



Polyaniline/zinc/cerium nitrate pigment for epoxy based anticorrosion coatings

Zhihua Li^{a,b,*}, Jiankang Hu^{a,b}, Yanbo Li^{a,b}, Jun Liu^{a,b}

^a Key Laboratory of Nonferrous Metal Materials Science and Engineering of Ministry of Education, Central South University, Changsha 410083, People's Republic of China

^b School of Materials Science and Engineering, Central South University, Changsha 410083, People's Republic of China



ARTICLE INFO

Keywords:

Polyaniline
Hollow microspheres
Anticorrosion
Composite coating
Cerium ions doping

ABSTRACT

Polyaniline (PANI) hollow microspheres were synthesized by self-assembly method in poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) aqueous solution. Ce^{3+} ions were doped onto PANI hollow microspheres and further blended with Zn particles to prepare polyaniline/zinc/cerium nitrate composites. PANI/Zn/Ce (NO_3)₃ was applied as additives and dispersed in epoxy resin by mechanical grinding. Anticorrosion properties were investigated by electrochemical impedance spectroscopy (EIS). Bode plots showed that impedance value in low frequency region maintained at $10^6 \Omega\text{-cm}^2$ after 70 days of harsh corrosion in 3.5 wt% NaCl aqueous solution. EIS results revealed that PANI/Zn/Ce(NO_3)₃-epoxy coating has excellent anticorrosion properties.

1. Introduction

Polyaniline (PANI) has attracted great attention owing to its good environmental stability, low cost, easy preparation and biocompatibility [1,2]. These characteristics enable PANIs to be used in many fields such as tissue engineering [3], anticorrosion coatings [4,5], solar cells [6], supercapacitors [7] sensors [8] etc. Nowadays, different morphologies of PANIs such as nanoparticles, nanorod, nanofiber, nanobelt, nanotube have been prepared with various approaches including electrochemical polymerization [9], interface polymerization [10], “template” method [11], self-assembly method [12] etc. For instance, PANI was considered as one of the most promising additives for anticorrosion coatings through deposition on metal substrate by electrochemical techniques [13] and electrospun [14] etc. PANI coating not only separates metal substrate from aggressive electrolytes but also electrochemically reduces corrosion rate of relevant [15]. However, there is still one remaining issue related to its poor solubility in many organic solvents which is difficult to disperse it uniformly in polymeric matrix. Besides, poor adhesion of PANI coatings has limited their wide applications. In order to improve processing ability, PANI was copolymerized with water-soluble polymer or blended with resin. For instance, PANI has been doped by inorganic acids, ions, organic acids such as Poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS) [16] etc. PAMPS was polymerized from 2-acrylamido-2-methylpropane sulfonic acid (AMPS) monomer and used as dopant in synthesis of PANI

with high electrical conductivity and water solubility [17]. In addition, PAMPS was employed as surfactant to form homogeneous suspension in self-assembly method [18]. PAMPS has been considered as good candidate to prepare ions doped PANI due to its sulfonic acid group in side chains.

Of distinctive optical, electrical, magnetic properties of rare earth elements, PANI/rare earth composites have received considerable attention. PANI/La³⁺, PANI/Tb³⁺, PANI/Eu³⁺ and PANI/Ce³⁺ composites have been explored [19,20]. Among those rare earth elements, Ce³⁺ has been chosen as an important corrosion inhibitor due to its high sustained-release effect, non-toxic and maximum corrosion protection efficiency. Moreover, composite with metals tend to enhance conductivity and anticorrosion property of PANI. For instance, PANI/Zn composite film prepared by Olad [21] showed better anticorrosion than PANI film. Gao and Liu [22] provided waterborne anticorrosion coatings containing PANI nanoparticles stabilized with thermoresponsive poly(vinyl alcohol) conjugated with 2-isobutyramidopropanoate moieties (PVA-AI). The coating containing 0.9% PVA-AI exhibited excellent corrosion inhibition and good adhesion. Ge and Yang [23] prepared four types inorganic acids doped PANI nanofibers. The results showed that H₃PO₄-doped PANI exhibiting the best protective effect, followed by H₂SO₄, HNO₃ and HCl doped ones.

The objective of this paper is to explore the effect and mechanism of PANI/Zn/Ce(NO_3)₃ anticorrosion coatings. PANI hollow microspheres will be co-doped with Ce³⁺ ions and PAMPS, and further composited

* Corresponding author at: Key Laboratory of Nonferrous Metal Materials Science and Engineering of Ministry of Education, Central South University, Changsha 410083, People's Republic of China.

E-mail address: ligfz@csu.edu.cn (Z. Li).

<https://doi.org/10.1016/j.reactfunctpolym.2018.07.002>

Received 16 March 2018; Received in revised form 30 June 2018; Accepted 4 July 2018

Available online 05 July 2018

1381-5148/ © 2018 Published by Elsevier B.V.

with Zn particles. Structural and morphological of PANI/Zn/Ce(NO₃)₃ will be examined and discussed in details. Anticorrosion properties of composite coatings containing PANI/Zn/Ce(NO₃)₃ will be examined through electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization in 3.5 wt% NaCl aqueous solution.

2. Experimental

2.1. Materials

Aniline (AR) was purchased from Sinopharm Group Chemical Reagent Co., Ltd. and used after distillation; Epoxy resin E-51 (Tech) and polyamide 651 (Tech) were purchased from Changsha Chemical Research Institute; Zinc powder with average particle diameter of 80 nm and purity of 99.9 wt% (Tech) was obtained from Shanghai China National Pharmaceutical Group Chemical Reagent Co., Ltd.; n-butanol (AR), cerium nitrate (AR) and ammonium persulfate abbreviated as APS (AR) were purchased from Sinopharm Group Chemical Reagent Co., Ltd.; PAMPS was polymerized from AMPS (Purity, 99.23% and supplied by Shouguang Yuyuan Green Technology Co. in China). The number-average molecular weight and weight-average molecular weight of PAMPS were 2006 and 2015 kg mol⁻¹, respectively. Its polydispersity index was 1.0045.

2.2. Preparation of PANI/Zn/Ce(NO₃)₃ composites

PANI hollow microspheres were prepared by self-assembly method in poly (2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) aqueous solution. PAMPS (1.08 g) and aniline (1.85 g) were added into a glass flask containing 85 mL ethanol aqueous solution (8 wt%) under ultrasonication. The suspension was heated in 80 °C water bath while 40 mL ammonium persulfate aqueous solution (0.45 M) was added pouring. After that, flask was transferred to iced water bath immediately. Polymerization was allowed to proceed for 12 h with continuous stirring. A dark green dispersion was obtained and demulsified by acetone. PANI precipitate were centrifuged and washed by deionized water and then dried at 60 °C for 24 h. These PANI precipitate were further dispersed in 40.0 mL cerium nitrate aqueous solution (4.5 g/L) and stirred at room temperature for 12 h. Then, products were obtained after centrifuged and washed with deionized water. Finally, PANI/Ce(NO₃)₃ precipitate were dried under vacuum at 70 °C, and ground with zinc particles with agate mortar to prepare PANI/Zn/Ce(NO₃)₃ composites.

2.3. Preparation of PANI/Zn/Ce(NO₃)₃-epoxy coatings

Composite coating was prepared using epoxy resin as binder, polyamide 651 as curing agent, PANI/Zn/Ce(NO₃)₃ as additives with n-butanol as adjuster for viscosity. Dosage of additives was changed from 0 to 20 wt%. PANI/Zn/Ce(NO₃)₃ were dispersed in n-butanol and re-dispersed in epoxy coating through mechanical grinding. Q235 steel sheet was used as substrate with dimension of 150.0 × 70.0 × 1.0 mm, ground to 1000-grits finish, degreased in acetone and dried in air. PANI/Zn/Ce(NO₃)₃-epoxy coatings were painted on Q235 steel substrate and cured at 60 °C for 2 h. Thickness of coatings was controlled at 35 ± 5 μm for corrosion test.

2.4. Characteristics

Morphologies of PANI/Zn/Ce(NO₃)₃ were characterized on Helios Nanolab 600i scanning electron microscope (SEM). X-ray diffraction was measured on D/Max 2500 X-ray diffractometer with Cu Kα radiation (k51.54Å) at scanning rate of 8°·min⁻¹ and covering 5°~80°. Structures of PANI/Zn/Ce(NO₃)₃ were characterized using Nicolet 6700 infrared spectrometer (using pellets with KBr) and TU-1900 UV/Vis spectrophotometer (PANI/Zn/Ce(NO₃)₃ was dispersed in N-

Methylpyrrolidone with concentration of 50 ppm). Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization test were carried out on three-electrode CHI660C electrochemical workstation. Uncoated or coated steel electrodes, platinum sheet, and saturated calomel electrode (SCE) were taken as working electrodes, counter electrode and reference electrode, respectively. NaCl aqueous solution (3.5 wt%) was used as supporting electrolyte. For EIS measurements, frequency was kept from 100 kHz to 10 mHz with signal amplitude of 10 mV at open circuit potential(OCP). Potentiodynamic polarization measurements were obtained by scanning electrode potential from -0.9 V to -0.3 V at scan rate of 10 mV·s⁻¹. Corrosion protection efficiency was evaluated from I_{corr} values with relationship, where I_{corr} and I_{corr}(C) are corrosion current density of bare steel and coated steel substrates, respectively. Adhesion between coating and steel plate was measured using cross-hatch tape test according to GB9212. Adhesion is divided into six grades: 0, 1, 2, 3, 4, and 5, representing peeling areas of 0, < 5%, 5–15%, 15–35%, 35–65%, and > 65%, respectively.

3. Results and discussion

3.1. Structures and morphologies of PANI/Zn/Ce(NO₃)₃ composites

Morphology of PANI/Zn/Ce(NO₃)₃ composites were characterized by SEM and TEM. As shown in Fig. 1a, PANI/Zn/Ce(NO₃)₃ composites were consisted of Zn particles and PANI/Ce(NO₃)₃ hollow microspheres with diameter of 400 ± 50 nm and shell thickness of 70 ± 5 nm. According to EDX surface element analysis, PANI/Zn/Ce(NO₃)₃ offered six elements including C (37.13 wt%), Zn (52.21 wt%), O (6.59 wt%), N (1.62 wt%), S (0.33 wt%) and Ce (0.12 wt%) (see Fig. 1b). The structure of PANI/Zn/Ce(NO₃)₃ was further affirmed by X-ray diffraction (XRD), where peaks observed at 2θ = 20.1° and 25.2° were attributed to PANI polymer chain. Peaks located at 36.29°, 38.99°, 43.22°, 54.32°, 70.08°, 70.63° and 77.05° were attributed to (002), (100), (101), (102), (103) and (110) of Zn particles, respectively.

FT-IR spectra of PANI, PANI/Ce(NO₃)₃ and PANI/Zn/Ce(NO₃)₃ composites were presented in Fig. 2. PANI hollow microspheres showed the following characteristic peaks: peaks at 3438 cm⁻¹ and 3221 cm⁻¹ were corresponded to stretching vibration of N–H and O–H, respectively; peaks belonging to C=C stretching vibration of quinone rings and benzene rings were observed at 1564 cm⁻¹ and 1485 cm⁻¹, respectively; peak of C–N plane stretching vibration in benzene rings was located at 1294 cm⁻¹; peaks at 1645 cm⁻¹ and 1032 cm⁻¹ were assigned to S=O and –SO₃H in PAMPS molecular, respectively. IR spectrum of PANI/Ce(NO₃)₃ was overlapped with PANI/Zn/Ce(NO₃)₃. Note here, the difference is mini compared with PANI. Peak at 1140 cm⁻¹ attributed to C–H plane bending vibration in quinone ring has shifted to 1301 cm⁻¹, which suggested coordination between Ce³⁺ and quinone structure in PANI backbone.

UV–Vis spectra of PANI, PANI/Ce(NO₃)₃ and PANI/Zn/Ce(NO₃)₃ composites was presented in Fig. 3. It can be clearly seen that peak centered around 272 nm was attributed to PAMPS. Absorption peak distributions of PANI were similar to PANI/Ce(NO₃)₃. Here, Hump at 373 nm was associated with inter band charge transfer of π-π* transition in benzene rings. In comparison with UV–Vis spectra of PANI and PANI/Ce(NO₃)₃, absorption peak assigned to π-π* transition of PANI/Zn/Ce(NO₃)₃ has blue-shifted from 373 nm to 354 nm. In addition, a broad peak of n-π* transition of quinone moieties centered at 630 nm was enhanced due to free electrons of Zn which excited under ultraviolet light. A large quantity of electrons have synergistic effect with unoccupied orbits of Ce³⁺ ions, which reduced coordination of Ce³⁺ ions with PANI, further indicated interaction between Ce³⁺ ions and quinone structure in PANI.

Download English Version:

<https://daneshyari.com/en/article/7826008>

Download Persian Version:

<https://daneshyari.com/article/7826008>

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