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A novel acid-responsive HNTs-based corrosion inhibitor for protection of carbon steel

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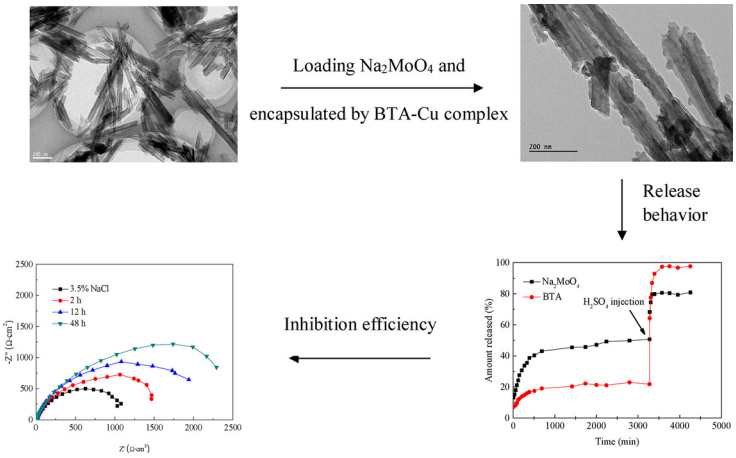
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a novel Cu-BTA-Na_2MoO_4-HNTs corrosion inhibitor was reported by loading Na_2MoO_4 and benzotriazole (BTA) into halloysite nanotubes (HNTs), followed by incorporated insoluble Cu-BTA complex stoppers at the end of tubes through the interaction between BTA and Cu^{2+}. For Cu-BTA-Na_2MoO_4-HNTs, BTA can not only participate in the stoppers preparation of Cu-BTA complex extending the release time of Na_2MoO_4, but also act as another corrosion inhibitor similar with Na_2MoO_4. Very importantly, the obtained Cu-BTA-Na_2MoO_4-HNTs is also responsive to acid medium, owing to the decomposition of the insoluble Cu-BTA complex in acid solution. In addition, the Q235 steel in 3.5% NaCl + 1.0 g/L Cu-BTA-Na_2MoO_4-HNTs shows higher inhibition efficiency than Q235 steel in 3.5% NaCl, such as the inhibition efficiency can be improved to 60.39% at 48 h by the synergistic effect between Na_2MoO_4 and BTA. Therefore, Cu-BTA-Na_2MoO_4-HNTs is a promising efficient and acid-response corrosion inhibitor for carbon steel.

1. Introduction

Corrosion is regared as one of the main problems in the usage of metal materials, because it will change the properties of metal, resulting in the huge economic losses and even heavy accident events [1]. Several methods have been developed to overcome it, including

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material selection, electrochemical protection, addition of corrosion inhibitor and insulating coating [2–4]. Among these methods, the insulating coating owns very wide applications in the metal surface, especially in marine industries. However, the conventional coating is not sufficient in practical applications such as seawater, because the ineluctable partial destruction of coating will accelerate Cl^- ions to permeate the metal surface through the damaged parts, leading to serious corrosion [5]. Recently, two new alternative coatings have been used to overcome this problem: (a) conducting polymer coating, including polyaniline and polypyrrole [6], graphene/polyaniline [7] and carbon nanoparticles/polyethylene/acrylonitrile butadiene rubber nanocomposites [8] so on; (b) inhibitors-enhanced coating. The conducting polymer coating not only owns the mechanical shielding effect on insulating metal from the external environment, but also poesseses a unique protective mechanism against corrosion, which can transfer the produced electrons at defects into polymers, reducing the corrosion rate at defects. Moreover, the conducting polymers coating is a unique anticorrosive coating, but the processability difficulties limit the practical application. Compared with conducting polymers coating, the inhibitors-enhanced coating is a more efficient and easier available method. The corrosion inhibitors in coating can interact with released metal ions once the coating is damaged, which can inhibit the further deterioration of corrosion [9].

In the early stage, the chromate-containing metal coating was commonly used to protect metals for its high inhibition efficiency. However, the chromate was proved to cause cancer, leading to the prohibition in Europe [10]. Therefore, it is important to develop the environment friendly corrosion inhibitors. Afterwards, large amount of attention was paid to some nontoxic or less polluted corrosion inhibitors, including molybdate, tungstate, vanadate, silicate, imidazolines, amides, amines, rare earth salts, gluconate and natural products inhibitors [11–17]. But the directly addition of inhibitors into coatings is not sufficient [9]. On the one hand, the inhibitors can react with other components of coatings. For example, amine corrosion inhibitors can react with epoxy resin, which will weaken the protective effect of coatings. On the other hand, the appropriate solubility is needed when corrosion inhibitors are added into coatings. Because the low solubility of corrosion inhibitors will cause their low concentration in coatings, which will limit their inhibit efficiency. But when the corrosion inhibitors have good solubility, they will be easily washed away and leave empty holes in the coating, which decreases the barrier properties of coatings [18]. Therefore, the introduction of micro/nanocontainers to encapsulate inhibitors is necessary before adding them into coatings [19,20].

Recently, many micro/nanocontainers have been studied, mainly including polyelectrolyte and polymer microcapsules, porous silica particles, layered double hydroxides (LDH), nanotubes. Li et al. [21] successfully encapsulated benzotriazole (BTA) into polystyrene (PS) matrix by the polymerization reaction, and the modification on the surface of PS can effectively decrease BTA release rate. Shchukin et al. [22] demonstrated that the layer-by-layer technique can be used to fabricate polyelectrolyte capsules, which are sensitive to the surrounding media, leading to control the release rate of loaded corrosion inhibitors through the shift of pH. Chenan et al. [23] synthesized hollow mesoporous silica spheres by the sol-hydrothermal method, and then they were used as nanocontainers to encapsulate corrosion inhibitor 2-mercaptobenzothiazole (MBT), which can decrease the release rate of MBT. Yan et al. [24] successfully synthesized three kinds of LDH by using co-precipitation method, and their inhibition behaviors showed that the ZnAlCe LDH intercalated by molybdate own the highest inhibition efficiency compared to ZnAl-NO_3 LDH and ZnAl-MoO_4 LDH. Arunchandran et al. [25] synthesized TiO_2 nanotube by the rapid break down anodization and then used to encapsulate BTA, leading to release loaded BTA in a controlled manner. However, the preparation of these nanocontainers is costly and energy-consuming, which limits their practical application. Compared with other nanocontainers, natural HNTs is abundant, biocompatible and environment friendly, which can be used as very promising nanocontainers for different corrosion inhibitors [26–32].

In our study, the Na_2MoO_4 was loaded into HNTs (namely Na_2MoO_4-HNTs) through vacuum negative pressure method, and then BTA was also loaded into Na_2MoO_4-HNTs, followed by introducing the barrier of Cu-BTA complex to control the release rate of Na_2MoO_4 and BTA (defined as Cu-BTA-Na_2MoO_4-HNTs). The surface morphology and release behavior of obtained samples were investigated by transmission electron microscopy (TEM) and UV–vis spectrophotometer, respectively. Finally, the inhibition efficiency of Cu-BTA-Na_2MoO_4-HNTs was investigated on Q235 steel in 3.5% NaCl solution by electrochemical impedance spectrum (EIS) measurements.

2. Experimental

2.1. Materials

HNTs were obtained from Shanghai Shiye Company (China). $Na_2MoO_4{\cdot}2H_2O$, BTA, $CuSO_4{\cdot}5H_2O$, H_2SO_4 and NaCl were purchased from Tianjin Yuanli chemical company. Moreover, all reagents were analytical grade and used without further purification.

2.2. Preparation of Na_2MoO_4-HNTs and Cu-BTA-Na_2MoO_4-HNTs

Firstly, $Na_2MoO_4{\cdot}2H_2O$ (10.0 g) was dissolved into the distilled water (100 mL), followed by adding HNTs (4.0 g) and stirred to form a suspension. Then, a beaker containing the obtained suspension was transferred into a vacuum jar, which was evacuated using a vacuum pump. With the increasing vacuum degree of the system, the slight fizzing of the suspension suggested that the gas in HNTs was replaced with Na_2MoO_4 solution. The vacuum condition must be maintained for a period of time to complete this loading process, and then was cycled back to atmospheric pressure. After the above process was repeated for two times, the loaded HNTs was collected, washed with ethanol and dried. One portion of these loaded HNTs completed the third loading process in the Na_2MoO_4 water solution (100 mg/mL), and the product was separated by centrifugation, washed with ethyl alcohol and dried to receive Na_2MoO_4-HNTs.

Another portion of the loaded HNTs completed the third loading process in BTA alcohol solution (20 mg /mL). Then the obtained samples were washed with water and dispersed into the $CuSO_4$ solution (0.08 M) for 1 min under stirring to form the end stoppers of insoluble Cu-BTA complex at the end of HNTs. Finally, the product was separated, washed and dried to produce Cu-BTA-Na_2MoO_4-HNTs.

2.3. Characterization

The TEM measurements of HNTs, Na_2MoO_4-HNTs and Cu-BTA-Na_2MoO_4-HNTs were carried out at 200 kV accelerating voltage.

The X-ray diffraction (XRD) patterns of HNTs, Na_2MoO_4-HNTs and Cu-BTA-Na_2MoO_4-HNTs were measured using an X-ray diffractometer (Rigaku D/MAX 2500X) from 5 to 90° (2θ) with steps of 4 min^{-1}.

Fourier transform infrared (FTIR) spectra of samples were measured with a Perkin-Elmer Paragon-1000 FTIR spectrometer in the range of 4000–400 cm^{-1}.

The concentrations of Na_2MoO_4 and BTA were determined by a UV–vis spectrophotometer (UV-2700) with the peaks at 460 and 259 nm, respectively.

2.4. The release tests

The release tests were carried out in the distilled water medium at room temperature, as follows: Cu-BTA-Na_2MoO_4-HNTs (0.05 g) were added into distilled water (100 mL). The dissolution medium (5 mL) was taken out and replaced with the same volume distilled water at