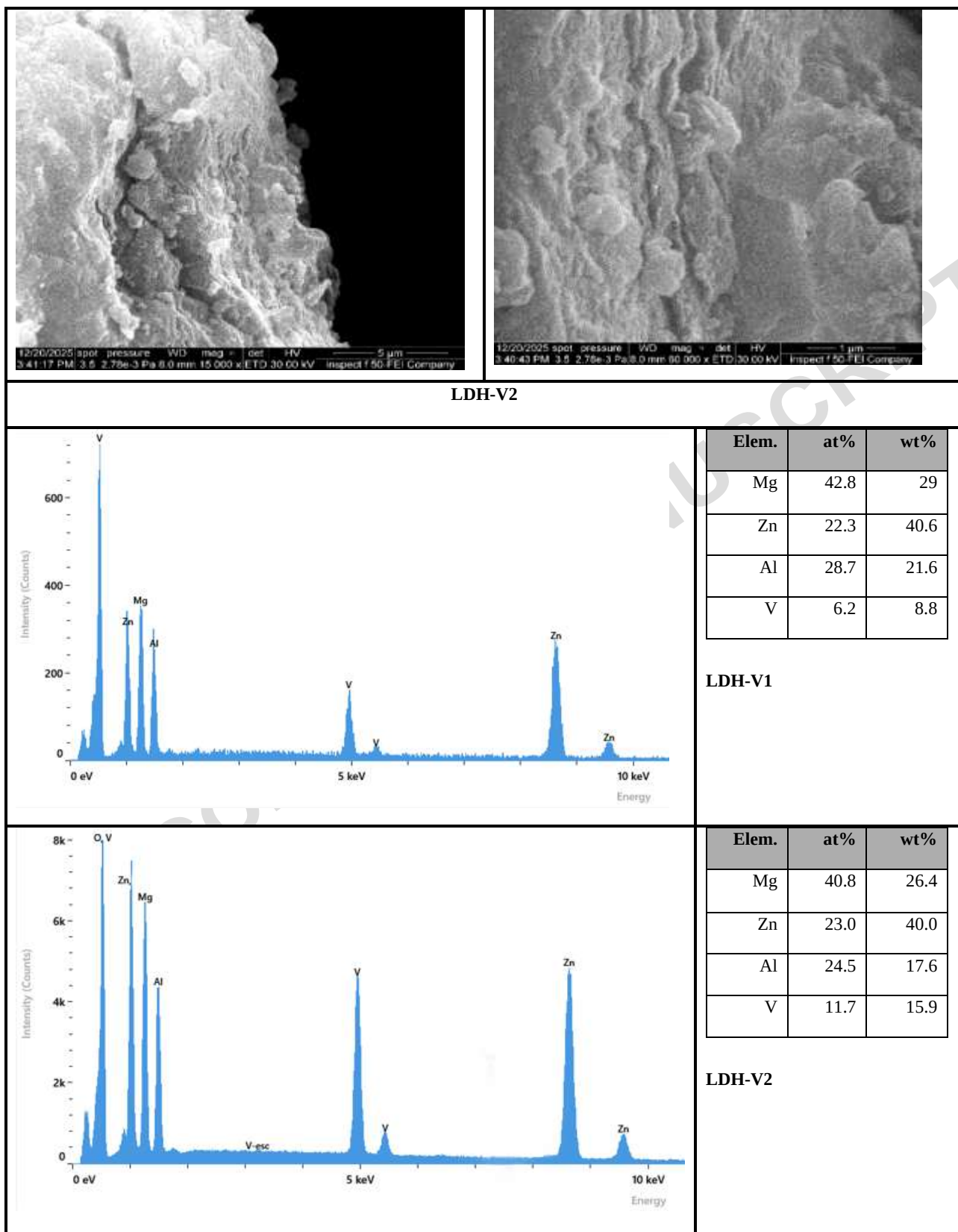
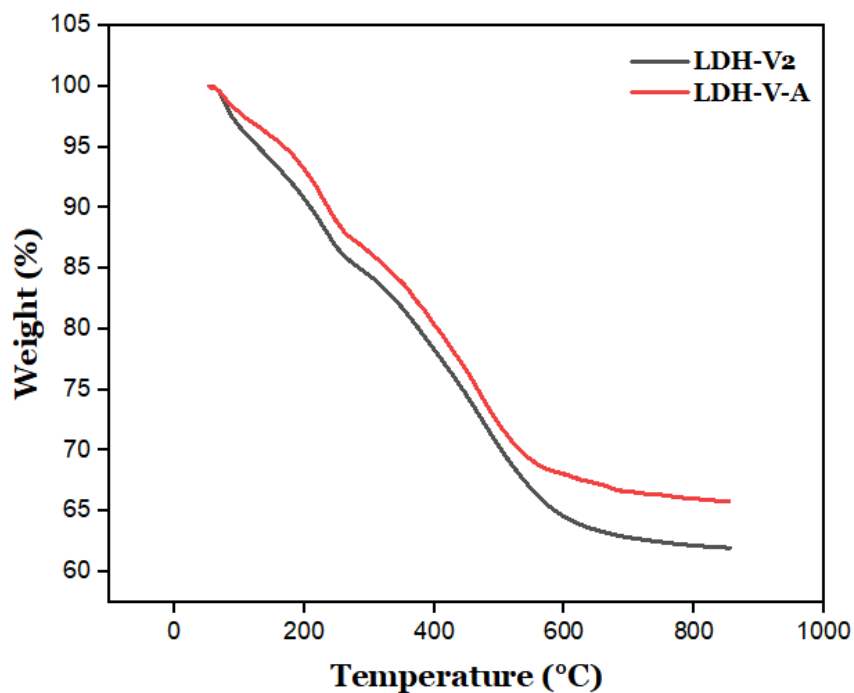
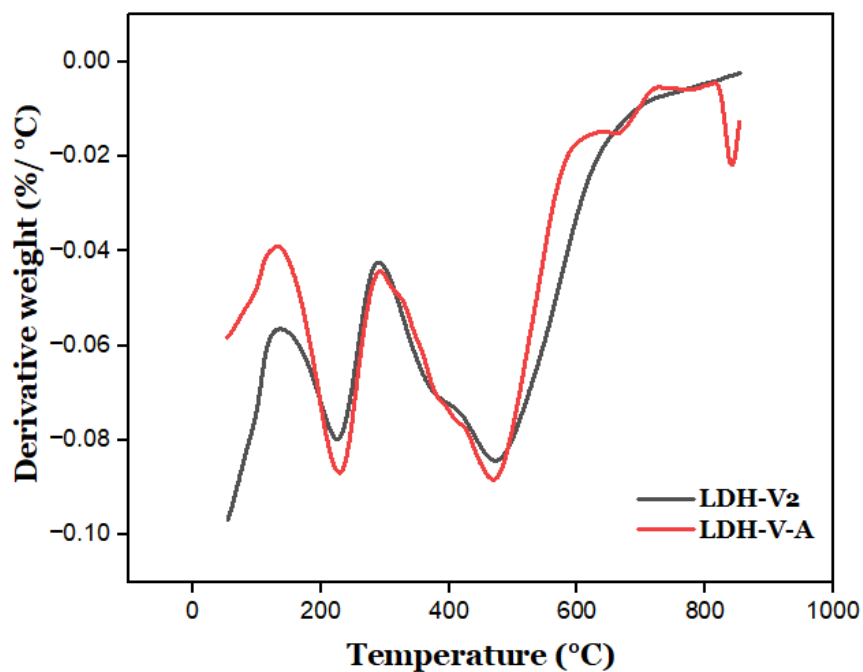


Figure 4: FESEM images of LDH-V2 and corresponding EDS graph of the LDH-V1 and LDH-V2 powders.



(a)



(b)

Figure 5: (a) TGA curves and (b) DTG curves of LDH-V2 and LDH-V-A powders.

3.2. Vanadate ion release behavior

A calibration curve was constructed from standard vanadate solutions analyzed under the same experimental conditions to quantify the release of vanadate ions from the LDH-V-A nanocontainers. A linear calibration equation, $A = 0.01027C + 0.00936$, was obtained, with a correlation coefficient ($R^2 = 0.995$). The calibration curve was linear in the range of concentration 1-25 ppm and all the vanadate release concentrations measured were within this validated range. This equation was used to determine the concentration of vanadate ions released into the 3.5 wt.% NaCl solution. All measurements were performed in duplicate. Figure 6 shows the release profile of vanadate ions from LDH-V-A in 3.5 wt.% NaCl solution. A relatively rapid release was observed in the first 24 hours of immersion. The concentration of vanadate rose from about 12 ppm after 3 hours to 18.75 ppm after 24 hours. The release rate subsequently decreased gradually, and the concentration of released vanadate ions reached 24.4 ppm after 336 h, confirming a sustained and controlled release behavior. The initial rapid release is attributed to the ion exchange between chloride ions and easily accessible vanadate species located on the external surface and at the edge sites of the LDH particles. The second release stage is controlled by the diffusion of the intercalated vanadate species, along with the continued chloride/vanadate anion exchange within the interlayers of the LDH particles [26]. Moreover, the APTES surface modification is expected to retard ion diffusion, thereby suppressing rapid leaching and promoting sustained inhibitor release. The gradual release of vanadate ions during the immersion period leads to the conclusion that LDH-V-A is a stable source of delivery of corrosion inhibitor, which enables the vanadate ions to be present throughout the immersion period.

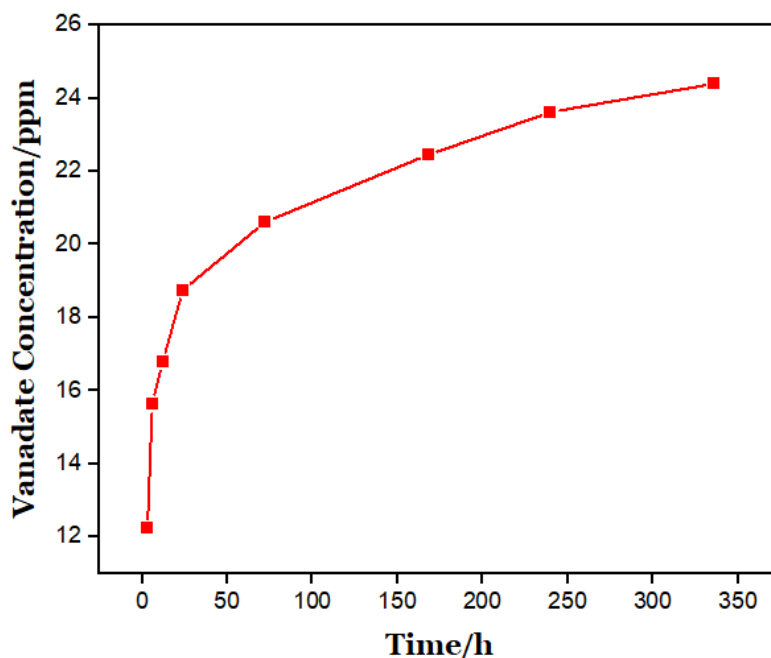
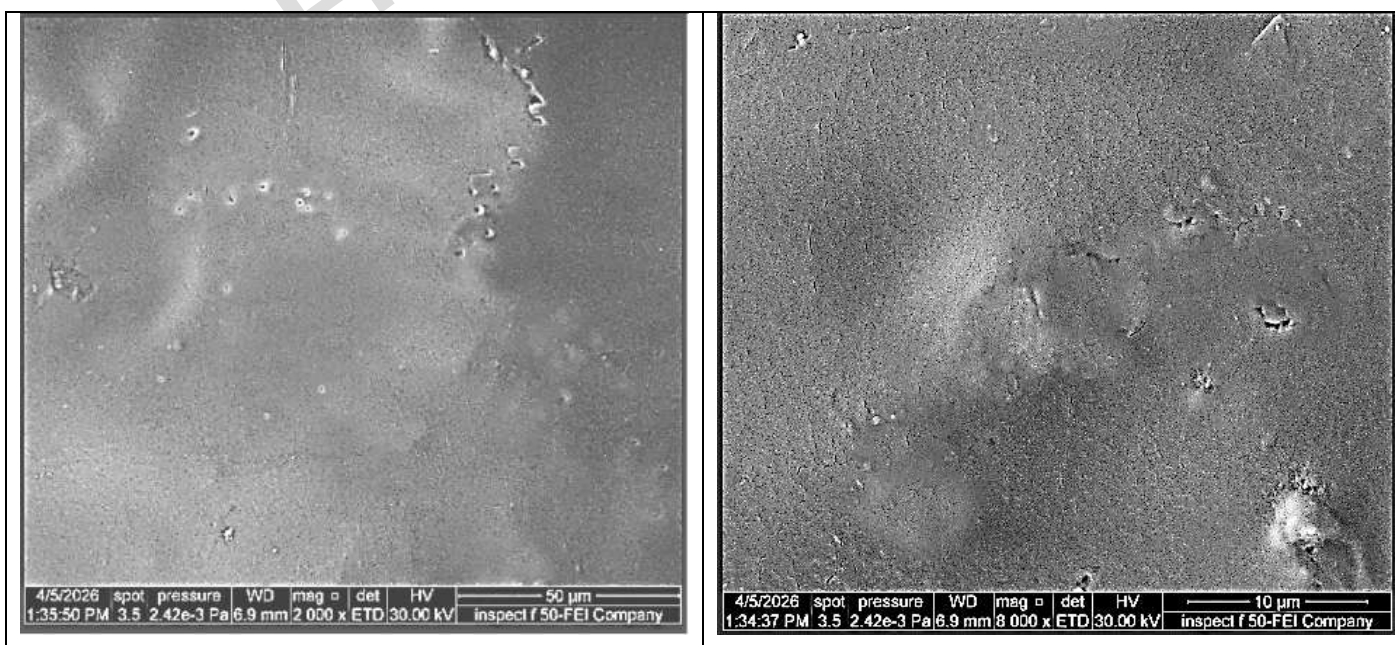


Figure 6: Time-dependent release profile of vanadate ions from LDH-V-A in 3.5 wt.% NaCl solution.

3.3. Morphological characterization of coatings and its correlation with corrosion resistance

The surface morphology of the pure epoxy and epoxy with 2 wt.% LDH-V-A (optimal ratio) was observed using FESEM analysis, as shown in Fig. 7. The neat epoxy coating exhibited a relatively smooth appearance but was found to contain several microdefects such as microcracks and localized voids. These imperfections are generally explained by solvent evaporation, curing shrinkage and developing internal stress that can lead to coating failure, as well as atmospheric and climatic species penetration. The surface structure of epoxy coating containing well-dispersed layered double hydroxides (LDH) was notably improved. The introduction of LDH-V-A gave rise to a denser and more uniform morphology with significantly reduced surface defects. These well-dispersed LDH platelets appropriately filled in the microvoids and restrained crack propagation for

improved barrier properties. Another specimen of the same composition (2 wt.% LDH-V-A) was analyzed by EDS elemental mapping to confirm the incorporation and distribution of the LDH-V-A filler as shown in Figure 8. Elemental maps verified the uniform distribution of the elements Mg, Al, Zn and V in the epoxy matrix. The existence of vanadium indicates that the vanadate was successfully intercalated into LDH structure, and the uniform distribution of the elements indicates good dispersion of the LDH-V-A particles in the epoxy coating. These results are in accordance with the results obtained from SEM and confirm that the filler is uniformly distributed throughout the epoxy matrix. The increased compactness, lower density of defects and better interfacial integrity led to superior barrier properties able to restrict penetration of the corrosive species. As a result, this significantly improves the corrosion resistance of the coated aluminum base [24, 27]. In conclusion, the epoxy/LDH-V-A composite coating had better surface quality, fewer defects formed and improved structural performance compared with the neat epoxy coating.



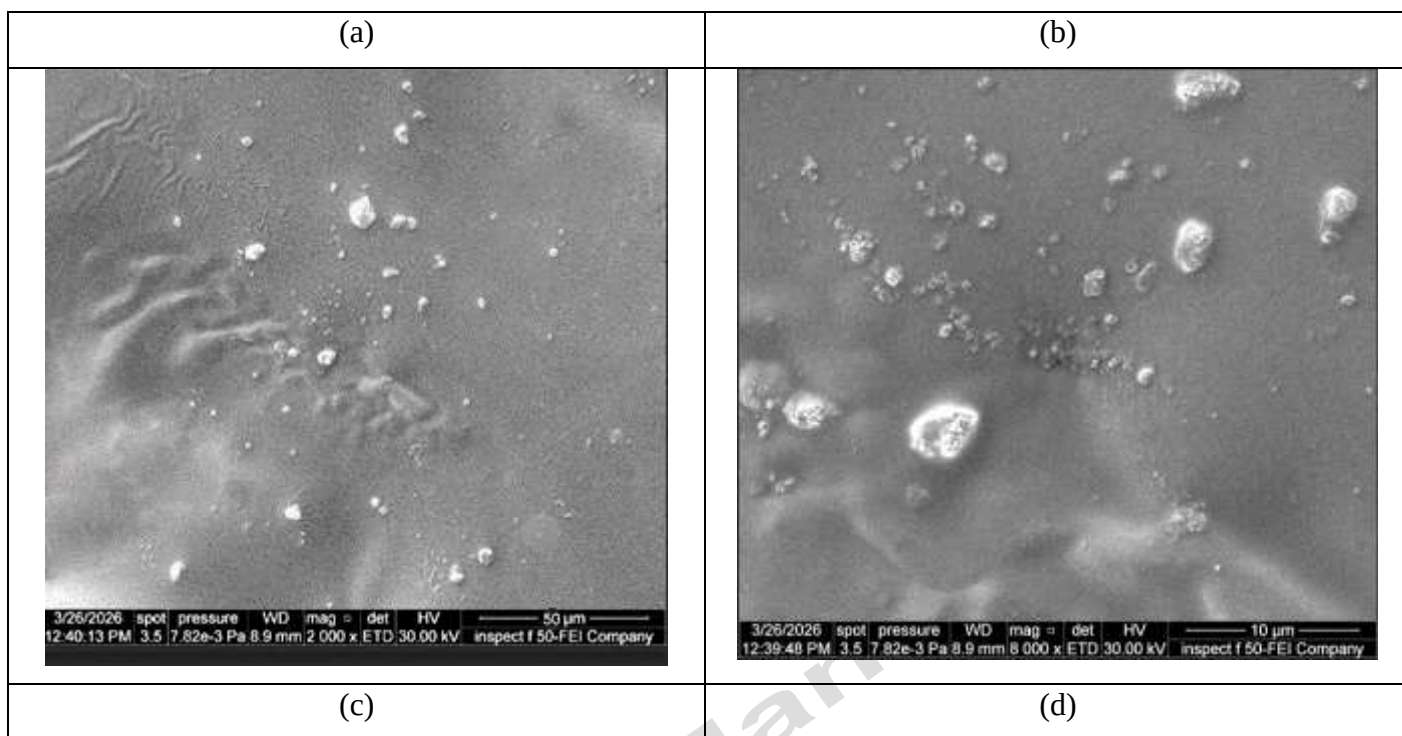


Figure 7: FESEM images showing the surface morphology of epoxy (a, b) and 2wt.%LDH-V-A/epoxy (c, d) coatings.

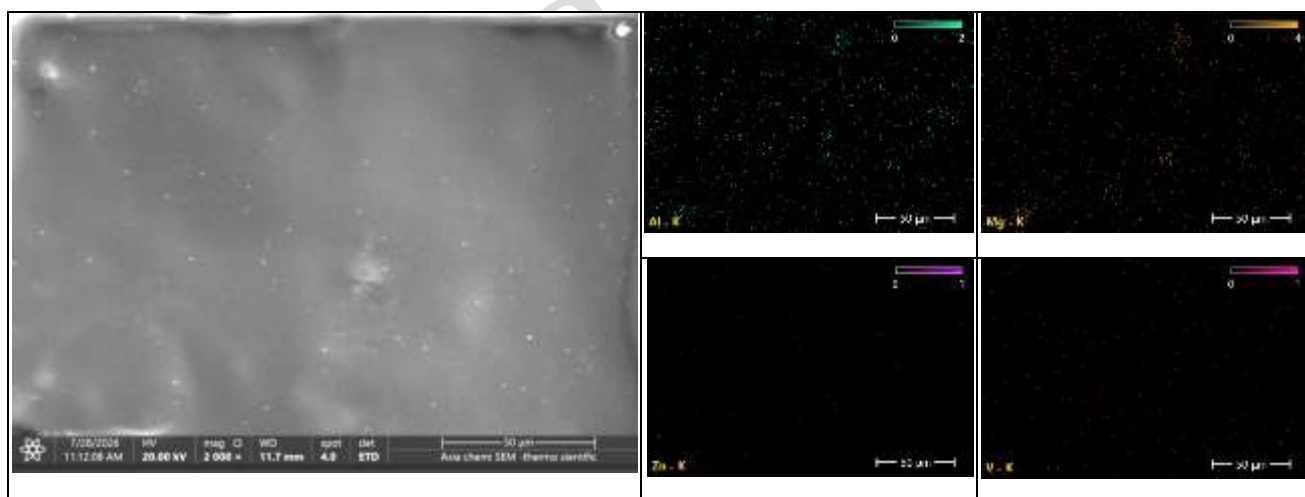


Figure 8: SEM image and corresponding EDS elemental mapping of the epoxy coating containing 2 wt.% LDH-V-A, showing the homogeneous distribution of Mg, Zn, Al, and V throughout the epoxy matrix.

3.4. Surface topography and roughness analysis

AFM analysis was conducted to study the effect of the incorporation of LDH on the

topography of the epoxy coatings. The three-dimensional AFM images provide qualitative information about the surface morphology, whereas the roughness parameters (S_a , S_q , and S_y) quantitatively describe the changes in surface topography. The AFM images and the roughness values are shown in Figure 9 and in Table 3, respectively. The neat epoxy showed a smooth surface compared with the other LDH/epoxy coatings. The surface roughness was slightly increased by the addition of 2 wt.% LDH-V-A, suggesting that the surface topography was altered due to the incorporation of nanoscale surface irregularities introduced by the LDH nanosheets. An additional 5 wt.% LDH-V-A led to a larger increase in the roughness parameters. This behavior indicates a more heterogeneous surface topography at higher loading of LDH, which causes larger variations in surface height observed in AFM images. Overall, the AFM results show that the surface topography and roughness of the epoxy coating were progressively changed as the LDH content increased. However, surface roughness alone does not determine the corrosion protection efficiency. The barrier performance is governed by nanoparticle dispersion, coating compactness, and the ability of LDH particles to enhance the tortuous diffusion path against corrosive species [28]. The AFM results are therefore discussed together with the FESEM morphology and electrochemical results to illustrate how the coating structure is related to corrosion resistance.

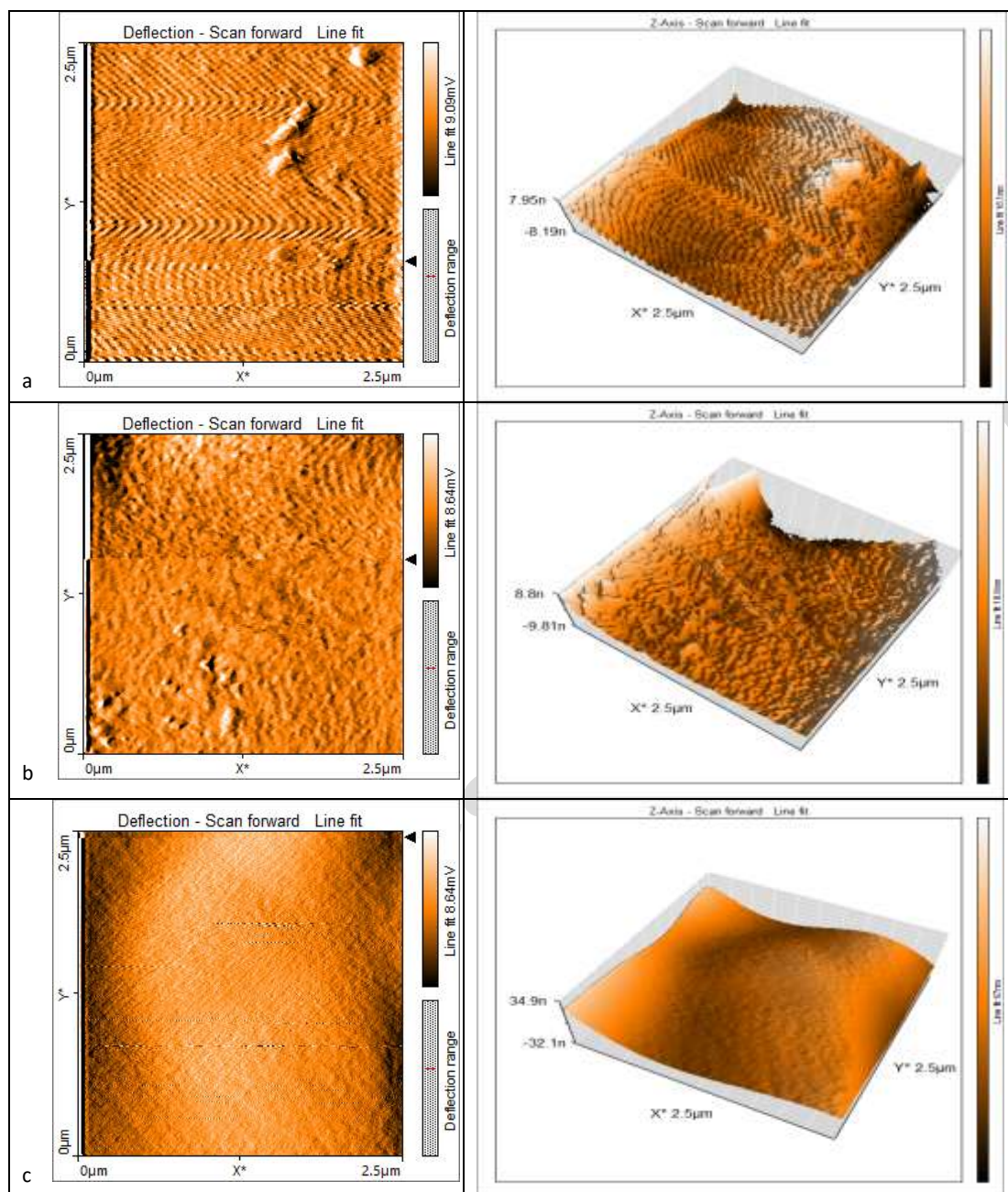


Figure 9: Three-dimensional AFM images of (a) Epoxy, (b) 2 wt.% LDH-V-A/ Epoxy, and (c) 5 wt.% LDH-V-A/ Epoxy.

Table 3. Surface roughness parameters obtained from AFM analysis

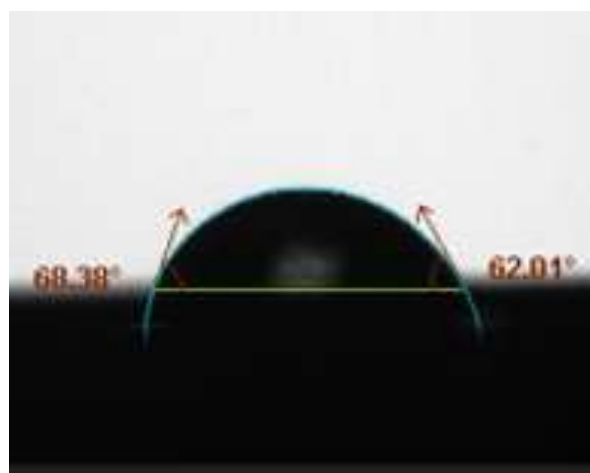
Sample	Sa (nm)	Sq (nm)	Sy (nm)
Epoxy	2.248	2.965	31.988
2 % LDH-V-A/ EP	2.826	4.597	62.513
5 % LDH-V-A/ EP	5.19 ^Y	6.260	41.941

3.5. Contact angle result

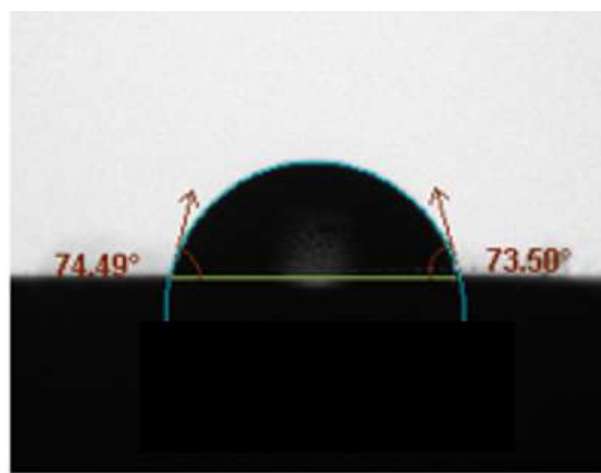
To study the impact of LDH-V-A incorporation on the coating hydrophobicity, the water contact angle was measured. Water contact angle is an important parameter for water interaction with a surface. A surface that exhibits a larger contact angle is hydrophobic, while a surface that exhibits smaller contact angles is hydrophilic; this, in turn, increases the ability of water to spread on the surface, thereby increasing its susceptibility to corrosion. By determining the contact angle on a coating's surface, it is possible to predict which coatings will provide better protection in corrosive environments [29]. According to experimental results, the bare Al alloy exhibited a contact angle of 65.1°, which increased to 74° with the epoxy coating. The addition of LDH-V-A further enhanced the contact angle, reaching a maximum of 79.7° at 2 wt.% LDH-V-A, after which it declined with higher loadings, dropping to 69° at 5 wt.% LDH-V-A, as presented in Table 4 and Figure 10. This improvement is attributed, according to Wenzel's theory, to the better dispersion of LDH sheets, the consequent reduction of surface energy, and the creation of micro-nano surface roughness [30]. Beyond an optimal LDH content, the tendency of the sheets to aggregate limits their dispersion, leading to a decline in hydrophobicity with further increases in LDH loading [31].

Table 4: The Contact Angle Results for Bare Al Alloy and Prepared Coatings.

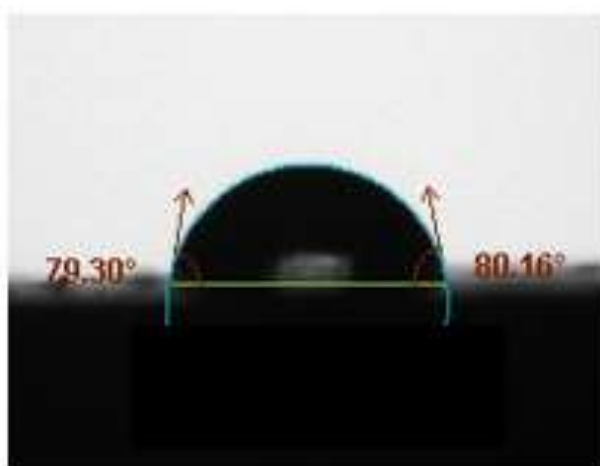
Sample	Al	Ep/Al	Ep/ with varying wt% LDH-V-A				
			1%	2%	3%	4%	5%
Contact angle (°)	65.1	74	74.7	79.7	78	77.1	69



a- Al alloy



b- EP/Al



c- 2wt% LDH-V-A/EP

Figure 10: Contact angle of the water droplet on bare Al alloy (a), epoxy coated (b), and 2 wt.% LDH-V-A / epoxy coated (c) surfaces.

3.6. Hardness

Shore D hardness was measured using a durometer (model HS-D, China) following ASTM D2240. Neat epoxy and LDH-V-A modified epoxy systems (both prepared in the disc shape, 10 mm in height and 32 mm in diameter) were prepared. The hardness of each sample was measured at five different locations after 14 days of curing, and the results are presented as mean $\pm$ SD ($n = 5$). The pure epoxy showed a Shore D hardness value of 62 ± 0.27 , which increased to 65.8 ± 0.46 after loading with 1 wt.% LDH-V-A,

suggesting an initial improvement of hardness. Nevertheless, with the increase in LDH content, hardness gradually decreased and reached its lowest value at 5 wt.% LDH-V-A loading, as shown in Figure 11. At low loadings of LDH-V-A, only effective mechanical interlocks between polymer chains are formed, and the mobility of chains decreases, which improves filler–matrix interfacial adhesion and increases hardness. The presence of the silane coupling agent (APTES) further assists with chemical bridging between LDHs and the epoxy matrix, leading to uniform dispersion [25, 32]. At 5 wt.% LDH-V-A loading, the reduction in hardness may be attributed to partial particle agglomeration resulting from less homogeneous dispersion within the epoxy matrix. The FESEM micrographs and the elemental mapping of the particles (Figure 12) confirm this interpretation, showing particle clusters associated with the enrichment of the constituents of the LDH, namely Mg, Al, Zn and V, which suggests a less homogeneous distribution of the LDH constituents. Moreover, the AFM analysis (Figure 9 and Table 3) indicates that the surface roughness increases with the addition of 5 wt.% LDH-V-A, consistent with the less homogeneous distribution of the filler seen in the FESEM and EDS analyses. These observations show that particle agglomeration adversely affects the interfacial interaction between the filler and the matrix, thus reducing the stress-transfer efficiency, as reflected by the decrease in hardness [25, 32].

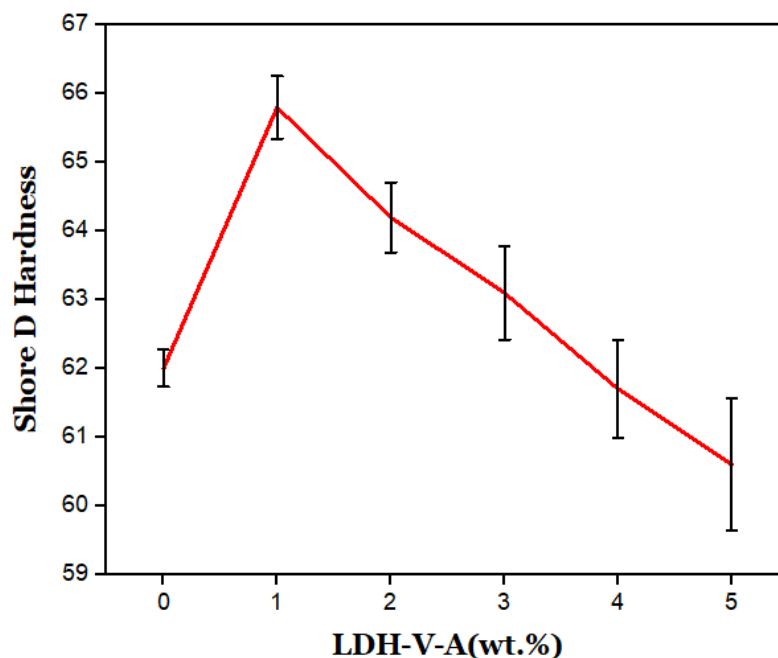


Figure 11: Effect of LDH-V-A content (wt.%) on the Shore D hardness of epoxy coatings. Data are presented as mean $\pm$ SD. Error bars represent the standard deviation.

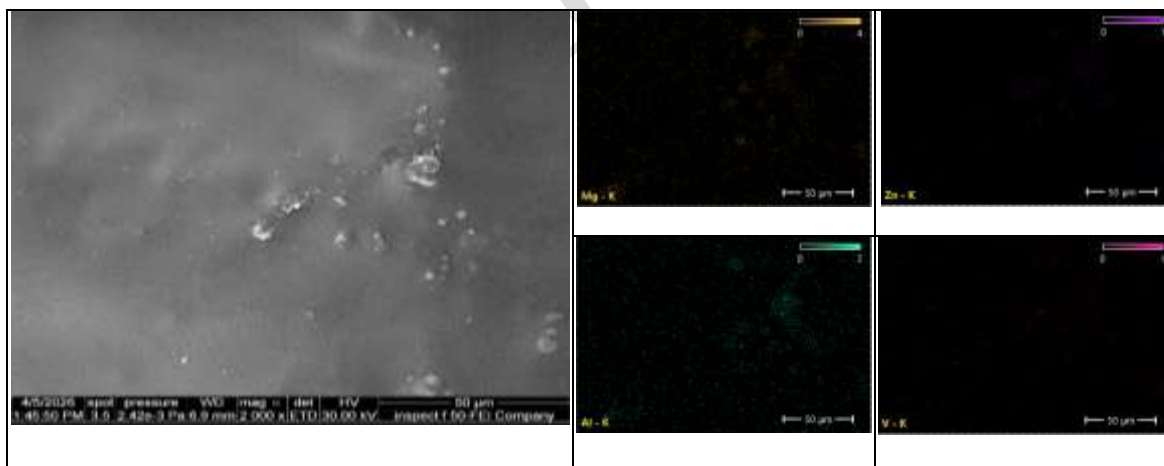


Figure 12: FESEM micrograph and corresponding EDS elemental mapping (Mg, Al, Zn, and V) of the epoxy coating containing 5 wt.% LDH-V-A.

3.7. Pull off result

ASTM D4541 was used for measuring the pull-off adhesion strength. Steel dollies, 10 mm in diameter, were glued onto the coated substrates using a two-component adhesive

that cured at room temperature for 7 days. Specimens were then pull-off tested in a universal testing machine by applying a tensile load at a 1 mm/min crosshead speed until failure [33]. For each coating formulation, the pull-off adhesion test was repeated three times using separate specimens, and the results are presented as the mean $\pm$ standard deviation (SD) of three measurements ($n = 3$). The method indicates the highest adhesive state of the coating until it splits off. The adhesion strength of the pristine epoxy and 2 wt.% LDH-V-A was measured to be 4.7 ± 0.23 MPa and up to 9.2 ± 0.47 MPa, respectively, revealing that this filler amount represents the optimal ratio of LDH. But then going up to 5 wt. % LDH-V-A decreased it to 4.5 ± 0.44 MPa. As depicted in Fig. 13, adhesion strength initially improves with increasing LDH content, reaching a maximum at 2 wt.%, before deteriorating at higher loadings, and it falls below the epoxy's adhesion strength. At low loading, the partially exfoliated LDH presented good dispersion and strong interfacial interaction with the epoxy, thus allowing very effective stress transfer and improved adhesion, while high loadings resulted in agglomeration and lower performance [34]. The LDH framework is rich in hydroxyl groups on the outer surface and on edge planes, which bond favorably with epoxy functional groups to improve coating adhesion on the metallic substrate. Moreover, APTES works as a successful coupling agent that links LDH and the epoxy matrix, thus enhancing the interfacial compatibility [24].

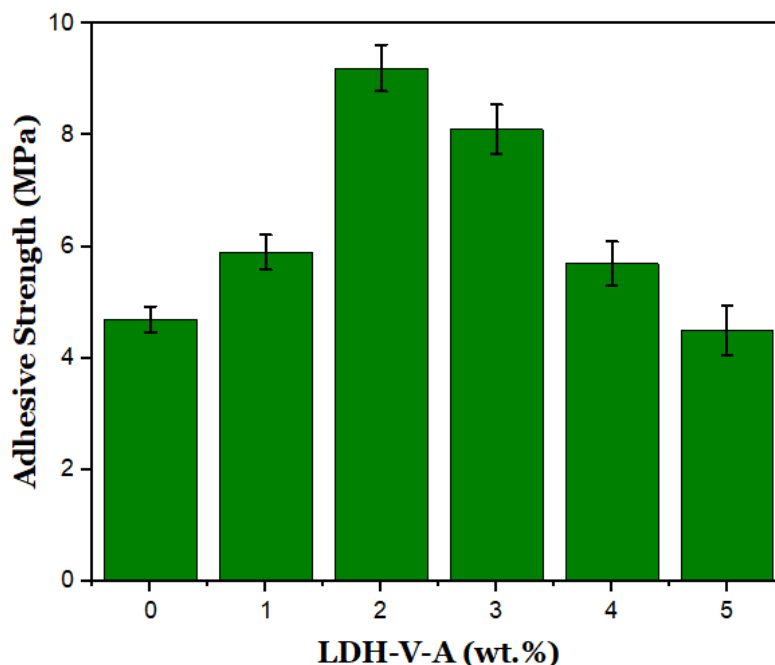


Figure 13: Effect of LDH-V-A content (wt.%) on the pull-off adhesion strength of neat epoxy and LDH-V-A/epoxy coatings. Data are presented as mean $\pm$ SD. Error bars represent the standard deviation.

3.8. Effect of salt solution immersion on corrosion resistance

Different methods were adopted to study the anticorrosion properties of the final epoxy coatings. Bare epoxy and 2 wt.% LDH-V-A/epoxy samples were sliced into an X-shaped pattern and soaked in a 3.5% NaCl aqueous solution for a period of 10 days, as illustrated in Fig. 14. Pure epoxy coatings showed extreme corrosion in scratched areas and beneath the coating after 10 days. In comparison, the 2 wt.% LDH-V-A/epoxy coating exhibited better barrier performance and a significant reduction in corrosion. Corrosive species can diffuse through the epoxy matrix and cause electrochemical corrosion and pitting of the substrate. The LDH-V-A particles alleviate this problem by two complementary mechanisms: first, the platelike nanoparticles serve as a passive barrier that restricts the migration of aggressive ions [24]; second, they protect the

substrate actively through anion exchange and release of inhibitor anions (vanadate ions) from interlayer spaces that reduce the concentrations of corrosive ions in solution and trap aggressive chloride ions [4, 20]. To further investigate the self-healing behavior, the scratched region of the 2 wt.% LDH-V-A/epoxy coating was examined by FESEM and EDS after 10 days of immersion, as shown in Figure 15. Deposition products were observed along the scratch and partially filled the damaged region. EDS analysis performed directly on these deposits confirmed the presence of vanadium, indicating that the released vanadate species migrated from the LDH particles toward the damaged area. The deposits containing vanadium accumulated in the scratch indicate that the inhibitor released was involved in the development of a protective layer on the exposed substrate, thus reducing further corrosion.

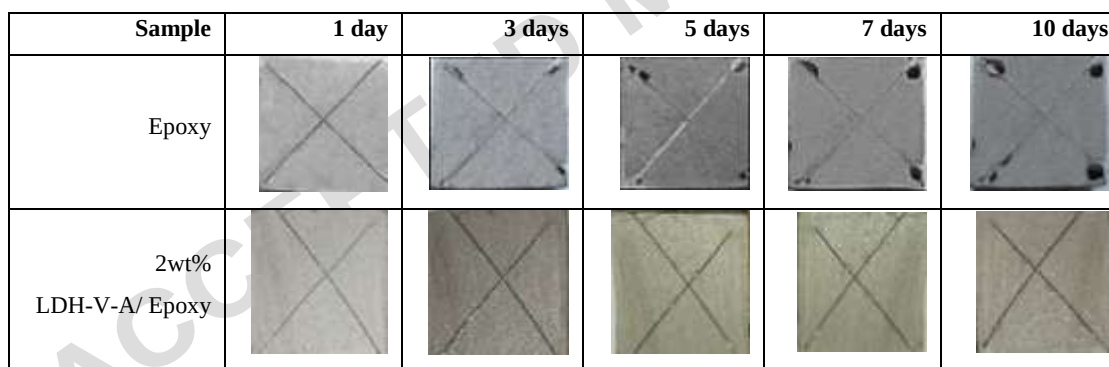


Figure 14: Epoxy vs. 2wt%LDH-V-A/Epoxy coating surfaces after 1–10 days immersion in 3.5wt.% NaCl

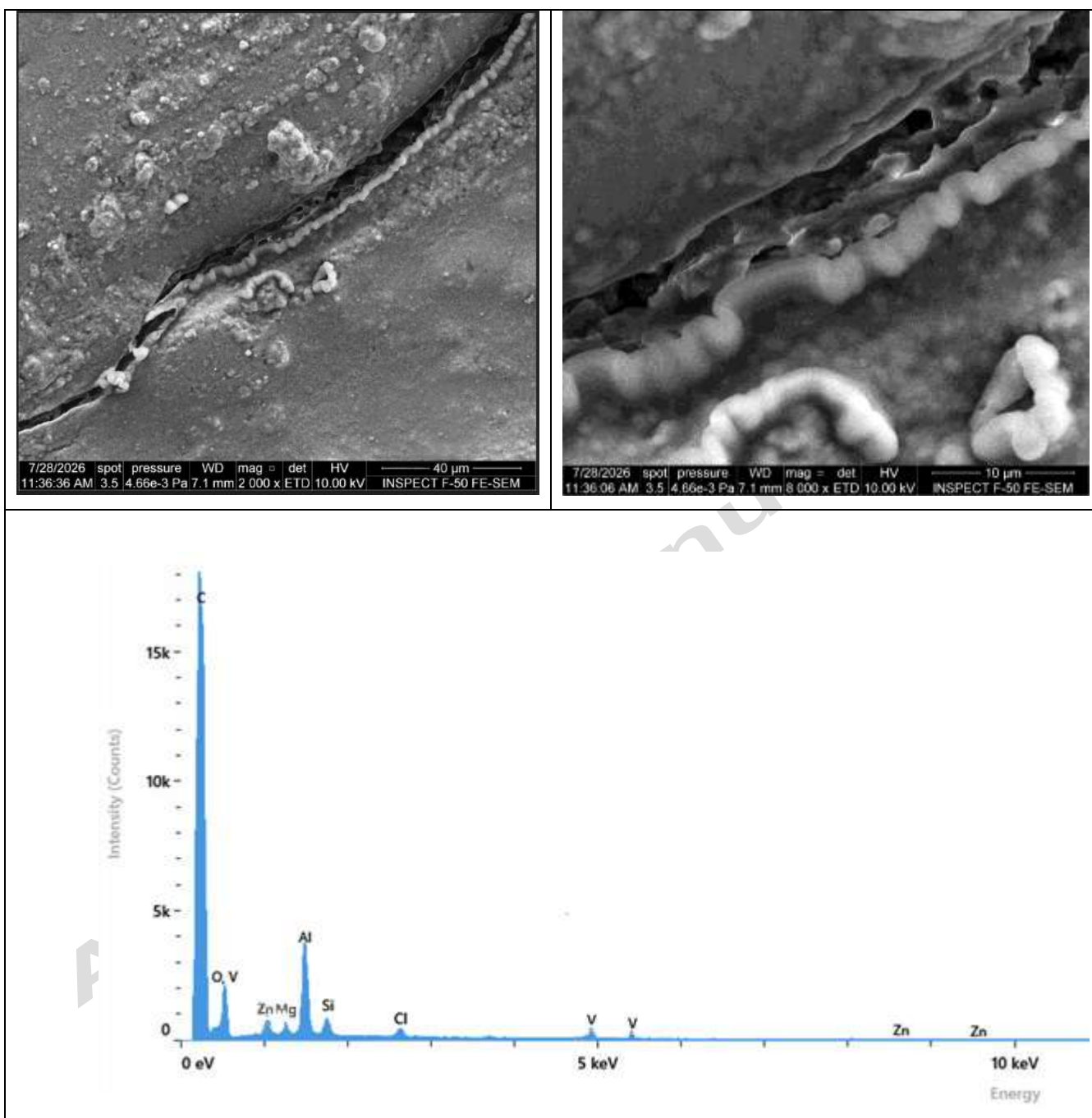


Figure 15: FESEM images of the scratched region and the corresponding EDS spectrum after 10 days of immersion in 3.5 wt.% NaCl solution for the 2 wt.% LDH-V-A/epoxy coating.

3.9. The potentiodynamic polarization test

To investigate the corrosion protection properties, the polarization performance of epoxy and composite coatings was scanned from cathodic to anodic regions. Potentiodynamic polarization properties, including corrosion current density (i_{corr}), corrosion potential (E_{corr}) and corrosion rate, can be calculated using the Tafel extrapolation method. To increase the protection against corrosion, I_{corr} should decrease, and E_{corr} should be shifted to a more positive region [16]. Hence, the corrosion resistance of epoxy and LDH-V-A/epoxy coated samples was tested by potentiodynamic polarization after soaking for 1 hour and 30 days in a 3.5 wt.% NaCl solution. All potentiodynamic polarization measurements were performed in triplicate using independently prepared specimens ($n = 3$), and the results are presented as mean $\pm$ standard deviation (SD). The Tafel plots, along with the electrochemical parameters obtained, are summarized in Table 5 and displayed with Figure 16. The quantitative parameters calculated with Tafel extrapolation show that the composite coating containing 2 wt.% LDH-V-A demonstrated significantly higher E_{corr} (-0.521 V) and lower I_{corr} (1.0×10^{-8} A/cm²) compared to the epoxy coating (-0.589 V, 5.36×10^{-7} A/cm²) with the best protection efficiency (98.13% vs. epoxy and 99.97% vs. bare metal). After one month of immersion, the epoxy coating was severely degraded (-0.636 V, 7.08×10^{-6} A/cm²) due to the electrolyte penetration and barrier breakdown, as shown in Table 6 and Figure 17. On the contrary, the epoxy/2 wt.% LDH-V-A coating maintained a high level of stability (-0.353 V, 1.17×10^{-8} A/cm²), with only a slight decrease in protection; this clearly suggests that LDH-V-A can greatly improve the long-term corrosion resistance and durability of epoxy coatings. This improvement in corrosion performance is mainly due to LDH nanosheets that can seal the defect of the

epoxy and act as a physical barrier to the substrate. In addition, the impressive corrosion resistance of LDH-V-A composite coating is attributed to its capability of trapping corrosive chloride ions and liberating vanadate species, which can actively inhibit corrosion at the metal/coating interface [17]. This is consistent with the results of Ying et al. [17]. Finally, it should be stated that potentiodynamic polarization test results are in accordance with the data analysis of the water contact angle study.

Table 5: Electrochemical parameters, corrosion rate, and protection efficiency of bare aluminum and coated aluminum samples determined by potentiodynamic polarization in 3.5 wt.% NaCl solution (mean $\pm$ SD, $n = 3$).

Sample	E_{corr} (V)	i_{corr} ($\mu A.cm^{-2}$)	CR (mm/y)	η (%) vs. Al	η (%) vs. EP
Al	-0.620 ± 0.017	36.00 ± 1.44	$3.8 \text{ E } -1$	-----	-----
Ep/ Al	-0.589 ± 0.010	0.536 ± 0.0123	$5.67 \text{ E } -3$	98.51	-----
1% LDH-V-A/ EP	-0.467 ± 0.013	0.0262 ± 0.00079	$2.77 \text{ E } -4$	99.93	95.11
2% LDH-V-A/ EP	-0.521 ± 0.011	0.0100 ± 0.00026	$1.06 \text{ E } -4$	99.97	98.13
3% LDH-V-A/ EP	-0.624 ± 0.014	0.0396 ± 0.00115	$4.2 \text{ E } -4$	99.89	92.61
4% LDH-V-A/ EP	-0.638 ± 0.022	0.0324 ± 0.00136	$3.42 \text{ E } -4$	99.91	93.96
5% LDH-V-A/ EP	-0.510 ± 0.021	0.0482 ± 0.00231	$5.09 \text{ E } -4$	99.87	91

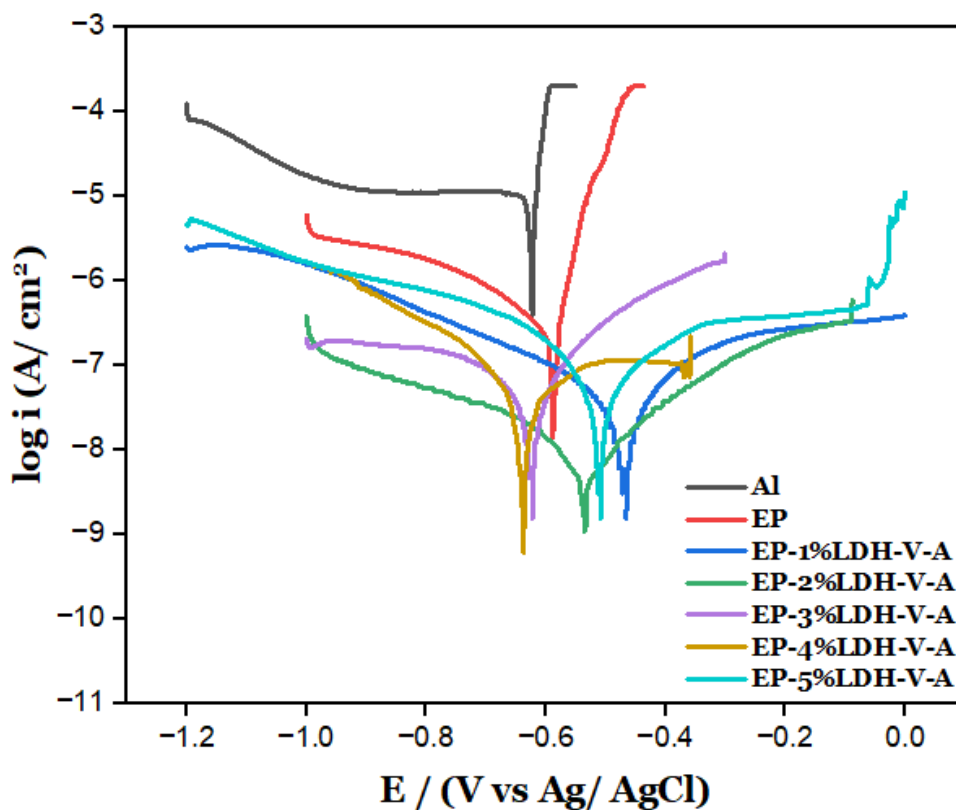


Figure 16: After One Hour of Immersion in a 3.5wt.% NaCl Aqueous Solution, PDP Curves of Coated and Bare 2024 Al Alloy Samples.

Table 6: Electrochemical parameters, corrosion rate, and protection efficiency of epoxy-coated and LDH-V-A/epoxy-coated aluminum after 1 h and 30 days of immersion in 3.5 wt.% NaCl solution, determined by potentiodynamic polarization (mean $\pm$ SD, $n = 3$).

Sample	immersion time	E_{corr} (V)	i_{corr} ($\mu\text{A} \cdot \text{cm}^{-2}$)	CR (mm/y)
Ep/ Al	1 hr	-0.589 ± 0.010	0.536 ± 0.0123	$5.67 \text{ E } -3$
Ep/ Al	30 days	-0.636 ± 0.020	7.08 ± 0.28	$7.49 \text{ E } -2$
2% LDH-V-A/ EP	1 hr	-0.521 ± 0.011	0.0100 ± 0.00026	$1.06 \text{ E } -4$
2% LDH-V-A/ EP	30 days	-0.353 ± 0.0095	0.0117 ± 0.00047	$1.2 \text{ E } -4$

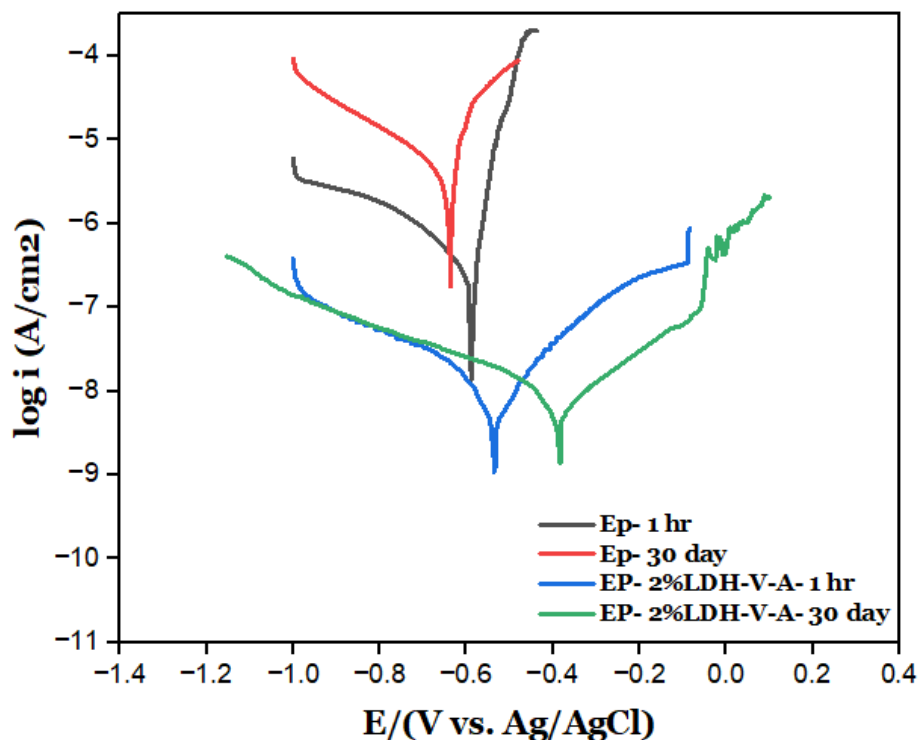


Figure 17: After one hour and 30 days of immersion in a 3.5wt.% NaCl aqueous solution, PDP curves of epoxy and 2%LDH-V-A/ epoxy coatings.

3.10. Electrochemical impedance spectroscopy (EIS)

The Nyquist plots and Bode impedance modulus of the epoxy coatings for 1 h immersion in 3.5 wt.% NaCl solution are shown in figure 1[^]. Compared with the neat epoxy coating, all LDH-V-A containing coatings showed a higher value of impedance and larger capacitive semicircles, showing a better barrier property against electrolyte penetration. The 2 wt.% LDH-V-A/epoxy coating exhibited the highest low-frequency impedance modulus and the highest semicircle diameter among the investigated coatings, thus providing the best corrosion protection performance. The excellent behavior is similar to that observed under SEM for which the dispersion of LDH-V-A particles in the epoxy matrix was found to be homogeneous at 2 wt.%. Such a uniform distribution makes the

diffusion path more tortuous and impedes the penetration of aggressive chloride ions [28]. The released vanadate species may also play a role in corrosion resistance, as they can inhibit the electrochemical reactions at the coating/substrate interface [24]. On the other hand, an LDH-V-A loading higher than 2 wt.% led to a decrease in the impedance response, in accordance with the localized particle clustering observed in the SEM images. The agglomerates can create defects at the localized areas, allowing electrolytes to penetrate and thereby decreasing the barrier efficiency of the coating [35]. The overall results from the EIS experiments are seen to be in good agreement with the results of the PDP measurements, and thus the results obtained prove that the 2 wt.% LDH-V-A/epoxy coating has the best corrosion resistance among the tested coatings.

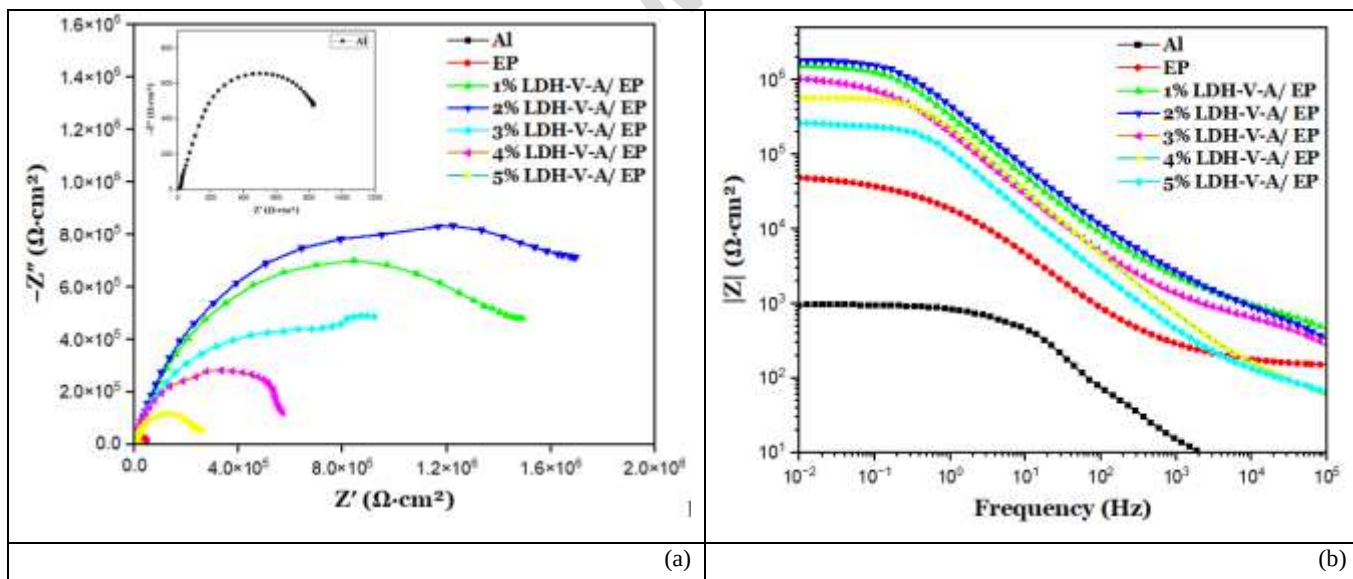


Figure 18: (a) Nyquist plots and (b) Bode impedance modulus plots of bare Al, epoxy-coated Al, and LDH-V-A/epoxy-coated Al after 1 h of immersion in 3.5 wt.% NaCl solution.

To further assess the electrochemical performance of the developed coating, Table 7 compares the obtained results with those of recently reported epoxy/LDH coating systems. The comparison is based on the available electrochemical parameters in the literature, including E_{corr} , i_{corr} , and the low-frequency impedance modulus ($|Z|$ at 0.01 Hz).

Table 7. Quantitative comparison of the electrochemical performance of the developed epoxy/LDH coating with recently reported epoxy/LDH coating systems in 3.5 wt.% NaCl solution.

Ref.	Coating system	Substrate	Coating thickness (μm)	E_{corr} (V)	i_{corr} (A/cm^2)	$ Z $ at 0.01 Hz ($\Omega \cdot \text{cm}^2$)
This study	MgZnAl-LDH-Vanadate	AA 2024-T3	50 ± 3	-0.521	1.0×10^{-8}	$\approx 2.2 \times 10^6$
[36] (2025)	ZnAl-LDH-TA	2024Al	33 ± 4	-	-	$\approx 1.4 \times 10^5$
[37] (2025)	PEO-MgAl-LDH	AA 2024-T3	PEO $\approx 43 \pm 6$ Epoxy $\approx 40 \pm 10$ (Ep-topcoat)	-	-	$\approx 6 \times 10^7$
[38] (2022)	ZnAl-LDH/DEDTC - MMT-Ce	AA 2024-T3	90 ± 2 (Ep-topcoat)	-	-	$\approx 10^9$
[4] (2022)	CaAl-MBT LDH	Q235 steel	40 ± 5	-0.23	1.1×10^{-8}	5.52×10^7
[24] (2024)	Zn-Al LDH- $(\text{V}_{10}\text{O}_{28})^{6-}$	mild steel	-	-0.006	1.2×10^{-6}	-

As shown in Table 7, the proposed coating exhibits competitive electrochemical performance compared with recently reported epoxy/LDH coating systems. Although two of the selected studies employed steel substrates, they were included because they investigated epoxy/LDH coatings with similar corrosion-protection mechanisms.

Therefore, the comparison is intended to provide a general performance benchmark rather than a direct substrate-to-substrate comparison.

4. Conclusion

A novel dual-step intercalation strategy involving co-precipitation and ion exchange was suggested for incorporation of vanadate in ternary MgZnAl-LDH to the highest extent. To improve the compatibility of the LDH with the epoxy coating, APTES was used to functionalize it. The functionalized LDH significantly improved the corrosion resistance of epoxy coated AA2024-T3 aluminum alloy in 3.5 wt.% NaCl solution. The surface hydrophobicity, adhesion strength and hardness of the epoxy coatings were also increased by incorporating LDH, although the optimum LDH loading varied depending on the property evaluated. At higher LDH loadings, the coating properties slightly deteriorated due to the localized accumulation of LDH particles within the epoxy matrix. The salt-solution immersion and electrochemical test results showed the best LDH/epoxy coating has better corrosion resistance than neat epoxy. The electrochemical results showed improved corrosion protection, owing to the dual effect of the LDH fillers, namely the ability to adsorb aggressive ions and the release of corrosion-inhibiting species.

5. References

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