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Active corrosion protection of Mg-Al-PO₄³⁻ LDH nanoparticle in silane primer coated with epoxy on mild steel

E. Alibakhshi^{a,b,c}, E. Ghasemi^a, M. Mahdavian^{b,*}, B. Ramezanzadeh^b, S. Farashi^d

^aInorganic Pigment and Glazes Department, Institute for Color Science and Technology, Tehran, Iran

^bSurface Coating and Corrosion Department, Institute for Color Science and Technology, Tehran, Iran

^cDepartment of Chemical Engineering, Payame Noor University, Tehran, Iran

^dFaculty of Medicine, Shahid Beheshti University of Medical Sciences, Tehran, Iran

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ABSTRACT

Mg-Al-PO₄³⁻ layered double hydroxide (LDH) nanoparticle was synthesized through an anion exchange method and characterized by XRD, IR spectroscopy and SEM. The phosphate and Mg²⁺ release ability of Mg-Al-PO₄³⁻ LDH in the 3.5 wt. % NaCl solution was measured by inductively coupled plasma-optical emission spectrometer (ICP-OES). Results showed the release of Mg²⁺ from the LDH scaffold along with phosphate anion from LDH gallery, illustrating importance of solubility rather than ion-exchange mechanism. Then, the corrosion inhibitive behavior of Mg-Al-PO₄³⁻ LDH in 3.5 wt. % NaCl solution was assessed by electrochemical measurements and FE-SEM in comparison with the Mg-Al-NO₃⁻ LDH. The results showed that Mg-Al-PO₄³⁻ LDH forms inhibitive film on the mild steel and significantly mitigate corrosion compared to Mg-Al-NO₃⁻ LDH. The LDHs were also employed in a silane primer top-coated by epoxy-polyamide on mild steel. The results of electrochemical measurements showed significant active corrosion protection ability of Mg-Al-PO₄³⁻ LDH in the coating with an artificial defect. Furthermore, the adhesion strength of the coating including Mg-Al-PO₄³⁻ LDH to mild steel after exposure to salt spray (5% NaCl solution) was improved.

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1. Introduction

Over recent decades, phosphate-based corrosion inhibitive pigments have been employed as replacement for chromates [1–4]. The corrosion inhibition performance of the phosphate based pigments is connected to their solubility, which led to dissociation of PO₄³⁻ and formation of complex insoluble precipitates on the metal surface [5]. The phosphate based pigments can protect damaged areas of the coatings by corrosion inhibition effect of phosphate ion dissolved in the penetrated water in the coating [6]. A low solubility of the pigment leads to too low concentration to initiate corrosion inhibiting reaction, whereas high solubility leads to the coating damage by osmotic blistering [7,8]. To overcome this obstacle, increasing attention has been focused on the development of novel materials such as nanoparticles [9,10] and ion-exchange pigments [11,12].

The potential of ion-exchange pigments, such as zeolites [13], calcium-exchanged silica [14] and aluminosilicate-based clay particles

(montmorillonite and bentonite) [15] as corrosion inhibitor is of growing interest in recent years. The active corrosion protective performance of clays modified with benzimidazole and zinc cations in the epoxy-ester coating has been investigated by Ghazi et al [16]. It was illustrated that incorporation of the clay particles intercalated by benzimidazole and zinc cation into the coating significantly enhanced its corrosion resistance due to the on-demand release resulted from the cation-exchange capability of the clay particles.

Layered double hydroxides (LDHs) are another type of ion-exchange pigments [17,18]. For some decades, LDHs, also known as the anionic clay or hydrotalcite like compounds, due to the great capability of anion exchange properties have been found great potential to be used in medicine, energy, and environment technologies. The general formula of LDHs is [M_{II}(_{1-x})M_{III}(OH)₂]^{x+}(Aⁿ⁻)_{x/n}.mH₂O, where M_{II} is a divalent metal such as Mg, Zn, Ni, Co, Ca, Cu; M_{III} is a trivalent metal such as Al, Fe, Ga, Cr; Aⁿ⁻ is an anion with a valency of n; and x, defined as [M_{III}]/([M_{III}]+[M_{II}]), is usually between 0.25 and 0.33 [19–25].

There are a few investigations on the application of LDHs as corrosion inhibitor reservoirs [26–33]. In the previous studies, LDHs were used as reservoir for organic inhibitors such as

* Corresponding author.

E-mail address: mahdavian-m@icrc.ac.ir (M. Mahdavian).

mercaptobenzothiazolate [26], 2,5-dimercapto-1,3,4-thiadiazolate [27] and inorganic inhibitors such as vanadate and tungstate [34,35]. Zheludkevich et al. [28] have studied the active corrosion protection performance of Mg–Al and Zn–Al layered double hydroxides with divanadate anions located in the interlayer regions. They demonstrated that both nanocontainers provided active corrosion protection on defective areas of the coating. Hang et al. have used Mg–Al layered double hydroxides loaded with 2-benzothiazolylthio-succinic acid in an epoxy coating for corrosion protection of carbon steel [36]. They illustrated that inclusion of LDHs intercalated with benzothiazolylthio-succinic acid in coating led to an improvement of corrosion protection due to the inhibitor release. In the previous works [37,38], we showed that incorporation of the Zn–Al- PO_4^{3-} LDH in the silane primer coatings can increase corrosion protection performance of the coating. However, the relatively small ionic radius of magnesium as compared to zinc can result in differences in the structure and solubility of the synthesized LDHs and consequently, its corrosion inhibition performance.

The present work intends to evaluate the role of phosphate in anion-exchange and corrosion inhibition properties of Mg–Al-LDHs nanoparticles. For this purpose, Mg–Al-nitrate LDH was synthesized by the co-precipitation route. Then, the phosphate intercalated Mg–Al-LDH nanoparticles were synthesized by ion-exchange method and characterized by XRD, IR spectroscopy and SEM analysis. To obtain insight into the mechanism of ions release, the phosphate anion and magnesium cation release ability of LDHs in the chloride-containing electrolyte was investigated by taking advantages of inductively coupled plasma-optical emission spectrometer (ICP-OES). The corrosion inhibition performance of the phosphate intercalated Mg–Al-LDHs nanoparticles was studied by electrochemical impedance spectroscopy (EIS) and polarization measurements in the 3.5 wt. % NaCl solution on the mild steel samples. The LDHs were also employed in a silane coating top-coated by epoxy-polyamide. Then, the coatings were scratched and immersed in the 3.5% NaCl solution and examined by EIS to evaluate active corrosion protection ability. The scratched coatings were also examined by EN to evaluate electrochemical corrosion activity on the defect site.

2. Experimental

2.1. Materials

Synthetic grade magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), sodium nitrate (NaNO_3), sodium phosphate tribasic dodecahydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) and sodium hydroxide (NaOH) were obtained from Sigma-Aldrich and all the materials were used as received without further purification. The mild steel with the mass percent composition of C 0.19, Mn 1.39, S > 0.005, Si 0.42, Cu 0.04, Cr 0.03, Mo 0.02, Co 0.06 and Fe (balance) was prepared from Foolad Mobarake (Iran) and used for corrosion studies.

The synthetic grade of tetraethylorthosilicate (TEOS), aminopropyltriethoxysilane (APTES) and acetic acid were purchased from Merck to prepare the silane coatings. Industrial grade epoxy resin (Epikote 1001) and polyamide resin (Versamid 115) were obtained to prepare epoxy-polyamide coatings. Double distilled water was used to prepare all the aqueous solutions.

2.2. Synthesis of Mg–Al LDHs

2.2.1. Mg–Al- NO_3^- LDH

Mg–Al- NO_3^- LDH nanoparticles were prepared using the co-precipitation route at room temperature ($30 \pm 1^\circ\text{C}$) by mixing of

two solutions, one containing nitrate salts of Mg^{2+} and Al^{3+} and another containing NaNO_3 and NaOH . The preparation was performed under a nitrogen atmosphere to exclude carbonate from the LDH. The Mg: Al mole ratio chosen for the synthesis was 2:1 to obtain stable layered compounds. In the first step, a solution containing 0.02 M $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.01 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ($V = 40\text{ mL}$) was slowly added to 0.02 M NaNO_3 ($V = 70\text{ mL}$), under vigorous stirring for 1.5 h. During this reaction, the pH was kept constant (9.8 ± 0.3) by simultaneous addition of 0.2 M NaOH . Afterward, the obtained slurry was centrifuged and washed several times with boiled deionized water. Finally, the resultant slurry was dried at 70°C in an oven.

2.2.2. Mg–Al- PO_4^{3-} LDH

Mg–Al- PO_4^{3-} LDH nanoparticles were prepared by the anion-exchange method. Accordingly, nitrate anions intercalated in the synthesized LDH nanoparticles (first step) were replaced by phosphate via an anion-exchange reaction (second step). The anion-exchange was carried out under nitrogen atmosphere and all the solutions were prepared using boiled deionized water, in order to avoid contamination with carbonate anions.

For the anion-exchange reaction, a 0.4 M $\text{Na}_3\text{PO}_4^{3-} \cdot 12\text{H}_2\text{O}$ aqueous solution ($V = 500\text{ mL}$, $\text{pH} = 11$) was prepared, then 0.5 g of Mg–Al- NO_3^- LDHs was dispersed in it. The suspension was held at room temperature under constant stirring for 48 h. During the ion exchange reaction, the pH of phosphate containing solution was measured using Metrohm 744 pH meter.

Finally, the phosphate-loaded LDHs nanoparticles were washed and centrifuged with boiled deionized water, and then dried.

2.3. Characterization

The X-ray diffraction (XRD) of the synthesized LDHs was conducted using PW 1800 Philips X-ray spectrometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54060\text{ \AA}$) over the 2θ range from 10° to 80° at rate of $2.5^\circ/\text{min}$. Chemical structure of the LDHs was characterized using IR spectroscopy (Perkin Elmer-Spectrum One) by placing each material into a KBr pellet in the region of $400\text{--}4000\text{ cm}^{-1}$.

The morphology and structure of the LDHs were investigated using a Mira field emission-scanning electron microscope (FE-SEM—model Tescan). LDHs were dispersed in the ethanol by ultrasonication for 3 min, after which a droplet of each LDH suspensions was dropped on an aluminum foil and allowed to dry for SEM imaging.

2.4. Ion release ability of LDHs

The release behavior of the phosphate ions loaded in the nitrate base Mg–Al LDH nanoparticles was analyzed in 3.5% NaCl solution. For this purpose 50 mg of the phosphate intercalated Mg–Al LDH powder was dispersed in 10 cc, 3.5% NaCl solution, and stirred for 48 h at 300 rpm. It should be mentioned that ion release ability of phosphate intercalated Mg–Al LDH was examined at 48 h as the solution reached to a constant pH after 48 h exchange reaction.

Then, the amount of magnesium and aluminum ions released from the Mg–Al- PO_4^{3-} LDHs nanoparticles was measured with ICP-OES. The analysis was carried out using the ICP-OES of Varian Company (Australia), model Vista-PRO.

2.5. Corrosion inhibition studies in extract solutions

The corrosion inhibition of the synthesized LDHs was investigated by means of EIS and polarization on the mild steel samples. An extract solution of Mg–Al- NO_3^- and Mg–Al- PO_4^{3-} LDH in 3.5% NaCl was prepared for corrosion inhibition studies. To prepare the

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