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Improvement of active corrosion protection of carbon steel by water-based epoxy coating with smart CeO_2 nanocontainers

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ABSTRACT

Water-based epoxy coating containing CeO_2 nanocontainers was successfully applied on carbon steel for corrosion protection. CeO_2 nanocontainers were loaded with the corrosion inhibitor benzotriazole (BTA). Polyelectrolyte multilayers were deposited on the loaded nanocontainers by layer-by-layer assembly method. Responsive release of BTA molecules were studied in water media at different pH values using UV–vis spectroscopy. The anticorrosive performance of the epoxy coatings doped with 0.5 wt% of smart nanocontainers was tested by immersion of the coated carbon steel in 0.5 M NaCl solution. Electrochemical impedance spectroscopy (EIS) was used to estimate the influence of smart nanocontainers on the passive corrosion resistance. The self-healing performance of the coating with modified CeO_2 nanocontainers was studied by scanning Kelvin probe (SKP). From results of EIS and SKP, the addition of pH-sensitive nanocontainers into the epoxy resin inhibited the corrosion activities on the metal surface, showing a promising strategy for developing water-based epoxy coatings with long term protection performance.

1. Introduction

Corrosion is a widespread problem faced by hundreds of industrial applications. Large sums of money are spent to protect the metal surface from corrosion all over the world. Polymer coatings are widely applied to protect corrosion on the metal surface against aggressive corrosive environment [1,2]. However, most of the organic coatings cannot provide a long term corrosion protection due to coating integrity degradation. Once the passive coating is in defect, corrosive agents such as oxygen, water and ions can diffuse into the organic resin and lead to the corrosion of metals. Therefore, there is a great need for developing a new coating system which possess both passive and active corrosion protection ability. The effective coating for active anticorrosion of metals is known as chromate-containing conversion coating, but the toxicity of the chromates limits its industrial applications [3]. One strategy to replace chromates is by the direct addition of friendly corrosion inhibitor into the coating system. However, this method leads to degradation of coating integrity and undesired leaching of corrosion inhibitor which is not an optimum idea to promote active protection efficiency [4,5].

One of the solutions for developing active anticorrosion coatings is the encapsulation of the corrosion inhibitors in micro and nanocontainers. There are reports on micro and nanocontainers adopting as inhibitor carriers incorporation into classic passive coatings by several authors [6–10]. The as-prepared coatings improved both the passive and active anticorrosion performance of the coatings, providing long term corrosion protection ability due to controlled release of active inhibiting species [11–14]. Many templates are adopted as host vehicles to load with corrosion inhibitors, such as porous inorganic nanoparticles, layered double hydroxides, polymer containers and halloysite nanotubes [15–21]. The stimuli for release of corrosion inhibitors include local pH changes, humidity, temperature and light [22–25]. Among the various stimuli, the most promising systems for controlled delivery of inhibitors rely on the pH-sensitive smart nanocontainers. Some research work has been reported in the literature using inhibitor-loaded nanocontainers coated with polyelectrolyte shells as pH-responsive reservoirs [26–29]. These reported results confirm the effectiveness of nanocontainers with polyelectrolyte multilayers for fabrication of self-healing coatings. More insight into the smart self-healing coatings with feed-back functionality has been focused on the hybrid sol-gel coatings for active protection of aluminum alloy. Few reports have been focused on the water-based epoxy coatings loading with pH-

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sensitive reservoirs for active protection of carbon steel. In earlier reports, water-based epoxy coatings doped with smart $CaCO_3$ microbeads and polyelectrolyte nanocapsules impregnated with corrosion inhibitors are applied on AA2024 substrate [30,31].

CeO_2 particles have been used as effective fillers to improve the corrosion protection performance of silane coatings [32,33]. In this study, we prepare hollow CeO_2 nanocontainers as reservoirs loading with BTA molecules. The loaded CeO_2 nanocontainers were coated with polyelectrolyte multilayers to form a core-shell structure of CeO_2/BTA/(PEI/PSS)$_2$. Release behavior of BTA inhibitors from the nanocontainers was determined by UV–vis spectroscopy. Corrosion tests were conducted in 0.5 M NaCl solution. Electrochemical testing techniques provide powerful tools to evaluate the active anticorrosion performance of as-prepared self-healing coatings. The common electrochemical methods adopted in the self-healing analysis include electrochemical impedance spectroscopy (EIS), scanning vibrating electrode technique (SVET), scanning electrochemical microscope (SECM), localized electrochemical impedance spectroscopy (LEIS), scanning ion-selective electrode technique (SIET), scanning Kelvin probe (SKP) [34]. Recently, large numbers of the papers devoted to the nanocontainer-based self-healing coatings using SVET method to evaluate the self-healing performance of the coating system [7,8,13]. To date, there has been limited work investigating the efficiency of the nanocontainer-based coatings using SKP technique [35,36]. Therefore, in our study, both EIS and SKP technique have been introduced to investigate the passive and active corrosion behavior of the coatings. EIS results showed that the addition of CeO_2/BTA/(PEI/PSS)$_2$ particles improve the passive protection performance of the coating when compared with the blank coating and coating with free inhibitors. SKP measurements demonstrated that the released inhibitors present on the corrosion site was crucial for termination of the corrosion process on the steel/film interface.

2. Material and methods

2.1. Materials

All chemicals used were commercially available and used without further purification. Cerium(III) chloride heptahydrate ($CeCl_3·7H_2O$), $CO(NH_2)_2$, benzotriazole (BTA), sodium chloride (NaCl), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH), and ethanol were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Poly(sodium-4-styenesulfonate) (PSS, MW ~ 70,000) was obtained from Shanghai Mackin Biochemical Co., Ltd., China. Polyethyleneimine (PEI, MW ~ 70,000) was purchased from Shanghai Aladdin Industrial Corporation, China.

In this work, the substrate material was Q235 carbon steel with chemical compositions (wt%) C 0.16%, Si 0.26%, Mn 0.52%, S 0.03%, P 0.02% and Fe balance. The working electrodes were ground with emery paper up to 800 grit, and cleaned by distilled water and ethanol. One-component water-based epoxy coating was obtained from Marine Chemical Research Institude (Qingdao, China).

2.2. Preparation of CeO_2 nanocontainers

Hollow CeO_2 spheres were synthesized by a simple hydrothermal reaction. In a typical procedure, 0.186 g of $CeCl_3·7H_2O$ and 0.30 g of $CO(NH_2)_2$ were dissolved in 75 mL of distilled water. After continuous stirring for 10 min, the homogenous solution was then transferred into a Teflon-lined autoclave (100 mL) which was then placed in the oven and maintained at 180 °C for 4 h. After that, the solution was cooled to room temperature. The as-prepared CeO_2 samples were separated, washed, and dried in an oven at 60 °C for 24 h. Finally, the obtained CeO_2 nanocontainers were calcined at 350 °C for 3 h with a ramping rate of 1 °C min^{-1}.

2.3. Filling of particles with inhibitor

For encapsulation of BTA inhibitor, about 300 mg of CeO_2 nanoparticles were added to a solution of BTA in 40 mL ethyl alcohol (10 mg mL^{-1}) and the vial was sealed in order to avoid any evaporation of ethanol. After being stirred for 20 h, the suspension was collected by centrifugation and cleaned several times in ethanol. Finally, the loaded CeO_2 nanocontainers were dried at 60 °C overnight.

2.4. Deposition of polyelectrolyte shells on inhibitor-loaded CeO_2 nanocontainers

The loaded CeO_2 nanocontainers were modified with PEI/PSS polyelectrolyte multilayers by layer-by-layer (LBL) technique. In the first step, 20 mL of 15 wt% CeO_2 nanoconainers suspension was mixed with 5 mL of 2 mg mL^{-1} PEI solution stirring for 10 min. Then, the CeO_2/PEI sample was obtained and washed several times with distilled water. After that, negative PSS layer adsorption was carried out using 2 mg mL^{-1} PSS solution for a period of 10 min. The PEI/PSS adsorption was repeated once more to form a CeO_2/BTA/(PEI/PSS)$_2$ structure. Finally, the resultant composite nanoparticles were dried in an oven at 60 °C for 24 h.

2.5. Preparation of the water-based epoxy coating

The water-based epoxy for coating preparation was loaded with as-prepared nanoparticles and stirred for 10 min. The epoxy mixture was applied on the carbon steel substrate with a brush at room temperature. The as-prepared coatings were dried at 50 °C for 24 h. The modified CeO_2 nanocontainers were incorporated into the epoxy coating at a concentration of 0.5 wt%. For comparison, a blank epoxy coating, coating with empty CeO_2 nanocontainers (0.5 wt%), and coating directly loaded with BTA inhibitor (0.5 wt%) were prepared. The thickness of each coating was approximately 30 ± 2 μm which was measured by a QuaNix 4500 magnetic instrument.

2.6. Characterization

The microstructures of the products were obtained by field scanning electron microscopy (FE-SEM; S4800, Hitachi Ltd., Tokyo, Japan) at an operating voltage of 8 kV. Transmission electron microscopy (TEM) images were obtained using a Hitachi HT7700 TEM operating at 100 kV. The surface area and porosity measurements were performed on an Micromeritics TriStar II 3020 apparatus. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 10 transform infrared spectrometer in the region of 525 cm^{-1} to 4000 cm^{-1}. X-ray diffraction (XRD) spectra were performed on a Shimadzu XRD-6000 diffract meter (Japan) using Cu kα radiation. To investigate the release behavior of BTA from the smart CeO_2 nanocontainers, the experiments were conducted at different pH values of 4, 7, 10 at room temperature. About 1 mg of the BTA-loaded nanocontainers was dispersed in 10 mL of distilled water. Concentration of benzotriazole from the release medium was determined at an absorption wavelength of 256 nm using a TU-1900 UV–vis spectrophotometer (Beijing Purkinje General Instrument Co. Ltd., China).

Electrochemical impedance spectroscopy (EIS) measurements were performed on coated steel in a conventional three-electrode cell at ambient room temperature. A rectangular platinum foil was the counter electrode and a saturated calomel electrode (SCE) was employed as the reference electrode. The carbon steel was the working electrode with an exposed surface area of 1 cm^2. EIS measurements were performed using a Gamry Reference 3000 electrochemical work station in the frequency range from 100 kHz to 10 mHz. All the spectra were recorded at open circuit potential while applying a 10 mV amplitude sinusoidal voltage. EIS measurements were taken after exposure to the 0.5 M NaCl solution.