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A review: Hydrotalcite layers as protective coatings on zinc and zinc alloys

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Abstract. In recent years, there has been significant research and development in area of corrosion prevention and protection, focusing on hydrotalcite layers on zinc and zinc alloys due to their distinct attributes, such as their capability to accommodate anions, ability to exchange anions, capability for structural memory, and its resistance to barriers. This review primarily aims to summarize findings related to how the formation of HT layers on zinc and zinc alloys is affected by various synthesis conditions. Besides, we compared and deliberated upon HT layers' anti-corrosion mechanism and corrosion protection.

Keywords: corrosion protection, hydrotalcite layer, zinc, zinc alloys.

Classification numbers: 2.5.3

1. INTRODUCTION

Recently, there has been a growing interest in zinc and its alloys as promising corrosion protection of metal substrates due to more negative electrode potential compared to iron [1, 2]. Unlike other active light metals like aluminum alloys, zinc alloys do not naturally develop a protective oxide film to slow down corrosion in aggressive environments, therefore, they present a distinctive and significant challenge in terms of corrosion protection. Several studies have focused on developing an effective method to inhibit the initial corrosion of zinc, which involves the preparation of a coating or some functional barrier layer on the surface for isolating base materials from corrosive environments [3 - 8]. Among coatings, hydrotalcite (HT) conversion layers show considerable promise, primarily due to their cost-effectiveness and easy application [9 - 12].

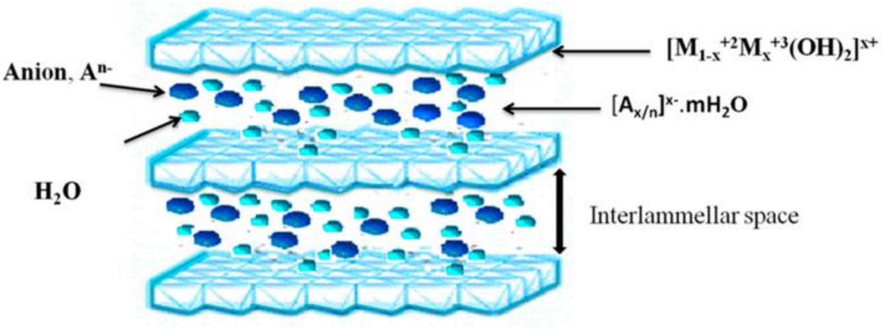

Figure 1. Schematic illustration of hydrotalcites (HTs) (reprinted with permission from [12]).

The chemical formula of hydrotalcite is represented as $[M_{1-x}^{2+}M_x^{3+}(OH)_2][A^{n-}]_{x/n}.mH_2O$, where M^{2+} and M^{3+} denote metallic ions with two and three positive charges, respectively, and, A^{n-} ions, which are exchangeable anions, are located in the interlayer region to balance the charge (Figure 1) [12 - 17]. The positive charge on the hydroxide layers arises when certain M^{2+} cations are substituted by M^{3+} cations, therefore, additional anions enter the HT gallery to offset the surplus positive charges on these hydroxide layers [7, 18 - 21]. This characteristic gives HT a capability to contain various anions, making it a valuable choice for various applications, including corrosion protection [19]. Thanks to their distinctive lamellar structure, the HTs have the capability to encase and release corrosion inhibitors, offering more additional benefits in terms of corrosion protection [22 - 27]. Moreover, the HTs possess capability to capture and retain corrosive anions such as Cl^- ions within positively charged layers (Figure 2) [19, 28]. They have the capability to grow directly on metal surfaces and create a firmly adhering protective layer using straightforward synthesis techniques [9, 10, 29 - 31]. They have been increasingly used for safeguarding zinc alloys against corrosion [32 - 36]. Furthermore, these HT layers can serve as a solid foundation for applying additional organic top coatings [37].

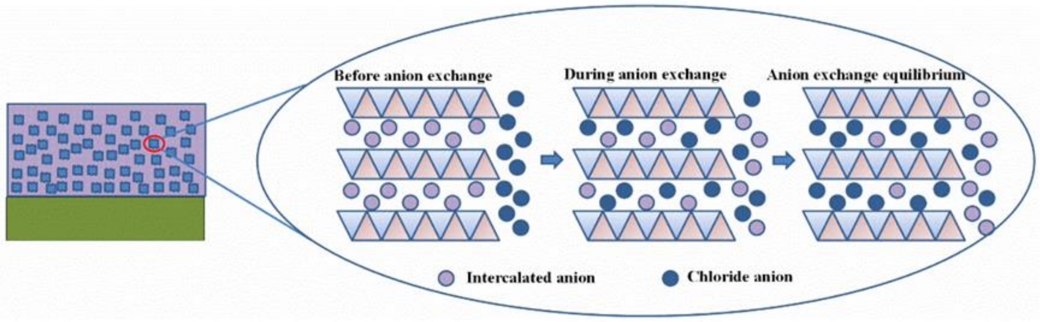

Figure 2. Schematic illustration of working mechanism of HT used in the anticorrosive coatings (reprinted with permission from [28]).

Recently, there has been a growing interest in utilizing HT layers on surface of zinc and its alloys. This review seeks to provide a comprehensive overview of the various techniques employed in creating standalone HT layers as well as composite coatings on zinc alloys. Additionally, this review aims to offer an in-depth analysis of the corrosion resistance capabilities exhibited by HT layers.

2. PREPARATION AND FORMATION MECHANISM OF HT LAYERS ON ZINC AND ZINC ALLOYS

2.1. Hydrothermal method

The hydrothermal method is the most commonly employed approach to prepare HT layer on magnesium and aluminum alloy substrates [10, 11, 15, 38, 39]. For the hydrothermal method used to produce HT conversion layers, the process involves dissolving metal salts, metal oxides/hydroxides, and alkali sources in water, subsequently, these cocktail solutions are exposed to hydrothermal treatment within a Teflon-lined stainless autoclave, maintained at a specific temperature for a designated duration [40, 41]. This method offers a distinct advantage compared to other techniques due to robust bonding strength of HT formed layer to surface of substrate [42].

Zheludkevich, *et al*. firstly synthesized ZnAl-HT with nitrates layer on zinc surface by dipping substrates in a closed vessel with the mixture solution of 1 mM $Al(NO_3)_3$ and 0.1 M $NaNO_3$ at 90 °C for various time intervals [15, 43, 44]. In the formation process of HT layers on zinc, $Al(OH)_4^-$ and $ZnOH^+$ species were also taken into account as the fundamental components for constructing HT [43]. The initial stage encompassed a series of swift chemical reactions:

$$Zn^{2+} + 2e^- \rightarrow Zn \tag{1}$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \tag{2}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{3}$$

$$Al^{3+} + OH^- \rightarrow Al(OH)^{2+},\ Al(OH)^{2+} + OH^- \rightarrow Al(OH)_2^+ \tag{4}$$

$$Al(OH)_2^+ + OH^- \rightarrow Al(OH)_3\downarrow \tag{5}$$

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \tag{6}$$

when the buffering capacity of aluminum containing species was exhausted, aluminum hydroxide began to precipitate on the zinc surface in solution in the second stage.

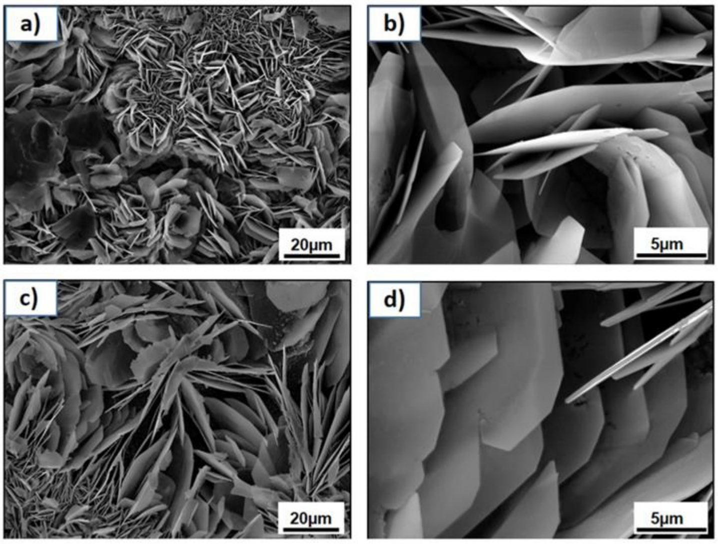

Figure 3. SEM images of Zn-LDH-NO_3 (a) and (b), Zn-LDH-Cl (c) and (d) (reprinted with permission from [15]).

During this stage, the concentration of Al in the solution decreases and that of Zn increases, while the pH grows due to the active electrochemical reduction reactions. In the third stage, the ZnAl-HT generated the building blocks of $Al(OH)_4^-$ and $ZnOH^+$ species. The HT layer, characterized by its typical plate-like structure, was applied onto the surface of zinc (Figure 3).

2.2. In-situ growth method

The microstructure of HT layers varies significantly depending on the specific synthesis conditions employed in the *in-situ* growth approach. The microstructure and structure of HT layers is influenced by crucial process parameters, including the pH of reaction baths, reaction time, M^{3+}/M^{2+} ratios, and composition and roughness of zinc coatings.

Buchheit, *et al*. initially fabricated ZnAl-CO_3 HT layers on hot-dip galvanized steel (HDG) by immersing the substrate into a strongly alkaline sodium aluminate solution [44]. The authors found that using an ammonium/ammonia source as the alkaline agent in the reaction solutions led to the formation and morphology of the coating.

Amanian, *et al*. produced *in-situ* growth of ZnAl-CO_3 HT conversion layers on electrogalvanized steel (EG steel) during 4, 8, 16 and 24 h, and, investigated the influences of treatment duration on appearance, internal structure, and surface characteristics of these layers [37, 46]. The results confirmed that irrespective of the treatment duration, the HT flakes exhibited a preference for growing perpendicular to the surface, forming a comprehensive covering on EG steel, however, the tightness and surface roughness of the HT coatings were influenced by the duration of immersion in the solution [37].

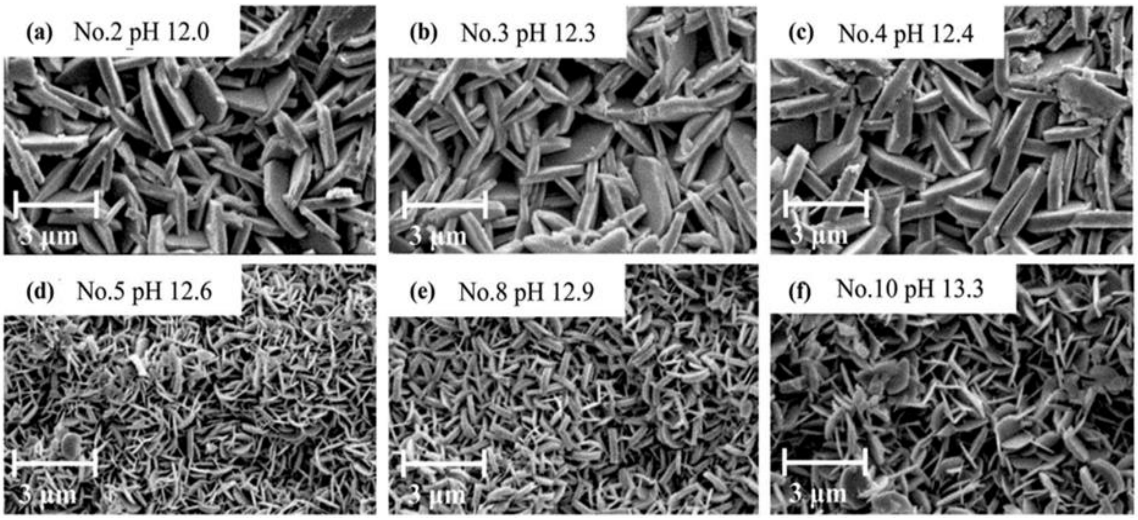

Figure 4. SEM images of HT-coated specimens. pH refers to the treatment solution conditions (reprinted with permission from [36]).

Pham, *et al*. prepared ZnAl-CO_3 HT layers on EG steel by immersion substrates in mixture solution containing $Al(NO_3)_3$ and $Zn(NO_3)_2$ with various Al:Zn ratios at pH 12 for 6 h with stirring and 16 h without stirring [33]. The XRD results confirmed that the Al/Zn ratios impacted the brucite layer, thickness of the interlayer distance and crystallite size of HT. In addition, the SEM and cross-section SEM results suggested that the Al/Zn ratios affected significantly on morphology and thickness of HT layers. The crystal size of the ZnAl-HT films slightly increased as the Al^{3+}/Zn^{2+} ratio decreased from 5/1 to 5/2. However, at a ratio of 5/3, the crystals exhibited a significant size reduction, becoming more uniform and denser. When the Al^{3+} /Zn^{2+} molar ratio was further decreased from 5/4 to 5/5, the crystal size continued to increase, while the thickness of the films decreased.

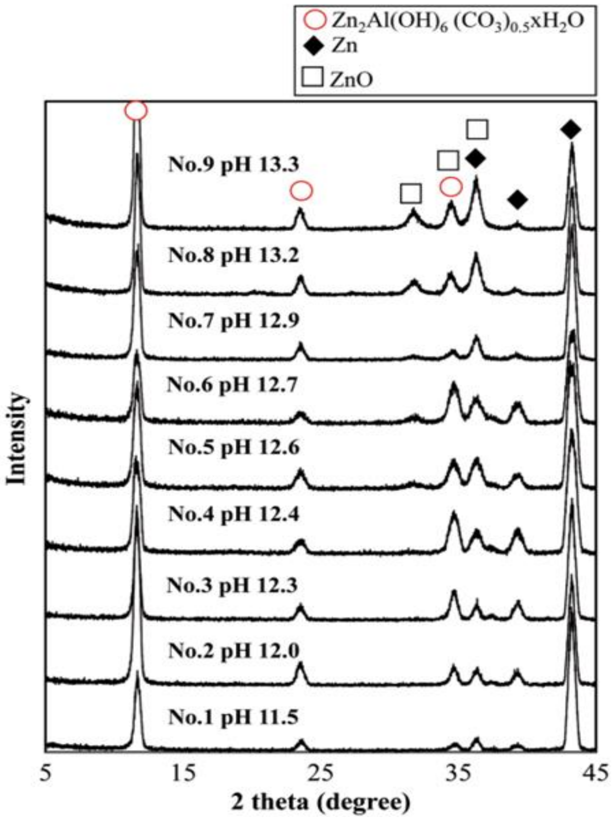

Figure 5. XRD patterns of LDH-treated specimens. pH refers to the treatment solution conditions (reprinted with permission from [36])

Hoshino, *et al*. demonstrated and highlighted that the pH of reaction baths had a direct influence on the composition and microstructure of HT layer on EG steel [36]. The observations confirmed the clear correlation between pH levels and the resulting microstructure in HT layer (Figure 4). The crystal size showed a slight increase as the pH was raised from 12.0 to 12.4, but above pH 12.6, there was a significant reduction, resulting in smaller crystals. The authors put forth a hypothesis suggesting that $Al(OH)_4^-$ and $Zn(OH)^+$ were the primary species responsible for ZnAl-HT formation. However, conducting the synthesis with a pH greater than 12.6 leads to the emergence of an extra ZnO phase (Figure 5).

The proposed that within the lower range of pH values, specific chemical reactions might take place, leading to the creation of ZnAl-CO_3 HT on EG steel:

$$2Zn(s) + O_2 + H_2O + OH^- \rightarrow 2Zn(OH)_3^- \tag{7}$$

$$CO_2(g) + 2OH^- \rightarrow CO_3^{2-} + H_2O \tag{8}$$

$$Al(OH)_4^- + 2Zn(OH)_3^- + 0.5CO_3^{2-} + xH_2O \rightarrow Zn_2Al(OH)_6(CO_3)_{0.5}.xH_2O + 4OH^- \tag{9}$$

At the upper limit of the pH range, the dissolution of Zn can be segmented into the following two reactions:

$$Zn(s) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^- \quad (10)$$

$$ZnO(s) + H_2O + OH^- \rightarrow Zn(OH)_3^- \quad (11)$$

Pham, *et al*. synthesized ZnAlCe HT layers on HDG substrates with the different pH values of reaction baths by *in-situ* growth method [34]. The findings revealed that the formation of ZnAlCe HT layers, with a molar ratio of Zn:Al:Ce at 3:4:1 occurred by addition of 1 M NaOH solution to water with a pH ranging from 11 to 13. The pH values of reaction baths significantly influenced the rate of zinc coating's dissolution reaction as well as the creation of HT layer. The thickness of HT layers increased as the pH value rose. At a lower pH (around 11), the concentrations of $Zn(OH)_3{}^-$ and $Al(OH)_4{}^-$ were reduced, resulting in fewer HT crystals being deposited on the HDG surface and the thinner HT conversion layer. However, at pH 12, the concentrations of these key species were sufficient to form and deposit HT building blocks on the HDG substrate. Additionally, pH 12 promoted the formation of initial ZnO crystals, which acted as a conditioning layer, leading to a denser deposition of HT crystals. When the pH increased to around 13, it accelerated the dissolution of the zinc coating and ZnO formation, affecting the porosity of the top layer and altering the microstructure and morphology of the HT layer. The precursor bath pH of 12 was found to be the optimal condition for both forming HT layer and facilitating incorporation of cerium within the HT network. In addition, the XRD results claimed that the cation-cation distance in brucite layer and interlayer distance also depended on pH values.

In-situ HT layers on different zinc alloys were investigated [32, 47, 48]. Huang *et al*. produced ZnAl-CO_3 HT on Zn-Al (ZA) alloys (Zn, Al: 5 wt.%) by immersion substrates in 5 mmol/L Na_2CO_3 (pH 8 with 1 M NaOH) for 4 h at 80 ℃ [47]. Holzner *et al*. prepared MgAl-CO_3 HT layer on Zn-Al-Mg (ZAM) coated steel (Zn, Al: 2.5 wt.%, Mg: 1.5 wt.%) by immersion substrates into mixture solution containing 3 mM CO_3^{2-} and 5 mM Mg^{2+} (pH 10.5) at 80 °C for 300 s [47]. Pham *et al*. produced ZnAl-CO_3 HT and investigated the effect of composition and roughness of top zinc alloys coated steel such as HDG (Zn, Al: 1.2 wt.%), ZA coated steel (Zn, Al: 9.4 wt.%), and ZAM coated steel (Zn, Al: 7.2 wt.%, Mg: 4.0 wt.%) on morphology and structure of HT layers [32]. The HT layers were prepared by immersion substrates in mixture solution concluding 0.3 M Zn^{2+} and 0.5 M Al^{3+} at pH 12 for 6 h with stirring and 16 h without stirring. These findings demonstrate that alterations in the composition and surface roughness of zinc coated steel substrates did not impact the structure of the HT layers, nevertheless, these changes had significant effects on the appearance, thickness, and porosity of these HT layers.

2.3. Anion-exchange method

Due to inherent property of HT to undergo anion exchange, the anion-exchange is a general technique for production of special HT compound [49 - 51]. Initially, HT precursors containing smaller interlayer anions are created, and subsequently, the interlayer anions of these prepared HT precursors are replaced with the target product's anions under specific conditions. Zheludkevich, *et al*. prepared ZnAl-Cl, ZnAl-SO_4, and ZnAl-VO_x HTs on zinc by replacing NO_3^- in interlayers [44, 52]. The results confirmed that the rate of exchange reactions for Cl^-, SO_4^{2-}, and VO_x^{y-} anions during anion exchange within LDH-NO_3 follows a decreasing order as follows: $Cl^- > SO_4^{2-} > VO_x^{y-}$ [52]. In addition, the ZnAl-V_2O_7 HT layer was also successfully produced by soaking ZnAl-NO_3 samples in a 0.1 M $NaVO_3$ solution (pH 8 - 9) for 4 h at room temperature (Figure 6) [44].

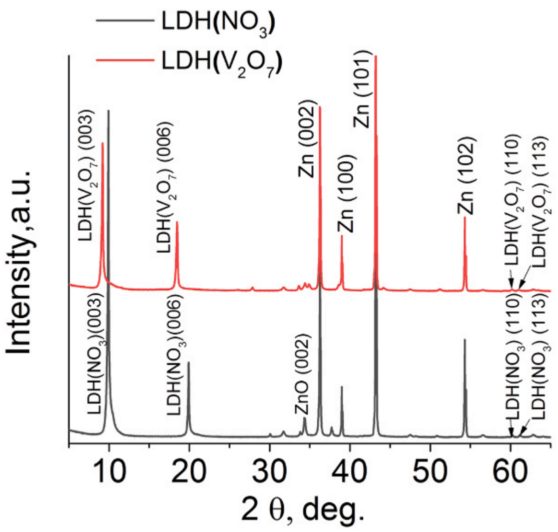

Figure 6. Diffractograms of zinc samples coated with LDH layers before and after anionic exchange (reprinted with permission from [44])

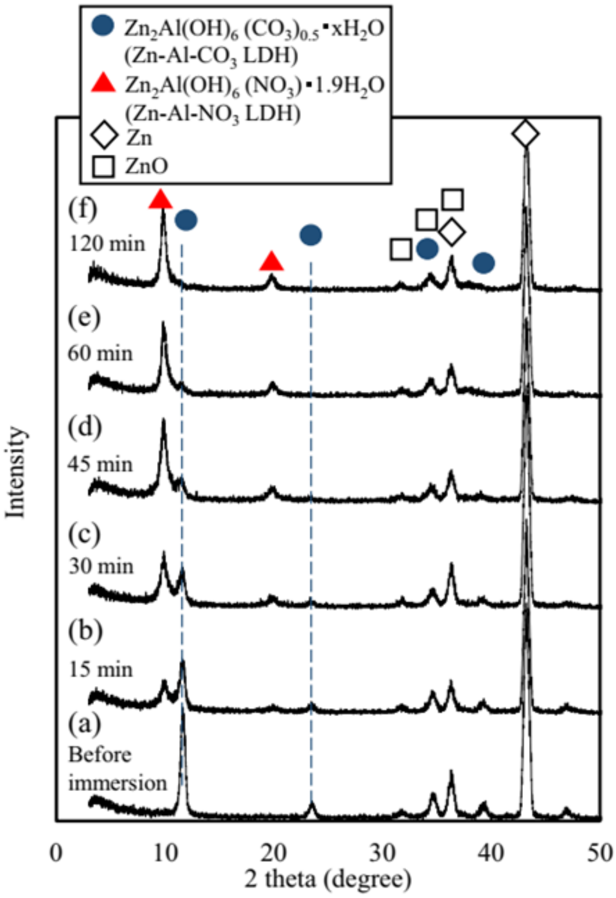

Figure 7. XRD patterns of Zn-Al-CO_3 LDH conversion coated EG steels. (a) before and (b-f) after immersion in $NaNO_3$ methanol solvent at 50 ^oC. Times refer to immersion in the $NaNO_3$ methanol solvent. (reprinted with permission from [35]).

Hoshino, *et al*. found that NO_3^- could successfully exchange with CO_3^{2-} in conversion coated ZnAl-CO_3 HT when the conversion coated substrate was immersed in a 0.24 M $NaNO_3$ methanol solvent at 50 °C for 2 h (Figure 7) [35]. Building upon their synthesis of ZnAl-CO_3 HT layers on EG steel, Amanian *et al.* acquired ZnAl-BTA HT layers (BTA: benzotriazole) through anion exchange [46]. To facilitate inhibitor anion loading, the ZnAl-CO_3 HT layers samples were immersed in a 0.1 M NH_4NO_3 solution in methanol under a nitrogen atmosphere at 30 °C for 2 h. Subsequently, these samples were immersed in an alkaline solution of BTA for 2 h under nitrogen atmosphere at 50 °C.

3. CORROSION PROTECTION OF HT LAYERS ON ZINC AND ZINC ALLOYS

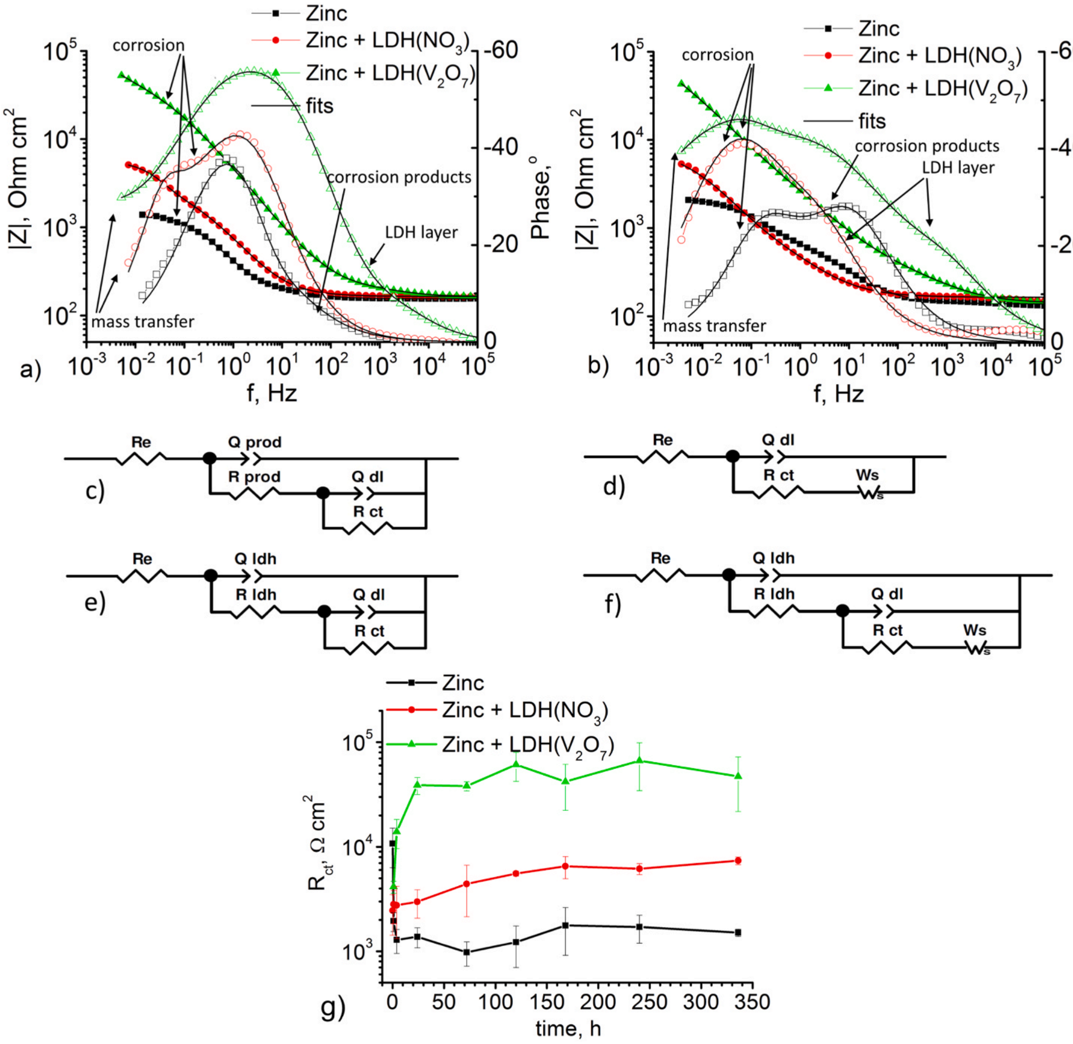

Figure 8. EIS spectra of bare zinc and zinc coated with LDH(NO_3) and LDH(V_2O_7) after immersion during 1 day (a) and 14 days (b) in 0.05 M NaCl solution where solid lines display fitting lines; equivalent circuit models used for fitting of bare zinc (c), LDH(NO_3) sample after 1 day (d) and 14 days of immersion (e), and LDH(V_2O_7) sample (f); temporal evolution of the charge transfer resistance (Rct) (g) (reprinted with permission from [44]).

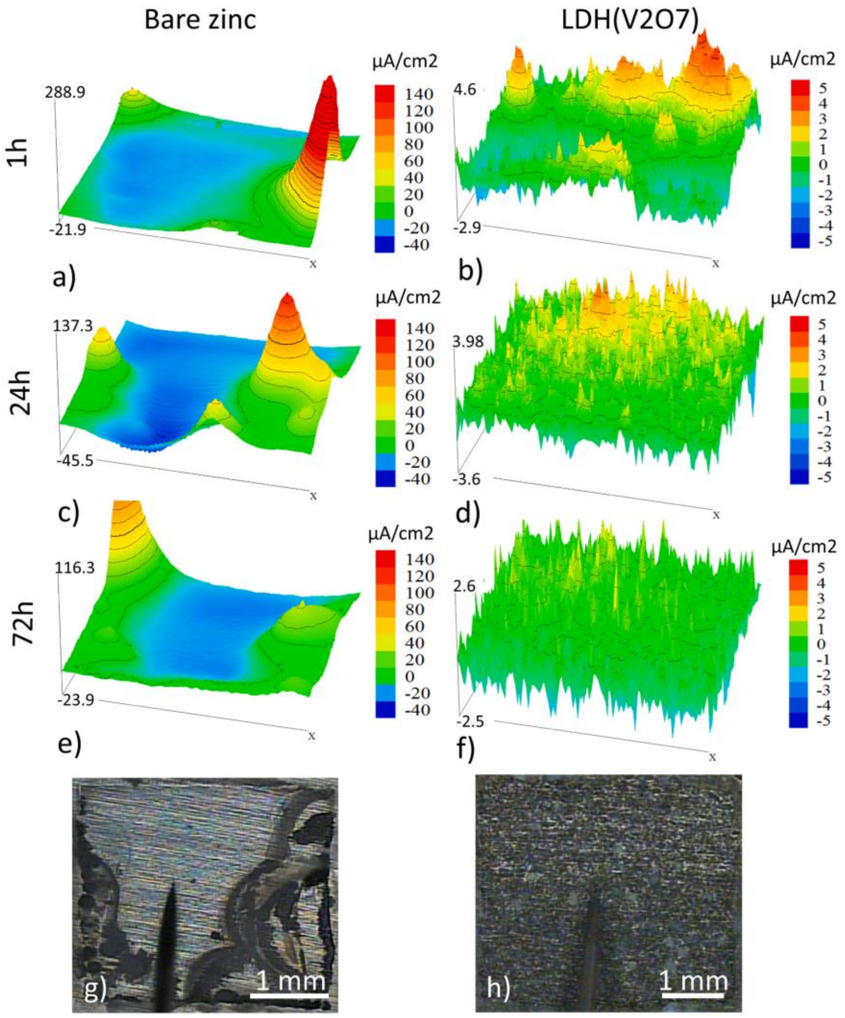

Figure 9. Ionic current density maps measured on zinc (a,c,e,g) and zinc coated with LDH(V_2O_7) (b,d,f,h) in 0.05 M NaCl during 1 h (a,b), 24 h (c,d) and 72 h (e,f), and optical images (g, h) acquired by the end of 72 h immersion (reprinted with permission from [44])

Recently, there has been significant interest in incorporating HT powders into polymer coatings as corrosion inhibitors for zinc and zinc alloy coatings [7]. The studies suggest that composites consisting of HTs intercalated with inhibitors have the potential for diverse applications in various coatings and demonstrate an efficient protective effect across a broad spectrum of substrates. Besides incorporating HT powder into organic coatings, *in-situ* developed HT layers can also be employed in conjunction with and without other coatings to enhance the corrosion protection of the underlying zinc and zinc alloy coatings [34, 35, 37].

The corrosion resistance of HT layers on zinc and zinc alloy coatings was measured and contrasted with that of the untreated substrates. Buchheit, *et al*. showed that the anti-corrosion of HT layers produced using optimal methods on HDG was higher than that of untreated substrates, however, their anti-corrosion effect was lower in comparison with Zn phosphate coatings [45]. The electrochemical results indicated that the presence of HT layers significantly enhanced corrosion protection of zinc and zinc coatings during exposure time to corrosive media.

Zheludkevich, *et al*. investigated the corrosion inhibitive properties of ZnAl-NO_3 and ZnAl-V_2O_7 HT layers on zinc substrates using EIS (Electrochemical Impedance Spectroscopy) and SVET (Scanning vibrating electrode technique) in a 0.05 M NaCl solution [44]. They discovered that the corrosion protection of zinc was significantly enhanced with the ZnAl-V_2O_7 layer compared to both the bare substrate and the ZnAl-NO_3 layer sample (Figures 8 and 9). In addition, after 72 hours of immersion in 0.05 M NaCl, the optical image reveals no obvious signs of corrosion, confirming the effective corrosion resistance offered by the ZnAl-V_2O_7 HT layer (Figure 9).

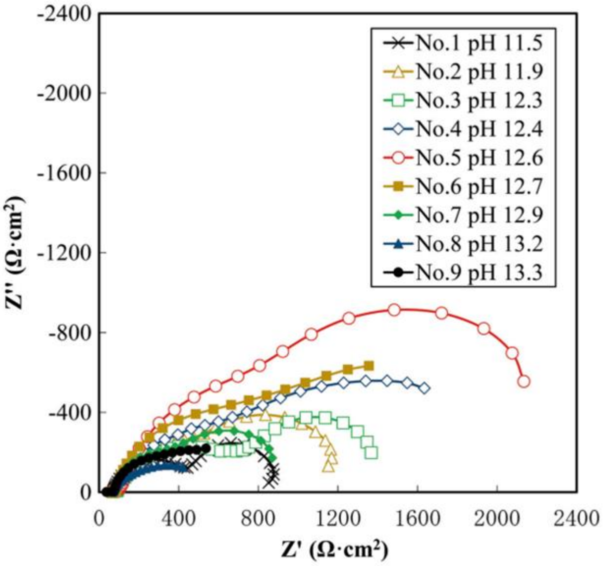

Figure 10. Evolution of EIS spectra for LDH-treated specimens during exposure to 0.1 M NaCl solution. pH refers to the treatment solution conditions (reprinted with permission from [36]).

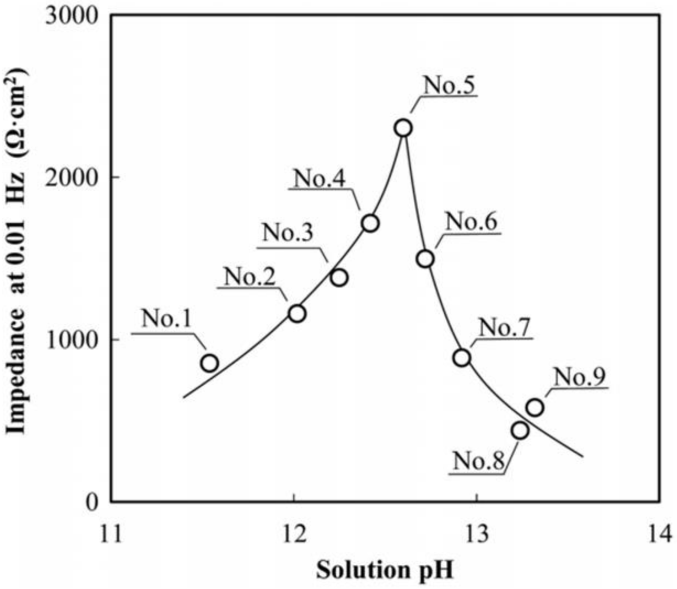

Figure 11. Relationship between impedance at 0.01 Hz and solution pH (reprinted with permission from [36]).

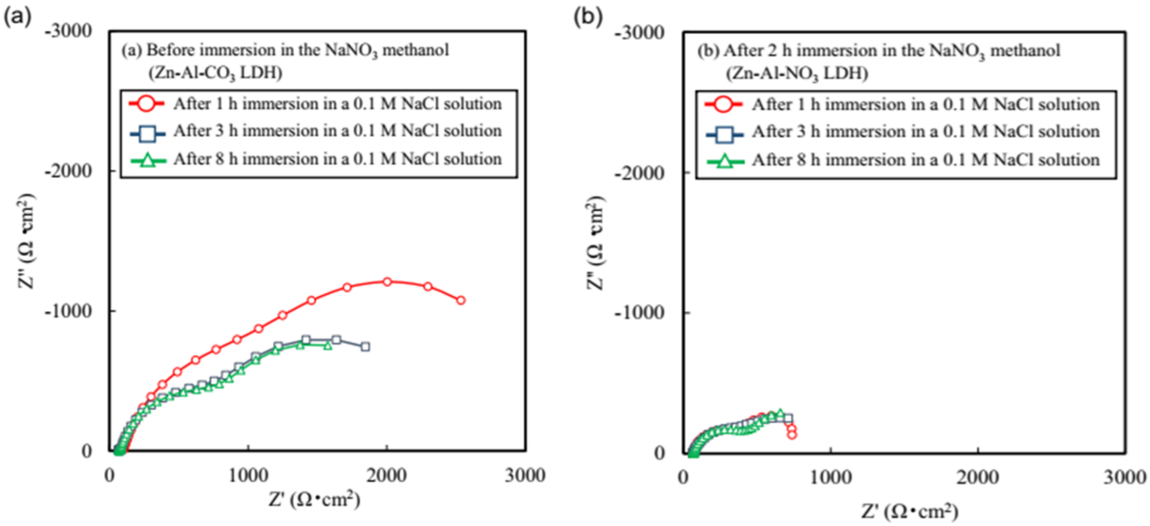

Figure 12. Results of EIS of LDH conversion coated EG steels (a) before and (b) after 2 h immersion in the $NaNO_3$ methanol solvent. The measurements were carried out in a 0.1 M NaCl solution after 1 h, 3h and 8 h immersion (reprinted with permission from [35]).

Hoshino, *et al*. investigated the effect of pH values on corrosion protection of HT layers on EG steel (Figures 10 and 11) [36]. The findings showed that the anti-corrosion of HT layers demonstrated an improvement as the solution pH rose, reaching its peak at pH 12.6. However, a significant decline in corrosion resistance was noticeable beyond this pH value. When the pH was below 12.6, corrosion resistance improved with thicker layers, but the protection provided by the HT layers was limited due to cracks and crevices in the crystals, allowing the electrolyte to reach the Zn substrate. At pH 12.6, higher corrosion resistance occurred despite thinner layers, likely due to the formation of a dense ZnO layer. As the pH rose above 12.6, the ratio of ZnO to HT in the coating increased, potentially reducing corrosion resistance, since ZnO, being highly soluble in NaCl solution, offered no protective effect. Hoshino *et al*. also investigated the corrosion protection of ZnAl-CO_3 and HT ZnAl-NO_3 layers on EG steel [35]. Compared with the ZnAl-CO_3 HT layers, the converted ZnAl-NO_3 HT coated specimens showed lower corrosion resistance by EIS and immersion test in 0.1 M NaCl, however, the results of 100 µL droplet testing with 0.1 M NaCl confirmed that ZnAl-NO_3 HT sample was higher corrosion protection (Figures 12 and 13). In addition, the solubility of the ZnAl-NO_3 HT layer was found to be greater than that of the ZnAl-CO_3 HT. This could affect the corrosion resistance of the coating when exposed to large amounts of solution.

Amanian, *et al*. confirmed that HT layers on HDG after 16 h immersion in mixture solution had better anti-corrosion effect [37]. Polarization and EIS analyses indicated that the HT layers for 16 h reduced the corrosion current density of EG steel by a factor of 10 and enhanced the impedance at 0.01 Hz by a factor of 6 in 0.1 M NaCl. The authors demonstrated that when HT layers were treated with BTA for corrosion protection, the impedance of the modified HT layers increased by a factor of four compared to the untreated HT layers [46]. Pham, *et al*. indicated that the corrosion resistance of HT with Al/Zn ratios 5/1, HT 5/2, and HT 5/3 films noticeably declined, on the contrary, the protective qualities of HT 5/4 and HT 5/5 remained consistent over time when subjected to immersion in 0.1 M NaCl [33].

The existence of HT layers on various zinc alloys had a notable effect on corrosion resistance of substrates. Huang, *et al*. indicated that the corrosion resistance ($R_{sum} = R_{cpf} + R_{ct}$) of HT layers on ZA alloy was higher than that of bare substrate during exposure time in 3.5 wt.% NaCl [47]. This suggests that the HT layers can enhance the durability of the corrosion product film and efficiently inhibit the infiltration of corrosive ions. Pham, *et al*. verified that the composition of zinc alloys had an impact on the corrosion protection provided by HT layers [32]. The corrosion protection properties were maintained in the HT layers on HDG, whereas the corrosion protection of HT layers on ZA and ZAM decreased after 24 h immersion in 0.1 M NaCl solution.

Pham, *et al*. examined how the pH of a solution influenced the corrosion resistance of ZnAlCe HT layers on HDG and compared their anti-corrosion on ZnAl HT layer prepared under pH conditions [32, 34]. The polarization and EIS results showed that the HT layer at pH 12 had sharply better corrosion protection than those of HT layers at pH 11 and 13. Moreover, incorporating cerium into the HT layer at pH 12 resulted in a noteworthy enhancement of corrosion resistance compared to the HT layer without cerium at the same pH solution.

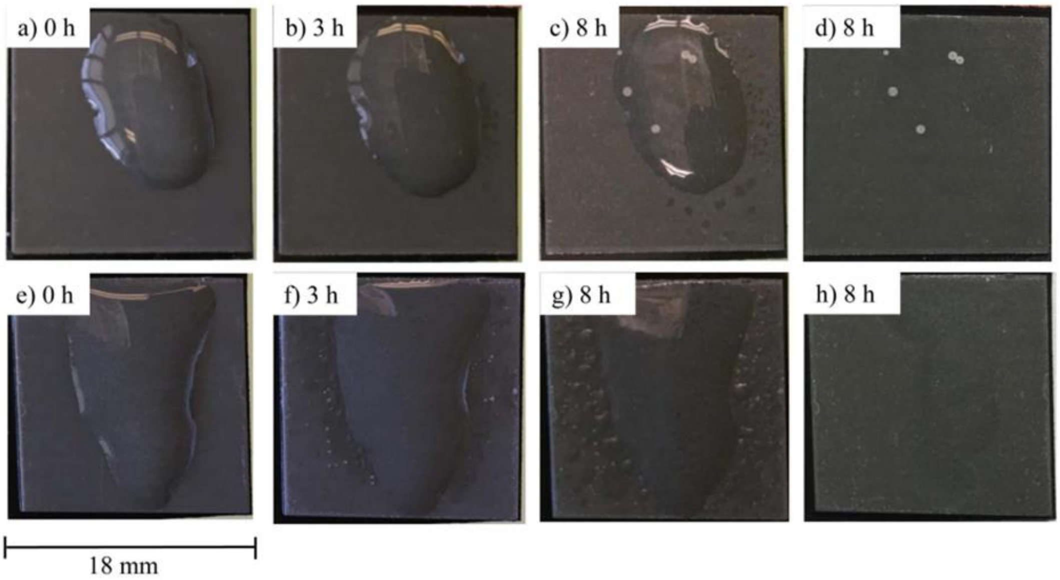

Figure 13. Physical appearance of specimens with either Zn-Al-CO_3 LDH coating (a-d) or Zn-Al NO_3 LDH coating (e-h) after subsequent exposure to 100 µl of 0.1 M NaCl droplet in 98 % HR chamber. Times refer to exposure. (d, h) after washing and drying (reprinted with permission from [35]).

In recent findings, the corrosion mechanism of HT layers has been explored, revealing that their ability against corrosion can be understood by considering key factors, including acting as a physical barrier, trapping aggressive ions, and facilitating the formation of self-repairing oxide or hydroxide layers. It had been previously discussed the effective barrier properties exhibited by HT layers in providing corrosion protection in prior publications [32 - 34]. In corrosive environments, the compact *in-situ* grown HT layers served as a physical protective barrier, effectively isolating aggressive ions from the top zinc and zinc alloy coatings [32 - 34, 47]. The reduction in aggressive ions concentration, associated with the aggressive ions trapping effect, is directly linked to the potential for reducing environmental aggressiveness and extending the operational lifespan of metallic materials [53]. In corrosive environment containing Cl^- ions, it was found that Cl^- ions can undergo an anion-exchange reaction with the anion's presence within the gallery, leading to their absorption into HT interlayer [32 - 34]. The self-repair ability of HT was one of the most important factors that helped increase the protective ability of HT layers [32 - 34]. The formation of metallic oxide/hydroxide crystallites within the corrosion cracking zone of HT layers was a result of a self-healing mechanism, which repairs corrosion pits and creates a protective layer [32 - 34]. Especially, significant improvement in the corrosion protection of HT coatings was involved the deposition of cerium oxides/hydroxides [34].

4. CONCLUSIONS

This review outlines the recent advancements in layer involving HT applied to zinc and its alloys to enhance their corrosion protection. Numerous valuable research endeavors have been conducted on a wide array of HT layers on zinc alloys, driven by their distinctive characteristics, which include modifiable structure and anion exchange capability. Researchers assert that HT layers have been widely recognized as robust physical barriers that effectively shield against the corrosive impact of aggressive ions. The HT layers can act as “nano-trap” of aggressive ions, effectively retarding the deterioration of zinc alloy coatings. In addition, one of the key factors contributing to the enhanced protective properties of HT layers can be their capability for self-repair. The HT conversion layers on zinc and its alloys, prepared through the "*in-situ*" growth method, have been effective for corrosion protection in chloride-containing corrosive environments. However, the majority of research discussed in this review has been conducted in laboratory settings, and there is a need for further refinement of experimental procedures to make them more applicable for industrial use.

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CRediT authorship contribution statement. Thu Thuy Pham: Formal analysis, Methodology, Writing. Thuy Duong Nguyen: Formal analysis, Review and editing, Marie-Georges Olivier: Supervision, Conceptualization, Review and editing. Thi Xuan Hang To: Methodology, Supervision, Conceptualization, Review and editing.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

ABBREVIATION

BTA: Benzotriazole

EG: Electrogalvanized

EIS: Electrochemical Impedance Spectroscopy

HDG: Hot-dip galvanized steel

HT: Hydrotalcite

LDH: Layered double hydroxide

SEM: Scanning electron microscopy

SVET: Scanning vibrating electrode technique

XRD: X-Ray diffraction analysis

REFERENCES

1. Meng Y., Liu L., Zhang D., Dong C., Yan Y., Volinsky A.A., Wang L.N. - Initial formation of corrosion products on pure zinc in saline solution, Bioact Mater. **4** (2019) 87-96. https://doi.org/10.1016/j.bioactmat.2018.08.003.
2. Pham T.T., Nguyen T.D., Nguyen A.S., Nguyen T.T., Gonon M., Belfiore A., Paint Y., To T.X.H., Olivier M.G. - Role of Al and Mg alloying elements on corrosion behavior of zinc alloy-coated steel substrates in 0.1 M NaCl solution. Materials and Corrosion, 2023, pp. 1-17. https://doi.org/10.1002/maco.202213549.
3. Bai X., Tran T.H., Yu D., Vimalanandan A., Hu X., Rohwerder M. - Novel conducting polymer based composite coatings for corrosion protection of zinc, Corrosion Science **95** (2015) 110-116. https://doi.org/10.1016/j.corsci.2015.03.003.
4. Pruna A., Pilan L. - Electrochemical study on new polymer composite for zinc corrosion protection, Composites Part B: Engineering **43** (2012) 3251-3257. https://doi.org/10.1016/j.compositesb.2012.02.041.
5. Pantoja M., Abenojar J., Martínez M., Velasco F. - Silane pretreatment of electrogalvanized steels: Effect on adhesive properties, International Journal of Adhesion Adhesives **65** (2016) 54-62. https://doi.org/10.1016/j.ijadhadh.2015.11.006.
6. Liu Y., Zhou X., Lyon S.B., Emad R., Hashimoto T., Gholinia A., Thompson G.E., Graham D., Gibbon S.R., Francis D. - An organic coating pigmented with strontium aluminium polyphosphate for corrosion protection of zinc alloy coated steel, Progress in Organic Coatings **102** (2017) 29-36. https://doi.org/10.1016/j.porgcoat.2016.02.020.
7. Rodriguez J., Bollen E., Nguyen T.D., Portier A., Paint Y., Olivier M.G. - Incorporation of layered double hydroxides modified with benzotriazole into an epoxy resin for the corrosion protection of Zn-Mg coated steel, Progress in Organic Coatings **149** (2020) 105894. https://doi.org/10.1016/j.porgcoat.2020.105894Get rights and content.
8. Savignac P., Menu M. J., Gressier M., Denat B., Khadir Y. E., Manov S., Ansart F. - Improvement of Adhesion Properties and Corrosion Resistance of Sol-Gel Coating on Zinc, Molecules **23** (2018) 1079. https://doi.org/10.3390/molecules23051079.
9. Zhou B., Wei X., Wang Y., Huang Q., Hong B., Wei Y. - Effect of lanthanum addition on microstructures and corrosion behavior of ZnAl-LDHs film of 6061 aluminum alloys, Surface and Coatings Technology **379** (2019) 125056. https://doi.org/10.1016/j.surfcoat.2019.125056.
10. Wang X., Li L., Xie Z. H., Yu G. - Duplex coating combining layered double hydroxide and 8-quinolinol layers on Mg alloy for corrosion protection, Electrochimica Acta **283** (2018) 1845-1857. https://doi.org/10.1016/j.electacta.2018.07.113.
11. Tang Y., Wu F., Fang L., Guan T., Hu J., Zhang S. - A comparative study and optimization of corrosion resistance of ZnAl layered double hydroxides films intercalated with different anions on AZ31 Mg alloys, Surface and Coatings Technology **358** (2019) 594-603. https://doi.org/10.1016/j.surfcoat.2018.11.070.
12. Iqbal M. A., Fedel M. - Effect of Synthesis Conditions on the Controlled Growth of MgAl–LDH Corrosion Resistance Film: Structure and Corrosion Resistance Properties, Coatings **9** (2019). https://doi.org/10.3390/coatings9010030

13. Ahmed A. A. A., Talib Z. A., Hussein M. Z., Zakaria A. - Zn–Al layered double hydroxide prepared at different molar ratios: Preparation, characterization, optical and dielectric properties, Journal of Solid State Chemistry **191** (2012) 271-278. https://doi.org/10.1016/j.jssc.2012.03.013.
14. Ahmed A. A. A., Talib Z. A., Hussein M. Z. - Influence of Metallic Molar Ratio on the Electron Spin Resonance and Thermal Diffusivity of Zn–Al Layered Double Hydroxide, Journal of Nanomaterials **2013** (2013) 1-9. https://doi.org/10.1155/2013/673173.
15. Bouali A. C., Iuzviuk M. H., Serdechnova M., Yasakau K. A., Wieland D. C. F., Dovzhenko G., Maltanava H., Zobkalo I. A., Ferreira M. G. S., Zheludkevich M. L. - Zn-Al LDH growth on AA2024 and zinc and their intercalation with chloride: Comparison of crystal structure and kinetics, Applied Surface Science **501** (2020) 144027. https://doi.org/10.1016/j.apsusc.2019.144027.
16. Bukhtiyarova M. V. - A review on effect of synthesis conditions on the formation of layered double hydroxides, Journal of Solid State Chemistry **269** (2019) 494-506. https://doi.org/10.1016/j.jssc.2018.10.018.
17. Fedel M., Zampiccoli M. - Insight into the Role of Cerium (III) Addition to a MgAl-LDH Coating on AA6082, Applied Sciences **11** (2021) 8252. https://doi.org/10.3390/app11178252.
18. Nguyen T. D., Nguyen A. S., Tran B. A., Vu K. O., Tran D. L., Phan T. T., Scharnagl N., Zheludkevich M. L., To T. X. H. - Molybdate intercalated hydrotalcite/graphene oxide composite as corrosion inhibitor for carbon steel, Surface and Coatings Technology **399** (2020) 126165. https://doi.org/10.1016/j.surfcoat.2020.126165.
19. Nguyen T. D., To T. X. H., Nicolay A., Paint Y., Olivier M. G. - Corrosion protection of carbon steel by solvent free epoxy coating containing hydrotalcites intercalated with different organic corrosion inhibitors, Progress in Organic Coatings **101** (2016) 331-341. https://doi.org/10.1016/j.porgcoat.2016.08.021.
20. Iqbal M. A., Fedel M. - The effect of the surface morphologies on the corrosion resistance of in situ growth MgAl-LDH based conversion film on AA6082, Surface and Coatings Technology **352** (2018) 166-174. https://doi.org/10.1016/j.surfcoat.2018.08.006.
21. Iqbal M.A., Sun L., LaChance A. M., Ding H., Fedel M. - In situ growth of a CaAl-NO3(-)-layered double hydroxide film directly on an aluminum alloy for corrosion resistance, Dalton Trans. **49** (2020) 3956-3964. DOI: 10.1039/C9DT01773A.
22. To T. X. H, Trinh A. T, Nguyen T. D, Pébère N., Olivier M. G. - Layered double hydroxides as containers of inhibitors in organic coatings for corrosion protection of carbon steel, Progress in Organic Coatings **74** (2012) 343-348. https://doi.org/10.1016/j.porgcoat.2011.10.020.
23. To T. X. H, Trinh A. T, Nguyen T. D, Thai H., Dinh T. M. T., Daopiset S., Boonplean A. - Effects of hydrotalcite intercalated with corrosion inhibitor on cathodic disbonding of epoxy coatings, Journal of Coatings Technology and Research **12** (2015) 375-383.
24. Nguyen T. D., To T. X. H, Gervasi J., Paint Y., Gonon M., Olivier M. G. - Corrosion inhibition of carbon steel by hydrotalcites modified with different organic carboxylic acids for organic coatings, Progress in Organic Coatings **124** (2018) 256-266. https://doi.org/10.1016/j.porgcoat.2017.12.006.

25. Smalenskaite A., Vieira D. E. L., Salak A. N., Ferreira M. G. S., Katelnikovas A., Kareiva A. - A comparative study of co-precipitation and sol-gel synthetic approaches to fabricate cerium-substituted Mg Al layered double hydroxides with luminescence properties, Applied Clay Science **143** (2017) 175-183. https://doi.org/10.1016/j.clay.2017.03.036.
26. Tabish M., Zhao J., Wang J., Anjum M. J., Qiang Y., Yang Q., Mushtaq M. A., Yasin G. - Improving the corrosion protection ability of epoxy coating using CaAl LDH intercalated with 2-mercaptobenzothiazole as a pigment on steel substrate, Progress in Organic Coatings **165** (2022) 106765. https://doi.org/10.1016/j.porgcoat.2022.106765.
27. Mohammadi I., Shahrabi T., Mahdavian M., Izadi M. - A novel corrosion inhibitive system comprising Zn-Al LDH and hybrid sol-gel silane nanocomposite coating for AA2024-T3, Journal of Alloys and Compounds **909** (2022) 164755. https://doi.org/10.1016/j.jallcom.2022.164755.
28. Cao Y., Fang S., Chen K., Qi H., Zhang X., Huang C., Wang J., Liu J. - Insight into the Preparation of MgAl-Layered Double Hydroxide (LDH) Intercalated with Nitrates and Chloride Adsorption Ability Study, Applied Sciences **12** (2022). https://doi.org/10.3390/app12094492.
29. Zhang F., Liu Z. G., Zeng R. C., Li S. Q., Cui H. Z., Song L., Han E. H. - Corrosion resistance of Mg–Al-LDH coating on magnesium alloy AZ31, Surface and Coatings Technology **258** (2014) 1152-1158. https://doi.org/10.1016/j.surfcoat.2014.07.017.
30. Wang F., Guo Z. - Insitu growth of durable superhydrophobic Mg–Al layered double hydroxides nanoplatelets on aluminum alloys for corrosion resistance, Journal of Alloys and Compounds **767** (2018) 382-391. https://doi.org/10.1016/j.jallcom.2018.07.086.
31. Chen J., Song Y., Shan D., Han E. H. - In situ growth of Mg–Al hydrotalcite conversion film on AZ31 magnesium alloy, Corrosion Science **53** (2011) 3281-3288. https://doi.org/10.1016/j.corsci.2011.06.003
32. Pham T. T., Nguyen T. D., Nguyen A. S., Gonon M., Noirfalise X., Paint Y., To T. X. H., Olivier M. G. - Study of the formation and anti-corrosion properties of Zn Al hydrotalcite conversion films grown “in situ” on different zinc alloys coated steel, Progress in Organic Coatings **173** (2022) 107221. https://doi.org/10.1016/j.porgcoat.2022.107221.
33. Pham T. T., Nguyen T. D., Nguyen A. S., Paint Y., Gonon M., To T. X. H., Olivier M. G. - A comparative study of the structure and corrosion resistance of ZnAl hydrotalcite conversion layers at different Al^{3+}/Zn^{2+} ratios on electrogalvanized steel, Surface and Coatings Technology **429** (2022) 127948. https://doi.org/10.1016/j.surfcoat.2021.127948.
34. Pham T. T., Nguyen T. D., Nguyen A. S., Gonon M., Belfiore A., Paint Y., To T. X. Hang, Olivier M. G. - Influence of solution pH on the structure formation and protection properties of ZnAlCe hydrotalcites layers on hot-dip galvanized steel, Surface and Coatings Technology **472** (2023) 129918. https://doi.org/10.1016/j.surfcoat.2023.129918.
35. Hoshino K., Furuya S., Buchheit R. G. - Effect of NO_3^-Intercalation on Corrosion Resistance of Conversion Coated Zn-Al-CO3LDHs on Electrogalvanized Steel, Journal of The Electrochemical Society **165** (2018) C461-C468. https://doi.org/10.1149/2.0091809jes.
36. Hoshino K., Furuya S., Buchheit R. G. - Effect of Solution pH on Layered Double Hydroxide Formation on Electrogalvanized Steel Sheets, Journal of Materials Engineering and Performance **28** (2019) 2237-2244. https://doi.org/10.1007/s11665-019-03963-x.

37. Amanian S., Naderi R., Mahdavian M. - The Role of an In-Situ Grown Zn-Al Layered Double Hydroxide Conversion Coating in the Protective Properties of Epoxy Coating on Galvanized Steel, Journal of The Electrochemical Society **169** (2022). https://doi.org/10.1149/1945-7111/ac5d95.
38. Wu L., Yang D., Zhang G., Zhang Z., Zhang S., Tang A., Pan F. - Fabrication and characterization of Mg-M layered double hydroxide films on anodized magnesium alloy AZ31, Applied Surface Science **431** (2018) 177-186. https://doi.org/10.1016/j.apsusc.2017.06.244.
39. Zhang F., Zhang C. L., Song L., Zeng R. C., Liu Z. G., Cui H. Z. - Corrosion of in-situ grown MgAl-LDH coating on aluminum alloy, Transactions of Nonferrous Metals Society of China **25** (2015) 3498-3504. https://doi.org/10.1016/S1003-6326(15)63987-5.
40. Abd-Elhamid A. I., Soliman H. M. A., Aly H. F. - Hydrothermal Preparation and Characterization of Co-based Layered Double Hydroxide and their Catalytic Activity, Journal of Advances in Nanomaterials **4** (2019). https://dx.doi.org/10.22606/jan.2019.41001.
41. Wang X., Zhang J., Yang S., Yan H., Hong X., Dong W., Liu Y., Zhang B., Wen Z. - Interlayer space regulating of NiMn layered double hydroxides for supercapacitors by controlling hydrothermal reaction time, Electrochimica Acta **295** (2019) 1-6. https://doi.org/10.1016/j.electacta.2018.10.021.
42. Cao Y., Zheng D., Zhang F., Pan J., Lin C. - Layered double hydroxide (LDH) for multi-functionalized corrosion protection of metals: A review, Journal of Materials Science & Technology **102** (2022) 232-263. https://doi.org/10.1016/j.jmst.2021.05.078.
43. Mikhailau A., Maltanava H., Poznyak S. K., Salak A. N., Zheludkevich M. L., Yasakau K. A., Ferreira M. G. S. - One-step synthesis and growth mechanism of nitrate intercalated ZnAl LDH conversion coatings on zinc, Chem Commun (Camb) **55** (2019) 6878-6881. https://doi.org/10.1039/C9CC02571E.
44. Yasakau K. A., Kuznetsova A., Maltanava H. M., Poznyak S. K., Ferreira M. G. S., M. L. Zheludkevich - Corrosion protection of zinc by LDH conversion coatings, Corrosion Science **229** (2024). https://doi.org/10.1016/j.corsci.2024.111889.
45. Buchheit R., Guan H. - Formation and characteristics of Al− Zn hydrotalcite coatings on galvanized steel, JCT research **1** (2004) 277-290.
46. Amanian S., Naderi R., Mahdavian M. - Benzotriazole modified Zn-Al layered double hydroxide conversion coating on galvanized steel for improved corrosion resistance, Journal of the Taiwan Institute of Chemical Engineers **150** (2023) 105072. https://doi.org/10.1016/j.jtice.2023.105072.
47. Huang Q., Wang Y., Zhou B., Wei Y., Gao F., Fujita T. - The effect of ZnAl-LDHs-CO3 on the corrosion behaviour of Zn-5Al alloys in 3.5 wt.% NaCl solution. Corrosion Science, **179** (2021) 109265. https://doi.org/10.1016/j.corsci.2020.109165.
48. Holzner T., Luckeneder G., Strauss B., Valtiner M. - Environmentally Friendly Layered Double Hydroxide Conversion Layers: Formation Kinetics on Zn-Al-Mg-Coated Steel, ACS Appl Mater Interfaces **14** (2022) 6109-6119. https://doi.org/10.1021/acsami.1c19573.
49. Conterosito E., Gianotti V., Palin L., Boccaleri E., Viterbo D., Milanesio M. - Facile preparation methods of hydrotalcite layered materials and their structural characterization

by combined techniques, Inorganica Chimica Acta **470** (2018) 36-50. https://doi.org/10.1016/j.ica.2017.08.007.

50. Forano C., Hibino T., Leroux F., Taviot-Guého C. - Layered double hydroxides. Developments in Clay Science, **1** (2006) 1021-1095. https://doi.org/10.1016/S1572-4352(05)01039-1.
51. Olfs H. W., Torres-Dorante L. O., Eckelt R., Kosslick H. - Comparison of different synthesis routes for Mg–Al layered double hydroxides (LDH): Characterization of the structural phases and anion exchange properties, Applied Clay Science **43** (2009) 459-464. https://doi.org/10.1016/j.clay.2008.10.009.
52. Iuzviuk M. H., Bouali A. C., Serdechnova M., Yasakau K. A., Wieland D. C. F., Dovzhenko G., Mikhailau A., Blawert C., Zobkalo I. A., Ferreira M. G. S., Zheludkevich M. L. - In situ kinetics studies of Zn-Al LDH intercalation with corrosion related species, Phys. Chem. Chem. Phys. **22** (2020) 17574-17586. https://doi.org/10.1039/D0CP01765E.
53. Tedim J., Kuznetsova A., Salak A. N., Montemor F., Snihirova D., Pilz M., Zheludkevich M. L., Ferreira M. G. S. - Zn–Al layered double hydroxides as chloride nanotraps in active protective coatings, Corrosion Science **55** (2012) 1-4. https://doi.org/10.1016/j.corsci.2011.10.003.