



Corrosion behaviors and physical properties of polypyrrole-molybdate coating electropolymerized on carbon steel



Zhihao Chen^a, Wenzhong Yang^{a,*}, Bin Xu^{b,*}, Yangyang Guo^a, Yun Chen^a, Xiaoshuang Yin^a, Ying Liu^a

^a College of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 210009, China

^b Nanjing Institute of Environmental Sciences, Ministry of Environmental Protection, Nanjing 210042, China

ARTICLE INFO

Keywords:

Polypyrrole
Electropolymerization
Corrosion protection
Physical properties
Mechanism

ABSTRACT

Polypyrrole (PPY) and polypyrrole-molybdate (PPY-MoO₄²⁻) coatings have been successfully electropolymerized on carbon steel by cyclic voltammetry method in aqueous oxalic acid solutions. These coatings were characterized by FTIR, XPS, EDX, FESEM and AFM methods. It was found that the incorporation of MoO₄²⁻ enhanced the corrosion resistance of PPY coating and improved the physical properties, such as thermostability, wettability, adhesion and hardness. The corrosion protection performance of PPY and PPY-MoO₄²⁻ coated steel in 0.1 M HCl solution was investigated by electrochemical impedance spectroscopy and Tafel polarization. Moreover, molecular dynamic simulations were engaged to assess the interactions between the metal surface and complex coatings. The exceptional anti-corrosion performance of PPY-MoO₄²⁻ coating was associated with the complex passive film on the metal surface and the barrier effect of the coating.

1. Introduction

Among all metal alloys, the carbon steel (CS) was commonly used in varieties of industries and engineering structures for its excellent mechanical properties and low cost [1]. However, it was highly susceptible to be corroded in acidic solutions, leading to a huge economic loss [2]. Because of the unique electronic, chemical and biochemical properties, conducting polymers (CPs) had attracted much attention in various fields such as gas sensor [3], capacitor material [4], electrode material [5] and corrosion protection [6,7]. Of the class of CPs materials, PPY was one of the most attractive alternatives for corrosion protection because of its eco-friendly synthesis, good stability and satisfactory biocompatibility [8]. Current polymerization methods of PPY coating could be chemical and electrochemical synthesized through the oxidation of the pyrrole (PY) monomers. Electrochemical synthesis method was used in our paper because of easy polymerization processes, better control of coating thickness and morphologies, and cleaner coating when compared with the chemical oxidation synthesis [9]. Moreover, the advantage of the electrochemical technique also included the promotion of the anodic passivation of the metal surface followed by the formation of polymer coating on the substrate [10].

In recent years, the incorporation of dopants in the PPY coating to improve its anti-corrosion performance and electrical conductivity was a hot topic, due to the highly ordered polymeric chain attained by the

interaction between polymer and dopants [11]. P. Herrasti et al. [12] investigated a novel composite coating consisting of PY and titanate nanotubes on a stainless steel surface. The anti-corrosion properties of the composite increased with respect to the stainless steel by approximately 400 times and twice that obtained on the PPY coating without nano-titanate inclusions. Y.H. Lei et al. [13] demonstrated that adherent and homogeneous benzotriazole (BTA) doped PPY coating can be achieved on an electrode by using the constant current control in oxalic acid aqueous. They investigated the corrosion behaviors in 3.5 wt % NaCl solution for a long time period and found that after 480 h of immersion, copper dissolution was inhibited with an 80% protection efficiency relative to the bare copper, indicating that the presence of BTA in the PPY coating provided much better corrosion protection. B.N. Grgur et al. [14] deposited the strongly adherent and smooth PPY coatings from an aqueous solution of PY and oxalic acid. The total impedance of the corrosion system increased with the immersion time, which was attributed to the difficulties for counter ion exchange along pores presented in PPY coatings. These tests showed that PPY coating could provide corrosion protection to mild steel. W. Su and J.O. Iroh [15] investigated the effect of electrochemical process parameters on the formation of PPY coatings on steel substrates from aqueous oxalate solution. They found that the PPY coatings formed in lower pH solution had higher adhesion strength. The PPY coatings significantly raised the corrosion potential and reduced the corrosion current and corrosion

* Corresponding authors.

E-mail addresses: yangwznjtech@163.com (W. Yang), xubinnies@163.com (B. Xu).

rate of steel.

In this study, we electropolymerized the PPY and PPY-MoO₄²⁻ coatings on CS from aqueous oxalic acid by using the CV method. Then we investigated the influence of MoO₄²⁻ anions on the electropolymerization process, corrosion behaviors and the physical properties such as thermostability, wettability, adhesion and hardness of the coatings. To our best knowledge, the influence of the MoO₄²⁻ anions on the electropolymerization and physical properties was seldom discussed. Furthermore, molecular dynamic simulation calculation was used to study the interaction between the metal surface and the coating. In addition, a complex corrosion protection mechanism was deduced to explain the anti-corrosion performance.

2. Experimental

2.1. Pre-treatment of CS

CS, containing 0.17 wt % carbon, 0.20 wt % silicon, 0.37 wt % manganese, 0.03 wt % sulfur, 0.01 wt % phosphorus and iron making up the remaining percentage, was selected as the base material. The exposed square working area was 4 cm², which was embedded in epoxy resin. Before the experiments, it was polished mechanically with different SiC papers (600, 800, 1000, 1200, 1500 grit), then degreased and cleaned with acetone and ultrapure water, finally dried at room temperature.

2.2. Chemicals

PY, sodium molybdate (Na₂MoO₄), oxalic acid dihydrate (C₂H₂O₄·2H₂O) and hydrochloric acid were analytical grade and were used without further purification unless specially emphasized. Before electropolymerization, PY monomer was distilled under nitrogen in order to remove the oligomers and oxidized form substance, then stored in the dark at low temperature (4 °C). All the solutions were prepared with ultrapure water.

2.3. Electropolymerization on CS

The PPY and PPY-MoO₄²⁻ coatings were electropolymerized by CV technique with the Gamry Reference 4000 electrochemical workstation. The electropolymerization solutions were prepared, which contained (a) 0.3 M oxalic acid + 0.1 M PY and (b) 0.3 M oxalic acid + 0.01 M Na₂MoO₄ + 0.1 M PY, respectively. Prior to the electropolymerization, all the solutions were purged with N₂ gas. The CV technique was carried out with potential range from -0.5 V to + 0.9 V for 20 scanning circles, with a scan rate of 20 mV s⁻¹. After the electropolymerization, PPY and PPY-MoO₄²⁻ coated electrodes were rinsed with ultrapure water for several times, blow-dried with a N₂ flow to remove excess acid solution on the surface, finally dried at 60 °C overnight.

2.4. Characterization

The Fourier Transform Infrared Spectra (FTIR) of PPY and PPY-MoO₄²⁻ coatings were recorded with Thermo Scientific Nicolet IS5. The Escalab 250Xi X-ray photoelectron spectroscopy (XPS) was used to determine the chemical valence of the particular elements in the coatings. The morphologies of the samples were observed by Zeiss Merlin Compact field-emission scanning electron microscope (FESEM) equipped with an IE 250X-Max50 Energy Dispersive X-ray (EDX) detector to analyze the compositions. The average roughness (R_a) of PPY and PPY-MoO₄²⁻ coated steels were investigated using Bruker ICON atomic force microscope (AFM).

2.5. Physical properties

The thermostability of these coatings were performed by TG Q500

Thermogravimetric analysis (TGA). The sample, about 5 mg, was heated from 50 to 800 °C with a heating rate of 10 °C min⁻¹ under a nitrogen flow of 40 - 50 mL min⁻¹. The wettability of these coatings were investigated by using DropMeter A-100 P contact angle analyzer with 5 μL liquid drops. The images were captured immediately by a digital camera and the contact angles were calculated by computer. Adherence of the coating was tested through scratch experiments by a WS-2005 coating adhesion automatic scoring instrument. The hardness of coating was measured by using an FM-ARS 9000 Vickers hardness instrument.

2.6. Corrosion protection tests

The corrosion protection of the coating was evaluated by EIS and Tafel polarization in 0.1 M HCl solution at 298 K by using the Gamry Reference 4000 electrochemical workstation with ESA 410 analysis software. All the electrochemical measurements were performed with a conventional three-electrode system where a platinum sheet worked as the counter electrode (CE), a saturated calomel electrode (SCE) was the reference electrode and the CS behaved as the working electrode (WE).

Prior to each test, the WE was requested to reach a stable open-circuit potential (OCP) after 30 min immersion in the electrolyte. Then, the electrochemical impedance spectroscopy (EIS) measurement was conducted over a frequency range from 100 kHz to 100 mHz with an amplitude of 10 mV. For Tafel polarization, potentiodynamic polarization curves were obtained by shifting the electrode potential automatically from -700 mV to -300 mV at a scan rate of 1 mV s⁻¹. All experiments were replicated at least three times in order to guarantee the repeatability of the experiments.

2.7. Molecular dynamic simulations calculation

Molecular dynamic simulations performed by Material Studio 5.5 software were used to simulate the interactions between metal and the coating. The Fe (1 1 0) surface was initially cleaved from Fe cell and optimized in Forcite Module, followed by enlarging to a (16 × 16) supercell. Meanwhile, the PPY molecules and the MoO₄²⁻ anion were built. All of Fe plane, the PPY molecules and the MoO₄²⁻ anion were conducted in a process of optimization. Then a vacuum slab was built above the Fe (1 1 0) plane and the thickness was set as 30 Å. The energy minimized PPY molecules and the MoO₄²⁻ anion were put onto the surface of Fe plane, which allowed to freely interact with the Fe plane. The simulations were carried out with a time step of 1 fs and simulation of 500 ps. The interaction energy ($E_{\text{interaction}}$) of the coating on the iron surface was calculated as follows:

$$E_{\text{interaction}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{polymer}}) \quad (1)$$

where E_{total} is the total energy of the Fe surface and the polymer, E_{surface} is the energy of the energy of the Fe surface and E_{polymer} is the energy of the polymer taken independently.

3. Results and discussion

3.1. Electropolymerization of PPY and PPY-MoO₄²⁻ coatings by CV on CS

Fig. 1a showed the CV curves for the electropolymerization of PPY coating in 0.3 M oxalic + 0.1 M monomer between -0.5 V and + 0.9 V (vs. SCE) with a scan rate of 20 mV s⁻¹. For the first cycle, the anode current peak appeared at - 0.25 V, which corresponded to the dissolution of iron. The C₂O₄²⁻ and Fe²⁺ formed an insoluble complex (FeC₂O₄), which covered the CS surface before the electropolymerization of the PPY and inhibited the dissolution of iron [16]. During subsequent scanning, the surface of the steel was in a passive state. It was noticeable that the oxidation of the PY monomer occurred as the potential reached about 0.6 V and the oxidation current increased sharply at about 0.9 V. At the same time, a black PPY coating started to deposit on the CS. When the scanning cycles increased, the degree of

Download English Version:

<https://daneshyari.com/en/article/7105527>

Download Persian Version:

<https://daneshyari.com/article/7105527>

[Daneshyari.com](https://daneshyari.com)