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

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ABSTRACT

Poly-5-aminoindole (P5AIn) 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 (5AIn) 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. 5AIn, 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 5AIn onto a metallic electrode surface is difficult because the substituent inhibits film formation [19]. Although the electrochemical synthesis and electrochemical behaviour of P5AIn have been studied [20–22], there has been no study reporting the use of P5AIn for the prevention of stainless steel corrosion.

P5AIn is a conducting, electroactive polymer that can be synthesized via the anodic oxidation of 5AIn in various electrolytes. P5AIn 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 P5AIn 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 cm^2 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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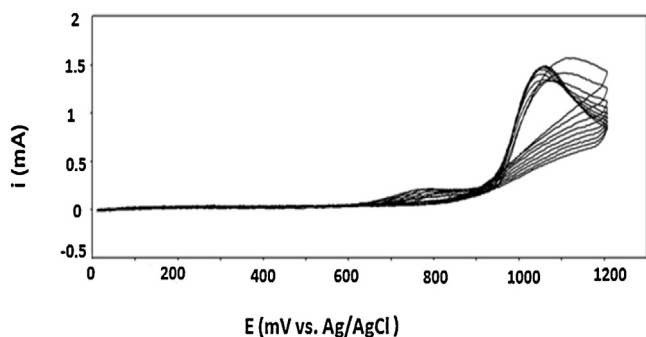E-mail address: mdudukcu@mersin.edu.tr (M. Düdükcü).

Fig. 1. Cyclic voltammograms for electrodeposition on SS in 0.3 M oxalic acid containing 0.05 M 5AIn 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 5AIn (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 P5AIn 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 P5AIn films was examined using SEM (Zeiss/Supra 55).

3. Results and discussion

3.1. Electrosynthesis of P5AIn on stainless steel

In the first step of the preparation of the SS/P5AIn electrodes, a single forward scan from −0.4 to +0.4 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 P5AIn film was grown by scanning a potential range from 0.0 to 1.2 V in a 0.05 M 5AIn with 0.3 M oxalic acid solution. Fig. 1 shows the successive cyclic voltammograms (CVs) during electropolymerization of the 5AIn using a scan rate of 50 mV s^{-1}. During the first cycle (Fig. 1), the onset potential of the 5AIn is approximately +0.5 V. As the CV scan continues, the peak current first decreases and then increases. The increase in the current indicates that the P5AIn 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: P5AIn, 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/P5AIn electrodes after a 1-h immersion in a 3.5% NaCl solution. The P5AIn-coated steel exhibits substantially smaller anodic currents compared the uncoated steel. In the case of the SS/P5AIn 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. P5AIn 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 P5AIn 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/P5AIn, 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/P5AIn 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/P5AIn electrodes after immersion times of 24 and 96 h in a 3.5% NaCl solution. The features of the curves
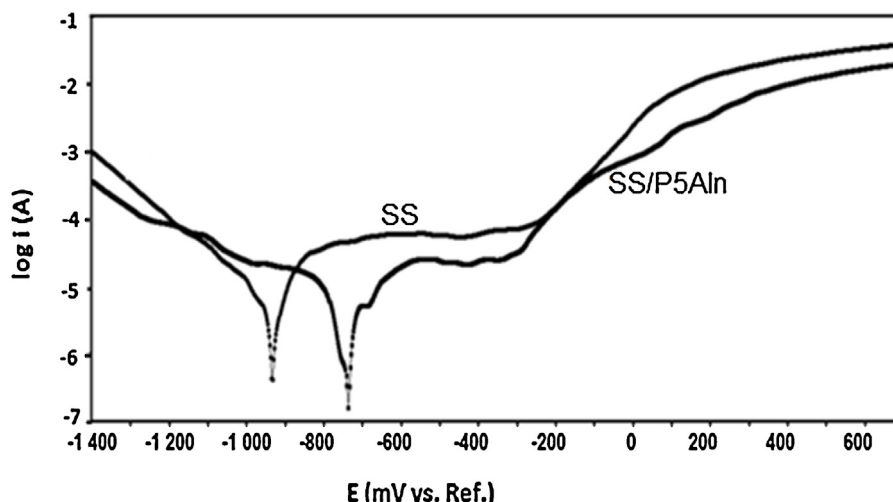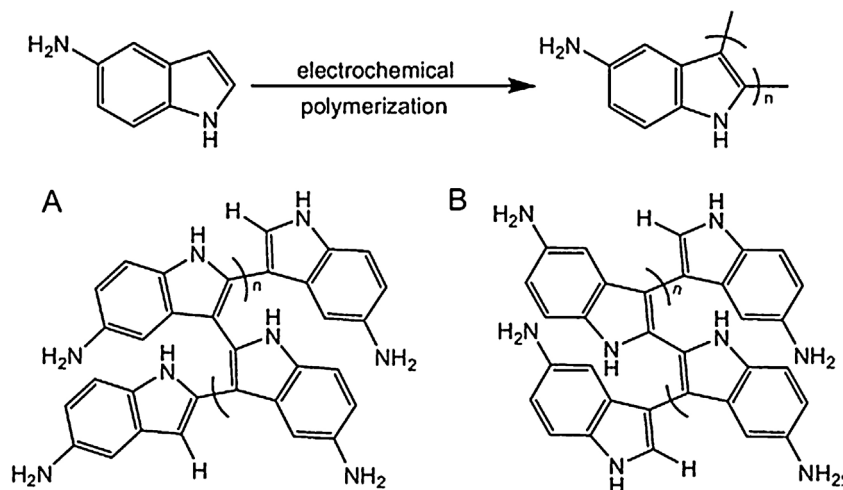

Fig. 2. The polarization plots for SS and SS/P5AIn electrodes in 3.5% NaCl solution after 1 h immersion time at a scan rate of 4 mV s^{-1}.

Scheme 1. Electrochemical polymerization of 5AIn in oxalic acid solution and the most probable structures of P5AIn: 2,3-coupled (A) and 2,2-3,3-coupled (B).
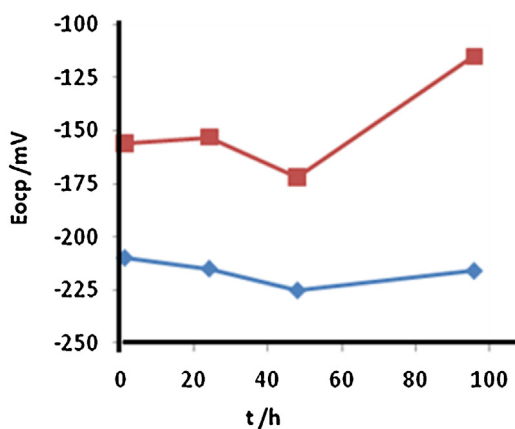

Fig. 3. The change of E_{OCP} as a function of immersion time for SS (♦) and SS/P5AIn (■) electrodes in 3.5% NaCl solution.
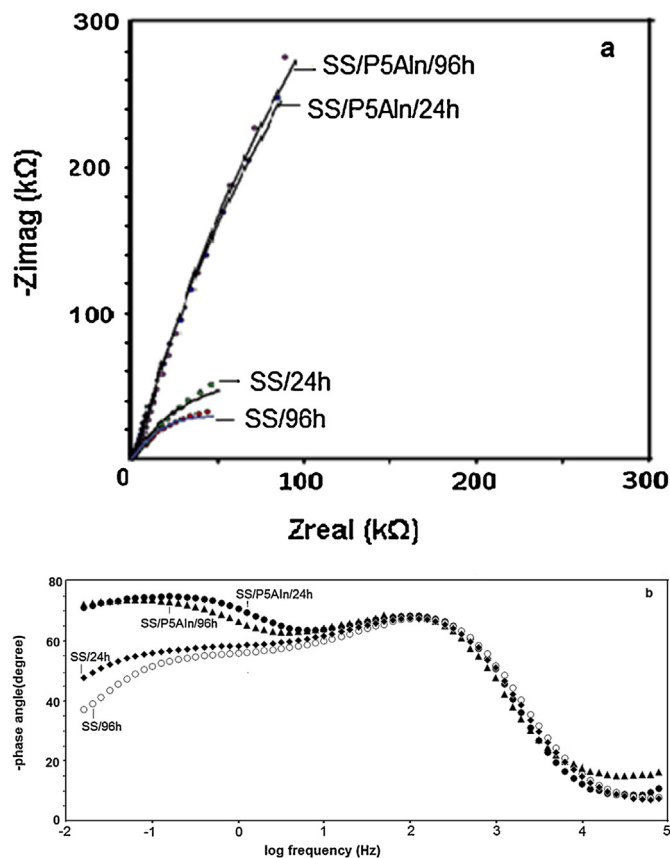

Fig. 4. Nyquist (a) phase angle-log(frequency) (b) plots for SS and SS/P5AIn electrodes in 3.5% NaCl solution after 24 h and 96 h immersion times.

for the SS/P5AIn system are different from those of the SS electrode. In the low-frequency region, the straight line with respect to the real axis represents the presence of a diffusion-controlled process. This response indicates that the P5AIn coating acts as a barrier against the diffusion of charge carriers to the metal surface. In the phase angle-log (frequency) diagram (Fig. 4b), two regions of distinct electrochemical response are present for both the SS and SS/P5AIn electrodes. The high-frequency region consists of the pore resistance (R_{po}) and the film resistance (R_f). R_{po} arises from a kinetically controlled electrochemical reaction occurring between the metal and the corrosive solution [29]. The straight lines at an angle of 45° with respect to the real axis in the lower frequency region are related to the Warburg diffusion parameter [30]. In the low frequency region, the phase angle values of SS/P5AIn are higher than those of SS.

The oxide film is composed of stable chromium and nickel compounds that protect the steel surface [31]. However, the corrosive species diffuse through the pores of the oxide layer and corrode the metal surface. The total resistance of the uncoated steel electrode is equal to the sum of the resistance against the corrosion process occurring within the pores and the resistance of the oxide film. In the presence of P5AIn, the film resistance includes both the oxide film and polymer film resistances.

An equivalent circuit model was fitted to the experimental Nyquist curves (Fig. 5). The equivalent circuit model consists of a solution resistance (R_S), film and pore resistances, a constant-phase
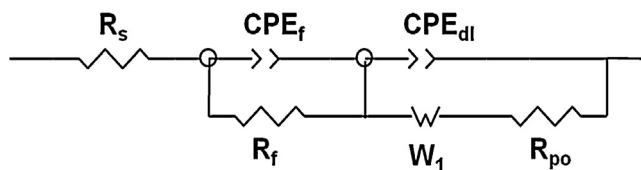

Fig. 5. Equivalent circuit used to fit the EIS data for SS and SS/P5AIn electrodes.

Table 1
Fitting results of impedance spectra for the corrosion of the SS and SS/P5AIn electrodes % in 3.5 NaCl solution at open circuit potential.

Electrodes	t (h)	R_s (Ω)	CPE_f (F)	CPE_{dl} (F)	n_2	R_f (Ω)	W_1 (Ω)	R_{po} (Ω)
SS	24	14.54	57.62×10^{-6}	62.75×10^{-6}	0.77	1352	23,960	149.30×10^3
	96	14.79	45.07×10^{-6}	61.06×10^{-6}	0.76	1246	1179	86.15×10^3
SS/P5AIn	24	22.71	33.20×10^{-6}	26.87×10^{-6}	0.86	867	6.34×10^6	2.34×10^6
	96	26.19	42.35×10^{-6}	24.97×10^{-6}	0.87	2868	3.72×10^9	2.33×10^6
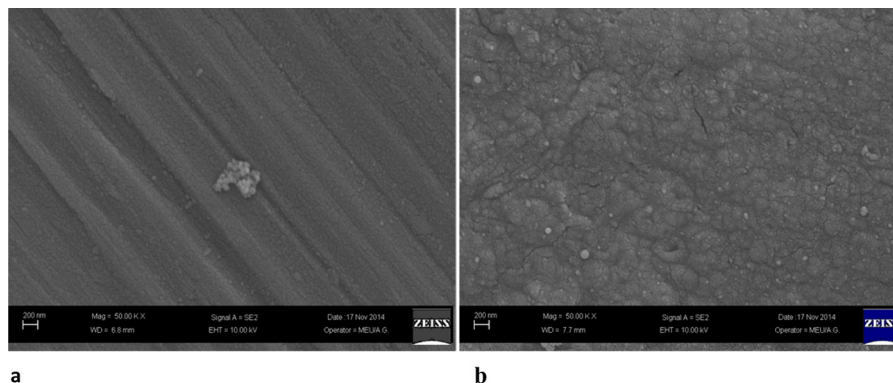
Fig. 6. SEM photographs of SS (a) and SS/P5AIn (b) electrodes in 3.5% NaCl after 96 h immersion.

element for the film (CPE_f), a constant-phase element for the double layer (CPE_{dl}), and a Warburg impedance (W_1), which accounts for diffusion of the mobile charges in the polymer backbone and the mobile anions throughout the P5AIn coating [32]. Here, a constant-phase element (CPE) is used instead of capacitance (C) to define homogeneities in the system. Expression of the impedance of the CPE is as follows:

$$Z_{CPE} = C^{-1}(iw)^{-n} \tag{1}$$

where C is the real capacitance, w is the angular frequency, i is an imaginary unit, and n represents the phase shift with the values between 0 and 1 [33].

Table 1 presents the values of the impedance parameters obtained from the fitting of the experimental data. R_{po} includes the charge transfer resistance (R_{ct}) and the resistance of accumulated species (R_a) such as corrosion products and any existing molecules or ions [34]. The corrosive solution must diffuse first through the polymer film and then through the oxide layer to reach and corrode the metal surface. As shown in Table 1, the sum of R_f and R_{po} for the coated electrode is greater than that for the uncoated SS after the 24 and 96 h immersion periods. For SS/P5AI, the increase in R_f with exposure time is consistent with the fact that the redox chemistry of the conducting polymer film can facilitate an increasingly thicker layer of oxide at the metal-polymer interface [35]. The decrease in the double layer capacitances for the coated electrode can result from a decrease in the local dielectric constant or an increase in the thickness of the electrical double layer. This indicates the substitution of water molecules with 5AIn molecules with a lower dielectric constant, which leads to the formation of a protective film on the electrode surface [36]. Table 1 shows that the Warburg resistances (W_1) of the SS/P5AIn electrode are much higher than those for the SS electrode. The EIS results indicate that P5AIn is an effective anticorrosion coating for SS.

The electrode surfaces were imaged using SEM to determine if the corrosion inhibition was due to the formation of the film on the metal surface through adsorption. Fig. 6 shows SEM images of the SS and SS/P5AIn electrodes after a 96-h immersion in a 3.5% NaCl solution. The P5AIn coating (Fig. 6b) is compact and homogenous and its surface morphology is a cauliflower-like structure.

4. Conclusions

P5AIn was successfully coated onto SS surfaces using a potentiodynamic technique. The results indicated that after the two-stage procedure, the polymer film adhered to the steel surface. Corrosion tests showed that the polymer coating on the steel acted as a physical barrier to decrease the amount of corrosion on the SS surface. P5AIn has the potential to be used as a protective coating on SS for considerable time periods in chloride solutions.

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