Review

Layered Double Hydroxide Protective Films Developed on Aluminum and Aluminum Alloys: Synthetic Methods and Anti-Corrosion Mechanisms

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Abstract: This work reviews the characteristics of layered double hydroxides (LDHs) in the context of protective thin films to enhance the corrosion resistance properties of aluminum alloys. A discussion is made in detail about the LDH protection mechanism and the effect of synthesis approaches on LDH structural variations and the corresponding anti-corrosion behavior. LDHs anion-exchange behavior to host inorganic/organic anions makes them a potential material to investigate for anti-corrosion film. This unique advantage and the availability of a wide range of metal oxide-based layers, interlayer anions, and self-healing properties make LDH family an attractive choice for the development of compact LDHs based smart coating systems.

Keywords: layered double hydroxide; aluminum alloys; nanocontainers; corrosion resistance; reaction mechanisms

1. Introduction

Aluminum alloys are considered optimum materials for various applications, due to their promising characteristics: for instance, conductivity, strength to weight ratio, natural abundance, and ready availability at low cost. However, aluminum alloys demonstrate compromising corrosion resistance properties and become susceptible to localized corrosion, especially pitting and intergranular corrosion, on contact with aggressive media which causes the destruction of the surface aluminum oxide protective layer [1–4]. Aluminum thin oxide layers are formed when a surface is exposed to the atmosphere. The metal remains protected unless the surface is exposed to conditions i.e., alkaline ones, which can damage the oxide layer. The microstructural features are other factors that significantly affect the properties of aluminum. Intermetallic phases are found to decrease/improve physical and mechanical properties, depending upon the distribution, type and morphologies of the phase [5,6]. Several intermetallic phase particles, like Al3Mg2, Mg2Si, Al2CuMg, and MgZn2 are anodic to the aluminum matrix and corrode preferentially with respect to the aluminum matrix, while the particles like AlFeMnSi, AlCuFeMn, Al3Cu (θ phase) and AlCuFeSi are found to be cathodic with respect to the aluminum matrix and cause peripheral trenches in the aluminum matrix adjacent to the intermetallic particles [7]. Iron, which is major class of secondary phase (AlFe and/or AlFeSi), induces a decrease of both mechanical and corrosion resistance properties but it reduces the tendency to adhere to metal molds [8]. The anodic behavior of intermetallic particles regarding the aluminum matrix can cause localized corrosion [9]. On the other hand, it is most likely that pitting corrosion or other forms of localized corrosion attack enhance fatigue...
crack initiation [10]. Chromate-based conversion coatings systems have been employed for a long time to protect aluminum alloys but due to the presence of hazardous Cr(VI) groups, much attention has been paid to develop suitable alternatives [11,12]. Various coating systems, for example, anodization [13,14], sol-gel synthesis [15,16] conversion coatings [17,18], magnetron sputtering [19,20], polymer coatings [21,22] and self-assembly [23,24] are widely investigated approaches to develop non-chromate based corrosion resistance coatings. Layered double hydroxides, also referred to as hydrotalcite, are a group of anionic clays and are actively investigated in different fields due to their unique characteristics. They are generally represented by the expression \[ \text{M}^{2+}\cdot\text{A}^x\cdot\text{mH}_2\text{O}, \]\ where \( \text{M}^{2+} \) are divalent cations, while \( \text{M}^{3+} \) are trivalent metal cations. “A” represents the \( x \)-valent anions. The LDH structure is organized when \( \text{M}^{2+} \) is substituted by \( \text{M}^{3+} \) and \( \text{A}^x \) anions are used to balance the net positive charge [25–28], and the molar ratio of \( \text{M}^{2+}/(\text{M}^{2+} + \text{M}^{3+}) \) range from 0.20 to 0.33 [29,30]. Due to the anion exchange capability of LDHs, various anions can be successfully incorporated inside the LDH interlayer to modify the chemistry of LDH for specific applications: for instance, supercapacitors, environmental sciences, catalysts, adsorption, etc. [31–37]. Recently, according the subject of anti-corrosion materials, layered double hydroxide (LDH)-based coating systems have also been widely explored, due to LDHs’ peculiar morphology, a wide range of cationic/anions combinations, environmental friendliness, barrier properties, high surface to volume ratio and multifunctional design along with the capability to intercalate various species, such as metal ions of mixed valences, complex inorganic, organic molecules in the in LDH interlayers, and thus can be utilized as multifunctional coating systems. The LDHs’ film thickness, number of layers, composition, surface geometry, and morphology are found to influence the ability of LDHs to encapsulate various functional groups and can be controlled with the adjustment of synthetic conditions, fabrication methodology, and initial salt concentrations etc. [38–40]. Furthermore, the interlayer anions and ratio of metal cations can largely impact orientation, crystal structure, and surface geometry [41]. A wide range of divalent metal cations (M = Mg, Ca, Zn, Ni, etc.) have been used to develop MAI-LDH on aluminum/aluminum alloys, along with various combinations of anions inside the LDHs interlayers (complex anions, corrosion inhibitors, pigments, etc.). The LDH protective mechanism includes the following key features; (a) the anion-exchange ability, (b) self-healing mechanism, and (c) barrier effect, which are found to improve the anti-corrosion properties. Considering the ion exchange equilibrium constant, the nitrate ions demonstrate the lower value in the following order: \( \text{NO}_3^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{MoO}_4^{2-} < \text{SO}_4^{2-} < \text{CrO}_4^{2-} < \text{HAsO}_4^{2-} < \text{HPO}_4^{2-} < \text{naphthol yellow}^{2-} < \text{CO}_3^{2-} \) [42]. That’s the reason a lot of research has been conducted on LDH-NO\(_3\) where nitrate groups act as active precursors to modify the LDH chemistry with different anticorrosion inhibitors through ion-exchange and can design multifunctional coating systems for corrosion protection.

To develop a compact LDH coating system, two main strategies have been pursued: (a) loading of corrosion inhibitors/anticorrosion pigments inside the LDHs; (b) LDHs dispersed/coated with polymeric coating matrix to protect the metallic surface. This work provides an overview of the utilization of the LDHs for the surface functionalization of aluminum surfaces to develop a compact LDH based system to enhance corrosion resistance properties.

2. Synthesis of LDH on Aluminum and Aluminum Alloys

In the context of LDH-based protective coatings, coprecipitation and in situ growth methods are the widely investigated approaches with various customized reaction/host modifications to develop LDH based systems. Here, we discussed in detail these two approaches and their modifications in terms of coating resistance properties.

2.1. Coprecipitated Synthesis

The coprecipitation approach is an illustration of the ex-situ method where the LDH precursors are initially synthesized in powder form and applied on the aluminum surface by using certain techniques. The coprecipitated LDH precursors are synthesized by the combination of divalent and trivalent cationic salt solutions and exhibit advantages of high purity, crystallinity, controlled chemical
composition, and significant interaction with organic/inorganic inhibitors. On the other hand, the
adhesion to the surface is inconsistent. In recent years, a number of reviews have summed up the
work on the synthesis of layered double hydroxides and the parameters/conditions affecting their
formation [43–48]. Theiss et al. presented a comprehensive review of the synthesis of LDHs by the
coprecipitation method [48]. Recently, Bukhtiyarova et al. [41] concisely reviewed LDHs’ synthesis and
discussed in detail the various parameters that affect the growth of LDHs, i.e., synthetic solution pH,
salt concentration, the nature of the alkaline solution (NaOH, urea, ammonia, ammonium carbonate,
etc.), aging time, reaction temperature, and molar cationic ratios. The synthetic conditions—including
the initial concentration of salts, crystallization time, solution pH, precipitating agents—and the ratio of
divalent to trivalent cations have been found to have an influential impact on LDH structure, functional
properties and crystal structure parameters [49]. To enhance the corrosion resistance properties, LDH
coating systems can also be modified either with various corrosion inhibitors/anticorrosion pigments
by taking the advantage of LDHs’ anion-exchange properties, or by the utilization of LDHs dispersed
in polymeric/organic systems. Both approaches are found to significantly inhibit the interaction
of aggressive species with the substrate and actively enhance the corrosion resistance properties.
The self-healing capability of LDHs also makes them a viable material to enhance the corrosion
resistance properties. A detailed summary of reaction conditions and general chemistry for the
synthesis of coprecipitated LDHs is listed in Table 1 for a comparative study.

Buchheit et al. initially developed a ZnAl-LDH-based coating system by using the coprecipitation
method and further applied it on the aluminum 2024 alloy [50] and reported the intercalation of
decavanadate corrosion inhibitor inside LDH galleries [51]. William et al. [52] synthesized ZnAl-LDH
intercalated with nitrate, carbonate, and chromate and processed it on organic coated AA2024 alloy.
They also investigated the various anti-corrosion pigments (oxalate, benztetrazolate, ethyl xanthate)
to protect the AA2024 [53]. They also investigated the LDHs intercalated with nitrate-, carbonate-, and
chromate, and dispersed in polyvinyl butyral (PVB), and applied on AA2024-T3 surface [54].
Poznyak et al. [55] developed MgAl-LDH and ZnAl-LDH loaded with different anticorrosion inhibitors
(quinaldate and 2-mercaptobenzothiazolate) on AA2024 and reported the kinetics of anions released
on contact with the aggressive solutions. Zheludkevich et al. [56] synthesized MgAl and ZnAl-LDH
loaded with divandate anions in the LDH interlayers and investigated the controlled release behavior
and corrosion resistance properties of resultants to protect the aluminum AA2024. Stimpfling et al.
prepared ZnAl-LDH modified by aniline and benzene derivatives, 3- and 4-aminobensulfonylic acid
(ABSA) and 3,4-dihydroxybenzoic acid (HHBA), on organo-modified aluminum AA2024 to enhance
the corrosion resistance properties [57,58]. Liu et al. [59] develop cerium-modified ZnAl-CO$_3^{2-}$
LDH on aluminum alloy through the sol-gel approach to enhance the corrosion resistance properties.

Galvao et al. reported the effect of temperature and time on the particle growth and crystallite
formation to understand the growth mechanism of LDHs developed by the co-precipitation method.
They described the nature of particle growth as being consistent with an Ostwald ripening and
dissolution mechanism, where extended synthesis time and temperature have found a significant effect
on particle size and crystallite size of LDHs [60].

2.2. In Situ Growth Method

The in situ growth approach is considered a promising choice to develop LDHs directly on
the substrate with the advantage of a more facile approach, controlled film thickness/size, distinct
surface morphologies, strong adhesion between LDH and the substrate, and feasible to coat complex
geometries. The successful intercalation with various inorganic/organic anions can be achieved by
controlling the differential growth of LDH islands on the surface-active intermetallic/active zones.
Figure 1 describes the general pattern of LDH synthesis on an aluminum substrate. The aluminum
alloys act as a source of Al$^{3+}$, where the aluminum surface starts dissolution in a basic solution to
form aluminum oxides. Al(OH)$_3$ reacts with water to form a mixture of precipitated divalent cations
and OH$^{-}$ on the surface of Al(OH)$_3$. The substitution of divalent cations with Al$^{3+}$ ions results in the
coexistence of Al(OH)$_3$ and M(OH)$_2$ to form the LDH structure. On the other hand, the hydroxyl ions present inside the galleries were exchanged by the solution anions (depending on the ionic radii). LDHs formed a compact layer at LDH/interface, followed by a comparatively porous LDH network (Figure 1). Initially, Buchheit et al. developed LDH directly on the aluminum alloys as corrosion resistance films and patented that work [61].

![Diagram of LDH structure](image)

**Figure 1.** (a–c) Synthesis procedures of in situ growth LDH and possible modification approaches, (d) general representation of an LDH structure.

In recent years, the introduction of various corrosion inhibitors in in-situ growth LDHs has been reported (Table 1) to develop long term stable hybrid LDH/polymeric structures that were studied to achieve better stability. A polymeric primer layer can provide enough binding support and inhibit diffusion reactions. However, the basic issue of self-healing is still not thoroughly investigated in different situations, and defects/scratches may remain open for continuous interference of aggressive species with the coating systems. Recently, the concept of double-doped LDH structures was also introduced, where trivalent cations are used in LDHs structure construction (Figure 2c). High corrosion resistance is reported where cerium and lanthanum trivalent cations were used in the presence of an aluminum source [62,63]. However, the addition of larger particles inside the LDH system may cause a plasticizing effect due to the trapped corrosion inhibitors inside the LDH framework.

Synthetic conditions have many crucial parameters to control the in situ growth of LDHs; reaction temperature and aging time strongly affected the crystallinity and geometry of LDH. The pH of the synthetic solution is another factor that can influence the composition of developed LDH. For example, in the case of Zn-based LDH, it is reported that a solution pH higher than 12.6 causes an increase in the wt.% ratio of ZnO/LDH, while ZnO is found to be highly soluble in NaCl solution, thus a reduction in corrosion resistance properties is reported. Elevated pH can also cause cracks and defects and can favor the formation of secondary phases.

Surface morphology/surface area is another property that is found to have an influence on the LDH corrosion resistance properties. Various surface morphologies in that regard are reported in our previous work, for instance, platelet structure, rod-like, cauliflower-like, spiral shape, sand rose [40,64]. The SEM images of LDHs synthesis at elevated condition is reported in Figure 2 to understand the growth pattern of LDHs.

Initially at low synthetic conditions LDH granules form, which turns into net/flower-like structure at optimum conditions. Better corrosion properties were observed at extended reaction conditions (100 °C, 18 h), where a compact structure was observed compared to the traditional LDH structure [40].
The urea hydrolysis is another approach to obtain the fine distribution of crystallites and a high degree of crystallinity, but urea hydrolysis promotes the formation of carbonate ions in the system which restricts the anion exchange capabilities of LDHs [65]. Numerous aluminum substrates have been studied to develop LDHs directly on them i.e., AA2024, pure aluminum, AA6061, AA6082, AA5005, and A6N01. The anodization of substrates is found to promote higher, denser growth of LDHs with additional underlying protection. But the formation of LDH growth in such cases depends upon the PEO tortuosity and the pores which are responsible for the accessibility of the $\text{Al(OH)}_3^-$ [66]. Plasma electrolysis modification is found to develop highly stable in situ growth LDH structure and dense LDH geometry [66,67]. Meanwhile, the electrochemical deposition approach is another way to develop LDHs directly on the substrate with the advantage of controlled deposition rate and higher growth rate, but the synthetic procedure is complex and not completely discussed yet. The complete overview of synthetic approaches and relevant parameters is mentioned in Table 1 and Table 2. Synthesis of DHs can be explained with the general reactions expressed in Equations (1)–(6):

\[
\text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad (1)
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (2)
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2\uparrow + 2\text{OH}^- \quad (3)
\]

\[
\text{Al}_2\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{Al(OH)}_3 \quad (4)
\]

\[
\text{M}^{2+} + \text{OH}^- \rightarrow \text{M(OH)}^+ \quad (5)
\]

\[
\text{M(OH)}^+ + \text{Al(OH)}_3 + \text{A}_n^- + \text{H}_2\text{O} \rightarrow \text{MAl-LDH} \quad (6)
\]

Due to elements segregation and the presence of secondary phases in aluminum alloys, a possible potential difference can form which causes the formation of corrosion microcell on the aluminum surface (Equations (1)–(3)), while hydrogen bubbles can also be formed during LDH preparation (Equation (3)). Porous outer and inner compact $\text{Al}_2\text{O}_3$ layers are formed and transformed into $\text{Al(OH)}_3$, which act as a precursor to form LDHs on the aluminum surface upon reaction with divalent cations. The anion exchange step further allows one to incorporate various anti-corrosion inhibitors inside the LDH interlayers and also can precipitate on the metal/LDH interface (Equations (1)–(6)) [63]. It can be said that the thickness of the LDH correlates with the number of cations, pH, reaction temperature, aging time, alkali solution and so on [41]. However, consistent values of all the describe that the morphological quality of LDH nanostructures increases with the increase of nitrate concentration in the solution. In an aqueous solution containing metallic aluminum and nitrate anions several electrochemical processes involving anodic dissolution of aluminum and cathodic reduction of nitrates and oxygen can occur. The cathodic processes generate hydroxyl ions and create a pH gradient. Although the reduction of nitrates to nitrite has been proven, there are other possible reactions involving nitrate and nitrite anions, producing nitrogen gas or ammonia, which may contribute to the overall reduction process [68] and thus can affect the film thickness as well surface morphology.
Table 1. Synthesis approaches to LDHs at various synthetic conditions with various precursors.

<table>
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<th>Anion-Exchanger</th>
<th>Precursors</th>
<th>Alkaline Media</th>
<th>Method</th>
<th>Al Alloy</th>
<th>Synthetic Condition</th>
<th>Aging Time (h)</th>
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<td>ZnCl₂, Al₂O₃</td>
<td>NaNO₃</td>
<td>coprecipitation</td>
<td>2024 V</td>
<td>6.3-6.5</td>
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<td>NaNO₃</td>
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<td>2024 V</td>
<td>6.3-6.5</td>
<td>12</td>
<td>[51]</td>
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<td>Mg₄Al₂O₅</td>
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<td>-</td>
<td>NaNO₃</td>
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<td>2024 V</td>
<td>9.3</td>
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<td>2024 V</td>
<td>9.3</td>
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<td>2024 V</td>
<td>10</td>
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<td>MgAl</td>
<td>-</td>
<td>Zn(NO₃)₂</td>
<td>NH₄OH</td>
<td>In situ</td>
<td>2198</td>
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<td>80</td>
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<td>(GPTMS)</td>
<td>NH₄OH</td>
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<td>80</td>
<td>[81]</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>coprecipitated</td>
<td>2024 V</td>
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<td>[82]</td>
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<tr>
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<td>-</td>
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* LDHs layer developed over a Plasma Electrolytic Oxidation (PEO) coating.
Among the possible solutions, LDHs incorporated with corrosion inhibitors seem to be a feasible choice to protect the metallic surface, while the compatibility with organic matrices makes them a powerful option to provide long term stability and to effectively reduce the corrosion rate.

3. Corrosion Resistance of LDH Films

LDH-based coatings have been pursued to achieve high corrosion resistance. The mechanisms through which these materials can provide the underlying substrate with improved corrosion resistance are manifold. In addition to being a physical barrier against water and ions migration, LDH-based coatings are recognized for their capability to encapsulate functional species in between the charged lamellae. As a result of this specific property, coatings based on these materials have a self-healing potential if proper corrosion inhibitors are embedded and released in situ upon a specific trigger. LDH coatings commonly show a two-layered structure (schematically depicted in Figure 3): an inner relatively compact layer and an outer porous layer formed by the interconnection of the different platelets.

Figure 3 depicts a schematic representation of the LDH coatings as well as a FIB-SEM image of the section of MgAl-LDH coating developed on AA6082. Liang et al. described the formation of LDHs on AA2099-T83 Al–Cu–Li alloy, and further explained the role of intermetallic particles on the formation of LDHs and on their corrosion resistance properties. Iron-containing intermetallic particles act as a preferential site for the formation of nucleation and growth of LDHs and a compact, uniform LDHs layer is developed on the aluminum surface [93]. Overall, intermetallic particles which are cathodic compared to the matrix, contribute to the formation of LDHs. Due to the localization of the cathodic reactions in correspondence with the intermetallic particles, LDHs nest-like morphology [64] is observed.

Table 2. Effect of synthetic conditions on the growth of LDHs developed directly on the AA6082 substrate [40]: Evolution of the morphology by combining different temperatures (from 40 °C to 100 °C, vertical axis) and times (from 12 h to 24 h, horizontal axis). Image reproduced with permission from the publisher (MDPI).
Figure 3. Structure of LDH based coatings: (a) schematic representation of the structure of the film; (b) schematic representation of the structure of the film in presence of intermetallic particles; (c) FIB-SEM image of MgAl-LDH coating on AA6082 (courtesy of Jönköping University).

Notice that in correspondence of the active intermetallic particles (Figure 3b), a differentiated growth of island-like LDHs occurs [60]. The inner compact layer is responsible for the physical barrier effect of the coating while the platelets, which form the outer layer, mainly provide the ion exchange reactions.

Regardless of the synthesis technique employed for the development of LDH films either by the in-situ method or the two-step method, LDHs suffer from corrosion induced by halogen ions such as chlorides. The film thickness and compactness cause an increase in LDHs barrier properties and help to reduce the diffusion of aggressive media to interact with the substrate. The film thickness can be controlled with synthetic conditions and can be modulated from a few microns to several micrometers. In our recent study, we observed that corrosion resistance varies with the effect of film thickness and high film thickness may cause a reduction of corrosion resistance due to higher porosity [40,76,77,88]. The durability of LDH coatings can also be increased with embedding corrosion inhibitors in between the platelets. In this regard, coatings based on Zn, Ca and Mg were developed directly or indirectly on aluminum substrates and have been tailored by entrapping various functional species. LDHs anion exchange reactions are generally assumed to take place too tactically, even if precipitation mechanisms have been also proposed [94,95]. Nitrate-based LDHs might be a possible
option to enhance the corrosion resistance by trapping the chloride ions through anion exchange process and release corrosion inhibitors [96]. Tedim et al. [96,97], described the synthesis of ZnAl-LDH (NO$_3$) and ZnAl-V-LDH developed on AA2024 and the chlorides entrapment capability of LDH-NO$_3$ and possible diffusion process which affects the stability of the coating against corrosion and leads to the damaging of the LDH/substrate interface.

LDHs with intercalating corrosion inhibitors are a better choice, as they are expected to deliver the inhibitors upon damaging of the matrix and can provide self-healing properties. Vanadate-exchanged LDHs were utilized by various research groups, either directly on the aluminum substrate (in-situ) or co-precipitated on the substrate, but, in both cases, the vanadate’s were found to enhance the corrosion resistance of LDH [17,45,50,51,69,73]. In another work, on AA2024 substrate, ZnAl-LDH was synthesized and modified with 2-mercaptopbenzothiazole and further treated with hydrophobic hexadecyltrimetoxisilane in order to functionalize the surface to obtain significant anti-corrosion and anti-biofilm characteristics [98]. To enhance the corrosion resistance properties of LDH, Zhang et al. [86] designed a graphene-based LDH, where graphene is found to act as sealing the LDH pores and improve barrier properties while MoO$_4^{2-}$ corrosion inhibitors further help to provide a stable corrosion resistance system. Kaidong et al. [92] introduced LiAl-LDH modified with disodium vanillin L-aspartic acid to protect the A6N01 aluminum alloy. The developed coating demonstrated an enhanced corrosion resistance compared to the bare Al alloy, but pitting corrosion after 120 h of exposure in 3.5% NaCl solution was observed to take place in the presence of coating defects. CaAl-LDH was introduced by our group [77] and found to improve corrosion resistance with limited long term stability. Wang et al. [82] investigated superhydrophobic LDH coatings produced by modifying the chemistry of LDH by intercalating with oleate, stearate and laurate groups in order to modify the LDH hydrophilic nature to superhydrophobic. A remarkable improvement of the microbiological corrosion resistance properties was achieved, and such systems have shown the potential to retard the biofilm formation and significantly enhance the corrosion resistance properties. Chen et al. [99] demonstrated a simple approach to prepare an oriented NiAl-LDH on PAO/Al substrate and further modify it with sodium laurate solution to endorse super-hydrophobicity. Wang et al. [100] synthesized superhydrophobic MgAl-LDH directly on AA6061 alloy and achieved specific characteristics by modifying the LDH chemistry with triethoxy-1H,1H,2H,2H-tridecafluoro-n-octylsilane to obtain superhydrophobic LDH properties. They showed that improved mechanical and electrochemical stability can be achieved by this method, along with high durability and anti-icing properties. LDHs also exhibited the so-called shape memory effect, where calcination causes dehydroxylation and decomposition of anions inside the galleries. Calcination strongly affects the oriented growth of the LDH, causes an increase in the surface area and contraction of the basal spacing, and increases the likeliness for anion exchange, which in turn causes a compact structure that substantially influences the LDH corrosion resistance properties [101].

To promote the barrier properties, the synthesis of LDHs on the anodized aluminum substrate can provide significant active and passive corrosion protection to obtain a compact coating system [90]. Conceptually, the LDHs grown on the anodic film may seal the micropores of the anodized surface (strong barrier properties), and LDHs itself provides active protection via entrapment of aggressive species and through self-healing properties [75]. Moreover, LDH preferentially grows on the entire surface of the anodic film including the bumpy areas and on the complicated surface providing a suitable approach to protect the aluminium alloys [102]. Recently combined effect of LDH coatings grown on a “plasma electrolytic film” have become an interesting research area due to combined attractive properties of active and passive protection [74,89,103].

Rare earth elements are found to have a significant inhibiting effect and are the object of considerable scientific interest [104], and generally exhibit a non-toxic nature [105]. Among rare earth elements, cerium-based coatings attract significant attention, specifically in case of incorporation inside the LDH network [59]. The synthesis of LDHs on anodized aluminum alloys is also reported and successfully proven helpful to develop a comparatively stable protective system where anodization of Al alloy support to develop a dense network of LDHs, and also the LDH solution treatment causes the sealing
effect of anodized surface, and such synergistic effect is found to improve the corrosion resistance of Al alloys [73–75]. Li et al. [73] developed ZnAl-LDH modified with vanadate corrosion inhibitors directly on anodized 2198 alloy and reported the long-term stability of the LDHs system. Kuznetsov et al. [75] developed an LDH-based sealing method for anodized AA2024. AA2024 sheets were grounded and anodized in a solution of 0.53 M C₆H₅O₃, 0.46 M H₂SO₄ at 37 °C for 25 min with an applied voltage of 14 V. It demonstrated the corrosion protection performance of actively sealed anodized aluminum surface with smart nano-containers. From the above discussion, we can say that composite hybrid LDH systems can provide multifunctional coating systems and can provide self-healing, self-wash ability, and biocompatibility as per applications. However, to analyze the LDHs self-healing capability and further, the response time and release rate of embedded inhibitors is still an issue and very little work is reported on that topic. This is discussed in more detail in Section 3.3.

3.2. Corrosion Resistance Co-Precipitated LDHs in Organic and Hybrid Matrices

LDH dispersions in polymeric matrices (see schematic representation in Figure 4) have been studied in order to enhance the coating stability against corrosion and provide better mechanical properties along with stress dissipation ability. In order to achieve an enhancement in terms of corrosion properties, LDH particles are embedded inside an organic or organic/inorganic hybrid (OIH) matrix in order to: (1) act as a physical barrier against moisture and oxygen permeation and (2) provide a controlled release of corrosion inhibitors. layered double hydroxides dispersed inside a polymeric matrix improves the barrier properties of organic coatings by increasing the length of the pathway water and other species take to reach the metal interface, similar to other lamellar pigments [106].

ZnAl-LDH intercalated with EDTA via co-precipitation and further coated on AA2024 was discussed and the capability of EDTA for anion exchange and corrosion resistance behavior is reported and the nature of ZnAl-CrO$_4$-LDH, ZnAl-CO$_3$-LDH, ZnAl-Cl-LDH are completely revealed [58]. Liu et al. [59] developed the cerium based LDH protective system with the combination of hybrid sol-gel on aluminum 2024 alloy and described the synergistic inhibiting effect of ZnAlCe-LDH and CeO$_2$ nanoparticles on the corrosion resistance properties of aluminum.

![Figure 4](image-url) Schematic representation of the co-precipitated LDH dispersed into an organic coating.

The inhabitation effect of MgAl-LDH mixed at various proportions with hybrid sol-gel compose of (tetra-n-isopropyoxizirconium (TPOZ) and 3-glycidoxypropyltrimethoxysilane (GPTMS)) were synthesized, and enhancement in corrosion resistance was monitored [87]. In another work, molybdate-intercalated MgAl-LDHs were synthesized by the coprecipitation method, dispersed in water-soluble (polyvinyl alcohol) PVA polymeric matrix, and the composite matrix coated onto Al5054 alloy. The prediction model was also introduced to estimate the release profile of the inhibitor from LDH [107]. Luo and coworkers [85] developed thin ZnAl-LDHs by the hydrothermal method on 6N01 Al alloy, and to inhibit the chloride penetration, oxygen diffusion, and prevention of water interaction, reduced graphene oxides sheets were used to seal the porous LDHs layers. The system
provides very good corrosion protection owing to the barrier function, ion exchange, and self-healing ability. The reported examination remarks upon recent approaches in introducing sharp anti-corrosion functionalities in protective coatings, utilizing guest reservoir carriers of corrosion inhibitors. A thick PLA coating was used to seal the porous outer layer of the LDH coating provided a strong adhesion. A delay was found in the penetration of aggressive ions inside the composite coating which in turn provided longer protection. Subasri et al. [91] reported a comparative study of the utilization of various corrosion inhibitors in different proportions for instance, vanadate group, 2-mercapto benzothiazole, 8-hydroxyquinoline, phytic acid intercalated LDH and studied the effect of resultant dispersion in the sol-gel matrix to investigate the compactness and corrosion resistance properties of LDH to protect the AA2024 substrate. After 120 h salt spray exposure to 3.5% NaCl solution, ZnAl-LDH with corrosion inhibitors of phytic acid and 8-hydroxyquinoline were seen to show the lowest corrosion current densities. Another possible choice is the dispersion of LDHs in polymeric matrices which results in better mechanical and electrochemical properties and facilitates the barrier properties. Zhang et al. [108] synthesized Ce-doped ZnAl-LDH further dispersed in sol-gel matrix and applied on AA 2024 to enhance its corrosion resistance properties. The findings depicted that Ce ions were actively incorporated in LDH galleries and sol-gel modified ZnAl-Ce-LDH delay the degradation process on exposure with aggressive species and can be used as potential a corrosion inhibiting system with self-healing properties. The following progression is generally observed regarding the corrosion resistance properties of virgin LDHs; Mg–Al-LDH > Zn–Al-LDH > Li–Al-LDH > Ca–Al-LDH.

3.3. Kinetics and Controlled Release of Interlayer LDHs Corrosion Inhibitors

Corrosion inhibitors entrapped inside LDHs’ interlayers play a vital role to inhibit corrosion reactions, which is why the kinetics and understanding of inhibitors release rate on contact with aggressive species are crucial factors to develop a stable coating system. The controlled release rate of LDH anticorrosion inhibitors under different reaction stimuli and the self-healing capability predict the lifetime of LDH systems. Slow or/fast anion exchange speed caused either short time stability or poor corrosion resistance. It is found that the healing process depends on various factors, mainly on the film thickness, elastic modulus, dimension of the damaged area and so on and can be explained by mathematical models and theoretical expressions. Further, Mohar’s approach can be used to predict the chloride contents after LDH exposure with an aggressive solution to understand the anion exchange and system predictability [79]. Weight loss measurements (ISO 8407 Standard) [109] before and after intercalation of corrosion inhibitors and concentration gradient measurement also proposed predictability to measure the corrosion rate and kinetic modeling combined with physical characterizations.

Recently Imran et al. reported a prediction model and kinetics study to analyze the inhibitor release profile, where Fickian diffusion is considered as a molybdate release rate and the data were fitted with the Weibull model to study the MgAl–Mo-LDH/PVA behavior on contact with 3.5% NaCl [107]. Bendinelli et al. [110] investigated the release rate of MgAl-imidazole-LDH and analyzed the inhibiting efficiency and studied the interparticle diffusion model to understand the kinetics and release rate of inhibitors. The synthetic parameters, structural geometry, and pH of the contact solution are the prime parameters to affect the inhibitor’s release rate with physical characterization approaches, like basal spacing differences through XRD. Very few reports are published on that issue and there is a need for further investigation on those criteria for the reason of practical implementations of LDHs coatings. Although the studies cited do not refer specifically to the LDHs corrosion inhibitors kinetics, the following literature provides an idea of the kinetics measurement and modeling to predict the release rate and kinetics of different anions inside the LDHs galleries [111–113].

3.4. Testing and Evaluation of LDH Coatings or Co-Precipitated Particles

Electrochemical Impedance Spectroscopy (EIS) is considered a basic approach to evaluate the coating properties and barrier properties. In fact, impedance measurements are recognized to supply
valuable information about protective coatings applied on metals and about their degradation mechanism, as well [114–116]. Impedance modulus and impedance phase graphs (quite often referred to as “Bode plots”) and Nyquist plots are used to show the impedance spectra collected over coated metals immersed in different electrolytes. From these graphs it is possible to gain a preliminary knowledge of the protective properties of the coatings: scientists refer to the modulus of the impedance in the low-frequency range (commonly in the 0.015–0.010 range) as a rough estimation of the quality of the protection system, in accordance with the claims of Bacon [117] and Murray and Hack [118], as highlighted by Amirudin and Thierry in their review [119]. In order to get some insight into the mechanisms through which coatings are able to protect the substrate, very often the experimental EIS data are studied by means of the nonlinear least-squares fit technique [116,120] which has been recognized to be a valuable tool for analyzing complex frequency dispersion data [121]. For this purpose, passive circuit elements (called “e.e.c., electrical equivalent circuits”) are commonly employed to fit impedance data arising from different experimental systems. Despite the implicit ambiguity claimed by McDonald [122] for the different possible geometrical arrangements of the circuit elements, the exploitation of the e.e.c., for the fit of an experimental set of EIS spectra is definitely widespread. In this context, LDH developed in situ on aluminum alloys have been often investigated by EIS and diverse e.e.c., have been suggested by different groups to fit the EIS experimental data and to assess the corrosion protection properties of the coatings. Various equivalent circuits were used due to the dynamic nature of LDH coating systems, where capacitance is replaced generally by constant phase element (CPE), which describes the non-homogenous nature of the LDH system and how it deviates from the ideal capacitive behavior. CPE approach is used extensively in equivalent circuits for fitting the experimental data and is attributed to the surface activity, inhomogeneity, factual geometry, roughness, electrode porosity, etc. It is believed to describe the current and potential distribution associated with the electrode geometry [123].

Wang et al. [64] introduced the circuit depicted in Figure 5a to fit the experimental EIS data of MgAl-LDH developed on 99.9% Al. In the model employed by the authors, Rs refers to the solution resistance, $R_{pore}$, and CPE$_{pore}$ to the conductive path in the films and double layer capacitance in the pores of the films, respectively; $R_{ct}$ and CPE$_{dl}$ to the polarization resistance and double-layer capacitance, respectively; $R_{film}$ to the inner film resistance and CPE$_{film}$ the constant phase element of the film. A similar circuit (depicted in Figure 5b) has been proposed by Zhou [63] for the interpretation and fit of the EIS data set collected over ZnLaAl-LDHs developed on AA6061. Also, in this case, the presence of a three-time constant has been suggested. A time constant has been attributed to the Faradic process and modeled by a charge transfer resistance, $R_{ct}$, in parallel with the double layer capacitance (CPE$_{dl}$); a second time constant has been related to the oxide film between the aluminum substrate and LDHs: $R_{OX}$ represents the resistance of film in parallel with the capacitance (CPE$_{OX}$); a third time constant has been introduced to account for the contribution of the LDH layer itself: the LDHs film resistance ($R_{LDH}$) in parallel with the layer capacitance (CPE$_{LDH}$). Similarly, Tedim et al. [69] identified three-time relaxation processes in the EIS spectra collected over ZnAl-LDHs on AA2024. The time constant in the high-frequency range has been associated with the LDH layer response, a second-time constant attributed to the aluminum oxide present on the alloy surface, and a third-time constant attributed to the corrosion process. The same authors suggested a similar circuit (depicted in Figure 5b) [97].

Wang [100] introduced two relaxation processes e.e.c., (Figure 5c) where $R_{s}$ represents the solution resistance; $R_{ct}$ and $R_{f}$ are the charge transfer resistance and the film of the MgAl-LDHs resistance, CPE$_{f}$ and CPE$_{dl}$ are the capacitance of the LDH film and the electrical double layer, respectively.

A two-time constant model (Figure 5c) has been employed also by Liang et al. when investigating the properties ZnAl-LDHs on AA2099 [93]. According to the attribution given by the authors, in addition to the resistance of the electrolyte $R_{s}$, $R_{f}$ and CPE$_{f}$ represent resistance and component of the constant
phase elements of the LDH/natural alumina film, respectively; $R_{ct}$ and $CPE_{dl}$ (charge-transfer resistance and component of the double layer constant phase, respectively) account for the faradic process.

Our impression is that among the different models to fit the EIS raw data set, the main difference resides in the interpretation of the contribution of the LDHs layer itself. In Section 3.1 it has been explained that the LDHs films consist of a barrier inner layer and a porous outer layer. In the literature, sometimes it has been possible to discriminate the contributions of the two different layers and, therefore, the e.e.c., like the ones depicted in Figure 5a,b are employed. In this case two different relaxation processes that can be attributed to the two different layers of the LDHs coatings are present in the EIS spectrum. Additionally, as far as the literature reports examined in this work are concerned, a time constant attributed to the corrosion process is always present (described by $R_{ct}$ and $CPE_{dl}$). In other cases, the overall contribution of the LDHs film has been interpreted as a single relaxation process and therefore modelled employing the circuit depicted in Figure 5c. Also in this case, an additional time constant to account for the corrosion is present (described by $R_{ct}$ and $CPE_{dl}$). Basically, both interpretations can be correct: it depends on the physical properties and morphological features of developed LDHs films. In fact, it is not always possible to clearly discriminate the different contributions of the two layers forming the LDHs film. For example, if the outer layer is very porous or very thin, its contribution to the EIS spectrum can be strongly reduced or negligible. Generally speaking, it is our opinion that a deep understanding of the physical and morphological structure of the developed LDHs film is needed to properly select the suitable e.e.c., which aims to fit the EIS raw data set.

As far as LDH dispersions in polymeric matrices are concerned, EIS spectra are fitted employing the well-established e.e.c., developed for organic coatings [118,124,125]. In particular, ionically conducting low resistive paths in the coatings, due to discontinuities or defects, are modeled with a resistance (namely “porosity resistance”, “pore resistance”, $R_{po}$) [126]. The dielectric behavior of the coating is modeled employing a pure capacitance (namely “coating capacitance”, $C_{c}$). The corrosion process occurring under the paint is modeled employing a charge transfer resistance ($R_{ct}$) in parallel with a double layer capacitance ($C_{dl}$). It has to be underlined that in some cases the response of an aluminum/coating/electrolyte system is also modeled employing a CPE which accounts for an oxide layer existing on the aluminum alloy electrode instead of the time constant attributed to the faradic process ($R_{ct}$, $C_{dl}$) [127].

In Table 2, the resistance of in situ developed LDHs obtained from the fitting of the experimental data set collected by different authors is listed. In particular, the value of $R_{po}$ and $R_{coat}$ are reported. The evolutions of pore resistance in the case of LDH provide a framework about the barrier properties and describe the dispersibility and compactness of LDH in the composite system. Regardless of the specific e.e.c., employed to model the physical properties of the LDH coating under investigation, a possible way to compare them in situ developed LDH layer is to employ the total resistance $R_{tot}$. This parameter corresponds to the sum of the resistance values obtained through the fitting and can be assumed as a sort of overall estimation of the protection extent of the LDH layer. A detailed comparison of literature data is not possible since the thickness of the different LDH protection layers is very different from one author to another and quite often the value is not reported at all. However, we calculated the $R_{tot}$ values of the in-situ developed LDH coatings on different aluminum alloys (mainly pure aluminum, AA6xxx, and AA2xxx) of different authors and we compared the obtained results with the $R_{tot}$ of the same system intercalated with corrosion inhibitors. Figure 6 shows the obtained results in the case of samples exposed in chloride-containing media (from 0.1 M to 3.5 wt.% NaCl) for a few hours. The huge dispersion of $R_{tot}$ data both for pristine and inhibitors containing LDH is due to the wide range of thicknesses of the different coatings. In addition, diverse concentrations in NaCl in the electrolyte have been used by the different authors (notice that as far as the literature reports considered in this review are concerned, no clear trend of $R_{tot}$ with the chloride content has been found). However, notice that the LDH layer without any inhibitor ranges from $10^{2}$ to $10^{8}$ $\Omega$ cm$^{2}$, while in presence of a corrosion inhibitor the $R_{tot}$ values tend to increase (they range between $10^{9}$ to $10^{12}$ $\Omega$ cm$^{2}$). These results, taken from literature reports, suggest that, in general terms, it is possible to
significantly increase the corrosion protection properties of LDH layers by exchanging the anions in the lamellar structure with corrosion-inhibiting species.

Figure 5. Schematic of the circuits employed to fit the experimental data set of LDH coatings developed on aluminum alloys: (a,b) three-time constants and (c) two-time constants.

Polarization curves are also quite often collected over LDH films developed on aluminum alloys to assess the corrosion protection properties. According to the mixed potential theory, anodic and cathodic reactions can be described by a straight line in the E versus Log(i) plot. For purely activation controlled anodic and cathodic processes, a linear extrapolation of the Tafel slopes from the experimental curves is possible [128], thus determining the corrosion current density. When one of the reactions (generally the cathodic reaction) is limited by the rate of transport of the reactant to the metallic surface (concentration-controlled processes) the extrapolation of the corrosion current density is still possible, even if it becomes more complex. If a dielectric coating is present over the metal surface, the ohmic drop due to its insulting nature affects the reliability of the Tafel extrapolation of the corrosion current density. In addition, the extrapolation of corrosion current density values over passive metals such as aluminum in a near-neutral chloride containing media is of doubtful scientific significance. However, there are many literature reports in which the corrosion current density is extrapolated...
from E versus Log(i) plots in presence of a dielectric film (LDH coating or organic coating) over the surface of aluminum electrodes immersed in neutral chloride containing media (see the References in Tables 2 and 3). It is our opinion that DC polarization curves collected over coated aluminum samples can provide mainly a qualitative assessment of the quality of the coatings. The flow of direct current in the case of metals coated with insulating materials is mainly possible thanks to the presence of defects and/or heterogeneity through which the electrolyte can reach the metallic surface. Therefore, the evolution of the anodic and cathodic current densities can be related to the amount of defect and homogeneity of the coatings.

Figure 6. Comparison of the total resistance obtained from EIS spectra fitting for neat and inhibitor exchanged LDH coatings; data taken from [102-117].

Despite our concerns, it must be highlighted that current density data are extrapolated by many different authors from the potential/current density plots collected over LDH or paint coated aluminum alloys, as reported in Tables 2 and 3.

DC techniques and EIS provide a general description of the LDH system but these techniques refer to the average surface response, and localized defects cannot be truly estimated by those approaches. Spatially resolved electrochemical techniques can be a possible alternative to analyze the local coating defects and evaluate the corrosion mitigation. The analysis of active coating defects has the great advantage of giving local information, regarding the evolution of the corrosion processes (progress and mitigation) on active defects of the coating. Scanning vibrating electrode technique (SVET) and scanning the ion-selective electrode technique is used in the work of Montemor [129] to investigate current density maps in order to quantify the overall electrochemical activity and the total anodic and cathodic current densities. SVET mapping has been also employed to evaluate the effect of organic corrosion inhibitors intercalated in between the lamellae of the LDH [101]. Tedim et al. [130] investigated the electrochemical activity of MgAl-LDH in the presence and absence of vanadates by SVET and assessed also the local intensity of corrosion currents and degree of localization of the corrosion attack. The potential of SVET to assess the effectiveness of corrosion inhibitor loaded LDH has been confirmed also when co-precipitated particles are embedded in an organic coating [131].
Table 2. LDH-based systems and measured corrosion resistance properties.

<table>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>MgAl-SA</td>
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<td>3.5 wt.%</td>
<td>(2.0 \times 10^{-8})</td>
</tr>
<tr>
<td>ZnAlNO_3</td>
<td>6N01</td>
<td>3.5 wt.%</td>
<td>(5.3 \times 10^{-6})</td>
</tr>
<tr>
<td>ZnAl/RGO</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnAlNO_3</td>
<td>2024</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnAlMOMG</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LiAlNO_3</td>
<td>A6N01</td>
<td>3.5 wt.%</td>
<td>(0.32 \times 10^{-6})</td>
</tr>
<tr>
<td>LiNO_3/Vanillin</td>
<td>6061</td>
<td>3.5 wt.%</td>
<td>(0.32 \times 10^{-6})</td>
</tr>
<tr>
<td>MgAl-PAS-10</td>
<td>5054</td>
<td>3.5 wt.%</td>
<td>(1.5 \times 10^{-4})</td>
</tr>
<tr>
<td>ZnAlV_2O_7</td>
<td>2024</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

8HQ: 8-hydroxyquinolate; C_6H_5COO: benzoate; AN: anodized; PEO: plasma electrolytic oxidation; VO_x: Vanadium oxide; SA: stearic acid; RGO: Reduced graphene oxide; GN: graphene.
Table 3. LDH particles dispersed in organic/polymeric matrix, and corresponding measured corrosion resistance properties.

<table>
<thead>
<tr>
<th>LDH</th>
<th>Substrate</th>
<th>Potentiodynamic Curves</th>
<th>Electrochemical Impedance Spectroscopy</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Electrolyte (NaCl)</td>
<td>i_{corr} sub. (A cm^{-2})</td>
<td>i_{corr} Film (A cm^{-2})</td>
</tr>
<tr>
<td>ZnAl-V/PVA</td>
<td>2024</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnAl-V/epoxy</td>
<td>2024</td>
<td>0.124 M</td>
<td>1 × 10^{-6}</td>
<td>2 × 10^{-8}</td>
</tr>
<tr>
<td>ZnAl/3-ABSA</td>
<td>2024</td>
<td>0.5 M</td>
<td>-</td>
<td>1.8 × 10^{-7}</td>
</tr>
<tr>
<td>ZnAl/3,4-HHBA</td>
<td>2024</td>
<td>0.5 M</td>
<td>-</td>
<td>6.4 × 10^{-7}</td>
</tr>
<tr>
<td>LDH/4-ABSA</td>
<td>2024</td>
<td>-</td>
<td>4.4 × 10^{-7}</td>
<td>-</td>
</tr>
<tr>
<td>ZnAl-EDTA</td>
<td>2024</td>
<td>0.5 M</td>
<td>-</td>
<td>2.9 × 10^{-7}</td>
</tr>
<tr>
<td>ZnAl-CO_3</td>
<td>2024</td>
<td>0.5 M</td>
<td>-</td>
<td>3.8 × 10^{-7}</td>
</tr>
<tr>
<td>ZnAl-Cl</td>
<td>2024</td>
<td>0.5 M</td>
<td>-</td>
<td>6.9 × 10^{-7}</td>
</tr>
<tr>
<td>ZnAl-Ce/sol gel</td>
<td>2024</td>
<td>-</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>MgAl-sol-gel</td>
<td>2024</td>
<td>-</td>
<td>-</td>
<td>0.1 M</td>
</tr>
<tr>
<td>ZnAl E3/E1</td>
<td>2024</td>
<td>3.5 wt.%</td>
<td>4.4 × 10^{-5}</td>
<td>1.4 × 10^{-6}</td>
</tr>
<tr>
<td>ZnAl-sol-gel</td>
<td>-</td>
<td>-</td>
<td>7.6 × 10^{-7}</td>
<td>-</td>
</tr>
<tr>
<td>ZnAl-sol-gel</td>
<td>-</td>
<td>-</td>
<td>1.8 × 10^{-7}</td>
<td>-</td>
</tr>
<tr>
<td>ZnAl-sol-gel</td>
<td>-</td>
<td>-</td>
<td>2.6 × 10^{-7}</td>
<td>-</td>
</tr>
</tbody>
</table>

ABSA: Acetamidobenzensulfonyl azide; HHBA: dihydroxybenzoic acid; V: Decavandate; PVA: polyvinyl alcohol; EDTA: Ethylenediaminetetraacetic acid.
4. Conclusions and Outlook

This work summarizes the significant approaches and synthetic conditions used to develop the LDHs on aluminum substrates to develop a smart coating system to protect the metallic surface from corrosion. In recent years, a lot of contributions have been made to develop compact LDH-based systems and have proven an efficient approach to protect Al alloys. It is common to synthesize LDH functional materials on aluminum surfaces to improve their corrosion resistance properties as well as obtain other multi-functional responses. The hybrid inorganic-organic coating systems, utilization, and investigation of the number of corrosion inhibitors/pigments have created a new generation of multifunctional responsive coatings, yet the size and geometry of the defects healed in accordance with the self-healing characteristics of LDHs, the controlled release of inhibitors in different reactive situations, the response of LDH on the occurrence of multiple damaging, pitting corrosion healing, and facile synthesis of defects free, low time-consuming LDH preparation are still open questions with limited solutions.

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