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## Layered double hydroxide (LDH)–based nanostructured materials as advanced anticorrosive agents: synthesis, properties, and applications

### ABSTRACT

*In recent years, layered double hydroxide (LDH) has developed strongly in the field of corrosion protection of materials due to its special properties, which include exceptional anion exchange capability with increased anion capacitance as well as barrier resistance and a recorded structural memory effect. This article reviews recent work on the properties of LDH in the form of powders and films. The possibilities and advantages of using this compound to protect materials from corrosion are analyzed in detail.*

**Keywords:** *nanomaterials; anticorrosive agents; anion exchange; LDH powder and ultrathin film*

### 1. INTRODUCTION

Nanotechnology deals with the research, production and application of nanoparticle architectures, tubular structures, films or sheets with a size of less than 100 nm in at least one dimension [2-4]. Nanomaterials appear as dimensionless entities – nanoparticles, one-dimensional entities – nanowires, nanorods and nanotubes or as two-dimensional entities in the form of nanolayers, nanofilms, nanosheets and nanoplates. These materials with nanoscopic dimensions exhibit altered, but also greatly improved physico-chemical behavior and properties, in particular electronic, optical, mechanical, thermal and magnetic [5]. This is mainly due to their very small dimensions and the very large influence of special conditions at the interfaces, which allow a higher surface unit volume to increase the effective interaction [6].

The inclusion of nanoparticles in organic units showed improved properties in terms of esthetics, corrosion protection, thermal stability (especially at high temperatures), mechanical strength (necessary for resistance to aging and erosion under difficult working conditions) and nano-architectural cross-linking (with the ability to effectively prevent the penetration of corrosive and biofouling entities).

All of this holds great promise for major advances in innovative techniques to develop nanoscopically thin coatings for applications in the packaging, aerospace, automotive, biomedical, marine and oil and gas industries, all of which offer superior protection against fouling, corrosion and self-healing effects on critical material surfaces. Therefore, nanomaterials have enabled the modification of (nano)coatings to effectively suppress corrosion, fouling and scratching on metallic materials. In addition, (nano)coatings can be self-healing in different architectures and under different environmental conditions, with all the associated and previously mentioned benefits.

Recent nanotechnological achievements have enabled promising innovations in protective nanocomposites – coatings for corrosion protection, antifouling and self-healing on material surfaces. Nanomaterials offer excellent prospects for minimizing the degree of corrosion on metal surfaces through surface modification - using nanocrystalline structural coatings. Various nanocoatings have proven to be very effective in reducing the negative effects of corrosion. The most commonly used are nanocoatings - coatings that contain components on a nanoscopic level or whose layer structure is less than 100 nm thick. The dimensions of the nanomaterials used and their very high layer density improve the adhesion and physical coverage of the coated surface. Nanocoatings can be applied to the outside, but also to the inner surfaces of the respective

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material, even if these are very smooth. Significantly, the successful use of nanocoatings to prevent or mitigate staining, corrosion and scratching or abrasion due to the ability to self-heal (which is realized by the inherent microarchitectural porosity) prevents the penetration of foreign bodies that are harmful to the respective surface. The inclusion of nanomaterials in protective coatings significantly improves their barrier protection performance.

Nanoparticles, which are used in the composition of nanolayers to protect materials, have been studied for more than two decades and there are many different products. However, it is only in recent years that research efforts have been crowned with adequate results that distinguish those whose price and properties fulfill their purpose. This certainly includes the layered double hydroxide (LDH) [7], which we will focus on here.

Layered double hydroxides are successfully used for surface protection and functionalization of metal materials due to their special structure, composition, controllability, anion exchange and other exceptional properties. This review focuses on the most common methods for producing LDH on magnesium alloys and summarizes the results of over 50 research papers. At the same time, based on the mechanism of corrosion protection by LDH materials, the performances of LDH films and LDH as a filler on metal substrates are briefly introduced. The surface of LDH materials was chemically modified to improve their compatibility with solvents, and their anti-corrosion function was developed as an additive. Finally, composite coatings based on LDH on Mg alloys were considered by pretreatment of the surface and chemical modification.

Magnesium (Mg) and its alloys, known as the lightest metallic structural materials, are widely used in the computer, electronics, automotive and aerospace industries due to their advantages (including low specific gravity, high specific strength and stiffness, ease of processing and recycling) [8]. By using magnesium alloys, the total mass of the vehicle could be reduced by 10% and fuel consumption could be reduced by about 20–30% without significant design changes. In addition, the modulus of elasticity of magnesium alloys is similar to that of the human skeleton, which can absorb external loads and is the main component of artificial skeletons. As a medical material, magnesium alloys are therefore ideal materials for cartilage repair and metal implants. Although magnesium alloys have many excellent properties, their poor corrosion resistance due to

their low standard potential (–2,36 V) has limited their further development and wider application [9]. Many approaches have been taken in researching this problem, including alloys, improved heat treatment processes and advanced surface treatment technology. Among them, surface treatment technology is the most comprehensive and effective method, including chemical conversion coatings, polymer coatings, micro-arc oxidation, layer-by-layer films and LDH coatings [9]. In recent years, LDHs have taken a key position, not only because of their environmental friendliness and low cost, but also because of their high anion exchange capacity [10]. As a result, intercalated materials have shown wide prospects for application as corrosion-resistant coatings.

## 2. WHAT IS LDH?

LDH is a type of material similar to hydrotalcite, consisting of two or more metal elements with a layered hydroxide structure [11]. LDH consists of positively charged mixed layers of metal ions  $M^{2+}/(M^{2+}+M^{3+})$  hydroxide anions with water molecules between the layers. As shown in Figure 1, the general crystal structure of LDH films is  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{m-})_{x/m} \cdot nH_2O$ , where  $M^{2+}$  refers to metal cations (e.g.  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ),  $M^{3+}$  denotes a trivalent cation (e.g.  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ),  $x$  is the molar ratio of  $M^{3+}/(M^{2+}+M^{3+})$ , and  $A^{m-}$  is an anion with valence  $m-$  [12], while the hydroxide layers are packed with water molecules during synthesis. Basically, the crystal structure, bond strength and anion exchange capacity of LDH depend on the size and charge of the metal cation, the charge of the anion and the relative amount of water of crystallization [13].

LDHs have potential applications in catalysis, functional materials, environmental protection and biomedicine due to their unique memory effect and interlayer anion exchange capacity [13]. Recently, prepared LDH coatings on alloys have been widely used due to the extensive raw material resources, simple synthesis methods and large quantities, especially on magnesium alloys and various kinds of LDH materials, on double compounds composed of Mg–Al LDH and carbonate.

### 2.1. Synthesis of LDH

There are several ways to synthesize LDH, of which the following stand out in terms of efficiency: co-precipitation, in situ growth methods, electrochemical deposition/deposition, spinning/spun coating and anion exchange. We will look at the good points of these processes individually, but also the difficulties that accompany them.

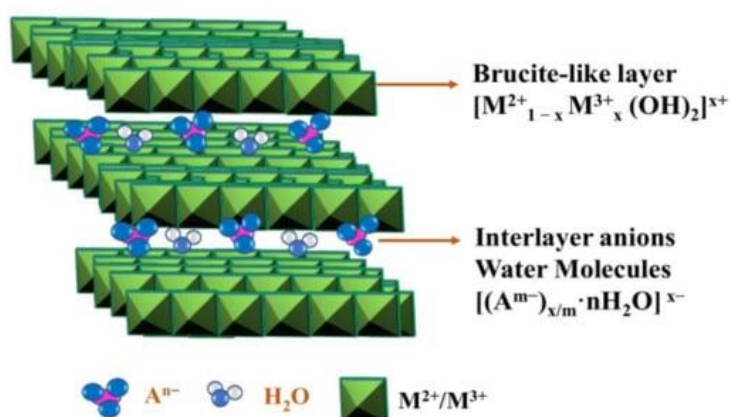


Figure 1. Schematic illustration of the LDH structure and its components (from [5])

### 2.1.1. Co-precipitation

Co-precipitation (CPT) means that two or more kinds of soluble salts with a layered structure of metal ions are uniformly mixed in a nitrogen atmosphere, and the corresponding solid particles are obtained by a precipitation reaction with an appropriate pH. The CPT approach is one of the most attractive techniques for the preparation of LDH intercalation materials of Mg, Al, Zn and other metals. The combination of CPT and hydrothermal

reaction can form LDH coatings of different systems, regardless of the chemical composition of the substrate, laminate and type of anions between the layers [14]. As can be seen in Figure 2, the LDH layers were well bonded together and no defects were observed at the interface. The overall Mg–Al LDH layers are smooth and compact, which improves the adhesion of the substrate and coating materials.

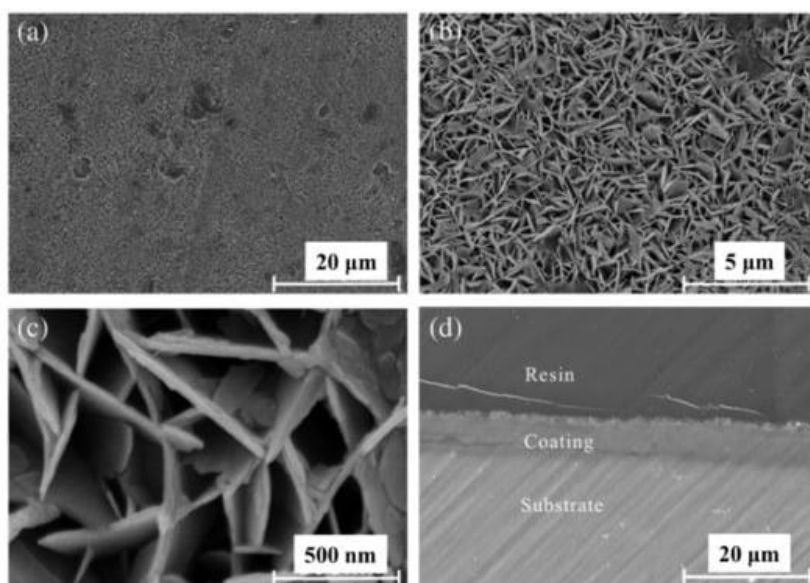


Figure 2. (a–c) SEM images of LDH coating on Mg alloy with different magnifications; (d) cross-sectional SEM images (from [5])

In the paper [15], the preparation of a Mg–Al LDH coating with a porous organic surface layer was presented by integrating the coprecipitation technique and the hydrothermal synthesis method for the extended application of Mg alloys. It has been shown that the appropriate addition of polyglutamic acid (PGA) can prolong the corrosion time of the composite coating when the pH value

reaches a minimum value, so that the corrosion resistance of the AZ31 alloy is improved by the described composite coating on the surface. Generally, the precipitated material needs to be heated at 60–80 °C for several hours –to improve the crystallinity of LDH. However, the CPT method is widely used in the preparation of LDH powder because it takes a long time and has poor

adhesion between the substrate and the coating, which is not suitable for coatings on metal substrates [16].

### 2.1.2. In-Situ growth methods

The in situ growth method refers to the choice of a special surface treatment of the metal plate that directly participates in the reaction and provides cationic metal on the metal substrate for the film formation technology. This is considered the most promising method due to the good adhesion between the LDH films and the substrate formed by chemical bonding. Currently, there are five methods for the in-situ synthesis of LDH films on Mg alloys.

#### A one-step grow-in-place method

The one-step in situ growth technique is a promising method because it can synthesize LDH films directly on the substrate and significantly improve the mechanical properties and adhesion of the coating to the substrate. In [17], it was reported that Mg–Al LDH films were first phosphorylated on cellulose microspheres (CM) and then prepared by in situ nano-growth. This finding provides a new approach that can improve not only the production and crystallinity of Mg–Al LDH, but also the loading of Mg–Al LDH and the porous structure of CM. Thus, Mg–Al LDH @CM are suitable for superhydrophobic treatment. Composite coating: inhibitor (2-mercapto-benzothiazole, MBT) in combination with Mg–Al LDH coatings (Mg–Al LDH/MBT) on an AZ31 alloy substrate at a relatively low temperature (95 °C) and ambient pressure was investigated in a one-step in situ growth process [18]. The corrosion protection of this coating was then evaluated.

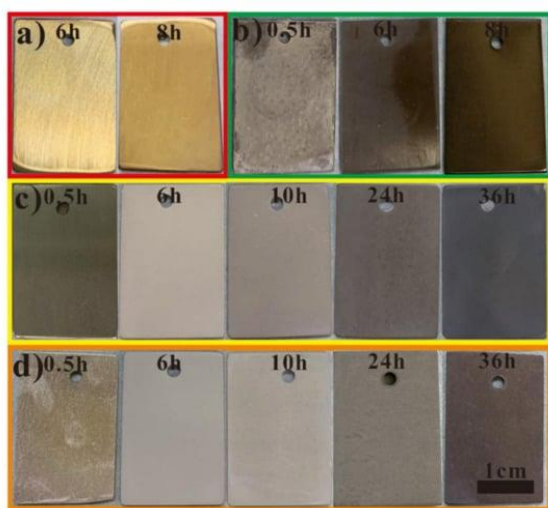


Figure 3. Digital images (a) blank; (b) MBT; (c) Mg–Al LDH; and (d) Mg–Al LDHs/MBT films synthesized with different reaction times at 95 °C and 1 bar pressure (from [18])

As can be seen in Figure 3, the corrosion current density of the LDH/MBT composite coatings is very low, and there is even no corrosion behavior when exposed to a NaCl solution or salt spray environment for 15 days, indicating very good corrosion resistance.

Mg–Al LDH coatings produced by the one-step growth technique on Mg alloys are able to eliminate the detrimental effects of the hydrothermal method at higher temperatures and higher pressures.

#### A two-step grow-in-place method

The two-stage in situ growth method consists of: Pre-treatment of ion incorporation into LDH coatings and post-treatment to maintain alignment by adding NaOH solution. In [19], it was found that this approach is also very suitable for other Mg alloys, regardless of whether they contain Al elements or not, as long as the process parameters are set correctly. Therefore, the corrosion resistance of most Mg alloys can be improved by a two-stage in situ growth process. So, with this method, a thick coating can be obtained under the condition of controlling the pH value, but the process is quite complicated. In this technique, the substrate is immersed in a solution of metal salts, the alkali of the solution is added to control the pH, and the metal substrate effectively becomes the metal source of the reaction, on which the film grows while sacrificing part of the substrate. Therefore, this method is only suitable for the preparation of LDH films directly on the metal matrix, but not for the preparation of LDH powders/particles.

#### Hydrothermal treatment

The hydrothermal treatment method refers to LDH obtained by mixing metal oxides or metal hydroxides with an alkaline solution in a high-pressure reactor for a certain period of time and under certain temperature and pressure conditions. As shown in [20], the closed porosity of the LDH layer and the absorption capacity of chloride ions limit the penetration of corrosive Cl<sup>–</sup> and provide effective corrosion protection for the oxide layer film. LDH is usually produced by heating the two mixed oxides in an autoclave with deionized water at 140 °C for several days. The advantages of hydrothermal synthesis are therefore the fully crystalline structure, the apparently layered structure and the uniform particle size distribution of LDH.

#### Hydrolysis of urea

Urea is a type of base with high water solubility; the rate of hydrolysis can be easily controlled. It can generate ammonium hydroxide by hydrolysis in water, while the CO<sub>3</sub><sup>2–</sup> obtained by hydrolysis can

be used as an interlayer anion for the synthesis of LDH in an alkaline medium [21]. By controlling the hydrothermal conditions, Mg–Al LDH was synthesized on a Mg alloy using the urea hydrolysis reaction. The advantage of this method is that the synthesized LDH has high crystallization and large volume. It was found that the nanostructure and ion exchange capacity of LDH can drastically improve the corrosion protection of AZ31 alloy, but it also tends to produce by-products, and  $M^{2+}$  or  $M^{3+}$  can be consumed during the process of by-product formation, which reduces the number of LDH in the following formations.

#### Steaming

Steaming is a method of producing an anti-corrosive magnesium alloy coating without chemical vapor using ultra-pure water as the vapor source. The protective Mg–Al LDH was prepared on magnesium alloys by chemical vapor deposition, which is a simple, environmentally friendly and cost-effective method. As reported in [7], KSRD analysis shows that the Mg–Al LDH coatings were successfully produced. Corrosion experiments also show that the film has a good protective effect on the substrate.

#### 2.1.3. Electrochemical deposition

Electrochemical deposition can be regarded as a valid method for the preparation of LDH films, which has the advantages of high purity, high deposition rate and simple equipment. The Mg–Al LDH film with nitrate is homogeneous and solid, thinner than the Li–Al LDH film, but has some small defects – cracks [22]. Potentiodynamic polarization and EIS measurements showed that the corrosion protection of the LDH-coated magnesium alloy is better than that of the uncoated magnesium alloy.

#### 2.1.4. Spinning / Twisted coating

Another method for producing a regenerative, smooth film is the twisted coating. The advantages of this method are that it is environmentally friendly, provides excellent adhesion between the film and the substrate, allows uniform film formation and achieves a good micro-concave and convex structure on the surface. LDH films with good corrosion protection and adhesion can be produced with a simple process. In [23], they combined LDH films on AZ31 Mg alloy by spin coating method with an aqueous solution as a vapor source. The resulting film surface is uniform and the electrochemical polarization curve of the film after the 7-hour coating shows a very low corrosion current density, which is much lower than that of AZ31 magnesium alloy without coating.

#### 2.1.5. Anion exchange

The anion exchange method is based on the intracellular anion exchange of LDH, which not only preserves the original lamellar structure of LDH, but also selects the type of intracellular anions. The corrosion-inhibiting anions can be released slowly, and the corrosive medium can be adsorbed thanks to the LDH produced in this way, so that the matrix is doubly protected. As can be seen in Figure 4, the surface of the matrix is completely covered with a dense and distorted lamella, the coating is thick, smooth and almost free of microcracks [24]. However, this method is demanding and the degree of crystallinity of LDH is lower than the previously mentioned methods.

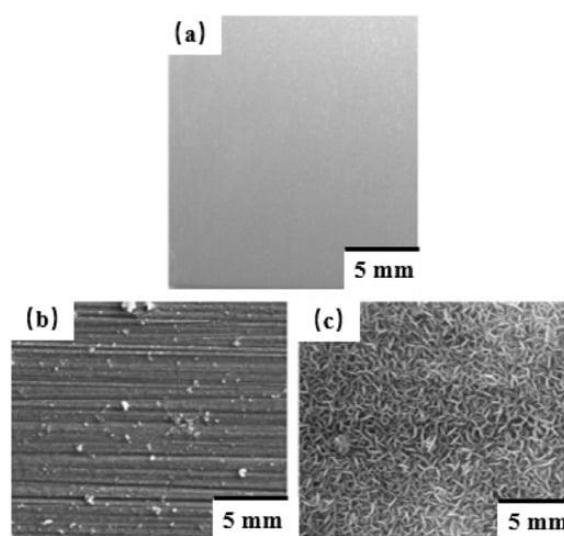


Figure 4. Images of LDH film: (a) optical microstructure; (b) SEM images at low magnification and (c) high magnification (from [24])

#### 2.2. Anti-corrosive mechanisms

In recent years, LDH films have been considered as the next potential coatings for magnesium alloys due to their stable lamellar structure and tunable interlayer anions, which can not only protect the metal matrix but also absorb corrosive ions. The corrosion properties and the mechanism of corrosion resistance of LDH materials have been intensively studied and presented in papers and articles [1-14].

##### 2.2.1. Interlayer mechanism of anion exchange

LDHs are the best nanotubes for corrosion inhibitors due to their stable layered structure, high efficiency, low cost, and ease of use. The addition of only small amounts of trace chemical substances into the corrosive medium through a physical or chemical reaction can slow down the corrosion rate of the metal and leave the physical



and chemical properties of the metal unchanged. Interlamellar anion exchange is an important property of LDH, and its anions can be exchanged with different anions to obtain materials with different functions.

Thanks to the ability of anion exchange between the LDH layers, this is an efficient way to incorporate corrosion inhibitors into a protective layer with a lamellar structure in order to achieve high corrosion protection of the substrate. In [25], the preparation of a corrosion inhibitor on the Mg alloy AZ31 by incorporating aspartic acid (ASP) into Mg–Al LDH using a one-step hydrothermal method was reported. Due to the high porosity coverage and lamellar nanostructure, Mg–Al–ASP LDH has a very good anticorrosion performance and a much larger specific surface area for the intercalation of invasive anionic species such as  $\text{Cl}^-$ . Therefore, it is an effective anti-corrosive and environmentally friendly coating for the transformation of light metals and alloys.

#### 2.2.2. Composite synergistic mechanisms of corrosion resistance

In recent years, water-based epoxy resins have proven to be effective adhesives and coatings for complex substrates due to their good adhesion, stable chemical properties, and excellent corrosion resistance. However, when cured at high temperatures, these resins can form numerous micropores through which the external corrosive medium can penetrate the protective matrix material, severely limiting their wider application. However, it has been observed that the addition of LDH nanocontainers to the ZRE film can capture the corrosive  $\text{Cl}^-$  and release the corresponding substances so that the carbon steel matrix has stronger anti-corrosion performance. Secondly, the two-dimensional layered structure of LDH can block some voids in the coating to effectively limit the penetration of corrosive ions into the film and improve the corrosion resistance of the matrix material.

Thanks to its special layered structure, graphene can effectively prevent the diffusion of oxygen and water molecules on the metal surface. The synergistic effect of adding other nanomaterials and LDH interlayer inhibitor ions to graphite composites can improve the corrosion protection of LDH films. In [25], the deposition of graphene-modified LDH nanocephalic films on the surface of Mg alloy using a two-step in situ method is pointed out. These experimental results showed that the modified graphene layer can close the nest-shaped pores of the LDH films, making the LDH films hydrophobic (CA 127.8°) and thus exhibiting improved corrosion resistance.

Organic coating is currently one of the most common and effective methods of protecting metals. The corrosion inhibitor is mixed directly with the organic coating, which allows corrosive ions to penetrate the metal matrix from the outside and can even cause the corrosion inhibitor to lose its effect. Due to the peculiarity of the layered structure of LDH and its anion exchange performance, direct contact between the inhibitor and the organic coating can be effectively avoided. Therefore, the addition of a corrosion inhibitor such as LDH to an organic coating can effectively increase the protection of the coating on the surface of metallic materials.

#### 2.3. LDH modified coating on magnesium alloy

LDHs grow directly on the metal substrate by forming chemical bonds through in-situ growth technology, resulting in strong adhesion between the LDH films and the metal matrix. On the other hand, the use of in-situ growth leads to an alignment of the LDH perpendicular to the substrate, resulting in different crystal orientations. This orientation of the film is generally associated with crystallization defects and consequently with the formation of corrosion channels. Therefore, to maximize the lifetime corrosion resistance of LDH films, anion exchange, and surface modification [26] are often used to achieve better corrosion resistance and superhydrophobic properties.

##### 2.3.1. Anticorrosive intercalated structure

LDH films have good corrosion protection due to their anion exchange capacity and their special layer structure, which slows down the corrosion rate of the Mg alloy. Compared to conventional coatings, LDH nanosheets usually grow perpendicular to the substrate surface, and there are many pores between the layers, which provide diffusion paths for anion exchange. In addition, different anionic intercalation structures can provide different protection mechanisms. For example, [27] used an in situ hydrothermal method for the growth of Mg–Al LDH on the surface of AZ31 alloy, followed by vanadate intercalation reactions to produce Mg–Al– $\text{V}_2\text{O}_7^{4-}$  LDH coatings, while [28] investigated Mg–Al LDH intercalated with  $\text{CO}_3^{2-}$  as a multiple adsorbent with anion exchange capacity, which was used to remove HCl,  $\text{SO}_2$  and  $\text{NO}_x$ . Table 1 illustrates the characteristic values of the corrosion protection parameters.

In general, higher  $E_{\text{corr}}$  and a lower  $I_{\text{corr}}$  can prevent corrosion under thermodynamic and kinetic conditions. As the table shows, the corrosion protection is successive in the same sodium chloride solution:  $\text{CO}_3^{2-} > \text{V}_2\text{O}_7^{4-} > \text{Cl}^- > \text{NO}_3^-$ . Among these coatings, it was observed that the  $I_{\text{corr}}$  coating of MgAl– $\text{CO}_3^{2-}$  LDH is four orders of

magnitude lower than that of  $\text{MgAl-NO}_3^-$  LDH and up to two orders of magnitude lower than other LDH coatings. It is worth noting that for some high-temperature superconducting materials [29–32], thin films have a stronger ability to absorb chloride ions in the corrosion solution, thereby improving corrosion protection. Therefore, film thickness and density are also key factors for corrosion resistance as they can limit the direct contact between the

matrix and the corrosive medium. Due to the excellent anion exchange ability and the special lamellar structure of LDH, this intercalation process is therefore efficient and time-saving in corrosion protection. From the perspective of the application of LDH films on Mg alloys, the intercalation of inorganic anions into LDH films is an optimal and effective method of corrosion protection.

Table 1. Corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ) of samples in NaCl solutions (from [28])

Sample	Electrolyte	$E_{\text{corr}}$ (V/SCE)	$I_{\text{corr}}$ ( $\mu\text{Acm}^{-2}$ )
$\text{CO}_3\cdot\text{Mg-Al}$ LDH	3.5 wt.% NaCl	– 0.805	$1.13 \times 10^{-7}$
$\text{Cl}\cdot\text{Mg-Al}$ LDH		– 1.300	$2.52 \times 10^{-7}$
$\text{NO}_3\cdot\text{Mg-Al}$ LDH		– 1.357	$5.58 \times 10^{-7}$
$\text{V}_2\text{O}_7\cdot\text{Mg-Al}$ LDH		– 0.920	$0.13 \times 10^{-7}$

### 2.3.2. Super-hydrophobic modification

Biologists discovered that the lotus is a self-cleaning plant and linked its self-cleaning mechanism to the microscopic morphology of its superhydrophobic surface. They discovered that the superhydrophobic properties of the surface of the lotus leaf are due to a certain roughness on the nanoscopic surface [33]. Inspired by the "lotus effect", scientists began to produce an artificial hydrophobic coating on a metal surface to obtain rough surface materials with low surface energy.

Mg–Al LDH films intercalated with corrosion inhibitors on magnesium alloys were thus prepared by the in situ growth method and the effect of synergistic multicomponent effects, such as molybdate intercalation and minor surface modification of lauric acid to protect the films from corrosion, was investigated. Electrochemical measurements showed that the superhydrophobic LDH coatings significantly reduce the corrosion current density, which proves that the corrosion protection of the Mg alloy can be improved by the combined effect of molybdate and lauric acid. It can be concluded that the surface of the superhydrophobic film cannot be infiltrated so easily. As a result, water molecules,  $\text{Cl}^-$  and other corrosive ions can be prevented from reaching the surface of the matrix and the metal can be better protected against corrosion.

### 2.4. Biocompatible coatings

In recent years, biocompatible materials have been in great demand due to their special, outstanding properties, and the surface modification of magnesium alloys has attracted more and more attention, especially because of their better biocompatibility. There are two types of biocompatible materials: the original biocompatible materials and those that require surface modification and other means to achieve biocompatibility.

PVA is currently one of the most widely used polymer materials. It is a biodegradable polymer with good biocompatibility, stability and chemical resistance. The modified Mg–Al– $\text{CO}_3$  LDH with organic acid coprecipitation method can promote the intercalation of LDH into the polymer matrix, which can achieve an appropriate degree of dispersion. To promote intercalation in the LDH polymer matrix and improve the ideal dispersion, an organic diacid was prepared from tetrabromophthalic anhydrides and L-aspartic acid in refluxing acetic acid with pyridine [34]. Under ultrasonic irradiation, the base spacing between the layers of lactate dehydrogenase was modified by the method of coprecipitation with an organic diacid, which effectively reduced the polymerization time and nanocoherence. The modification process showed that the tensile strength and modulus of PVA/mLHDH-NCs were improved due to the hydrogen bonding and good dispersion of mLHDH in the polymer matrix.

To further extend the long-term protective effect of the absorbent magnesium alloy, the preparation of PGA (a kind of synthetic peptide with good hydrophilicity and biodegradability) sealed with Mg–Al LDH coating on AZ31 magnesium alloy was presented in [15] by a combination of hydrothermal and vacuum freeze-drying methods, whereby a composite coating of LDH and PGA coating was synthesized. Electrochemical polarization, impedance spectroscopy and hydrogen evolution tests showed that these composite coatings provide effective corrosion protection for the AZ31 alloy. The composite coating acts as a physical barrier to seal the porous LDH coating, which improves the corrosion protection of the film and provides long-term protection to the AZ31 substrate. The authors [35] synthesized a conjugate of PGA and rose bengal (PGA–RB), which improved the pharmacokinetics

and antitumor effect. In addition, hydrophobic polycaprolactone (PCL) and PGA were used as raw materials to synthesize tissue-reinforced menisci with good biomechanical and biodegradable properties. Based on this, they successfully applied PGA coating on Mg–Al LDH by hydrothermal treatment in [36], and the results show that LDH has good corrosion resistance. The study on cell adhesion of stem cells from rat bone marrow also showed that PGA/LDH composite coatings can significantly improve the cell compatibility of the substrate and have a broad application prospect in orthopedic surgery [37–40].

### 3. CONCLUDING SUMMARY AND PERSPECTIVE

LDH materials are widely used in the field of metal protection due to the rapid development of LDH in the field of anion exchange, preparation technology, modification methods and corrosion mechanism. However, there are too few studies on the anion exchange mechanism between LDH layers and the recombination mechanism of the layer structure from a microscopic point of view. In this review, the synthesis methods of LDH coatings are summarized. The mechanism of corrosion resistance of LDH material on magnesium alloys is briefly discussed. The surface of LDH material was chemically modified to improve solvent compatibility, and the anti-corrosion function was developed in the form of additives, resulting in composite coatings with special functions.

To summarize, LDH coatings have a good protective effect on magnesium alloys, but there are still problems that need to be further investigated. In-situ growth is the most commonly used method, but the degree and thickness of LDH coating are sometimes insufficient. This shows the importance of multiple synthesis methods for LDH coatings. The binding force between the LDH and the substrate can be changed by changing the ratio of metal cations, and the corrosion resistance can be improved to extend the life of the film. To achieve this goal and other functional effects of Mg alloy, it is necessary to investigate the recombination mechanism of LDH interlayer structure, which can maximize the release of inhibitory ions and the absorption of corrosion ions. Chemical modification or incorporation of synergistic ions can improve the compatibility between LDH and organic polymers, thereby increasing the compactness of the composite coating and improving its corrosion resistance.

In addition to researching the preparation of the Mg–Al LDH coating system on the surface of the Mg alloy to improve corrosion resistance, it is

particularly important to better understand the selection of suitable key parameters and the synthesis process. Since the LDH film has the main characteristics of positive anti-corrosion function, it is necessary to find new regulation parameters for realizing the preparation of multifunctional LDH film with controlled values of boundary parameters on specific interfaces, in addition to improving the protective performance of composite films on Mg alloys. Therefore, Mg–Al LDH composite films produced on the surface of Mg alloys have great prospects for wide application in corrosion protection.

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## IZVOD

### PREZENTACIJA METODA DOBIJANJA, SVOJSTAVA I MOGUĆNOSTI PRIMENE NOVIH ANTIKOROZIVNIH SREDSTAVA – NANOSTRUKTURIRANIH MATERIJALA NA BAZI LHO

*Posljednjih godina, slojeviti dvostruki hidroksid (LDH) se snažno razvio u oblasti zaštite materijala od korozije zbog svojih posebnih svojstava, koja uključuju izuzetnu sposobnost anjonske izmene sa povećanim anjonskim kapacitetom, kao i otpornošću na barijeru i zabeleženim efektom strukturne memorije. Ovaj članak daje pregled nedavnih radova o svojstvima LDH u obliku prahova i filmova. Detaljno su analizirane mogućnosti i prednosti korišćenja ovog jedinjenja za zaštitu materijala od korozije.*

**Ključne reči:** Nanomaterijali, antikorozivna sredstva, anjonska izmena, LDH prah, ultratanki film

*Naučni rad*

*Rad primljen:*

*Rad prihvaćen:*