



## Fabrication of oriented layered double hydroxide films by spin coating and their use in corrosion protection

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### ABSTRACT

MgAl-Layered Double Hydroxide (LDH) films have been prepared by spin coating a nanodispersed MgAl-LDH sol on an AZ31 magnesium alloy substrate. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) of the as-prepared films demonstrated their uniform and compact structure composed of LDH platelets stacked parallel to the substrate surface. The anti-corrosion properties of the LDH films were investigated by measuring dc polarization curves and electrochemical impedance spectroscopy (EIS). EIS results demonstrated that the densely packed oriented LDH platelets are effective in restricting penetration of aggressive ions and thus inhibit corrosion of the underlying metal surface. The corrosion resistance imparted by the LDH films increased with film thickness.

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### 1. Introduction

The costs of metal and metal alloy corrosion amount to several percent of the GDP of an industrialized country and the development of effective corrosion inhibitors is therefore an issue of major economic importance [1]. Mg alloys are being increasingly used as advanced structural and functional materials in the ship, automotive, aerospace and electronic industries, because of their high strength-to-weight ratio. The low corrosion resistance of the alloys is, however, a limitation on their applications. Anodizing methods are generally used to form a ceramic layer on the surface of the alloy in order to increase its corrosion resistance, but the conventional methods involve the use of environmentally undesirable species such as chromate, fluoride or phosphate [2]. Conductive polymer coatings have been shown to be a promising alternative [3–5]. Other protective films, such as epoxy ester resin, were used as anticorrosion material for aluminum [6]. However, the thermal stability and adhesion are concerns for pure polymer coatings.

Recently, Layered materials such as anionic clays (e.g. layered double hydroxides (LDHs) [7–11] and cationic clays (e.g. montmorillonite) [12,13] have been widely investigated as additives in organic anti-corrosion coatings or as polymer-clay nanocomposite corrosion resistant coatings. In addition, zeolites [14–17] have also been explored as corrosion resistant coating materials. For LDHs, the composition may be varied over a wide range allowing mate-

rials with a wide variety of properties to be prepared. By taking advantage of the most attractive feature of LDH chemistry, *viz.*, the ability to modify the properties of the coatings by varying the layer composition and the intercalation of other anions, LDHs coatings have been shown to be a promising alternative for corrosion prevention of metal alloy.

LDHs are generally prepared in powdered form [18–20], but in order to be used as materials for functional coatings or in devices [21–31] they must be fabricated into well-oriented supported or self-supporting films. There have been a limited number of reports of the formation of oriented LDH films. For example, Gardner et al. [27] and Wang et al. [31] found that colloidal suspensions of LDHs can be used to form multilayered transparent films, either self-supporting or on a glass substrate. By employing ultrasonication, Lee et al. obtained a monolayer film of LDHs on a Si wafer [28,29]. Layer-by-layer self-assembly techniques have also been used to fabricate LDH films by using pre-exfoliated LDH nanosheets [30] or as-synthesized LDH nanocrystals [32] as building blocks. When using all of the above methods, it was found that the LDH platelets adopted a preferred orientation with their *c* axis perpendicular (i.e., *ab* face parallel) to the substrate surface; this reflects the intrinsic propensity of LDH crystallites to align in an orientation that leads to maximum face-to-face contact between the crystals and the substrate [28–30,32]. More recently, we found that uniformly aligned polycrystalline LDH films directly grown from an aluminium oxide substrate, with the *c* axis of the crystallites parallel to the substrate surface can be prepared by an *in situ* hydrothermal crystallization method and that the films showed excellent “slippy” (Cassie-Baxter regime) superhydrophobicity after simple treatment with lauric

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acid [33]. In spite of the recent progress made in the study of LDH films, the development of a convenient approach for the fabrication of oriented films with controllable properties, such as film thickness, crystal orientation and packing manner, remains a considerable challenge.

There have been a small number of studies of the use of LDH films as inhibitors of metal corrosion. Mixed slurries of LDHs and organic polymers such as polyvinyl butyral [9,10] or an epoxy resin [7] have been cast on AA2024-T3 aluminum alloy surfaces or lithium-aluminum based LDH films formed by exposure of 2024-T3 (Al–4.4Cu–1.5Mg–0.6Mn) metal surfaces to an alkaline solution of a lithium salt impart some corrosion resistance although additional organic coatings are required in order to give adequate protection [11,26,34]. To achieve effective anti-corrosion coatings, a densely packed LDH film structure is required.

Spin coating has been shown to be an effective approach for the fabrication of inorganic films or membranes with controlled structure and crystal orientation [35]. In its simplest form, a film can be cast directly from an aqueous suspension of precursor crystals without any pre-treatment. The spin-coated films may be used in large scale as corrosion protection agent, especially potentially and nicely fit into some certain current semiconductor processes [36,37]. In this work, we describe the corrosion protection properties of oriented LDH films prepared by spin coating an LDH sol on an AZ31 magnesium alloy substrate.

## 2. Experimental

### 2.1. Preparation of MgAl-LDH films

The MgAl-LDH sol was prepared using a procedure reported by Gardner and co-workers [38], since aluminum component has been demonstrated effective to enhance the anticorrosion properties for magnesium or magnesium alloy [39–41]. In brief, methoxide anion-intercalated derivatives of MgAl-LDHs were prepared by a coprecipitation method from magnesium and aluminum nitrates dissolved in methanol in the presence of NaOH. The precipitated LDH was then dispersed in water, leading to complete hydrolysis of the methoxide ions and the formation of a nearly transparent colloidal suspension.

The AZ31 (composition: 3.0% Al, 1.0% Zn, 0.1% Cu, 0.15% Mn, and 0.03% Ni, with the balance being Mg) substrates (10 mm × 10 mm) were mechanically polished with SiC paper (400, 800, 1200 and 4000 grit) to obtain smooth surfaces and subsequently cleaned for 5 min in an ultrasonic bath in 95% acetone.

Spin coating was carried out using a KW-4A spin coater (Institute of Microelectronics, Chinese Academy of Sciences). The substrate was placed on the spin coater tray and 100  $\mu$ L LDH sol was applied by syringe as the substrate was spun at 600 rpm for 10 s. The substrate was then spun for an additional 30 s at 1500 rpm. This process was repeated a varying number of times (5 or 10) for preparing multilayers of LDHs. The resulting films were dried in a vacuum oven for 24 h at room temperature.

### 2.2. Characterization

XRD data were collected on a Shimadzu XRD-6000 powder X-ray diffractometer under the following conditions: 40 kV, 30 mA, Cu K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ), and scan rate of  $5^\circ/\text{min}$  in the range  $3\text{--}70^\circ$ .

The morphology of the films was investigated by using a scanning electron microscope (SEM, Hitachi S-4700). The accelerating voltage applied was 20 kV. For transmission electron microscopy

studies (TEM, Hitachi H-800, accelerating voltage 200 kV), LDH powder samples were scraped from the spin coated LDH film under a microscope, diluted to approximately 0.01 g/mL and finally pipetted onto uncoated copper TEM grids and allowed to dry under ambient conditions.

For the electrochemical tests, a three-electrode configuration was employed with the sample under test as the working electrode, a platinum electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. 3.5% NaCl aqueous solution was used as the electrolyte. Only a  $1 \text{ cm} \times 1 \text{ cm}$  area was exposed on the surface of each sample with the remaining part being sealed with wax during the tests. The polarization curves were recorded with a CS300 corrosion electrochemical testing system at room temperature with a sweep rate of 10 mV/s. EIS measurements were carried out using a Zahner IM6e impedance measurement unit. The data were acquired at room temperature from 100 kHz to 10 mHz using a 5 mV amplitude perturbation. Basically,  $E_{\text{corr}}$  data ( $E_{\text{corr}}$ ) were obtained from the plateaus at low current,  $i_{\text{corr}}$  data ( $i_{\text{corr}}$ ) were calculated from the extrapolation of Tafel line to pre-determined open circuit potential [42]. The adhesion of the LDH film on the surface of AZ31 magnesium alloy was performed according to the method reported in the previous literature [14].

## 3. Results and discussion

### 3.1. Microstructural characterization of LDH films

Fig. 1 shows the XRD patterns of the LDH films prepared with different numbers of coating cycles, as well as the XRD patterns of the bare AZ31 substrate and the LDH powder prepared by co-precipitation method for comparison. The XRD pattern of the precipitate (Fig. 1a) exhibited the characteristic reflections of LDHs. The strongest reflection at ca.  $11.7^\circ$  corresponds to a basal spacing ( $d_{003}$ ) of 0.751 nm, consistent with the values reported in the literature [43,44]. Other peaks at relatively high  $2\theta$  values can be indexed to non-basal (0 1 2), (0 1 5), (0 1 8), (1 1 0) and (1 1 3) reflections. For the three LDH film samples, well-defined series of basal and higher order (00 $l$ ) reflections at lower  $2\theta$  values were also observed (Fig. 1c–e). The peaks above  $30^\circ$   $2\theta$  in the patterns can be ascribed to the AZ31 substrate, by comparison with the XRD pattern shown in Fig. 1b. The fact that no non-basal reflections are

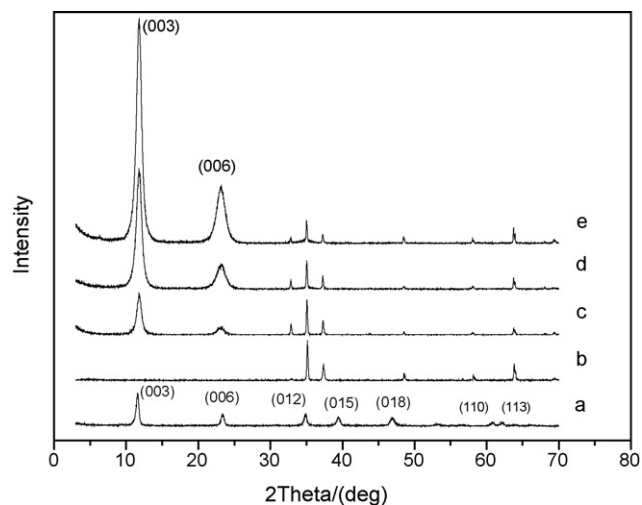


Fig. 1. XRD patterns of (a) MgAl-LDH prepared by using co-precipitation method, (b) bare AZ31 substrate, and oriented LDH films prepared with different numbers of spin coating cycles: (c) once, (d) 5 times, and (e) 10 times.

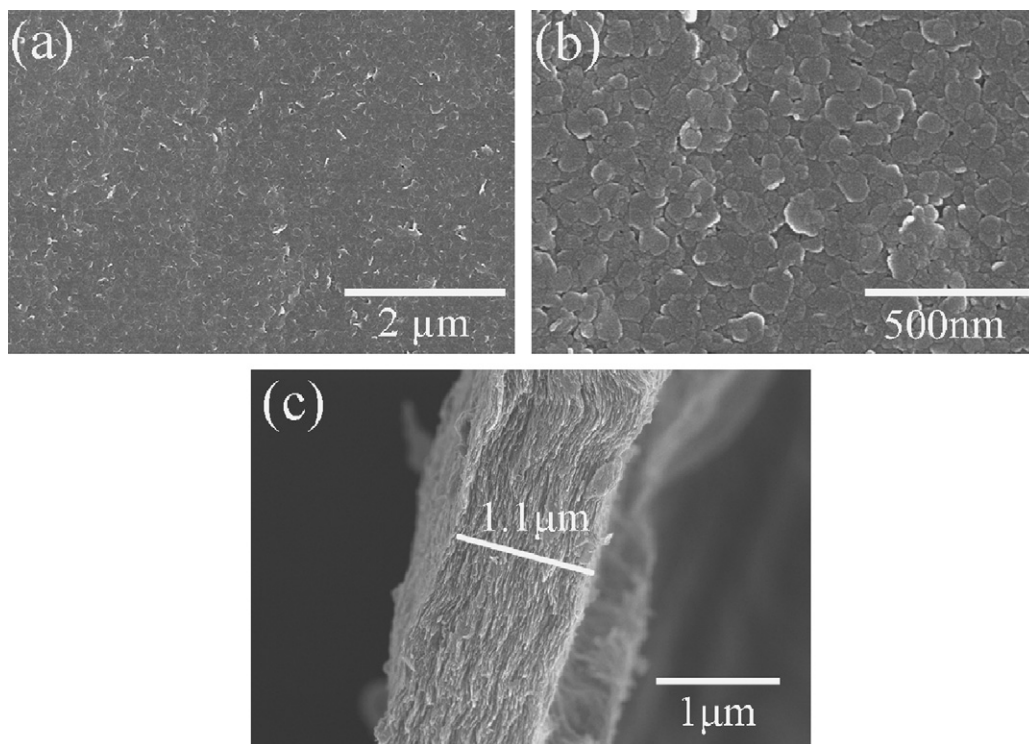


Fig. 2. SEM images of oriented LDH films prepared with a single coating step: (a) top view, (b) same as (a) at high magnification, and (c) edge view.

observed for the LDH films is good evidence for an extremely well-oriented arrangement of LDH platelets in the film samples, with their *c* axis perpendicular to, and *ab* face parallel to the surface of the substrate, as reported for the well-oriented LDH films prepared by other effective approaches such as casting, i.e., solvent evaporation method [27,38,45], combination of exfoliation of LDHs in organic solvents and layer-by-layer techniques [30], simple ultrasonic treatment [29], as well as via selective layer reaction of layer-by-layer assembly method [32]. In addition, when the spin coating process was repeated, the intensities of both (003) and the (006) reflections of LDH film samples increased, indicating that thicker LDH films had been formed. Also, the broadening of the basal reflections of spin-coated LDHs films with increase of spin coating times can be observed, which can be due mainly to the increase of defects or displacements between big crystals and the increase of crystals bearing broadening basal reflections. This inhomogeneous distribution of the different crystal sizes can eventually lead to the XRD result of the broadening of the basal reflections with spin coating times increased, albeit the enhanced intensity of the peaks of (003) and (006).

Fig. 2 shows the SEM micrographs of the LDH films prepared with a single coating step. The top-view images (Fig. 2a and b) clearly show that the LDH platelets, with a mean size of 60 nm, are parallel to the surface of AZ31 substrate with the edges of the particles only rarely being seen. The edge-view image (Fig. 2c) confirms that the platelets are closely packed in the two-dimensional plane, layer by layer. The film thickness is about 1.1  $\mu\text{m}$ . When the spin coating process was repeated 5 and 10 times, the measured film thickness increased to about 4.5 and 10.2  $\mu\text{m}$ , respectively (SEM images not shown).

The TEM image of the LDH powder sample scraped from the spin coated LDH film is illustrated in Fig. 3. Fine structure on the morphology of the LDH grain boundaries can be clearly observed. The LDH nanoparticles retain the characteristic platy crystal habit of LDHs.

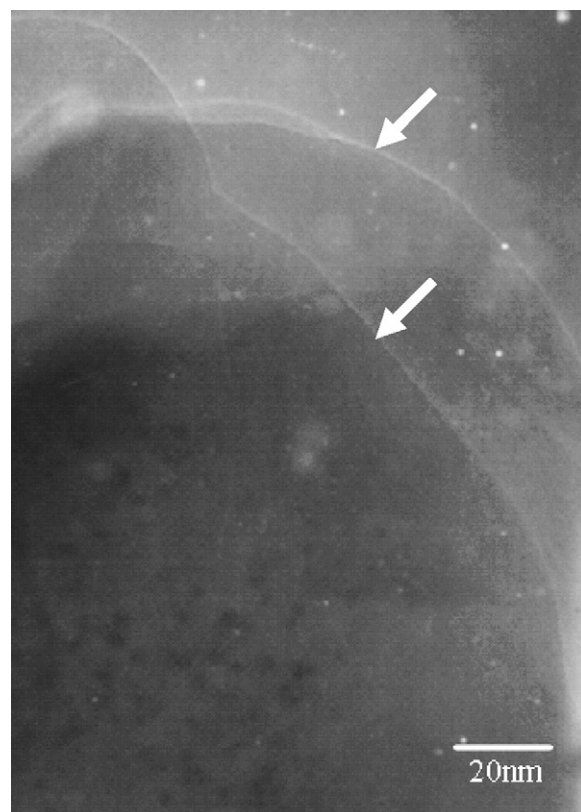
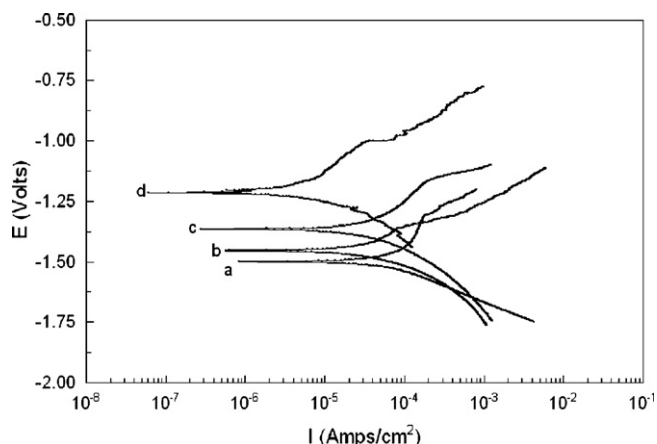


Fig. 3. TEM image of LDH powder sample scraped from the spin coated LDH film prepared with a single coating step.



**Fig. 4.** Polarization curves of (a) bare AZ31 substrate, and the oriented LDH films prepared with different numbers of spin coating cycles: (b) once, (c) 5 times, and (d) 10 times.

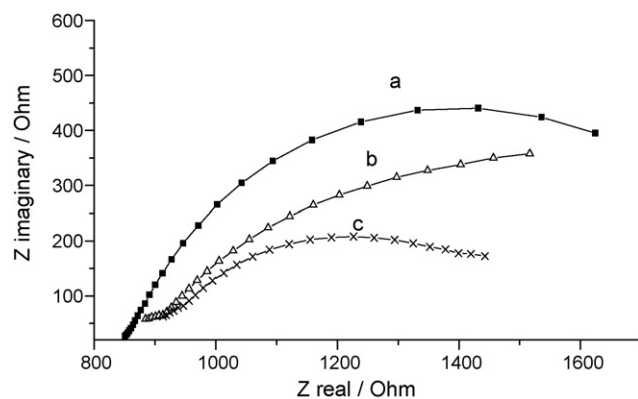
### 3.2. Corrosion resistance of the LDH films

The corrosion resistance of the LDH films was evaluated by dc polarization, a technique commonly used for this purpose [14,17]. In a typical polarization curve, the lower the polarization current, the better the corrosion resistance. Fig. 4 shows the polarization curves for the bare AZ31 substrate and the oriented LDH films. The curves were recorded after open-circuit exposure to 3.5% NaCl (pH 7.0) for 5 min. After coating the AZ31 substrate with LDH films of different thickness, the corrosion current density ( $i_{\text{corr}}$ ) was reduced, with the extent of the reduction increasing with the thickness of the film as shown in Table 1; there were concomitant shifts in the corrosion potential ( $E_{\text{corr}}$ ) of the materials to less negative values. Spin coating the substrate with a single coating of LDH afforded a reduction in  $i_{\text{corr}}$  to 35% of that of the bare substrate, whereas when the process was repeated 10 times, the value of  $i_{\text{corr}}$  was reduced to ca. 2.5% of that of the bare substrate. The high density of crystallite packing, shown by SEM and TEM, clearly provides an effective barrier to the transport of aqueous species to the AZ31 substrate, so that aggressive ions (in this case  $\text{Cl}^-$ ) are unable to penetrate the film, resulting in the observed excellent anti-corrosion performance. The enhanced properties of restacking could be attributed both to the “stickiness” or adhesion properties of the LDH [38] and to the intercalation of chloride anion into the LDHs thus preventing it from reaching the surface. The intercalation of chloride anion can be measured by using XRD, as reported previously [7,46]. We performed XRD measurements of LDH films exposed to immersion for 24 h in 3.5% NaCl. Our results of XRD clearly show the shifts of the peaks at (003) and (006) from  $11.45^\circ$  to  $11.25^\circ$  and  $22.56^\circ$  to  $22.98^\circ$ , respectively. The appreciable shifts could be attributed to  $\text{Cl}^-$  intercalated into the LDH upon exposure to 3.5% NaCl, in which the peaks at (003) and (006) of the post-exposed samples are in agreement with those of  $\text{Mg}_2\text{Al}-\text{Cl}$  (PDF#190748).

**Table 1**

Corrosion potential ( $E_{\text{corr}}$ ) and corrosion current density ( $i_{\text{corr}}$ ) of the bare substrate and LDH films prepared with different numbers of spin coating cycles

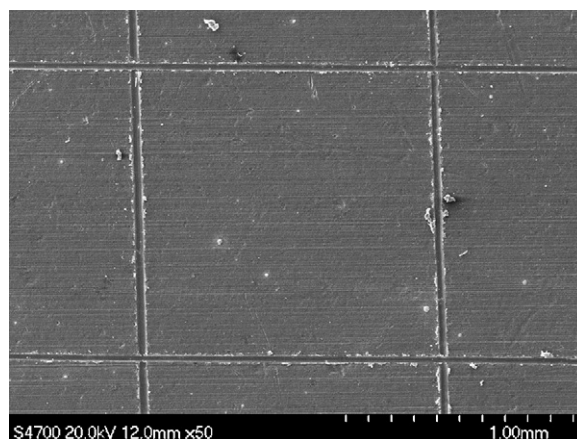
Sample	$E_{\text{corr}}$ (V)	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )
Bare AZ31	-1.4998	193.9
Spin coated once	-1.4536	67.67
Spin coated 5 times	-1.3655	60.27
Spin coated 10 times	-1.2139	4.914



**Fig. 5.** Nyquist plots of the impedance spectra of LDH films (prepared by spin coating 10 times) after immersion for different times in 3.5% NaCl: (a) 1 h, (b) 6 h, and (c) 12 h.

EIS was also used to evaluate the anti-corrosion performance of the LDH films. Fig. 5 shows the Nyquist plots of the impedance of LDH films prepared by spin coating 10 times after immersion in 3.5% NaCl for different times. For the film immersed for 1 h only, the Nyquist plot clearly shows a quasi-semicircle (Fig. 5a), revealing that the film effectively blocks the penetration of medium. This suggests that the substrate thus remain intact, as no electron transfer processes occur between medium and non-electronically conductive MgAl-LDHs. In contrast, for the films immersed for longer times (Fig. 5b and c), small depressed semicircles were observed at high frequency, followed by second larger semicircles at lower frequency. The depressed semicircles correspond to the frequency range where the impedance depended on charge transfer, indicative of infiltration and breakdown of the film [47–49]. The general shape of the complex plane plots was as expected for porous electrodes [50]. In the case of the spin-coated films, one possible explanation is that there exists some defect of pinholes open areas in the multilayers, consistent with the observation of SEM. These pinholes provide channels for medium to penetrate the multilayer to the electrode. This suggests that permeation of NaCl solution progresses along the LDH grain boundaries [51].

Fig. 6 shows the SEM result of the adhesion of the LDH film on the surface of AZ31 magnesium alloy analyzed according to the method reported previously [14]. Note that the tested LDH film was prepared by spin coating for 10 times, and the gap between the blades was about 1 mm. There was no significant peeling of either



**Fig. 6.** SEM images of MgAl-LDH coating on AZ31 magnesium alloy tested for adhesion.

material after cross cutting through the LDH coating, indicating that there is strong adhesion between the AZ31 magnesium alloy and MgAl-LDH coating.

#### 4. Conclusions

The anti-corrosion properties of in-plane oriented LDH films prepared by spin coating an MgAl-LDH sol on AZ31 magnesium alloy have been investigated. The microstructure of the LDH films was shown to involve a compact packing of LDH platelets oriented parallel to the surface of the substrate. Polarization curves showed that the spin coated AZ31 afforded a marked enhancement in corrosion resistance, the magnitude of which increased with film thickness. EIS results demonstrated that the densely packed LDH crystallites effectively block the penetration of aggressive ions such as  $\text{Cl}^-$ . The results demonstrate that MgAl-LDH films have the potential to provide an effective and environmentally friendly corrosion resistant coating for magnesium alloys.

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