Intelligent saline enabled self-healing of multilayer coatings and its optimization to achieve redox catalytically provoked anti-corrosion ability

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ABSTRACT

To obtain a coating with both self-healing and redox catalytic ability to protect a metal substrate from corrosion under aggressive environment is strongly desired. Herein, we report the design and fabrication of intelligent polyaniline-polyacrylic acid/polyethyleneimine (PANI-PAA/PEI) multilayer composite coatings by spin assembly. The main influencing factors, including solution concentration (c) and disk rotating speed (ω) were studied in order to gain excellent performance. The resulting multilayer coatings with thickness in a range from 0.47 to 2.94 μm can heal severe structural damages and sustain a superior anti-corrosive performance for 120 h in 3.5% NaCl. The PANI-PAA layer enhances the anti-corrosion property and PEI layer contributes to the self-healing ability as well as their multilayer combination strengthens them. The improved self-healing ability is attributed to the rearrangement and reversible non-covalent interactions of the PANI-PAA and PEI layers that facilitates electrostatic repairing.

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1. Introduction

Developing new conductive polymers (CPs) for corrosion protection application to replace environmentally toxic and banned heavy metals [1–3] has achieved a considerable interest. Fortunately, polyaniline (PANI) is considered the most extensively studied polymer, as its redox states maintain a passive film on the substrate [4–6] and facilitate the anodic protection for steel [7–9] and iron [10,11]. In addition to its well-known electro-active nature, PANI coatings marked as good anti-corrosive material. Electrodeposition of PANI on metal surface is considered to be the most facile method [12–14], but the resulting coatings would eventually fail due to porous morphology and appearance of large defects [15]. It is hard for a damaged coating to be healed due to the brittle nature of the CPs and the related self-healing mechanism is unclear so far.

Taking inspiration from nature [16], self-healing materials acquired much attention, particularly for corrosion protection because this intelligent system can repair damage by using their inbuilt resources [17,18]. The fabrication of self-healing coatings for anti-corrosion application is still at infancy despite it acted as an intelligent material because of the long healing time and com-

plex fabricating procedures [19,20]. Therefore, ideal self-healing coatings for anti-corrosion application should be capable of quickly repairing severe damage and restore substrate integrity for prolonged time. One of the viable routes to introduce self-healing functionality in the coating matrix is the incorporation of capsule loaded with active healing agents [21,22]. The crack propagation would rupture the capsules and the healing agent was released which repairs the coating matrix through extrinsic self-healing [23–25]. This method is advantageous and strengths the mechanical properties of the coating, however, large size of the capsule would result in thicker coatings. Moreover, the capsule based coating needs long time to repair with partial healing and needs high temperature as an external stimulus [26,27]. In addition, the damaged spot can be healed at once and would no longer enjoy the extrinsic self-healing at the same ruptured capsule site [17,28]. In contrast, intrinsic self-healing materials are capable of reversible repairing at the same damaged site with non-covalent interactions [29–31]. The coating, fabricated by intrinsic self-healing material, do not need the aid of healing agents and the obtained film prevents agglomeration caused by the healing capsules [29].

Taking advantage of Layer-by-Layer (LbL) assembly, oppositely charged polyelectrolyte multilayer coating could be fabricated to achieve the intrinsic self-healing for improved anti-corrosion application with multiple repairing at the same damage site [29]. The most probable self-healing mechanism proposed for polyelec-

trolyte multilayers are, the local neutralization of the pH in the damaged zone (buffering activity) [32] and water assisted mobility of polyelectrolytes to seal the surface defects [30,33]. Although polyelectrolyte coating exhibits enhanced self-healing ability, but its lifespan is short. In addition, its anti-corrosion property is significantly affected due to the diffusion of electrolyte that enhances the mobility of the polyelectrolytes. Efforts have been devoted and corrosion inhibitors were added in the polyelectrolytes multilayers to enhance the anti-corrosion property of the coating for aluminum protection [34]. Contrary to this, CPs (PANI) based coating exhibits exceptional anti-corrosion behavior [8,9,35], however, there is a lack of self-healing behavior and one should compromise between self-healing and marked anti-corrosion behavior.

In our previous publications, we proposed PANI-PAA composite as a good corrosion inhibitor [36] and PDDA/PAA multilayers with profound self-healing effect [37]. It is still problematic to achieve both the intrinsic self-healing and anti-corrosion ability to increase the lifespan of the metal. To address these issues, in the present paper, we demonstrate the self-healing ability with enhanced anti-corrosion performance at the same time of PANI-PAA/PEI multilayer coating.

2. Experimental

2.1. Materials

Polyacrylic acid (PAA) and Polyethyleneimine (PEI) of average $M_w \sim 450{,}000$ and $750{,}000$ (50 wt.%), respectively, were purchased from Sigma-Aldrich. All other chemicals were purchased from Shanghai Lingfeng Chemicals. Senda Decoration Materials Co. Ltd. (Haimen, China) provided the 316SS plates. Coupons of 316SS size $(2.5\,cm \times 2.5\,cm \times 0.1\,cm)$ were grounded successively by using 800, 1000, 1200 SiC papers and $3\,\mu m$ alumina slurry was used for polishing the SS surface. The surface of the coupons was treated with a piranha solution $(H_2SO_4/H_2O_2$, 70:30 v/v) for 1 h. Finally, the substrates were washed with excess of water and dried.

2.2. Fabrication of PANI-PAA/PEI coatings

Previously, we described the synthesis with detailed characterization of PANI-PAA composite [36] and herein we discuss the spin assembly of PANI-PAA/PEI multilayers on 316SS. Initially, PANI-PAA composite solution (1 ml) was added drop wise on 316SS surface (deposition). The substrate was started to rotate at a low speed (spin-up = 500 rpm). The disk rotating speed (ω) was then accelerated and determines the final thickness of the coating (spin-off = 1000–1500 rpm). Finally, the excess of solvent was evaporated by heating the substrate at 110 °C to obtain a uniform film (evaporation). For PEI layer, 1 ml of 10 mM PEI solution was deposited by following the same procedure used for the fabrication of PANI-PAA layer. Similarly, at different c and ω, PANI-PAA/PEI coatings at layer number ($n = 20$) with a multilayer structure were obtained and used further for characterization. In addition, for all the experiments when c was varied from 0.45 to 1.80%, the rotating speed was set at $\omega = 1000$ rpm, and when the ω was varied from 1000–4000 rpm, the c was set at 1.80%. The reason behind the selection of this specific c and ω will be discussed in later sections.

2.3. Instrumentation

The spin coating machine KW-4A/5 (China) was used for the spin assembly of PANI-PAA/PEI multilayers. Spectrum-GX of Perkin Elmer was used to obtain FTIR spectra. The morphology of PANI-PAA/PEI coatings was investigated by scanning electron microscope (SEM) of Hitachi S-4800. The surface roughness and thickness of the coatings were measured by Veeco Dektak 150 surface profilometer. The uncoated and coated samples were first immersed in 3.5% NaCl solution for 24 h then the coating was carefully removed to study the underlying SS surface. The passivating metal oxide layer was characterized by X-ray photoelectron spectroscopy (XPS) for chemical analysis (ESCA), which was performed on a Thermo Fisher Scientific K-Alpha XPS system with a monochromatic Al Kα X-ray source (1486.6 eV) and the pass energy is 50 eV. The pressure of the analysis chamber was $\sim 10^{-8}$ Pa.

The electrochemical measurements were conducted on Autolab PGSTAT30. An assembly of three-electrode cell, 316SS as working electrode, saturated calomel electrode (SCE) and platinum as a reference and counter electrode, respectively. All the samples were tested in 3.5% NaCl with the exposed circular region having a diameter 1 cm. The polarization measurements were performed at a sweep rate of 10 mV/s with the starting sweep potential of −0.1 V vs. open circuit potential (OCP). The EIS was carried out at OCP with the amplitude of 10 mV under the frequency range of 10^5 to 10^{-2} Hz. The evaluation of fitting parameters and the simulation of electrical circuits were performed on software Nova (version 1.1). Similarly, cyclic voltammetry was carried out by using the same three electrode assembly, except a platinum foil $(2 \times 2\,cm)$, which is used as a working electrode in 1 M H_2SO_4 solution.

To evaluate the self-healing property of the coating, digital and microscopic images were taken of the cross shaped scribe made by using a scalpel. Carl Zeiss Axio ImagerM2m Microscope System was used to obtain the optical microscopic images. Self-healing property of the coating was further supported with the electrochemical testing by exposing the scribe to 3.5% NaCl solution for 15 h.

3. Results and discussion

3.1. Coating composition and structure

The FTIR-RAS of PEI, PANI and their multilayer structure (PANI-PAA/PEI) is presented in Fig. 1. The peaks of PEI film (Fig. 1a) at $3335\,cm^{-1}$ and a small shoulder at $3281\,cm^{-1}$ is attributed to the −N−H stretching of primary and secondary amine, respectively. However, the peaks at $2945/2850\,cm^{-1}$ and $1475\,cm^{-1}$ corresponds to −C−H stretching and bending, respectively [33]. In addition to these peaks, a prominent interaction between oppositely charged layers of PANI-PAA/PEI coating was also observed. The band at $1595\,cm^{-1}$ and $1503\,cm^{-1}$ assigned to C=C stretching of quinoid and benzenoid rings (Fig. 1b) which indicates the formation of PANI structure [38]. The protonated PANI exhibits conductive C−N⁺ structure which is expressed by the peak at $1320\,cm^{-1}$ [39]. The peak at $1165\,cm^{-1}$ is ascribed to the plane bending vibration of C− [40]. At higher wavenumber ($>2000\,cm^{-1}$), a broad absorption band was observed in Fig. 1c which indicates the free charge-carriers in the protonated PANI [41]. The characteristic peaks exhibited by PANI-PAA/PEI coating (Fig. 1c) indicate the presence of PANI-PAA and PEI in a multilayer structure.

3.2. Effect of solution concentration (c) and rotating speed (ω) on coating thickness

The thickness of the coating depends on c and ω. Fig. 2a presents the relationship between the c and the thickness of PANI-PAA/PEI coating. The PANI-PAA composite was based on a series of PAA concentration (0.45, 0.90, 1.35, 1.80 and 2.25% w/v). Initially, the dependence of thickness on c was small, ranged from 0.47 to 0.85 μm at $c = 0.45$ to 0.9%. Whereas, the thickness is ranged from 1.99 to 2.75 μm at $c = 1.35$ to 1.8%. Finally, the thickness reached to 2.94 μm at $c = 2.25\%$. Therefore, the difference between the coating thicknesses of successive c becomes smaller at very high concen-