

Role of a Chelating Agent in the Formation of Polyaniline Films on Aluminum

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ABSTRACT: A chelating agent, alizarin, was used to pretreat an aluminum surface before the electrochemical synthesis of polyaniline. Alizarin had two main effects on the process: (1) it suppressed the hydrogen evolution reaction and increased the current efficiency and (2) it stabilized the open-circuit potential in a corroding environment, such as in

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INTRODUCTION

In recent years, because of environmental concerns and health risks, an intensive search for a substitute for the chromate conversion coating of steels and aluminum has been underway. The Cr(IV) ion is almost impossible to immobilize in nature and has been listed as toxic and carcinogenic.¹

Many studies have been devoted to the corrosion protection of steels with conductive polymers. Among various conductive polymers, polyaniline (PAni) is preferred because of its stability in strongly acidic environments and its appropriate redox potential, which is located in the potential range corresponding to the passivation of stainless steels.^{2–4} PAni for corrosion protection has been synthesized on iron and mild steels by both chemical and electrochemical methods. Doped and undoped PAni have been found to provide protection for steel.^{2,5–10}

PAni has been prepared electrochemically in the form of films on carbon steels, mainly from aniline solutions containing oxalic acid.¹¹ Recent studies have shown that this conducting polymer is also effective in the protection of aluminum and aluminum alloy surfaces.^{12–14} Epstein et al.¹⁴ used the casting process to prepare films on Al 3003 and Al 2024-T3, and they observed a 10-fold reduction in the corrosion current compared to that of uncoated surfaces.

However, the electrodeposition of PAni on aluminum presents a serious problem in the form of hydrogen evolution, which takes place in the potential window where PAni polymerizes. The hydrogen evolution reaction on pure aluminum electrodes occurs between -2.0 and $+0.6$ V versus a saturated calomel electrode (SCE).¹⁵ This wide potential range accompanied by hydrogen evolution leads to low efficiency during the electropolymerization process if no previous surface modification has been performed. This results either in nonpolymerization or nonuniform film formation. Chelating agents have been used extensively in the pretreatment of metallic surfaces in the electroplating industry to produce decorative aluminum surfaces. In particular, alizarin has been used to treat stainless steel before the chemical application of a conductive polymer coating.^{8,9} Alizarin is a heterocyclic compound, also called 1,2-dihydroxyanthraquinone (Fig. 1), which forms alizarin chelates with metallic cations.

Depending on its nature (hydrophilic or hydrophobic), a chelating agent can lead to the passivation of the metal by salt formation, or it simply forms a blocking compound. Alizarin, as used in this investigation, is the hydrophobic type and, like many other heterocyclic chelating agents, may also form a polymeric complex on a nonnoble metallic surface.¹⁶

In this work, the effective role of alizarin as a chelating agent on the electropolymerization of aniline on pure aluminum was studied with 0.4M aniline in 0.5M H₂SO₄ and 0.12M aniline in 0.5M H₂C₂O₄. Stabilization of the open-circuit potentials of the PAni films by suppression of the hydrogen evolution reaction was also examined.

EXPERIMENTAL

Coupons of pure aluminum (area = 1 cm²) were isolated in acrylic resin. Specimens were mechanically

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polished with emery paper with 320–1200 grades, degreased in ethanol and dried at 40°C. After this first step to clean the aluminum surface, the specimens were dipped in a 1.3% aqueous solution of alizarin for 20 min and were then dried at 40°C.

Aniline (99.5%, Aldrich, Milwaukee, WI, ACS reagent) was previously distilled *in vacuo* at 155°C. The electrolyte consisted of 0.4M aniline dissolved in 0.5M H₂SO₄. Aqueous solutions were prepared with Milli-Q water. A single-compartment electrochemical cell was used with the aluminum coupons as the working electrode, a platinum plaque (2 × 2 cm) as the counter-electrode, and an SCE as the reference electrode. The electrodepositions of PANi were performed by cyclic voltammetry at 50 mV s⁻¹ between -0.2 and 0.8 V with a potentiostat 273A (EG&G/PARC, Gaithersburg, MD) controlled by M270/M352 software (cyclic voltammetry/corrosion software). The galvanostatic depositions were performed with 0.12M aniline dissolved in a 0.5M H₂C₂O₄ solution. The open-circuit potentials were recorded in 0.1M NaCl solutions. Scanning electron microscopy (SEM) was used to study the morphology of the films.

The adhesion of the PANi films on the aluminum surfaces was verified by a Sellotape test. To perform the test, we attached a special tape for testing the adherence of paints on the PANi film and peeled it off by force. We characterized the remaining underlying surface of the PANi after each removal by cycling the electrode in monomer-free electrolyte. Films were considered to have good adherence when they remained intact after two operations. To study the polymer structure deposited as a film, we carefully scratched the polymer from the aluminum substrate with a knife and submitted it to an undoping process by stirring it in 0.1M NaOH solution for 24 h to neutralize the acid in the polymer. The undoped polymer was then filtered and dried at 60°C *in vacuo* for 24 h. Dried PANi was triturated with KBr and pressed into a tablet. The infrared spectrum in the absorption mode was measured in a BOMEM MB102 Fourier transform infrared (FTIR) spectrometer (St.-Laurent, Quebec, Canada).

RESULTS

Role of the chelating agent in the hydrogen evolution reaction during deposition by cyclic voltammetry

The sequence of cyclic voltammograms in Figure 2 indicates the effective role of alizarin on the film

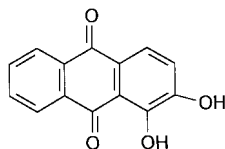


Figure 1 Structural formula of alizarin.

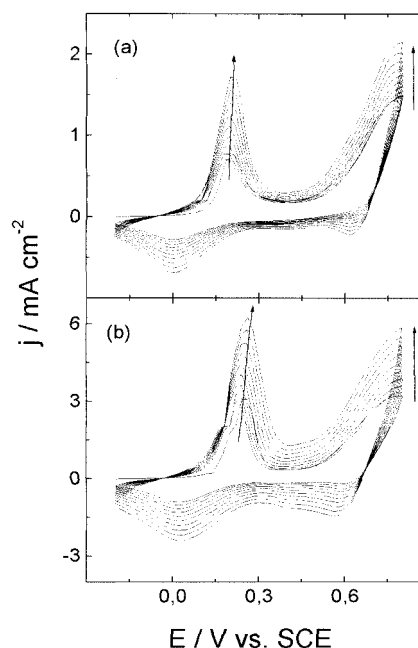


Figure 2 Cyclic voltammograms showing the last 10 cycles of 40 for the deposition of PANi on aluminum with 0.4M aniline in 0.5M H₂SO₄: (a) untreated and (b) treated in alizarin. Scan rate = 50 mV s⁻¹.

growth. This was marked by the peak height of the leucoemeraldine/emeraldine oxidation, in which the polymerization increased four times after alizarin pretreatment. The emeraldine formation peak attained 24 mA cm⁻² during deposition with 60 potential cycles; that is, it was 14 times higher than the deposition in Figure 2(a). The PANi degradation process to hydroquinone was absent during the deposition. Similarly, the overoxidation of the film by polarization to 0.8 V remained absent up to 60 cycles.

On the nonchelated surface, heavy hydrogen evolution was observed, and this effect visually disappeared after alizarin treatment. Therefore, alizarin acted as a surface blocker for the hydrogen evolution reaction. When hydrogen evolution was reduced to a minimum, the incubation time for the film growth was around 50 s. For example, during the deposition of PANi as shown in Figure 2, the film started to grow during the sixth cycle. For untreated electrodes with hydrogen coevolution, the induction time reached hours and even infinity, as indicated by an examination of the surface, which contained only polymer nuclei.

Role of the chelating agent in the hydrogen evolution reaction during galvanostatic deposition

The effect of chelation on the galvanostatic deposition of PANi on aluminum with 0.12M aniline dissolved in 0.5 M oxalic acid is presented in Figure 3(a,b). The deposition on nonchelated aluminum exclusively

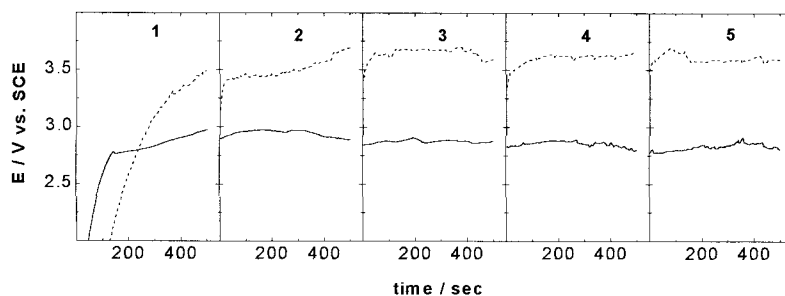


Figure 3 Galvanostatic deposition of PANi on aluminum (a) without and (b) after pretreatment with alizarin. The electrolyte was 0.12M aniline in 0.5M oxalic acid, and five depositions of 1 mA cm^{-2} for 500 s were performed.

showed copious hydrogen evolution, forming bubbles distributed on the entire surface; that is, no film was deposited on the aluminum even after five depositions for 500 s, and the surface presented only nuclei on the surface. During the first run, a potential peak that could be attributed to nucleation was observed at around 2.8 V followed by hydrogen bubble formation. By contrast, on alizarin-pretreated aluminum, PANi deposited immediately during the first deposition for 500 s. During the second galvanostatic run, a closed film was formed.

Similarly, the potential level, established at an alizarin treated specimen, was around 0.8 V higher than that for the nontreated electrode. This was attributed to the electropolymerization process. Depending on surface preparation and chelation, a major part of the hydrogen evolution could be suppressed by alizarin, and the film growth was not much hindered. A compact coverage of the electrode was then attained, and the resulting material could be used as a corrosion protection coating for aluminum in an aqueous environment.

Figure 4 displays schematically the aluminum surface before and after five successive galvanostatic dep-

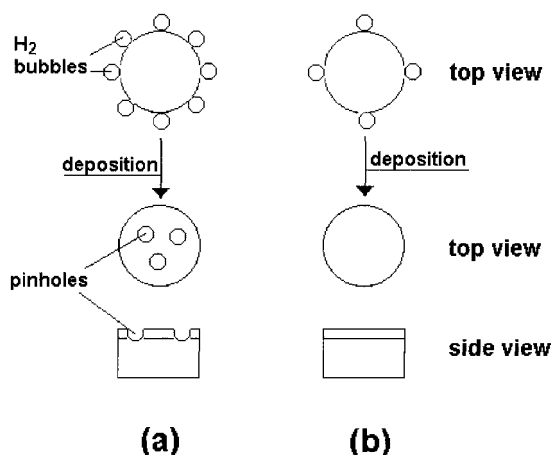


Figure 4 Observation of the aluminum surface by hydrogen evolution during the electrodeposition of PANi on (a) nontreated and (b) alizarin-treated surfaces.

ositions for the unchelated and chelated aluminum surfaces. Only the previously chelated surface led to the formation of a compact PANi film. The nonchelated surface was not completely covered by the PANi film, and the deposit contained pinholes.

To better observe hydrogen gas evolution, we prepared an artificial scratch on the aluminum surface with a knife on replicate specimens. One replicate sample was used for deposition in the freshly scratched state, and the second sample was treated in alizarin before deposition. Large amounts of hydrogen bubbles formed over the freshly prepared scratch in comparison to the alinarized one. The alinarized scratch became covered with PANi more rapidly than the nonalinarized one. This behavior was better observed on an aluminum wire electrode, in which a H_2 bubble was only observed on the tip of the freshly cut wire.

IR spectrum of PANi

Figure 5 shows the IR spectrum of undoped PANi, which was prepared by cyclic voltammetry with 0.4M aniline in 0.5M H_2SO_4 . Characteristic bands at 1578

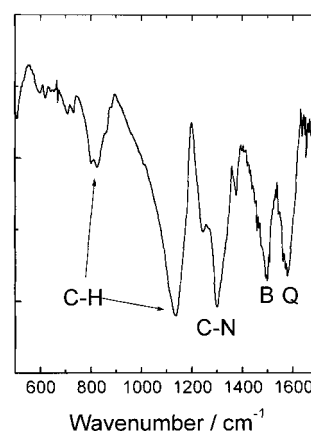


Figure 5 FTIR spectra of PANi deposited on aluminum by cyclic voltammetry with 0.4M aniline in 0.5M H_2SO_4 . The electrodeposited PANi was removed from the film and undoped in a 0.1M NH_4OH solution.

and 1496 cm^{-1} corresponded to the quinoid (Q) and benzenoid (B) rings, respectively. The bands at 1300 , 1138 , and 828 cm^{-1} corresponded to vibrations of the C—N bonds in the Q and B rings and to C—H bending in-plane and out-of-plane, respectively. These peaks were in agreement with the characteristic peaks of PANi reported in the literature.¹⁷ A B/Q ratio of 0.970 (ca. 1) indicated that the polymer was in the emeraldine base form, which theoretically contained the same number of both B and Q units.

SEM

Figure 6 shows the surface structure of PANi deposits grown on aluminum by cyclic voltammetry for different times. The films showed differences in morphology. The thin film prepared with 20 cycles of deposition was uniform. After 40 cycles, a second thick film started to form, which completely covered the electrode after 60 cycles. The structure of this outer layer was spongy.

Role of alizarin in stabilizing the open-circuit potentials

Another important result was the effect of alizarin in the stabilization of the open-circuit potential, as shown in Figure 7. The open-circuit potential of untreated aluminum was used for comparison. When gas evolution was suppressed by the alizarin complex, the open-circuit potential tended to be stable. Because the film obtained after 20 cycles contained small pinholes that were exposed to solution and penetrated into the aluminum substrate, the open-circuit potential was influenced by the hydrogen evolution in the pinholes, shown in Figure 7 as two hills between 1600 and 2400 s.

DISCUSSION

Alizarin probably has the ability to chemically bind the metal substrate and the PANi coating. According to

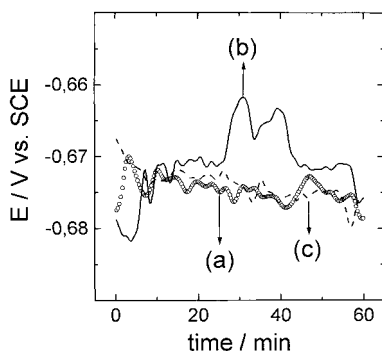


Figure 6 SEM micrographs of PANi obtained on aluminum with 0.4M aniline in 0.5M H_2SO_4 (a) after 20, (b) 40, and (c) 60 cycles.

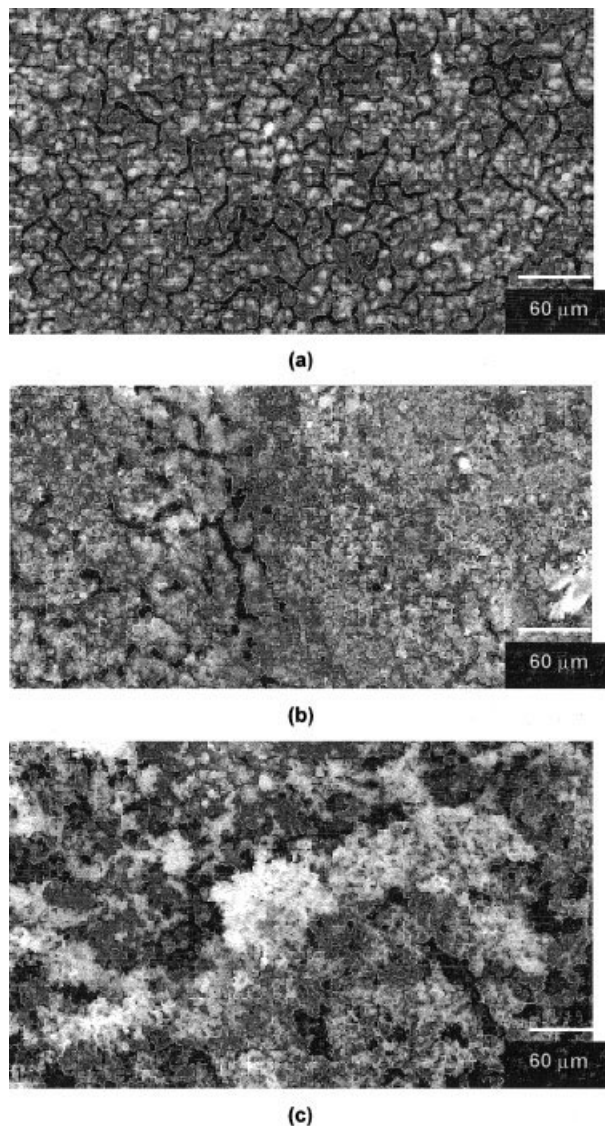


Figure 7 Open-circuit potentials of PANi-covered aluminum grown by cyclic voltammetry to 20 cycles on untreated and treated in alizarin substrates in 0.1M NaCl and open to the air.

the model proposed by Ahmad and MacDiarmid⁸ for iron, alizarin is supposed to form more than one coordinate bond with a metal. A two-branch alizarin bond to an aluminum cation is shown in Figure 8.

A critical point during electropolymerization was the formation of bubbles on the surface. When the surface was not pretreated with alizarin, big bubbles remained on the whole surrounding areas of the electrode, inhibiting the formation of a PANi film. For corrosion performance studies, those substrate-incongruent coatings, as schematically shown in Figure 4, were not suitable because of the formation of galvanic pairs between PANi and the bare aluminum.

In the solution containing aniline dissolved in oxalic acid, passivation by the oxalate and electropolymerization competed against each other. Therefore, an

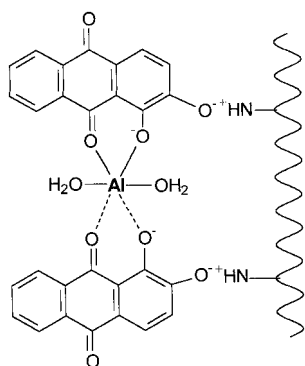


Figure 8 Model representation of the chelated aluminum cation bonded to the PANi chain.

appropriate surface preparation and a pretreatment with a chelating agent were important to the acceleration of the electropolymerization before preferential passivation by the formation of oxalate film took place. In addition, polymerization did not occur on oxalated or phosphated aluminum surfaces.

CONCLUSIONS

1. A chelating agent suppressed hydrogen evolution and increased the current efficiency for the deposition of PANi, as indicated by the first oxidation peak, which characterized the leucoemeraldine/emeraldine oxidation.
2. The chelating agent stabilized the open-circuit potential of the film.

3. To prepare closed and adherent PANi coatings on aluminum for corrosion protection, the deposition from oxalic acid solution was found to be the most effective. Thin films between 10 and 50 μm thick had good adherence, as confirmed by the Sellotape test, and would be convenient for corrosion protection studies.

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