



Electrochemical synthesis and corrosion inhibition performance of poly-5-aminoindole on stainless steel



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ABSTRACT

Poly-5-aminoindole (P5AIIn) was coated by potentiodynamic methods onto type-304 stainless steel (SS) using a 0.3 M oxalic acid solution containing 0.05 M 5-aminoindole (5AIIn) monomer. The corrosion protection ability of the polymer coating was studied using open circuit potential (E_{ocp})–time measurements, polarization curves, and electrochemical impedance spectroscopy (EIS) after the electrodes had been immersed in a 3.5% NaCl solution as the corrosive media. We used scanning electron microscopy (SEM) to examine the electrode surface characteristics. The results indicated that the polymer film adhered to the stainless steel surface and inhibited the SS corrosion for the 96-h immersion period.

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1. Introduction

Metals and alloys have wide industrial applications because of their high strength and ductility. The corrosion resistance of stainless steel, which is a particular type of alloy, arises from passive films that form on the surface. Although this thin oxide layer is strongly adherent and chemically stable, in specific aggressive environments, especially those containing chlorides, the film degrades, which causes initiation and propagation of localized corrosion.

Since the work by DeBerry, who first suggested that polyaniline could increase the corrosion resistance of stainless steel, there have been extensive investigations on conducting polymers (Cps) for corrosion protection applications [1]. The common Cps used for corrosion prevention for steel are polyaniline (PANI), polypyrrole (Ppy), polythiophene (PTh), polyindole (PIN), and their derivatives [2–8]. Anodic oxidation can be used to electrochemically synthesize most Cps onto the metal surfaces in a single step.

The polymers form a physical barrier and also stabilize the passive oxide layer on the surface [9]. Because Cps can store and transport charges, they protect metals against rapid rates of corrosion. The efficiency of the polymer coating depends on the redox state of the polymer and the conditions of the corrosive environment. Cps exhibit effective corrosion protection when they are in the doped state [10]. The primary advantages of using conducting

polymers for corrosion protection are their non-toxicity, relatively low costs, and ease of production on oxidizable metals using electrochemical techniques [11].

Previous studies have shown that indole [12] and some of its derivatives (e.g., indole-5-carboxylic acid [13], 5-aminoindole [14–16], 5-chloroindole [17], and indole-3-acetic acid [18]) inhibit the corrosion of copper and mild steel. 5AIIn, which is structurally similar to aniline and pyrrole, has also been reported to inhibit the corrosion of mild steel. There are reports that the electrochemical synthesis of 5AIIn onto a metallic electrode surface is difficult because the substituent inhibits film formation [19]. Although the electrochemical synthesis and electrochemical behaviour of P5AIIn have been studied [20–22], there has been no study reporting the use of P5AIIn for the prevention of stainless steel corrosion.

P5AIIn is a conducting, electroactive polymer that can be synthesized via the anodic oxidation of 5AIIn in various electrolytes. P5AIIn may function as a polymeric anodic inhibitor on steel due to its conjugated double bonds, which reduce the number of active sites on the metal surface through adsorption [23].

In this study, we electrochemically synthesized P5AIIn on SS from a monomer-containing oxalic acid solution and investigated the corrosion performance of the SS in a 3.5% NaCl solution.

2. Experimental

We used a 304 stainless steel rod embedded in a polyester block with an exposed area of 0.20 cm² as a working electrode. The chemical composition (wt.%) of the SS rod is 0.054 C, 1.66 Mn, 0.42 Si,

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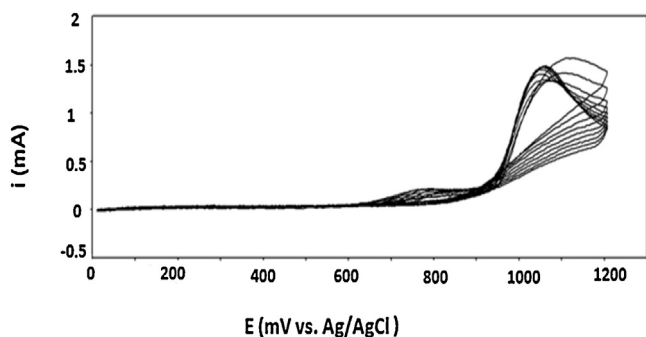


Fig. 1. Cyclic voltammograms for electrodeposition on SS in 0.3 M oxalic acid containing 0.05 M 5Aln at a scan rate of 50 mV s^{-1} .

0.039 P, 0.026 S, 0.039 P, 8.06 Ni, 18.20 Cr, 0.14 Cu, 0.125 Mo, and balance Fe. The electrodes were polished with different grades of emery paper, up to 1200 grit. Then the electrodes were washed with distilled water and dried. The potential was measured against an Ag/AgCl/KCl electrode with a platinum sheet (1 cm^2 surface area) as the counter electrode. The electrochemical measurements were performed using a conventional three-electrode set-up and a Gamry ZRA model electrochemical analyser controlled by a computer using Electrochemistry software version 5.30.

The aqueous solutions used for the electropolymerization contain 0.05 M 5Aln (Merck) and 0.3 M oxalic acid (Merck). A 3.5% NaCl solution was used as the corrosion test media. All chemicals used in the experiments were analytical grade. All experiments were performed at room temperature.

The electrosynthesis of P5Aln films on steel electrode was performed using a potentiodynamic technique. The anticorrosion properties of the films were investigated using E_{ocp} -time curves, polarization measurements, and EIS. The polarization curves were recorded with a sweep rate of 4 mV s^{-1} . The frequency used for the impedance measurements ranged from 100 kHz to 10 mHz with an amplitude of 5 mV. The morphology of the electrodes coated with the P5Aln films was examined using SEM (Zeiss/Supra 55).

3. Results and discussion

3.1. Electrosynthesis of P5Aln on stainless steel

In the first step of the preparation of the SS/P5Aln electrodes, a single forward scan from -0.4 to $+0.4 \text{ V}$ at a scan rate of 4 mV s^{-1} in

the 0.3 M oxalic acid solution was used to passivate the steel surface. The P5Aln film was grown by scanning a potential range from 0.0 to 1.2 V in a 0.05 M 5Aln with 0.3 M oxalic acid solution. Fig. 1 shows the successive cyclic voltammograms (CVs) during electropolymerization of the 5Aln using a scan rate of 50 mV s^{-1} . During the first cycle (Fig. 1), the onset potential of the 5Aln is approximately $+0.5 \text{ V}$. As the CV scan continues, the peak current first decreases and then increases. The increase in the current indicates that the P5Aln layer deposits onto the SS electrode. The current reaches a steady state value as the scan progresses. During the film growth, the peaks shift to lower potentials, which is attributed to the lower initial oxidation potential of the as-formed polymer or oligomer. Based on the literature [24,25], there are two possible polymerization paths for the backbone chain: P5Aln, 2,3-coupled and 2,2-3,3-coupled (Scheme 1).

3.2. Corrosion tests

Fig. 2 presents the potentiodynamic curves for the SS and SS/P5Aln electrodes after a 1-h immersion in a 3.5% NaCl solution. The P5Aln-coated steel exhibits substantially smaller anodic currents compared to the uncoated steel. In the case of the SS/P5Aln electrode, the E_{ocp} shifts in the anodic direction to 200 mV. The positive shift in the E_{ocp} is due to the more effective action exerted on the anode rather than on the cathode reaction. P5Aln exhibits anodic protective behaviour on SS by acting as a physical barrier that prevents the attack of corrosive species (dissolved oxygen and chloride ions) on the metal surface [26]. In this case, it could be concluded that P5Aln has a low permeability to the corrosive species. It has also been proposed that when a metal comes into contact with an electronically conducting polymer, an electric field is generated that would limit the flow of electrons from the metal to the oxidizing species, thus reducing the corrosion rate [27]. As shown in Fig. 2, SS is passive in the range of potentials from -0.8 to -0.3 V . The passive layer begins to degrade at potentials greater than -0.3 V . In the case of SS/P5Aln, the current increases at around -0.3 V due to oxidation of the polymer film and/or oxidation of the underlying substrate [28].

Fig. 3 shows the time dependence of E_{ocp} in a 3.5% NaCl solution for SS and SS/P5Aln electrodes. After 96 h of exposure, the measured potentials of the coated electrode are nobler than the potentials of the uncoated electrode.

Fig. 4 shows Nyquist and corresponding phase angle-log (frequency) plots of SS and SS/P5Aln electrodes after immersion times of 24 and 96 h in a 3.5% NaCl solution. The features of the curves

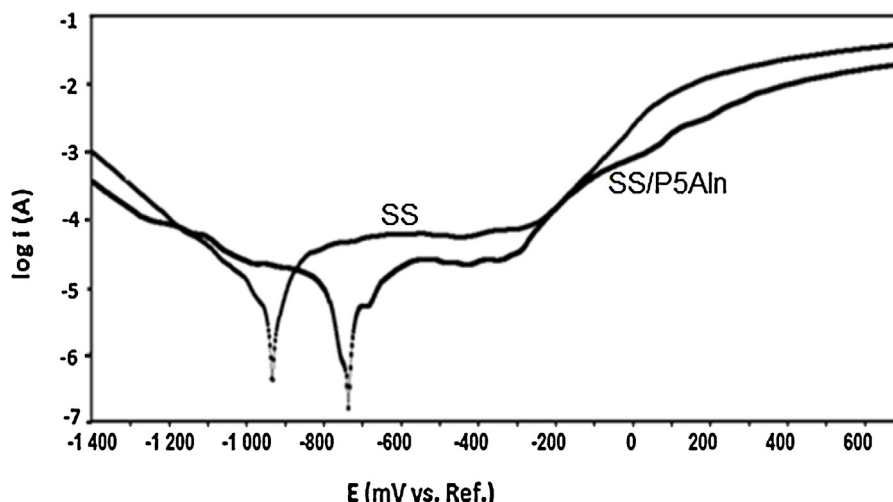


Fig. 2. The polarization plots for SS and SS/P5Aln electrodes in 3.5% NaCl solution after 1 h immersion time at a scan rate of 4 mV s^{-1} .

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