Influence of pH on corrosion resistance of electrodeposited Mg-Fe LDH composite films on Mg alloys WE43

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Abstract. Layered double hydroxide (LDH) are widely studied as corrosion inhibition coatings for magnesium (Mg) alloys due to their nano-lamellar structure and anion-exchange ability. The two common approaches in synthesising LDH films on Mg alloys are co-precipitation and hydrothermal treatment. Recently, electrodeposition has drawn more interest as a potential synthesis approach due to the low cost, ease of control, one-step method, and ability to create a compact film. In this work, Mg-Fe LDH film was synthesised on magnesium hydroxide, Mg(OH)₂ layer formed on Mg alloy WE43 by electrodeposition approach with the as-prepared iron solution at different pH values. The effect of pH of the solution (3.0, 5.0 and 7.0) on the formation of LDH films was investigated using Field Emission Scanning Electron Microscopy (FESEM). Additionally, the surface chemical components of the film were obtained by Fourier Transform Infrared Spectrometer (FTIR). All the LDH composite films synthesised at different pH values undergo electrochemical tests in Hank's Balanced salt solution (HBSS). All samples promote corrosion resistance of WE43 with the LDH film synthesised at pH 3.0 provided the highest inhibition efficiency (I.E) of 94.48 % and resistance polarisation value of 3559.07 Ωcm².

Keywords. Layered double hydroxide, magnesium alloys, surface modification, corrosion, coatings

1. Introduction
Magnesium (Mg) alloys received much recognition as biomaterials for implant applications due to their biocompatibility and biodegradability [1–3]. For instance, the similarity in density and mechanical properties of Mg alloys to human bone makes them a suitable biomaterial for orthopaedic implant applications [4, 5]. Secondary surgery can be avoided with the degradability properties, which reduces the patients' pain and cost [6]. However, the high electrochemical activity of Mg alloys in physiological environments limits their clinical applications. The rise in local alkalinity and hydrogen evolution hampers the post-surgery healing process [7, 8]. Thus, continuous efforts have been communicated to elevate the corrosion resistance of Mg alloys.

Generally, past literature has highlighted various surface modifications that could delay the fast corrosion activity of Mg alloys, such as conversion coatings [9, 10], plasma electrolytic oxidation (PEO) coatings [11, 12], and layer-by-layer coatings [13–15]. Nevertheless, these coatings can only provide a
passive barrier protection in which the protective ability will be at risk once their coating integrity is damaged. Thus, layered double hydroxide (LDH), an active coating system, has gained attention as a potential coating material for Mg alloys as LDH can react to physical and/or chemical damage [2, 16, 17]. As an active coating system, LDH can simultaneously entrap corrosive anions while releasing corrosion inhibitors from the interlayer space during physical and/or chemical damage.

LDH is an anion clay or hydrotalcite-like material stacked with alternative positive charged layers, with an exchangeable anionic layer in the interlayer space, allowing the entrapment of corrosive chlorine anions [18, 19]. Recently, LDH has been reported as a corrosion inhibition coating for Mg alloys due to the ion-exchange ability and flexible structure [19, 20]. Peng et al. [21] synthesised Mg-Al LDH film loaded with 5-Fluorouracil on AZ31 alloy. The LDH film constructively elevate the corrosion resistance of the substrate due to their ion-exchange ability. Similarly, Chen et al. [22] reported an excellent self-healing ability with improved corrosion resistance of the hydrothermally synthesised Mg-Al LDH film intercalated with aspartic acid.

Looking at the numerous reports on the enhanced corrosion resistance ability of LDH films on Mg alloys, various synthesis approaches have been explored to synthesise LDH on Mg alloys [23, 24]. In particular, in-situ growth method, such as co-precipitation [25], hydrothermal process [26, 27], and electrodeposition method [28, 29] is a common approach for forming LDH films on Mg alloys. Despite multiple works which looked into in-situ growth method as the synthesis approach for LDH films, the corrosion protection ability and surface morphology of LDH films based on synthesis parameters has not been thoroughly investigated. Based on the crystallography theories, the crystallization rate of LDH and the overall microstructure are affected by the reaction conditions [30, 31]. Kamiyama et al. [32] reported that the thickness of the Mg-Al LDH film through steam coating increased when the treatment time increase from 1 h to 9 h. The LDH film synthesised at 9 h showed excellent corrosion protection for the substrate, attributed to the excellent barrier effect.

Additionally, Chen et al. [33] studied the effect of different process parameters, including immersion time, pH of the solution, and treatment temperature, on the film properties on the corrosion inhibition ability of the film. They concluded that the LDH film achieved the best quality with excellent corrosion resistance when the film was synthesised at pH 10.5 at 80 °C for 1.5 h. Generally, even though past researchers have studied the effects of process parameters, however, the studies on the impact of pH on the microstructure of LDH film through the electrodeposition method is currently limited based on the author's knowledge.

In this work, Mg-Fe LDH film was prepared successfully by electrodeposition method on as-prepared Mg(OH)2 layer on WE43 alloy. The effect of pH of 3.0, 5.0, and 7.0 on the microstructure of Mg-Fe LDH films was studied. The selection of different solution pH assesses the impact on the surface morphology of Mg-Fe LDH films synthesised via electrodeposition. Additionally, the active protective function of LDH films is evaluated by electrochemical methods.

2. Experimental methods

2.1. Materials

Magnesium alloys WE43 with a composition of Y 3.56 %, Nd 2.20 %, Zr 0.47 % and Mg – balanced (all in wt. %) was used in this work. The WE43 alloys with a 10 x 10 x 6 mm measurement were ground using silicon carbide (SiC) paper of 240 grit to 1500 grit. Afterwards, the samples were ultrasonically cleaned in ethanol for 10 mins.

2.2. Preparation of precursor Mg(OH)2 layer and Mg-Fe LDH films at various pH

Synthesis of an Mg(OH)2 layer on WE43 alloy was carried out through hydrothermal process using DI water at 160 °C for 3 h, as previously reported by Zhu et al. [34]. The synthesis of Mg-Fe LDH film was adapted from Lin et al. [23], with some modification done for this work. Firstly, an aqueous solution containing Fe3+ ions was prepared. Next, the filtered Fe3+ solution was adjusted to pH 3.0 with 1.0 M of nitric acid (HNO3) solution before the electrodeposition of LDH film. Afterwards, Mg-Fe LDH film
was electrodeposited through a three-electrode setup at an applied potential of $-1.4 \text{ V}_{\text{SCE}}$ for 300 s at room temperature (25 °C) without stirring. After electrodeposition, DI water was used to rinse the sample and dried in the oven before any characterisation. Additionally, two other Fe$^{3+}$ solutions were prepared at pH 5.0 and pH 7.0 with 1.0 M of HNO$_3$ solution and 2.0 M of sodium hydroxide (NaOH) solution, respectively, before electrodeposition. The as-prepared samples were designed as LDH 3, LDH 5, and LDH 7.

2.3. Characterisation
Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi SU8010) was selected to determine the structure and surface morphology of Mg-Fe LDH films. The surface functional groups of the Mg-Fe LDH films were evaluated by Fourier Transform Infrared Spectrometer (FTIR, Thermo Fisher Scientific Nicolet iS10) under attenuated total reflectance (ATR) mode. All coated substrates were scanned from 4000 – 600 cm$^{-1}$ with 64 scans at 4 cm$^{-1}$ resolutions.

Electrochemical studies were conducted via a Gamry FAS2 with a PCI4 Controller Board. The selected medium is Hank’s Balanced Salt Solution (HBSS), whereby the temperature was maintained at 37 ± 0.1 °C through a thermostatic water bath. The open-circuit potential (OCP) was conducted for 1 h to stabilise the substrates. Potentiodynamic polarization (PDP) measurements were performed at a scan rate of 1 mV/s in the range of $-300 \text{ mV}$ to $+500 \text{ mV}$ vs OCP. The inhibition efficiency of the samples was calculated using:

$$I.E = [1 - \left( \frac{i'_{\text{corr}}}{i_{\text{corr}}} \right)] \times 100$$  \hspace{1cm} (1)

where $i'_{\text{corr}}$ and $i_{\text{corr}}$ are the corrosion current density of the LDH film and uncoated WE43 alloy.

3. Results and discussion

3.1. Physical and chemical characterisation of samples
The structures and surface functional groups of the electrodeposited Mg-Fe LDH films at different pH were examined through FTIR and FESEM.

The functional groups in the as-prepared Mg(OH)$_2$ layer and LDH films were examined through FTIR spectroscopy in wavelengths of 4000 – 600 cm$^{-1}$. The peaks distribution of the FTIR spectrum for all samples are shown in figure 1 below. Based on figure 1, all samples show a band at 3692 cm$^{-1}$ with LDH 3 showed a distinguish sharp and strong band, describing the stretching vibration of the Mg-OH group [36]. The appearance of a sharper absorption peak at 3692 cm$^{-1}$ for the LDH 3 sample indicates the participation of the Mg(OH)$_2$ layer in the synthesis of LDH film. Asides from the absorption peak at 3692 cm$^{-1}$, LDH 3 also presented peaks at 1640 cm$^{-1}$ and 1393 cm$^{-1}$. These peaks correspond to the bending vibration of the hydroxyl group in water molecules and asymmetric stretching of carbonate anions, respectively. Undoubtedly, with 1640 cm$^{-1}$ and 1393 cm$^{-1}$ peaks, it is clear that LDH film is successfully synthesised at a pH of 3.0. On the contrary, LDH 5 and LDH 7 samples presented weak absorption peaks compared to LDH 3, which suggests that the solution's pH at 5.0 and 7.0 are not ideal for forming LDH film via the electrodeposition method.
Figure 1. FTIR spectrum for (a) Mg(OH)₂ layer; (b) LDH 3; (c) LDH 5; (d) LDH 7.

The FESEM micrographs of the Mg(OH)₂ and Mg-Fe LDH samples electrodeposited at various pH values are demonstrated in figure 2. Figure 2 (a,a1) shows the presence of curled nano-plates microstructures, indicating the successful synthesis of Mg(OH)₂ layer on the surface of WE43 alloy. Nevertheless, it can be seen that the formation of the Mg(OH)₂ layer is not uniform as the Mg alloy’s polished surface is still visible. The Mg(OH)₂ morphology reported here is similar to the surface morphologies reported by past researchers [37, 38]. Thus, the Mg(OH)₂ layer cannot provide excellent corrosion protection for the substrate as the non-uniform layer will accelerate the penetration of corrosive anions to the substrate surface. The surface microstructure of the electrodeposited LDH films at different pH values is shown in figure 2 (b-d). LDH 3 represents the nano-blade structure, eviting the crystalline nature of the LDH film. However, smaller-sized flowers appear at pH 7.0, creating compact and more dense surface morphologies. The formation of flower-like morphology could be due to the decrease in crystallinity.

Nevertheless, the LDH film synthesised at pH 5 contains pores visible in the FESEM micrographs. Additionally, it can be observed from the figure (d, d4) that small needle-like morphology with the presence of cracks is seen in the LDH 7 sample. The presence of cracks and small needle-like morphology could form due to the selection of pH at 7.0 restrict the crystallography growth of the LDH film. These results agree with the FTIR spectrum of the samples. Thus, solution pH of 3.0 is regarded as the most suitable pH to grow a compact and dense Mg-Fe LDH film through electrodeposition.
Figure 2. FESEM micrographs of (a, a1) Mg(OH)2 layer, (b, b2) LDH 3, (c, c3) LDH 5, (d, d4) LDH 7.
3.2. Corrosion inhibition of Mg-Fe LDH films at various pH values.

Potentiodynamic polarisation (PDP) technique was selected to assess the electrochemical performance of the Mg-Fe LDH films. PDP curves of Mg-Fe LDH films prepared at different pH values in Hank's balanced salt solution (HBSS) are illustrated in figure 3. Polarization measurements were performed to obtain the values of corrosion potential (E_cor), corrosion current density (i_corr), polarization resistance (R_p), and inhibition efficiency (I.E), which are presented in Table 1. Based on the E_cor and i_corr values, it can be seen that both values for the LDH films at pH 3, pH 5, and pH 7 shifted to more positive and lower values, indicating that the LDH films showed improved corrosion resistance in terms of kinetics and thermodynamics as compared to WE43 alloy in HBSS. These results portray the reliability of the protective ability of the LDH films on WE43 alloy against corrosion attacks in the physiological environment. Above all, these results suggested that LDH 3 sample exhibited the best corrosion resistance, with I.E and R_p values of 94.48 % and 3559.07 Ωcm², respectively. Generally, the higher value of I.E and R_p indicated that the sample is less prone to corrosion attacks.

![PDP curves of WE43 alloy and Mg-Fe LDH films synthesised at different pH values.](image)

**Figure 3.** PDP curves of WE43 alloy and Mg-Fe LDH films synthesised at different pH values.

| Sample  | β_a (mVdec⁻¹) | β_c (mVdec⁻¹) | E_cor (V vs. SCE) | i_corr (μA.cm⁻²) | I.E (%) | R_p (Ωcm²) |
|---------|---------------|---------------|-------------------|------------------|---------|------------|
| WE43    | 0.3331        | 0.4063        | -1.71             | 0.000143         | -       | 556.52     |
| LDH 3   | 0.0804        | 0.3305        | -1.40             | 0.0000079        | 94.48   | 3559.07    |
| LDH 5   | 0.0798        | 0.3644        | -1.49             | 0.0000090        | 93.71   | 3162.51    |
| LDH 7   | 0.067         | 0.1165        | -1.56             | 0.0000098        | 93.14   | 1887.17    |

**Table 1.** Tafel plot values for Mg-Fe LDH samples in HBSS with pH of 7.4 at 37°C.
4. Conclusion
Mg-Fe LDH films were successfully synthesised on WE43 alloy with Mg(OH)$_2$ layer as the precursor layer via electrodeposition. The FTIR spectrum confirmed the formation of LDH film on the WE43 alloy. It is found that the pH value of 3.0 encourages the crystalline growth of LDH, which leads to the formation of a dense and compact nano-blades film. The obtained Mg-Fe LDH film at a pH value of 3.0 shows improved corrosion resistance for the underlying WE43 alloy in HBSS at 37 °C, rendering its potential for biomedical implant applications.

Reference

[1] Yin Z Z, Qi W C, Zeng R C, Chen X B, Gu C D and Guan S K 2020 Advances in coatings on biodegradable magnesium alloys. *J. Magnesium Alloys.* 42–65

[2] Tan J K E, Balan P and Birbilis N 2021 Advances in LDH coatings on Mg alloys for biomedical applications: A corrosion perspective. *Appl. Clay Sci.* 202 105948

[3] Liu J, Bian D, Zheng Y, Chu X, Lin Y, and Wang M 2020 Comparative in vitro study on binary Mg-RE (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) alloy systems. *Acta Biomaterial* 102 508–28

[4] Chen J, Tan L, Yu X, Etim I P, Ibrahim M and Yang K 2018 Mechanical properties of magnesium alloys for medical application: A review *J. Mecha Behav. Biomed. Mater.* 87 68–79

[5] Ding W 2016 Opportunities and challenges for the biodegradable magnesium alloys as next-generation biomaterials *Regen Biomater.* 3 79–86

[6] Mao L, Shen L, Niu J, Zhang J, Ding W and Wu Y 2013 Nanophasic biodegradation enhances the durability and biocompatibility of magnesium alloys for the next-generation vascular stents *Nanoscale.* 5 9517–22

[7] Kuhlmann J, Bartsch I, Willbold E, Schuchardt S, Holz O and Hort N 2013 Fast escape of hydrogen from gas cavities around corroding magnesium implants *Acta Biomaterialia.* 9 8714–21

[8] Mraied H, Wang W and Cai W 2019 Influence of chemical heterogeneity and microstructure on the corrosion resistance of biodegradable WE43 magnesium alloys *J. Mater Chem B* 7 6399–411

[9] Yan T, Tan L, Zhang B and Yang K 2014 Fluoride Conversion Coating on Biodegradable AZ31B Magnesium Alloy *J. Mater Sci. & Technol.* 30 666–74

[10] Abatti G P, Nunes Pires A T, Spinelli A, Scharnagl N and da Conceição T F 2018 Conversion coating on magnesium alloy sheet (AZ31) by vanillic acid treatment: Preparation, characterization and corrosion behavior *J. Alloys Compd.* 738 224–32

[11] Bakhsheshi-Rad H R, Hamzah E, Ismail A F, Aziz M, Najafinezhad A and Daroonparvar M 2019 Synthesis and in-vitro performance of nanostructured monticellite coating on magnesium alloy for biomedical applications *J. Alloys Compd.* 773 180–93

[12] Zhang G, Wu L, Tang A, Ma Y, Song G L and Zheng D 2018 Active corrosion protection by a smart coating based on a MgAl-layered double hydroxide on a cerium-modified plasma electrolytic oxidation coating on Mg alloy AZ31 *Corros. Sci.* 139 370–82

[13] Cui L Y, Xu J, Lu N, Zeng R C, Zou Y H and Li S Q 2017 In vitro corrosion resistance and antibacterial properties of layer-by-layer assembled chitosan/poly-L-glutamic acid coating on AZ31 magnesium alloys *Trans. Nonferrous Met. Soc. China.* 27 1081–6

[14] Zhao Y B, Liu H P, Li C Y, Chen Y, Li S Q and Zeng R C 2018 Corrosion resistance and adhesion strength of a spin-assisted layer-by-layer assembled coating on AZ31 magnesium alloy *Appl. Surf. Sci.* 434 787–95

[15] Cui L Y, Cheng S C, Liang L X, Zhang J C, Li S Q and Wang Z L 2020 In vitro corrosion resistance of layer-by-layer assembled polyacrylic acid multilayers induced Ca–P coating on magnesium alloy AZ31 *Bioact. Mater.* 5 153–63
[16] Wen T, Yan R, Wang N, Li Y, Chen T and Ma H 2020 PPA-containing layered double hydroxide (LDH) films for corrosion protection of a magnesium alloy. *Surf. Coat. Technol.* **383** 1252–55

[17] Wu L, Ding X, Zheng Z, Ma Y, Atrens A and Chen X 2019 Fabrication and characterization of an actively protective Mg-Al LDHs/Al2O3 composite coating on magnesium alloy AZ31 *Appl Surf Sci.* **487** 558–68

[18] Wu L, Yang D, Zhang G, Zhang Z, Zhang S and Tang A 2018 Fabrication and characterization of Mg-M layered double hydroxide films on anodized magnesium alloy AZ31 *Appl. Surf. Sci.* **431** 177–86

[19] Li L X, Xie Z H, Fernandez C, Wu L, Cheng D and Jiang X H 2020 Development of a thiophene derivative modified LDH coating for Mg alloy corrosion protection *Electrochimica Acta.* **330** 1351–86

[20] Shulha T N, Serdechnova M, Lamaka S V, Wieland D C F, Lapko K N and Zheludkevich M L 2018 Chelating agent-assisted in situ LDH growth on the surface of magnesium alloy *Sci. Rep.* **8** 1640–9

[21] Peng F, Wang D, Cao H and Liu X 2018 Loading 5-Fluorouracil into calcined Mg/Al layered double hydroxide on AZ31 via memory effect *Mater. Lett.* **213** 383–6

[22] Chen J, Fang L, Wu F, Xie J, Hu J and Jiang B 2019 Corrosion resistance of a self-healing rose-like MgAl-LDH coating intercalated with aspartic acid on AZ31 Mg alloy *Prog. Org. Coat.* **136** 1052–34

[23] Lin J K, Uan J Y, Wu C P and Huang H H 2011 Direct growth of oriented Mg–Fe layered double hydroxide (LDH) on pure Mg substrates and in vitro corrosion and cell adhesion testing of LDH-coated Mg samples *J. Mater Chem.* **21** 5011–20

[24] Guo L, Wu W, Zhou Y, Zhang F, Zeng R and Zeng J 2018 Layered double hydroxide coatings on magnesium alloys: A review *J. of Mater. Sci. & Technol.* **34** 1455–66

[25] Patil A S, Gunjakar J L, Lokhande C D, Patil U M, Sadavar S V and Padalkar N S 2020 Nanocrystalline copper-chromium-layered double hydroxide with tunable interlayer anions for electrochemical capacitor application *Synth. Met.* **264** 1163–71

[26] Cao K, Yu Z, Zhu L, Yin D, Chen L and Jiang Y 2021 Fabrication of superhydrophobic layered double hydroxide composites to enhance the corrosion-resistant performances of epoxy coatings on Mg alloy *Surf. Coat. Technol.* **407** 1263–67

[27] Cao Y, Zheng D, Li X, Lin J, Wang C and Dong S 2018 Enhanced corrosion resistance of superhydrophobic layered double hydroxide films with long-term stability on Al substrate *ACS Appl. Mater. Interfaces* **10** 15150–62

[28] Shamsayrei M, Yamin Y, Asabi H and Khataei M M 2020 Electrodeposition of layered double hydroxide intercalated with 2,3-dimercaptopropane sulfonate on carbon cloth and application for effective uptake of heavy metals *Appl. Clay Sci.* **196** 105747

[29] Wu F, Liang J, Peng Z and Liu B 2014 Electrochemical deposition and characterization of Zn-Al layered double hydroxides (LDHs) films on magnesium alloy *Appl. Surf. Sci.* **313** 834–40

[30] Wu L, Zheng Z, Pan F-S, Tang A, Zhang G and Liu L 2017 Influence of reaction temperature on the controlled growth of Mg-Al LDH film *Int. J. of Electrochem. Sci.* **12** 6352–64

[31] Hoshino K, Furuya S and Buchheit R G 2019 Effect of Solution pH on Layered Double Hydroxide Formation on Electrogalvanized Steel Sheets *J. Mater. Eng. Perform.* **28** 2237–44

[32] Kamiyama N, Panomsuwan G, Yamamoto E, Sudare T, Saito N and Ishizaki T 2016 Effect of treatment time in the Mg(OH)2/Mg–Al LDH composite film formed on Mg alloy AZ31 by steam coating on the corrosion resistance *Surf. and Coat. Technol.* **286** 172–7

[33] Chen J, Song Y, Shan D and Han E H 2016 In situ growth process of Mg–Al Hydrotalcite conversion film on AZ31 Mg Alloy *J. Mater. Sci. Technol.* **31** 384–90

[34] Zhu Y, Zhao Q, Zhang Y H and Wu G 2012 Hydrothermal synthesis of protective coating on magnesium alloy using de-ionized water *Surf. and Coat. Technol.* **26** 2961–6
[35] Zulfareen N, Kannan K, Venugopal T and Gnanavel S 2016 Synthesis, characterization and corrosion inhibition efficiency of N-(4-(Morpholinomethyl Carbamoyl Phenyl) Furan-2-Carboxamide for brass in HCl medium Arabian J. Chem. 9 121–35

[36] Zhang F, Zhang C, Zeng R, Song L, Guo L and Huang X 2016 Corrosion resistance of the superhydrophobic Mg(OH)2/Mg-Al layered double hydroxide coatings on Magnesium alloys Met. 6 85

[37] Jeong H and Yoo Y 2015 Synthesis and characterization of thin films on magnesium alloy using a hydrothermal method Surf. and Coat. Technol. 284 26–30

[38] Peng F, Li H, Wang D, Tian P, Tian Y and Yuan G 2016 Enhanced corrosion resistance and biocompatibility of Magnesium alloy by Mg–Al-Layered double hydroxide ACS Appl. Mater. Interfaces. 8 35033–44

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