Colloid and Interface Science Communications 24 (2018) 18–23

Contents lists available at ScienceDirect

Colloid and Interface Science Communications

journal homepage: www.elsevier.com/locate/colcom

Controlled Release of Nitrate and Molybdate Intercalated in Zn-Al-Layered Double Hydroxide Nanocontainers towards Marine Anticorrosion Applications

Weihua Li[a,b,c], Ang Liu[a,c], Huiwen Tian[a,c,*], Dapeng Wang[d,**]

[a] Key Laboratory of Marine Environmental Corrosion and Bio-fouling, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China
[b] School of Chemical Engineering and Technology, Sun Yat-sen University, Zhuhai 519082, China
[c] Qingdao National Laboratory for Marine Science and Technology, Qingdao 266071, China
[d] State Key Laboratory of Polymer Physics and Chemistry, Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

ARTICLE INFO

Keywords:
Mild steel
Layered double hydroxides
Nanocontainers
Anticorrosion

ABSTRACT

Zn-Al layered double hydroxides (LDHs) intercalating with molybdate anions was developed to inhibit the corrosion of mild steel in neutral chloride conditions. The LDH compounds were prepared by a method involving co-precipitation and anion-exchange and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), respectively. The anticorrosion capabilities of the LDHs hybrids were analyzed by using open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curve. A significant reduction of the corrosion rate is observed in the presence of a 2 g/L concentration of the LDHs hybrids in the corrosive media. The mechanism is that the intercalated molybdate anion can slowly diffuse out of the inner structure of LDHs in a controllable way and result in a relatively long-term effect of corrosion inhibition. The result presented here underlines the great potential of the controlled release mechanism for marine anticorrosion applications.

1. Introduction

Mild steel is wildly used in both industrial and domestic applications. However, corrosion is the major problem for use of mild steel in aqueous media. Chloride-induced corrosion is one of the main reasons causing the destruction of the steel structures in marine environments and coastal areas [1,2]. Notorious destructive effects of corrosion result in enormous economic loss and social harm. Therefore, it is necessary to take preventive measures for the anticorrosion. Thus far, there are various methods that are available to inhibit the surface corrosion, including the surface coating, using corrosion inhibitors, and electrochemical protection, etc. [3,4]. Among these methods, the use of corrosion inhibitors is one of the best-known methods for the preventive corrosion inhibition because of its advantages including low-cost, highly efficient, and easy to set up and deploy, etc. [5].

However, the use of corrosion inhibitors still confronts many problems and challenges, such as short effective time, and being toxic to the environment. It is desirable to design the next—generation of the corrosion inhibitor that can smartly protect where it has been corroded and therefore, leads to extended protection duration [6,7].

Designing such corrosion inhibitor has been intensively pursued in recent years. Nanocontainers, such as oxide nanoparticles [8,9], polymeric layer-by-layer (LbL) assembled shells [10], metal organic frames [11] and double layer hydroxides (LDHs) [12–15], have attracted considerable interest owing to their unique microporous structures and capability of controllable release of the loaded small cargo molecules by applying various strategies such as mechanical triggering, capsules shell damage, and ion exchange process, etc [8,9,12,13]. The key hypothesis is that the nanocontainer can slowly release the adsorbent molecules into the media by exerting the adsorbent—surface interaction. Among these controlled-release strategies, the anion exchange method becomes more attractive because it can release the inhibitive ions while absorbing the chloride [13,15]. The layered double hydroxides (LDHs) are well known as anion exchange substances because the inner microstructure of LDHs consists of stacks of positively charged, mixed-metal hydroxide layers [16,17]. LDH materials have succeeded in many potential applications such as electrochemical capacitors [18,19], catalysis [20,21], drug delivery [22,23] and water treatment [24,25], etc. The LDHs were commonly represented by the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}mH_2O$, where M^{n+} is the metal cation

---

[*] Corresponding author at: Key Laboratory of Marine Environmental Corrosion and Bio-fouling, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China.
[**] Corresponding author.
E-mail addresses: tianhuiwen1983@foxmail.com (H. Tian), wdp@ciac.ac.cn (D. Wang).

https://doi.org/10.1016/j.colcom.2018.03.003
Received 15 December 2017; Received in revised form 22 February 2018; Accepted 17 March 2018

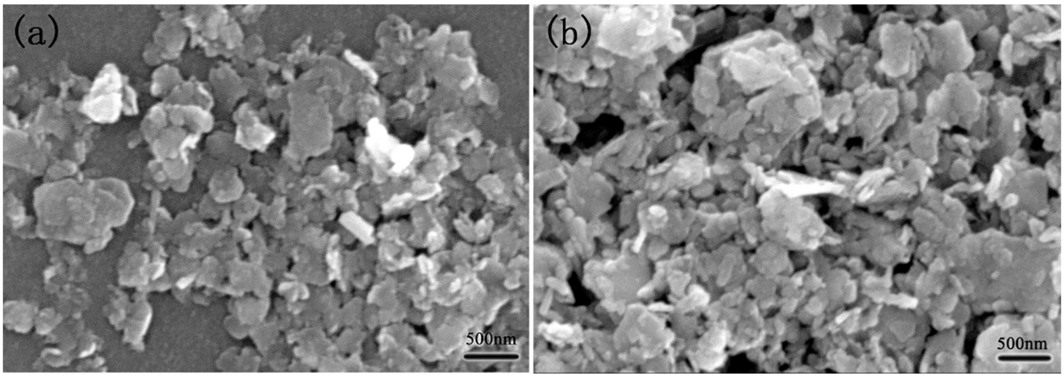

Fig. 1. SEM micrographs of (a) Zn-Al-NO_3^- and (b) Zn-Al-MoO_4^{2-} LDHs.

(e.g., M^{2+}: Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, Ca^{2+}, Cu^{2+}; M^{3+}: Al^{3+}, Fe^{3+}, Ga^{3+}, Cr^{3+}) and A^{n-} interlayer anion is loaded in hydrated interlayer galleries to compensate the positive charge.

In this paper, we describe synthesis, characterization, and the anticorrosion properties of hybrids consisting of Zn-Al LDHs and molybdate inorganic anions (MoO_4^{2-}) that are efficient corrosion inhibitive species for steel substrates [26,27]. The Zn-Al-MoO_4^{2-} LDHs were synthesized by a co-precipitation and ion-exchange method and characterized by SEM, XRD, and FTIR. The corrosion inhibition performances of the molybdate intercalated Zn-Al LDH nanoparticles on a mild steel substrate were studied by OCP, EIS and polarization tests in a 3.5 wt.% NaCl solution.

2. Experimental Section

2.1. Materials

The chemical composition of tested mild steel is: 0.16C, 0.53 Mn, 0.30 Si, < 0.045 P, < 0.055 S, 0.3 Ni, 0.3 Cu (wt.%), and Fe balance. All chemicals are analytical reagent and purchased from Sinopharm Chemical Reagent Co.

2.2. Synthesis of LDHs

In the first step, Zn-Al-NO_3^- LDHs were synthesized by a co-precipitation method [13,28]. Specifically, a solution ($V = 100$ mL) containing 0.5 M Zn $(NO_3)_2 \cdot 6H2O$ and 0.25 M $Al(NO_3)_3 \cdot 9H_2O$ was slowly added to 1.5 M $NaNO_3$ ($V = 200$ mL, pH = 10) under vigorous stirring at room temperature. During this process, pH = 10 ± 0.5 was adjusted by controllable addition of 2 M NaOH. Afterward, the obtained slurry was subjected to a hydrothermal treatment at 65 °C for 24 h for crystallization of the LDHs. The resulting residue was recovered by using centrifugation, followed by five-times wash with boiled distilled water, and dried at 70 °C for 8 h. In order to avoid introducing carbonate anion, the synthesis was carried out under nitrogen atmosphere and all solutions were prepared using boiled distilled water.

Zn-Al-MoO_4^{2-}LDH was obtained through an anion-exchange process [13,28]: 1 g of Zn-Al-NO_3^{2-} LDH was dispersed in a 0.2 M $Na_2MoO_4 \cdot 2H_2O$ aqueous solution ($V = 200$ mL, pH = 11); the suspension was held at room temperature with constant stirring for 48 h. Finally, the reaction product was centrifuged, washed, and then dried.

2.3. LDHs Morphology and Chemical Structure Characterization

The particle morphology was characterized via scanning electron microscopy (SEM; Hitachi S-3400 microscope with an electron beam energy of 15 kV). The structure of the LDH powders was studied via X-ray diffraction (XRD; Rigaku Ultima IV X-ray Diffractometer using Cu Kα radiation, the sample was tested from 5° to 80° at a scanning rate of 5°/min). FTIR spectrum was measured by using a Nicolet iS10 spectrometer in the range of 4000–400 cm^{-1}.

2.4. Electrochemical Measurements

The inhibition performances of LDHs and their hybrids were investigated by using OCP, EIS and polarization test in 3.5 wt.% NaCl solution. To prepare the LDHs-containing solution, 2 g of LDHs or hybrids was added to 1 L of 3.5% NaCl solution; the resulting mixture was stirred for 24 h. All electrochemical measurements were performed on an Autolab PGSTAT302N system (Metrohm AG) in a conventional three-electrode cell system. Mild steel (exposed area of 1 cm^2, abraded with emery paper) was used as working electrode. Pt and saturated calomel electrode were used as the counter and reference electrode, respectively. The OCP was continuously tested for 48 h. The EIS was implemented at OCP using 10 mV perturbation in a frequency range of 100 kHz ~ 10 MHz after 1, 4, 24 and 48 h immersion durations, respectively. The inhibition efficiency, ηe_R, was calculated as follows:

$$\eta e_R\% = \frac{R_{Rct} + R_{Rct}^0}{R_{Rct}} \quad (1)$$

where R_{Rct} and $R_{Rct}{}^0$ are the charge transfer resistance of mild steel in 3.5% NaCl solution with and without LDHs, respectively.

Polarization was conducted at a scan rate of 0.5 mV/s from −200 to 200 mV around OCP after the EIS measurement. The obtained inhibition efficiency, ηe_i, was calculated by:

$$\eta e_i\% = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \quad (2)$$

where i_{corr} and $i_{corr}{}^0$ are the corrosion current density of mild steel in 3.5% NaCl solution with and without LDHs, respectively.

3. Results and Discussion

3.1. LDHs Morphology Analysis

Fig. 1 shows typical SEM micrographs of LDH particles. LDHs have a well-defined plate-like crystalline structure whose size is about 500–1000 nm. The thickness of the LDH plates was approximately several tens of nanometers. After the anion exchange with MoO_4^{2-}, the crystalline structure of LDHs swells up due to the intercalation of anions decreasing the stacking density of the inner structure of LDHs [17,28].

3.2. LDHs Chemical Structure Analysis

The X-ray diffraction measurement was carried out in order to explicitly quantify the effect of the anion exchange on the structure of LDHs. As shown in Fig. 2a, all samples have the hydrotalcite-type clay character with typical diffraction peaks of (003), (006) relative to a