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Development of superhydrophobic layered double hydroxide directly on zinc substrate: structural and corrosion resistance properties

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Abstract. This study is aimed to study the functionalization of zinc metal surface with the development of layered double hydroxides (LDHs) and was modified further to develop superhydrophobic LDHs thin film. The influence of the protective LDHs on physical–electrochemical properties and the chemical state of the surface against different reagents (NaOH, NaCl, acidic solution) for self-cleaning characteristics are reported. The structural characteristics of developed coatings were evaluated by scanning electron microscopy (SEM-EDS) and X-ray diffraction (XRD), while electrochemical impedance spectroscopy (EIS) measurements were performed in NaCl solution to analyse the importance of protective coating. The research demonstrates that active and passive corrosion protection by the LDH conversion film against electrolytic species yields a substantial enhancement in corrosion resistance properties. The superhydrophobic surface, by incorporating $CF_3(CF_2)_9CH_2CH_2Si(O^-)_3$ groups (PDFTS) in ZnAl–LDHs, has shown significant corrosion protection efficiency after 7 days of immersion in 0.1 M NaCl solution with an increase of almost three orders of magnitude in the $|Z|_{10\ mHz}$ in comparison to untreated zinc surface, which can lead to important values for more potential applications.

Keywords. Pure zinc surface; LDHs; superhydrophobic; EIS.

1. Introduction

Zinc is an active metal with a wide range of industrial applications. It is also widely used for coatings, where about half of the consumed zinc finds its application in the protection of galvanizing steel [1]. However, when exposed to a humid atmosphere, zinc-coated articles undergo rapid corrosion (white rust), rendering the plated zinc materials unsuitable for industrial applications [2,3]. Different strategies can be employed to protect metals from corrosion, including the use of corrosion inhibitors, cathodic and/or anodic protection, and protective coatings. The latter is one of the most general and cost-effective measures to avoid the degradation of active metals by corrosion. In the past few years, researchers have focused on conversion/pseudo-conversion coatings to protect zinc substrates [4–8]. Chromate solution treatment was one of the prominent solutions to enhance the corrosion resistance of the zinc surface. However, due to their carcinogenic nature, recent environmental restrictions on the utilization of chromate solutions required the investigation of other non-toxic reagents to replace chromate coatings [9]. Recently, layered double hydroxides (LDHs) based coating systems have been widely explored due to peculiar morphology, a wide range of cationic/anions combination, environment-friendly characteristics, high surface-to-volume ratio, and their capability to intercalate with various species inside the LDHs interlayers [10,11]. A wide range of divalent and trivalent cationic sources has been used to develop LDHs directly on the various metallic substrates, where the layered structure of the LDHs is constructed by the periodic stacking of positively charged octahedral layers, which are bonded by the interlayered anions and water molecules. Recently, a broad variety of divalent metal cations (M^{2+} = Mg, Ca, Zn, Ni, etc.) have been employed to develop M–Al–LDH directly on light metallic alloys, coupled with diverse combinations of anions inside the LDHs interlayers (complex anions, corrosion inhibitors, pigments, etc.)

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[11–22]. Up to now, most research carried out on the study of *in-situ* grown LDH films is mainly focused on light metal alloys, mainly because the type of metal cations provided by these substrates give rise to stable, well-known LDH conversion films (e.g., Mg–Al, Zn–Al LDHs). However, there are few reports on the direct growth of LDHs on zinc substrates [23–25], and there is a need to investigate other aspects like the modification of film and corrosion resistance properties to consider the smart functional surface treatment for numerous applications.

In the present investigation, ZnAl–LDH–NO_3 is synthesized directly on the pure zinc surface and was further modified with PFDTS solution to obtain a superhydrophobic surface for enhanced corrosion resistance properties with self-cleaning characteristics. The LDHs play a double inhibition role as a superhydrophobic surface for corrosion inhibitors and also as a way to trap aggressive species inside the interlayers. For more attractive merits, ZnAl–NO_3 is synthesized with good crystallinity without the controlled environment for system simplicity and commercial feasibility.

2. Materials and synthesis

2.1 *Pretreatment*

The zinc substrate with a surface area of (4 × 4 cm) is used for the understanding of uniform LDH formation. The substrate was initially ground with 400, 1200 and 2400, SiC grit size papers, rinsed with distilled water, and etched with an aqueous NaOH solution. The composition of the zinc substrate is shown in table 1.

2.2 *Synthesis of superhydrophobic ZnAl–LDHs*

The zinc substrate was vertically immersed in a mixed solution of 0.05 M $Al(NO_3)_3$ (≥99%, Sigma-Aldrich) and 0.3 M NH_4NO_3 (≥99%, Sigma-Aldrich). The hydrothermal reaction was performed under hydrothermal treatment (100°C, 24 h) in three bottleneck flasks without any controlled environment. The pH value is an important factor in controlling the formation of LDHs where an increased pH (≥10) is found to easily adsorb CO_2 from the air in the reactive solution [25]. The exceptionally high affinity of CO_3^{-2} to intercalate with LDHs can result in a carbonated LDHs system. In the current work, the synthesis of the LDHs is conducted at low pH (6) by dropwise addition of 1 M NH_4OH. The obtained specimens, termed LDHs, were washed with deionized water several times and air-dried.

Table 1. Weight composition of zinc substrate.

Component	Cu	Cd	Ag	Fe	Si	Zn
wt%	0.003	0.006	0.0001	Trace	Trace	Balance

To obtain a superhydrophobic surface, the PFDTS solution is initially made by hydrolysis of 0.1 g of PFDTS in 200 ml pure ethanol by continuous stirring at 40°C for 1 h. This results in $CF_3(CF_2)_9CH_2CH_2Si(O^-)_3$ groups, which form Si–OH groups and can induce hydrogen bond formation with –OH groups of LDHs. The as-prepared LDHs specimen is immersed in hydrolyzed PFDTS solution and held for 2 h at 40°C at room temperature. The sample was removed from the solution, dried in the ambient atmosphere, and dried in the oven for 1 h at 60°C. The final product was termed LDH-F.

3. Characterization

The surface of the samples was characterized using scanning electron microscopy (JEOL-JSMIT300 equipped with an EDS detector). The crystal structure is analysed through X-ray diffraction (X'Pert High Score diffractometer/30 kV, 10 mA and Cu K-alpha radiation). After 10 seconds of dropping a 5 µl drop of various liquids on the surface, static contact angle measurements were acquired using a customized experimental setup. The standard deviation of the static contact angle measurement was ±2.0, considering different drops at various positions on the surface. The mechanical stability of the superhydrophobic surface is analysed by excessive ultrasonication (100 W, 99% amplitude) for 20 min. The protective ability and degradation in time of the developed coatings were estimated based on the results of electrochemical impedance spectroscopy (EIS) by using 'Parstat' equipment with a reference electrode of Ag/AgCl (+210 mV *vs*. SHE) and platinum foil as a counter electrode. The impedance measurements were made with an amplitude of 10 mV at the frequency range from 0.01 Hz to 100 kHz.

4. Results and discussion

Figure 1a–d depicts the top view of SEM images of the LDHs and modified LDHs. It can be seen that the LDH films grew on the entire zinc substrate where the curved plate-like LDH microcrystals are formed perpendicular to the substrate (figure 1a, b). The surfaces of developed ZnAl–LDH films highlighted the nano-hexagonal platelet morphology, which entirely covered the substrate and confirmed the LDH formation [26,27]. After treatment with PFDTS (figure 1c, d), the morphology of the LDHs-F film transformed from a packed sheet to a flower-like structure, which is in accordance with the literature data [28]. The introduction of PFDTS groups inside LDH interlayers caused stresses in the geometry, resulting in the disorder in the curvy platelet structure and arranged in a packed flower-like structure. The EDS results (figure 1e, f) of LDHs showed that zinc element appeared with an atomic percentage of 36.4 (mass %), aluminium (17.1 mass %) along

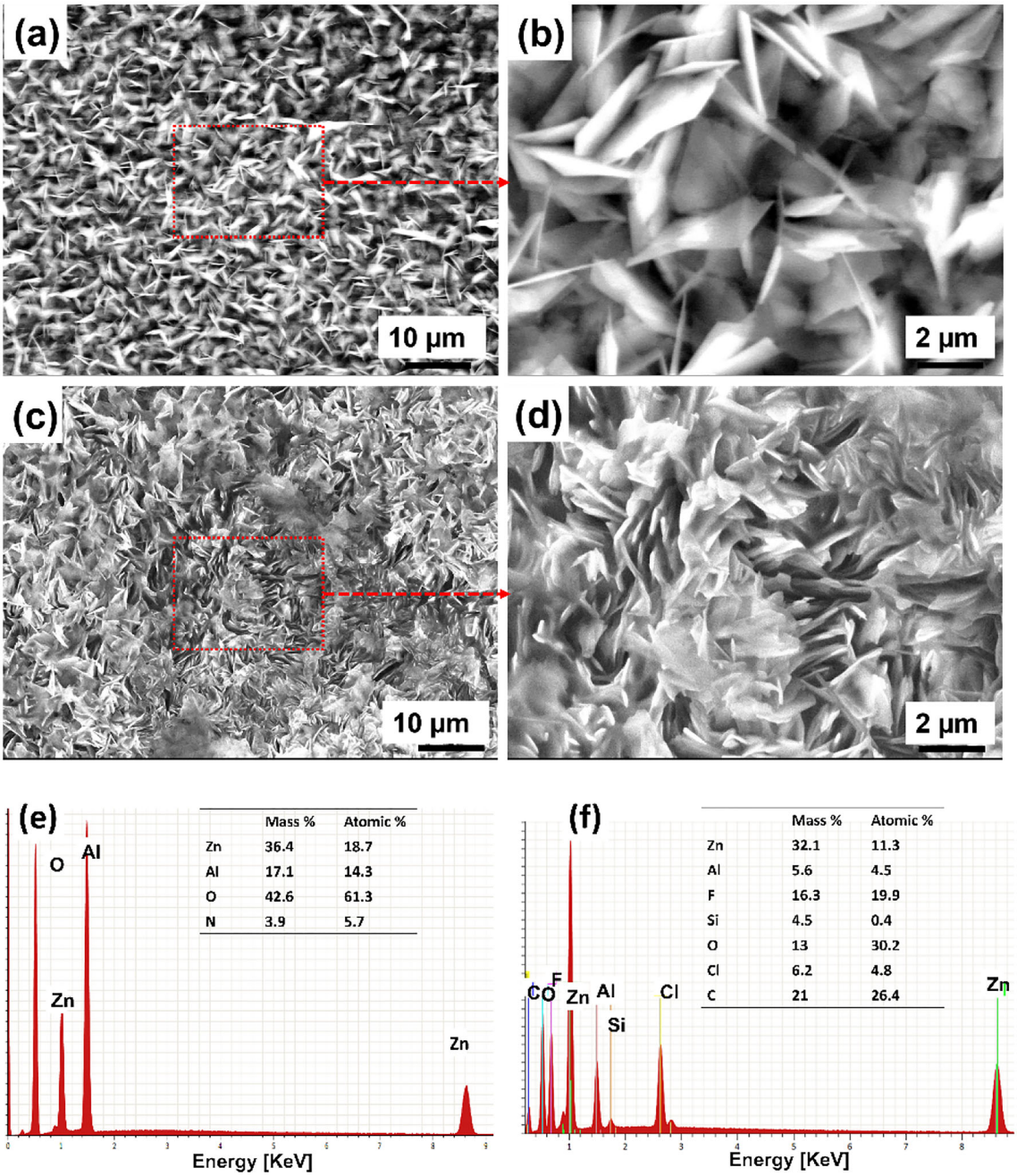

Figure 1. SEM images and EDS analysis of developed LDHs: LDHs (**a**, **b**, **e**) and LDHs-F (**c**, **d**, **f**).

with the presence of nitrogen (3.9 mass %), and higher O element contents (42.6 mass %). After the modification of LDH film with PFDTS solution, the additional element contents of carbon, fluorides, silicon and chlorine are introduced into the structure, indicating that PFDTS were successfully bonded/adsorbed with the ZnAl–LDHs. The zinc contents after modification reduced from 36.4 to 32.1%, while aluminium reduced from 17.1 to 5.6%, along with the appearance of carbon (21%), silicon (4.5%), fluoride (16.3%) and chloride (6.2%). The atomic ratio of Zn/Al was 2.1 in the case of LDHs, which changes to 5.75 for LDHs-F. These results supported the explanation of morphology variations after modification of LDHs with PFDTS.

The growth mechanism of LDHs on zinc substrate is discussed in the recent work of Mikhailau *et al* [23], which involves several electrochemical reactions, including the anodic dissolution of zinc and cathodic reduction of nitrates and oxygen in an aqueous solution containing metallic zinc and nitrate anions and produce hydroxyl anions, and deposition of aluminium hydroxide on the surface, followed by reprecipitation of $Al(OH)_4$ and $ZnOH^+$ species into the LDH phases. The overall kinetics of LDHs development

can be explained by the dissolution of zinc substrate leading to the formation of an active phase of LDHs growth when soluble aluminium is mainly precipitated as a hydroxide on the zinc surface and the formed film acts as a diffusion barrier and also slowing down the zinc dissolution process. Ammonium solution on one side supports the buffering of the pH and is also found to keep the CO_3^{2-} (absorption of CO_3^{2-} in solution is inevitable, especially in open synthetic conditions) in solution and thus prevents its intercalation into the interlayers and support nitrate intercalation [29]. ZnAl–LDHs nanosheets accumulate gradually to form the LDHs film that covers the entire zinc surface. From the cross-sectional morphology of the LDH coating (figure 2), it can be seen that the thickness of the ZnAl–LDH film was approximately 20.9 ± 0.8 μm, which after modification increased a bit with an average value of 24.3 ± 0.7 μm. After the intercalation of PFDTS anions in the gallery, the thickness of the films increased a bit with an approximate value of 3.4 μm.

The XRD pattern (figure 3) revealed the characteristic diffraction peaks of well-crystallized hydrotalcite-like LDH materials (JCPDS no. 38-0486) with a series of (*00l*) peaks around 9.8°, 19.9°, 33.8°, 61° and 63° corresponding to (003), (006), (012), (110) and (113) planes of the LDH crystals [30–32]. LDH X-ray diffraction pattern shows (*00l*) baseline peaks related to the lamellae stacking sequence. Non-baseline peaks, considered non-harmonic, are related to the lamellae structure [33,34]. The intense traditional reflection peak of (003) showed a basal spacing of ~0.89 nm, which defined the presence of nitrate inside the interlayers of LDHs. The diffraction peaks can be indexed in a hexagonal lattice (cell parameter for LDH-NO_3 equals c = 2.67 nm and a = 0.35 nm) with an R3m rhombohedral symmetry that is closer to the previous works for commonly used LDHs structure [24]. Other low-intensity reflection peaks attributed to the presence of secondary phases were also observed in the brucite-like structure [34]. An additional peak attributed to ZnO was at 34.36 (002), where ZnO with less intense peaks is only observed. After

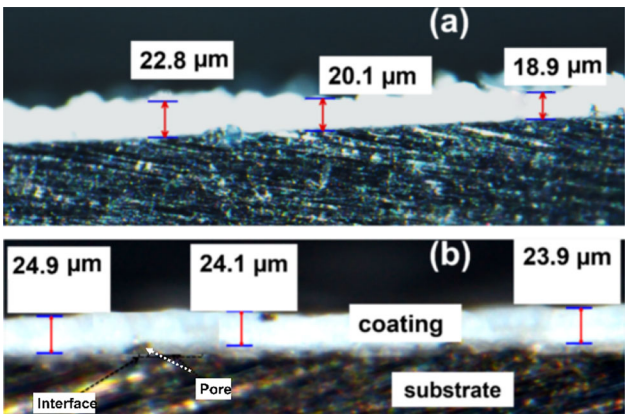

Figure 2. Cross-sectional optical images of the LDHs: (**a**) LDHs and (**b**) LDHs-F.

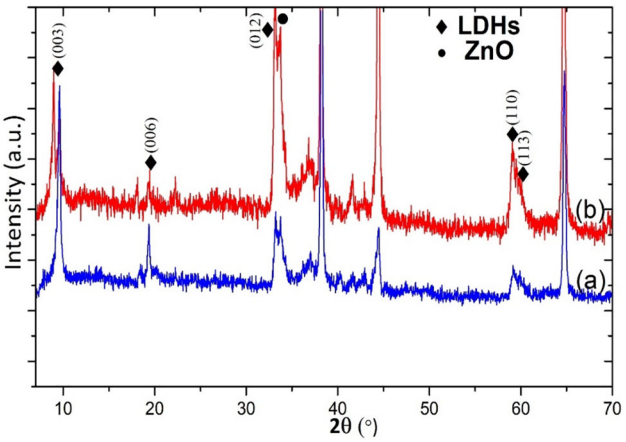

Figure 3. The XRD spectra of developed LDH films: (**a**) LDHs and (**b**) LDHs-F.

modification with PFDTS, a slight shift in the (003) peak towards the left side is observed, indicating the possible intercalation of PFDTS in ZnAl–LDHs. Hydrolysis of PFDTS in ethanol yielded Si–OH groups that can induce hydrogen bond formation between –OH groups of LDH and Si–OH groups which led to a slight increase in the gallery height (anionic layer thickness) and defined the functionalization of ZnAl–LDHs by long-chain PFDTS.

The superhydrophobicity of modified LDHs was estimated through the surface wettability evaluated by contact angle (WCA°) measurements. The static WCA° of water droplets is found to be higher than 150°. The changes in surface roughness and surface energy are the direct factors leading to the changes in surface wettability of LDH-F. The use of PDFTS not only reduces the surface energy of LDHs, but also adjusts the surface morphology of LDHs and contributes to the variation of surface roughness [35,36]. It can be concluded that the superhydrophobic property of LDHs-F results from the interaction between surface energy and surface roughness. From the Wenzel equation, in the case of an ideal interface contact angle greater than 90°, the roughness will increase the actual contact angle. The conclusion of the equation is consistent with the study's results. To understand the stability of the thin film against different household items, the contact angles are also calculated against acid, base and alkali. Figure 4 shows the optical images of liquid drops on the surface of LDHs-F, where the droplets of water, NaCl and NaOH stood almost spherical. However, acid droplets spread on the surface with a comparatively lesser contact angle.

Superhydrophobic coatings may experience mechanical damage when applied for indoor applications. The mechanical stability of LDHs-F is considered by conducting the excessive ultrasonic treatment for 20 min. The increase in surface roughness and the decrease in surface energy are conducive to improving the hydrophobic properties of the films and it is observed that the surface morphology of LDHs-F remains almost the same after ultrasonication

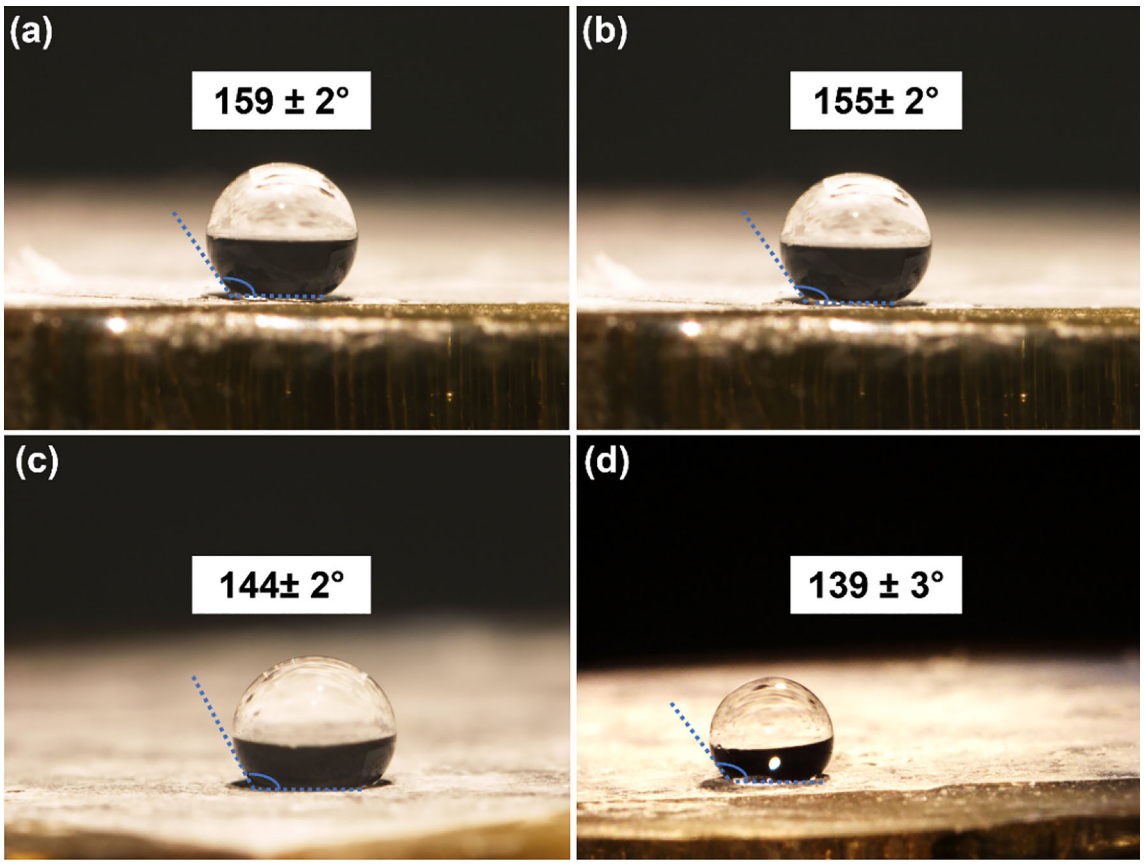

Figure 4. Digital photos of different liquid droplets on the LDHs-F surface: (**a**) water, (**b**) 1 M NaCl, (**c**) 1 M NaOH and (**d**) acidic solution (pH ∼3).

treatment (figure 5), where the randomly packed microcrystal appeared like the as-prepared ones and the film can still maintain stable hydrophobic properties. However, some platelets collapsed and caused the appearance of voids in the surface morphology (figure 5). Studying the superhydrophobic capability after ultrasonic treatment for practical solutions is significant and sufficient stable hydrophobicity against different liquid droplets is observed (figure 6).

To understand the corrosion resistance behaviour of developed LDHs, EIS spectra in Bode format were acquired in 0.1 M NaCl solution after 7 days of immersion in 0.1 M NaCl solution (figure 7). The developed LDHs showed an impedance value of 3.24 $\Omega{\cdot}cm^2$ at $|Z|_{0.01}$ Hz, while 5.48 $\Omega{\cdot}cm^2$ for LDH-F. The higher impedance magnitude of the LDHs-F suggested excellent inhibition properties, where the superhydrophobic surface effectively impedes the diffusion of corrosive species to the metal interface and

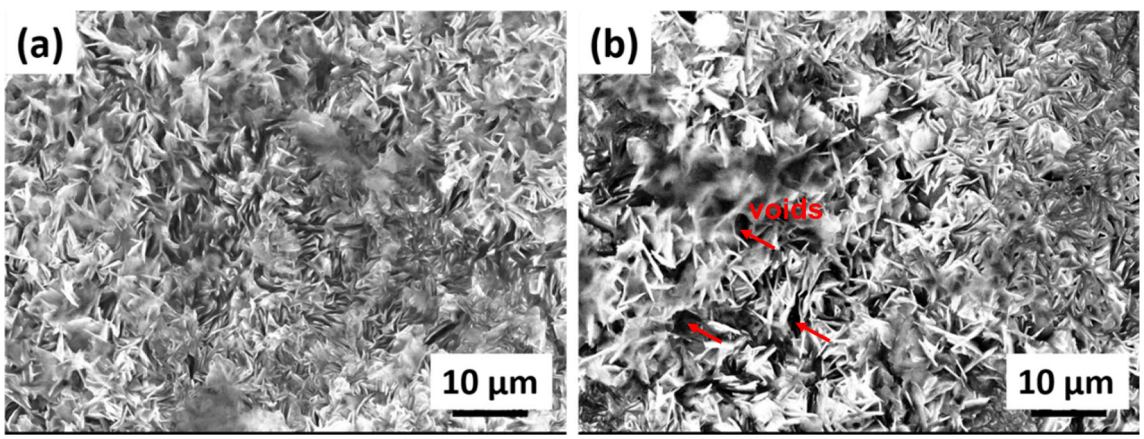

Figure 5. SEM images of LDHs-F: (**a**) before ultrasonication and (**b**) after ultrasonication.

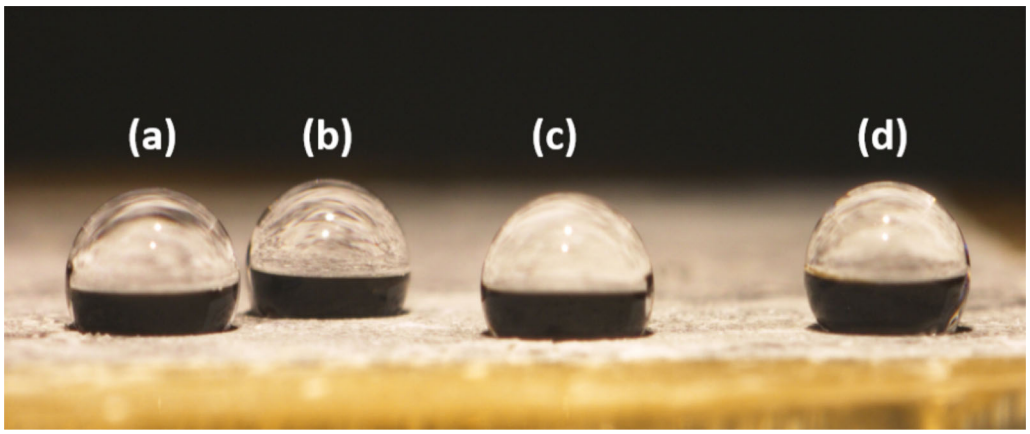

Figure 6. Optical images of water droplets on the surface of LDHs-F after ultrasonication treatment: (**a**) acidic solution (pH ~3), (**b**) 1 M NaOH, (**c**) 1 M NaCl and (**d**) water.

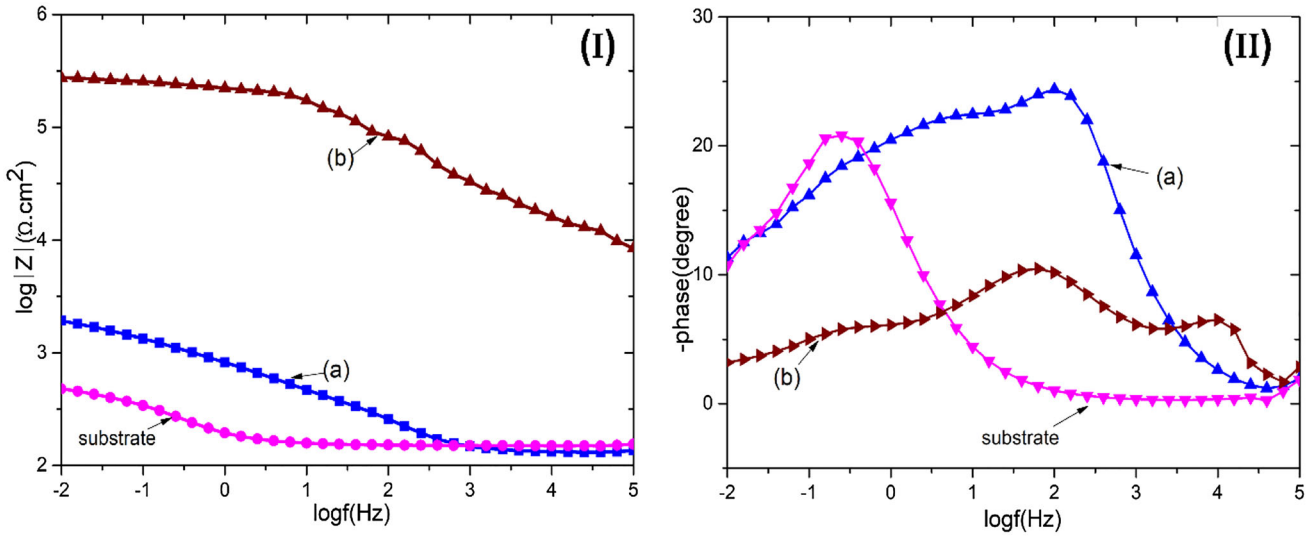

Figure 7. Bode plots and phase angle plots of developed LDHs after 1-week immersion in 0.1 M NaCl solution: (**a**) LDHs and (**b**) LDHs-F.

promotes the corrosion resistance of the zinc substrate. Considering the phase angle plots for the developed LDHs, the two-time constants are attributed to the inner barrier layer in the low-medium frequency range and the outer porous layer in the high-medium frequency range [37,38]. The time constants for LDHs-F shifted towards a higher frequency, which indicated that the metal surface was well protected.

In other words, it signifies that the formation of boundary layers acted as a barrier and prevented the corrosive species from penetrating. Modified LDHs have shown a better inner barrier layer and compact outer surface than the LDHs, which defined the concept of superhydrophobicity and higher corrosion resistance properties. The considerable corrosion resistance of developed LDHs can be explained by the following: (a) ability to anion-exchange with corrosive species that can uptake corrosive species in the galleries, behaving as nano traps, which is found effective to improve corrosion resistance properties, (b) superhydrophobic LDHs surface which did not allow the corrosive reagent to interact with the surface and promote the active protection conferring a self-healing ability.

To properly analyse the developed thin films, the evaluation tendency of porous layer resistance R_P and dense layer resistance R_b are obtained via EIS curves fitting by using 'ZSimpwin' software (table 2). The immersion of LDH in 0.1 M NaCl solution for 7 days, the corrosion reaction of so developed LDHs involved the outer porous structure and less involvement of the inner dense layer with high R_{ct} behaviour in the equivalent circuit diagram, as the penetration of Cl^- ions is restricted due to strong barrier effect of the dense layer of LDHs. Following equivalent circuit $R_s(CPE_P(R_P(CPE_bR_b)))$ is used to fit the EIS results (figure 8a), where R_P and CPE_P are porous layer resistance and corresponding constant phase element, respectively, which represents the dielectric properties of the layered double

Table 2. Evolution with a time of the fitting parameters R_P, Q_P, α_P, R_b, Q_b, α_b, R_{ct}, Q_{ct} and α_{ct}.

Sample	Immersion time	R_P Ω cm^2	Q_P Ω^{-1} cm^{-2} s$^{\alpha}$	α_P	R_b Ω cm^2	Q_b Ω^{-1} cm^{-2} s$^{\alpha}$	α_b	R_{ct} Ω cm^2	Q_{ct} Ω^{-1} cm^{-2} s$^{\alpha}$	α_{ct}	$\varkappa^2$ ($\times 10^{-3}$)
ZnAl–LDHs	7 day	215	5×10^{-3}	0.91	120	7×10^{-3}	0.87	—	—	—	2.1
ZnAl–LDHs-F	7 day	4852	4×10^{-6}	0.79	8860	1×10^{-7}	0.81	7736	1.08×10^{-5}	0.89	6.4

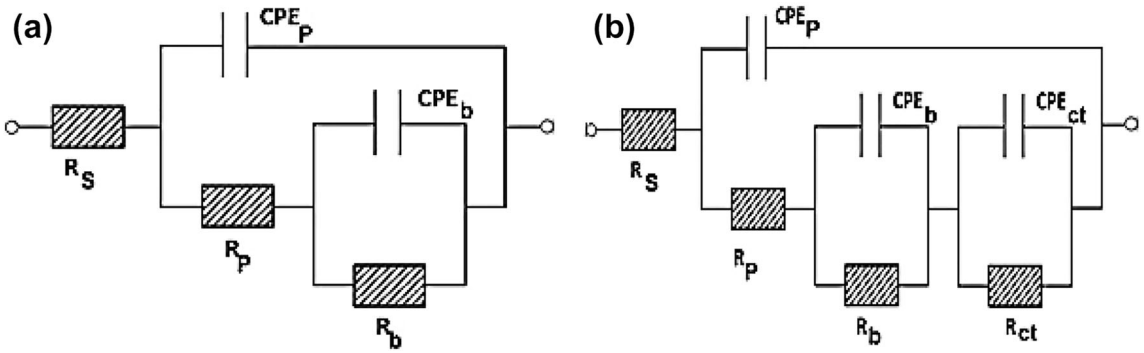

Figure 8. EIS fitting of developed LDHs for the equivalent circuit used to model the experimental results: (**a**) LDHs and (**b**) LDHs-F.

hydroxides coatings, while R_b is the LDH dense layer, constant phase element CPE_b. Constant phase element (CPE) provides the understanding of dielectric response and is represented by the general expression, i.e., $Z_{CPE} = 1/Q(\omega j)^{\alpha}$. However, due to the low value of 'α' than unity in our cases, it is not possible to demonstrate the precise physical meanings. In the case of LDHs-F, the following equivalent circuit model $R_s(CPE_P(R_P(CPE_bR_b)(CPE_{dl}R_{ct})))$ is used to fit the EIS results, where an additional R_{ct} parameter is involved (figure 8b) [28]. The measured values of each stage are demonstrated in table 2. R_P and R_b values describe the effective nature of PFDTS addition in the coating system where both porous and dense networks of LDHs are properly promoted and have shown significant corrosion resistance properties, where the fitting values were in good agreement with the corresponding experimental data and electrochemical equivalent circuit model spectra (chi-square values of 2.1×10^{-3} and 6.4×10^{-3}). The corresponding values of the exponent (α) of the CPE are in the 0.79–0.9 range during immersion time. This parameter is recognized to be dependent on the fractal nature of the surface (affected by roughness and porosity), as well as on the heterogeneities of the electrode surface. Within this framework, the obtained data suggest the significance of surface roughness after LDHs modification and CPE_b is believed to account for the dielectric properties of the LDHs, but a more defined description is not possible. The significant corrosion resistance properties were related to the superhydrophobicity of the LDHs film, surface compactness, effective anodic inhibitors on zinc corrosion, and ion exchange capacity for self-healing/self-cleaning characteristics.

Table 3 compares the impedance modulus $|Z|_{0.01}$ that can be used to measure the corrosion resistance and film wettability against the corrosive solution. $|Z|_{0.01}$ in this work is comparable to the values in the literature of previous LDH-based coating systems. However, one must also consider that there are no data on the development of

Table 3. Comparison of the wettability and corrosion resistance properties of the LDH-F with the literature data on aluminium alloys.

LDH	WCA°	NaCl (conc.)	Time (h)	$\lvert Z\rvert_{0.01}$	Ref.
LDHs-F	159.2	0.1 M	168	$10^{5.5}$	This work
MgAlCe–LDH-F	155.6	0.1 M	1200	$10^{6.5}$	29
Steartae–Ce–LDH	152.6	0.1 M	720	$10^{8.9}$	38
ZnAl–LDH–La	152.7	3.5 wt%	672	$10^{5.2}$	40
ZnAl–VOx–LDH–La	151.7	3.5 wt%	1680	$10^{5.9}$	41
MgAl–Stearate	121.3	3.5 wt%	—	$10^{6.3}$	42

superhydrophobic LDHs on zinc substrate and have compared the current results with different LDHs developed on aluminium substrates and further crystallization time to synthesize LDHs varied in the literature work [28,37,39–41], that make an influence on the film thickness and further on the corrosion resistance properties.

5. Conclusion

In summary, zinc substrate is functionalized through LDHs to develop a protective coating film. The developed superhydrophobic surface (LDH-F) has shown significant corrosion resistance properties. The surface has shown sufficient contact angles against the common household solution, suggesting the robustness of the LDHs-F surface to chemical damages and superhydrophobicity remain stable after ultrasonication. The EIS analysis of superhydrophobic LDHs has shown an increase of 3 orders at $|Z|_{0.01}$ impedance moduli, while one order of increase for unmodified LDHs in comparison to the zinc substrate. The electrical equivalent circuit modelling data best fit the generated plot where developed LDHs-F had maximum coating resistance with minimum capacitance. The simple synthesis approach confirms the effective process to improve the corrosion resistance of zinc substrate.

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