



# Optically transparent Li–Al–CO<sub>3</sub> layered double hydroxide thin films on an AZ31 Mg alloy formed by electrochemical deposition and their corrosion resistance in a dilute chloride environment

Jia-Han Syu<sup>a</sup>, Jun-Yen Uan<sup>a,\*</sup>, Meng-Chang Lin<sup>b</sup>, Zhi-Yu Lin<sup>a</sup>

<sup>a</sup> Department of Materials Science and Engineering, National Chung Hsing University, 250 Kuo-Kuang Rd., Taichung 40227, Taiwan, ROC

<sup>b</sup> Green Energy and Environment Research Laboratories, Industrial Technology Research Institute, 195 Sec. 4, Chung-Hsing Road, Hsin-Chu 31040, Taiwan, ROC

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## ABSTRACT

An optically transparent Li–Al–CO<sub>3</sub> layered double hydroxide (LDH) film was formed on an AZ31 substrate by applying DC voltage between the cathode (AZ31) and the anode (stainless steel) in a Li<sup>+</sup>/Al<sup>3+</sup> aqueous solution. The film thickness increased with electrolysis time. The LDH-coated sample exhibited low corrosion rate in NaCl solution, which was consistent with the results from long-term corrosion testing in a high-humidity environment. The LDH film exhibited good corrosion performance, which mainly resulted from its high hydrophobicity and its increased surface pH value during corrosion testing.

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## 1. Introduction

Magnesium has a density equal to 2/3 that of aluminum and 1/4 that of iron, providing great potential for magnesium to be used in automotive applications. However, magnesium exhibits poor formability, mainly because of its hexagonal close-packed structure [1]. Takuda et al. [2] confirmed that adding Al and Zn into magnesium (e.g., Mg–Al–Zn AZ31 alloy) effectively improves the workability of the Mg alloy. Importantly, magnesium alloys have high electrochemical activity [3,4], which leads to poor corrosion resistance. Therefore, a surface coating on AZ31 alloy is essential to protect it against corrosion. There are several surface coating methods for Mg alloys, including electroless Ni–P plating [5], electrochemical plating, conversion coatings, anodizing, hydride coatings, organic coatings and others [6]. Among the various surface treatments, chemical conversion coating is cost-effective and easy to perform on magnesium alloys [7,8]. Several chromate-free conversion coatings have been developed, including phosphate [9–11], phosphate–permanganate [12], cerate [13], stannate [12,14], lanthanite [15] and others [16]. In addition, conversion coatings on Mg surfaces exhibit various colors [17–19]. Many factors, such as solution composition, pH value, treatment time and solution temperature, strongly influence the color of the final coating [19]. However, the above conversion coatings on Mg alloys are not

optically transparent. Limited publications [20] focusing on the formation of an optically transparent conversion coating on Mg alloys were found. Liang et al. [20] applied a phytic chemical conversion bath to an AZ31 alloy sample; a transparent conversion coating subsequently formed on the sample surface [20]. It seemed that a chemical reaction occurred on the Mg alloy substrate before the phytic acid conversion treatment finished. The as-coated sample reveals a black color, although the phytic acid conversion coating itself was optically transparent [20]. Although Liu et al. [21] investigated the phytic acid conversion treatment on magnesium alloys, there were no conclusive findings for the production of a transparent phytic coating.

The authors of the present study have demonstrated a novel method for growing a highly oriented Li–Al–CO<sub>3</sub> layered double hydroxide (LDH) film directly on glass by dipping a glass sample in an aqueous alkaline solution containing Al<sup>3+</sup> and Li<sup>+</sup> [22]. Notably, Li–Al–CO<sub>3</sub> LDH film (~1.5 μm) exhibits a maximum transparency to visible light of 56% on glass [22]. However, it takes hours to coat the glass sample with a Li–Al–CO<sub>3</sub> LDH film [22]. The typical chemical formula of Li–Al–CO<sub>3</sub> LDH is [Li<sub>2</sub>Al<sub>4</sub>(CO<sub>3</sub>)(OH)<sub>12</sub>·mH<sub>2</sub>O] [23]. In this compound, Li<sup>+</sup> cations occupy the vacant octahedral sites of gibbsite (Al(OH)<sub>3</sub>) to produce [LiAl<sub>2</sub>(OH)<sub>6</sub>]<sup>+</sup> layers that are intercalated with interlayers of (CO<sub>3</sub>·4H<sub>2</sub>O)<sup>2-</sup> [24]. In previous studies, the authors [25–27] and Chen et al. [28] have developed an Mg–Al–CO<sub>3</sub> LDH layer on an Mg alloy surface in aqueous HCO<sub>3</sub><sup>-</sup>/CO<sub>3</sub><sup>2-</sup> solutions. Wang et al. [29] used a co-precipitation method to synthesize a Mg–Al–CO<sub>3</sub> LDH layer on AZ31 in a mixed

\* Corresponding author. Tel.: +886 4 22854913; fax: +886 4 22857017.

E-mail address: [jyuan@dragon.nchu.edu.tw](mailto: jyuan@dragon.nchu.edu.tw) (J.-Y. Uan).

solution of  $(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$  at  $60^\circ\text{C}$ ) at  $100^\circ\text{C}$  for 24 h. Ishizaki et al. [30] developed Mg–Al– $\text{NO}_3$  LDH on AZ31 in a mixed solution that contained 0.1 M  $\text{NH}_4\text{NO}_3$  and 1 ml of 0.1 M NaOH at  $120\text{--}180^\circ\text{C}$  for 1–24 h. Although the above studies successfully produced LDH coatings on magnesium alloys, Mg–Al LDH coatings are not optically transparent. The authors' previous work [22] on Li–Al– $\text{CO}_3$  LDH films grown on glass may contribute to the creation of an optically transparent Li–Al– $\text{CO}_3$  LDH film on AZ31 Mg alloy. Moreover, there is no information about the corrosion resistance property of the Li–Al– $\text{CO}_3$  LDH thin film on an Mg alloy. The present study will focus on the research and development of an optically transparent Li–Al– $\text{CO}_3$  LDH film with good corrosion performance on an AZ31 Mg substrate.

Wang et al. [31] found that the corrosion performance of Mg alloys in dilute chloride solutions remains ill-defined. The corrosion behaviors of AZ31 alloy [28,31,32] and Al alloy [33] in dilute chloride solutions (0.01–0.5 M NaCl) have been studied in recent years. The corrosion resistance of AZ31 Mg alloy in a high-humidity atmosphere without salt fog has not been investigated. In the present study, the effect of the applied voltage on the formation of the Li–Al– $\text{CO}_3$  LDH film was investigated between DC voltages of 2 and 4 V. Both AZ31 substrate sample and the electrodeposited AZ31 samples were tested in a high-humidity chamber for understanding the corrosion behavior of the samples in the dilute chloride environment.

## 2. Experimental

### 2.1. Mg alloy material

The AZ31 Magnesium alloy contained 2.9% Al, 0.82% Zn, 0.34% Mn, 0.02% Si, 0.0001% Fe, 0.0019% Cu and 0.0005% Ni (in weight percentages). Each sample had dimensions of  $20 \times 20 \text{ mm}^2$  and was 0.82 mm thick. The samples were ground with SiC paper (2000 grit) to ensure the same surface roughness across various samples and were then cleaned in ethyl alcohol in an ultrasonic cleaner. For long-term corrosion testing in a humidity environment, samples with larger exposed areas ( $20 \times 50 \text{ mm}^2$ ) were employed.

### 2.2. Preparation of $\text{Al}^{3+}$ - and $\text{Li}^+$ -containing electrolyte solution

Alli intermetallic compound (IMC) is the key material employed herein for synthesizing Li–Al– $\text{CO}_3$  LDH. The Alli IMC ( $19 \pm 0.5 \text{ wt.}\%$  of Li and the remainder balanced by Al) was produced by molten salt electrolysis, based on the method explored in our previous study [34]. Fig. 1(a) presents the IMC prepared in this investigation, revealing the brittleness of the compound. The crystal structure of the Alli IMC sample was verified by X-ray diffraction (Fig. 1b). This diffractogram is consistent with JCPDS card No. 3-1215, referring to Alli. This IMC can also be obtained by the vacuum metallurgy method. Due to its high activity in water, the Alli IMC hydrolyzes easily in water [34]. Firstly, highly pure nitrogen ( $\text{N}_2$ ) gas was bubbled through 200 ml of deionized (DI) water for 5 min. A sample of 0.4 g of Alli powder was then added into the DI water under continuous  $\text{N}_2$  bubbling for another 3 min at room temperature in the ambient atmosphere. Stirring generated  $\text{H}_2$  in the hydrolysis reaction. The reaction solution was then filtered through filter paper (No.5A; Advantec). The pH value of the filtered aqueous solution was approximately 12.4. The filtered solution had the concentrations of  $\text{Al}^{3+}$  ( $788 \pm 50 \text{ ppm}$  by weight) and  $\text{Li}^+$  ( $370 \pm 14 \text{ ppm}$  by weight), determined by means of ICP (ICP-AES, ULTIMA 2000, Horiba Jobin Yvon). Carbon dioxide in the ambient atmosphere dissolved in the solution, providing  $\text{HCO}_3^-$  (bicarbonate ions) and  $\text{CO}_3^{2-}$  (carbonate ions) [35]. The relative concentrations of

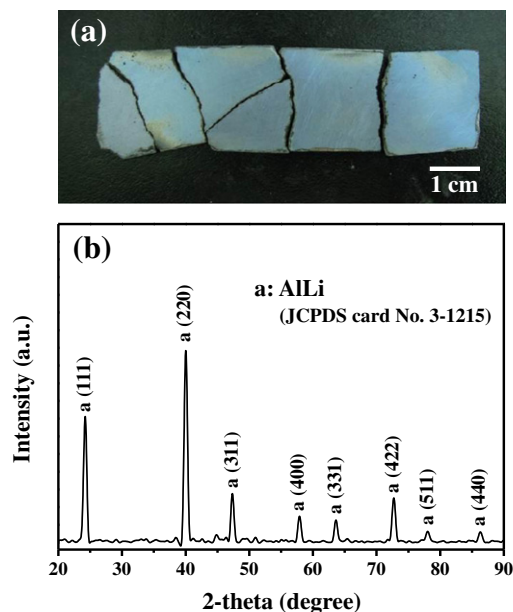


Fig. 1. (a) Bulk intermetallic compound (IMC), showing the brittle nature of the IMC; (b) X-ray diffraction pattern of the IMC. This diffractogram is consistent with JCPDS card No. 3-1215, referring to Alli.

$\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in aqueous depend on the pH of the solution [35]. In alkaline water with  $\text{pH} > 10$ ,  $\text{CO}_3^{2-}$  rather than  $\text{HCO}_3^-$  is the dominant anion [35]. Since the pH value of  $\text{Al}^{3+}/\text{Li}^+$ -containing solution was pH 12.4, exposing such solution to the ambient atmosphere causes sufficient  $\text{CO}_3^{2-}$  ions to be present in the solution to form Li–Al– $\text{CO}_3$  LDH. Our previous study [34] confirmed that Li–Al– $\text{CO}_3$  LDH precipitates would automatically form in the  $\text{Al}^{3+}/\text{Li}^+$ -containing solution at room temperature in ambient atmosphere. In present study, to prevent the LDH precipitation in each solution prior to conducting electrochemical deposition, highly pure nitrogen ( $\text{N}_2$ ) gas was bubbled through the solution to prevent the dissolution of  $\text{CO}_2$  at this stage of experiment. The inert gas bubbling method can effectively retard the formation of Li–Al– $\text{CO}_3$  LDH precipitates in the  $\text{Al}^{3+}/\text{Li}^+$ -containing solution in ambient atmosphere [22,34]. The  $\text{N}_2$  bubbling in the solution ceased as the LDH coating experiment started.

### 2.3. Growth of Li–Al– $\text{CO}_3$ LDH film electrochemically

Fig. 2 shows a schematic of the setup used to fabricate the Li–Al– $\text{CO}_3$  LDH coating on the AZ31 sample surface. As revealed in Fig. 2, a 304 stainless steel pipe was selected as the anode material. The 304 stainless steel pipe had dimensions of  $\phi 5.56 \times 13 \text{ cm}$

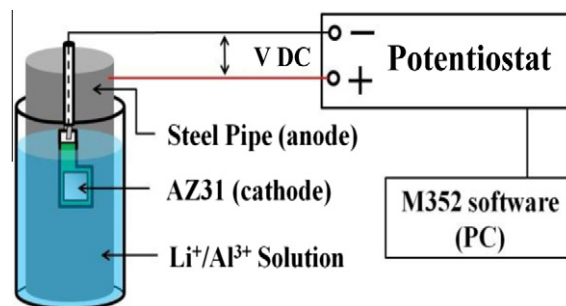


Fig. 2. A schematic of the apparatus used to fabricate a Li–Al LDH thin film on AZ31 electrochemically, with DC voltage being applied between the steel pipe (the anode) and the AZ31 sample (the cathode) in the  $\text{Li}^+/\text{Al}^{3+}$  aqueous electrolyte.

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