



Research paper

Preparation and characterization of nanocontainers of corrosion inhibitor based on layered double hydroxides

To Thi Xuan Hang*, Trinh Anh Truc, Nguyen Thuy Duong, Pham Gia Vu, Thai Hoang

Institute for Tropical Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

ARTICLE INFO

Article history:

Received 23 October 2011

Received in revised form 17 July 2012

Accepted 19 July 2012

Available online 30 August 2012

Keywords:

Layered double hydroxides

Nanocontainers

Corrosion inhibitor

Release

ABSTRACT

Nanostructured zinc aluminum and magnesium aluminum layered double hydroxide (ZnAl-LDH and MgAl-LDH) intercalated with corrosion inhibitor 2-benzothiazolylthio-succinic acid (BTSA) were prepared using co-precipitation method and characterized by infrared spectroscopy, X-ray diffraction, scanning electronic microscopy and transmission electronic microscopy. BTSA release from ZnAl(BTSA)-LDH and MgAl(BTSA)-LDH in 3 wt.% NaCl and 3 wt.% Na₂SO₄ solution was investigated with UV-vis spectroscopy, and inhibitive action of ZnAl(BTSA)-LDH and MgAl(BTSA)-LDH on carbon steel was examined by electrochemical methods. It was shown that the formula of synthesized ZnAl(BTSA)-LDH and MgAl(BTSA)-LDH is [Zn_{2.4}Al(OH)_{6.8}](BTSA)_{0.43}(NO₃)_{0.14}·4H₂O and [Mg_{2.1}Al(OH)_{5.96}](BTSA)_{0.62}·1.5H₂O, respectively. The BTSA release was dependent on the anion type in electrolyte and the BTSA release in the presence of SO₄²⁻ anion was higher than that in the presence of Cl⁻ anion. The polarization curves obtained on the carbon steel sample showed that the ZnAl(BTSA)-LDH and MgAl(BTSA)-LDH are anodic inhibitors. Inhibition efficiency is higher with ZnAl(BTSA)-LDH, at the concentration of 3 g/l, achieving approximately 97% and 88% for ZnAl(BTSA)-LDH and MgAl(BTSA)-LDH, respectively.

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1. Introduction

Organic coatings are widely used to prevent corrosion of metallic structures because they can be easily applied at a reasonable cost. Chromates have been widely used as excellent inhibitive pigments in anticorrosion coatings. However, their toxicity and carcinogenic effects necessitate the development of effective chromate-free organic coatings (Katz and Salem, 1993; O'Brien and Kortenkamp, 1995).

There are numerous non-toxic organic compounds showing excellent corrosion inhibitors in solutions such as amines, phosphonic acids, carboxylic acids or heterocyclic compounds. However, these materials have not yet found widespread applications in protective organic coatings (Amar et al., 2007; Ashry et al., 2006; Lebrini et al., 2006; Ochoa et al., 2005). The reason is that the active part of these compounds (—NH₂, —POOH, —COOH), which is responsible for the inhibitive effect (formation of strong bonds with the metal surface) can unfortunately react with the polymer resins used for coating. Thus, the corrosion inhibitor is trapped by the polymer chain and cannot diffuse across the coating to reach the metal/film interface to prevent corrosion reactions. In addition, most of these organic inhibitors are soluble in water. This could cause blistering of coatings in contact with moisture. One effective solution is to attach the inhibitor molecules to another compound and disperse the inhibitor containers in the coating. By this way, inhibitors could then be slowly released at the metal/coating interface and

react with the substrate. Recently research works on the use of ion exchange compounds containers for corrosion inhibitors as an other alternative have shown very interesting results (Bohm et al., 2001; Buchheit et al., 2003; Garea and Iovu, 2006; Hang et al., 2007, 2010; Truc et al., 2008; Williams and McMurray, 2004).

Environmentally friendly corrosion inhibitor additives based on bentonite clay like cerium (III) bentonite, and calcium (II) bentonite for protective coatings have been studied. The results showed that coatings containing Ce-exchanged bentonite provide good corrosion protection, but lower than that of coatings containing chromates (Bohm et al., 2001; Williams et al., 2002). Clay modified by organic corrosion inhibitors were studied for organic protective coatings. Incorporation of modified clays in epoxy coatings provides both good barrier properties due to lamellar structure of the clay and corrosion inhibition at the carbon steel/coating interface due to the presence of functional groups of the organic molecules (Garea and Iovu, 2006; Hang et al., 2007, 2010; Truc et al., 2008).

Layered double hydroxides (LDH) are known as anionic clays. They are composed of positively charged hydroxide layers similar to the brucite structure with intercalated anions and water molecules in the layers. The general formula can be expressed as [M_n²⁺M³⁺(OH)_{2+2n}][A^{m-}]_{1/m}·xH₂O, where M²⁺ and M³⁺ are divalent and trivalent cations occupying the octahedral positions within the hydroxide layers, *n* is the atomic ratio of divalent and trivalent cations and the *n* value should generally be between 2 and 4. The hydroxide layers are positively charged, and A^{m-} is an interlayer exchangeable anion balancing the positive charges on the layers. The

* Corresponding author. Tel.: +84 912178768; fax: +84 4 37564484.
E-mail address: hang@vnd.vast.ac.vn (T.T.X. Hang).

distance between hydroxide layers provides a wide range for anions insertion (both organic and inorganic) of different sizes and orientations (Costantino et al., 2008, 2009; Khan and O'Hare, 2002; Leroux and Besse, 2001; Newman and Jones, 1998; Perioli et al., 2011; Tammaro et al., 2009). The intercalated anions can be released and substituted by other anions from the environment. Applications of double layer hydroxide are complex and based on adsorption, anion exchanges capacity and the mobility of the anion between the layers. LDH and LDH-derived mixed oxides have been widely used as adsorbents, ion exchangers, base catalysts, polymer additives, and corrosion protection agents, thus receiving a great interest in the recent decade (Cavani et al., 1991; Costa et al., 2008; Costantino et al., 2007; Sels et al., 2001; Williams and McMurray, 2003).

Layered double hydroxides can be used to immobilize anionic inhibitors (Buchheit et al., 2003; Leggat et al., 2002; Mahajanam and Buchheit, 2008; Wang et al., 2004). In this case, the release of inhibitor anions can be triggered by the exchange with aggressive corrosive chloride ions. The anion-exchange pigment can play two roles: absorbing the harmful chlorides and releasing the inhibiting ions in response. The layered double hydroxide containing decavanate and molybdate has been studied in application overlay for corrosion protection of aluminum alloys. However, coatings containing ZnAl layered double hydroxide intercalated with decavanate are not capable of protection equivalent to coatings containing chromate.

MgAl-LDH and ZnAl-LDH doped with divanate anions as corrosion inhibitor were used in primers for corrosion protection of 2024 aluminum alloy. Electrochemical results and accelerated corrosion tests showed that coatings doped with ZnAl-LDH provide higher ability of corrosion protection compared to that of chromate-based coatings (Zheludkevich et al., 2010).

There are also studies on corrosion protection of aluminum alloy using coatings containing layered double hydroxide bearing organic anions such as benzotriazolot, ethyl xanthate and oxalate (Williams and McMurray, 2004). The results showed that inhibition efficiency depends on the structure of organic anion and inhibition efficiency increases in the order ethyl xanthate < oxalate < benzotriazolot. Benzotriazolot has been shown to interact specifically with the alloy surface. 2-benzothiazolylthio-succinic acid (BTSA) is well known as an organic corrosion inhibitor used in organic coatings (Braig, 1998). It was observed that BTSA can be adsorbed on the iron oxide layers which are always present on steel surfaces and can form insoluble precipitates with ferrous ions (Braig, 1998).

The objective of the present work is to prepare and characterize nanosized container of corrosion inhibitors based on layered double hydroxides which can be used in organic coatings like anticorrosion pigments. ZnAl and MgAl layered double hydroxide intercalated with 2-benzothiazolylthio-succinic acid were synthesized using the co-precipitation method. The BTSA release in 3 wt.% NaCl and 3 wt.% Na₂SO₄ solutions was investigated using UV–vis spectroscopy. The inhibition efficiency of ZnAl(BTSA)-LDH and MgAl(BTSA)-LDH was evaluated by electrochemical methods.

2. Experimental

2.1. Materials

Sodium hydroxide, magnesium nitrate hexahydrate, Mg(NO₃)₂·6H₂O, zinc nitrate hexahydrate, Zn(NO₃)₂·6H₂O, aluminum nitrate nonahydrate Al(NO₃)₃·9H₂O were purchased from Merck. Corrosion inhibitor, 2-benzothiazolylthio-succinic acid (BTSA), was obtained from Ciba Company. The chemical structure of BTSA is shown in Fig. 1.

To characterize the inhibitive efficiency of BTSA, MgAl-LDH, ZnAl-LDH, MgAl(BTSA)-LDH and ZnAl(BTSA)-LDH, a rod of XC 35 carbon steel with 1 cm² cross-sectional area was used as a working electrode. Its composition in percentage mass was C = 0.35, Mn = 0.65, Si = 0.25, P = 0.035, S = 0.035 and Fe to 100. A heat-shrinkable sheath was used to leave

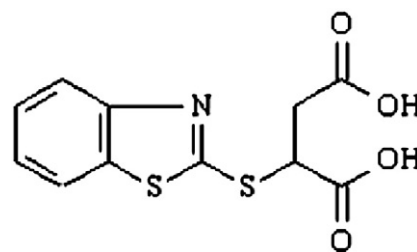


Fig. 1. Molecular structure of 2-benzothiazolylthio-succinic acid.

only the tip of the carbon steel cylinder in contact with the solution. For all experiments, the carbon steel samples were polished with SiC paper down to grade 1200, cleaned in distilled water, in an ultrasonic bath and dried in warm air.

2.2. Preparation of layered double hydroxides

The magnesium aluminum layered double hydroxide (MgAl-LDH) was synthesized using the co-precipitation method (Nyambo et al., 2009). The preparation was performed in a nitrogen atmosphere to exclude CO₂ which would lead to the incorporation of carbonate in the LDH. A solution of 0.125 mol of Mg(NO₃)₂·6H₂O and 0.0625 mol of Al(NO₃)₃·9H₂O in 125 ml of degassed distilled water was added drop by drop over 1 h to a solution of 0.313 mol of NaOH in 145 ml of degassed distilled water. The pH of the solution was maintained at 8–10 by adding 1 M NaOH solution as needed. The resulting white precipitate was aged for 24 h at 65 °C, and then filtered until all of the supernatant liquid was removed. The sample was washed several times with large amounts of degassed distilled water and dried at 50 °C in a vacuum oven.

The zinc aluminum layered double hydroxides (ZnAl-LDH) were also prepared by the same procedure as for MgAl-LDH, except that Zn(NO₃)₂·6H₂O was used instead of Mg(NO₃)₂·6H₂O.

2.3. Preparation of layered double hydroxides intercalated with BTSA

The magnesium aluminum layered double hydroxides intercalated with BTSA (MgAl(BTSA)-LDH) were prepared by the co-precipitation method (Nyambo et al., 2009). A solution of 0.125 mol of Mg(NO₃)₂·6H₂O and 0.0625 mol of Al(NO₃)₃·9H₂O in 125 ml of degassed distilled water was added drop wise to a solution of 0.313 mol of BTSA with the molar equivalent of NaOH in 145 ml of degassed distilled water with vigorous mixing under an inert nitrogen atmosphere. The pH of the solution was maintained at 8–10 by adding 1 M NaOH solution. The resultant slurry was aged at 65 °C for 24 h, cooled to room temperature, and repeatedly washed with large amounts of degassed distilled water before drying at a temperature of 50 °C in a vacuum oven.

The zinc aluminum layered double hydroxides intercalated with BTSA (ZnAl(BTSA)-LDH) were also prepared by the same procedure as for MgAl(BTSA)-LDH, except that Zn(NO₃)₂·6H₂O was used instead of Mg(NO₃)₂·6H₂O.

2.4. Analytical characterizations

2.4.1. Infrared Spectroscopy

The FTIR spectra of BTSA and synthesized LDHs were obtained using the KBr method on a Nexus 670 Nicolet spectrometer operated at 1 cm⁻¹ resolution in the 400–4000 cm⁻¹ region.

2.4.2. UV–vis spectroscopy

UV–vis spectra of solutions containing BTSA were obtained using GBC CINTRA 40 spectrometer operated in the 200–400 nm regions.

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