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Aspects of polyaniline electrodeposition on aluminium

Received: 17 February 2004 / Accepted: 4 July 2004 / Published online: 2 September 2004
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Abstract Electrodeposition of polyaniline (PAni) from acid solutions on spontaneous passivating electrodes such as Al is not so obvious as on active metals (Fe and Ni). The methods that can result in deposition are: (1) surface pre-treatment with a chelating agent (alizarin) to block the hydrogen evolution reaction on aluminium and (2) a suitable monomer concentration (critical monomer concentration) to decrease the polymerisation induction time. The oxidation of aluminium to thick porous film limits the growth kinetics of PAni during deposition by cyclic voltammetry. We found that after reducing hydrogen evolution by surface chelation, for film growing in 0.5 M H₂SO₄ a concentration of 0.4 M aniline is required.

Keywords Aluminium · Polyaniline · Chelating agent · Monomer concentration · Electrochemical synthesis

Introduction

The deposition of conducting polymers on spontaneously passivating metals such as titanium, lead and aluminium usually requires a pre-treatment of the substrate, because natural oxides, which protect the active surface, cover them. In the particular, on aluminium the hydrogen evolution reaction (HER) occurs between –2.0 and +0.6 V versus a saturated calomel electrode (SCE) that covers both the cathodic and anodic potential region of the metal [1]. This wide potential range accompanied by HER leads to a low efficiency in the electropolymerisation, resulting either in non-polymerisation or non-uniform film formation.

Polyaniline (PAni) can be easily formed on conductive oxide films of iron group metals without additional pre-treatment. On the other hand, the polymerisation on insulating oxides results in either non-deposition or formation of few conglomerated centers. Abalyaeva et al. [2] studied the electrosynthesis of PAni from sulphuric acid solutions. The authors paid special attention to the electrode pre-treatment consisting of anodic passivation and use of catalytic initiator, hexachloroiridic acid or its salts in the electrolyte, in order to reduce the induction time for the synthesis. It is almost impossible to synthesise PAni on thick compact alumina with high resistivity in the order of teraohms.

Chelating agents have been generally used in the pre-treatment of metallic surfaces in the electroplating industry in order to produce decorative aluminium surfaces. Depending on its nature, hydrophilic or hydrophobic, a chelating agent can lead to passivation of the metal by a salt or simply formation of a blocking compound. In particular, alizarin has been used to treat stainless steel before a chemical application of a conductive polymer coating [3, 4]. This chelating agent corresponds to the hydrophobic type and, like many other chelating agents, may also form a polymeric complex on a non-noble metallic surface [5].

Another aspect of polymer deposition on aluminium that has not been considered is the monomer concentration. Winand and co-workers pointed out that polypyrrole films cannot be formed in 0.1 M oxalic acid and 0.1 M pyrrole [6].

Much research work done on the corrosion inhibition properties of an electronically active coating such as PAni has focused on the protection of steels [4, 5, 6, 7, 8, 9, 10], while many fewer studies have been devoted to the protection of aluminium by PAni [11, 12, 13]. Tallman et al. [12] presented a review about the use of conducting polymers for corrosion control, paying special attention to the protection given by PAni to structural alloys for the aerospace industry, such as 2024-T3, 6061 and 7075. Conroy and Breslin [13] electrodeposited PAni from a tosylic acid solution containing aniline and

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observed that the electropolymerisation is strongly dependent on the applied potential and monomer concentration. Epstein and co-workers [14] reported high shifts of the corrosion potentials of the aluminium alloy 2024-T3 in 0.1 M NaCl solution with coating by drop-casting with emeraldine base, chemically synthesised (ca. 0.5 V vs SCE more noble than the bare alloy). Fujita and Hyland [15] coated PANi onto 5005 aluminium alloy pre-treated in various ways. The authors collected evidence about a chemical interaction between the coating and the metallic surface that varies with the pre-treatment of aluminium.

In the present study, results on the influence of the monomer concentration and the use of pre-treatment of the aluminium surface with alizarin are discussed. The main goal is to find the best conditions that lead to deposition of adherent PANi in acid solutions, paying special attention to the adhesion on the aluminium surface, along with possession of optimum properties for corrosion protection.

Materials and methods

Aluminium of the nominal composition 0.25 Si, 0.40 Fe, 0.05 Mg, 0.05 Mn, 0.05 Cu, 0.05 Zn, 0.03 Ti, 0.03 others, and the balance Al (according to ASTM-specification) was used. Aluminium coupons of 1 cm² surface area, with welded platinum wire as conductor, were embedded in acrylic resin leaving part of the wire free for electrical contact. After mechanically polishing with emery paper (320–1,200 grade) and degreasing with ethanol, the samples were dried at 40 °C. Following this first step to clean the aluminium surface, the specimens were dipped in a 1.3% aqueous solution of chelating agent, 1, 2-dihydroxiantraquinone (alizarin) for 20 min and then dried at 40 °C.

Aniline 99.5% (Aldrich, A.C.S. reagent) was previously distilled under vacuum at 155 °C. Electrolytic aqueous solutions consisted of 0.1–0.4 M aniline dissolved in 0.5 M H₂SO₄ (Mallinckrodt), prepared by using Milli-Q water (18 MΩ resistivity). A single-com-

partment electrochemical cell was used, having aluminium coupons as working electrode, a platinum plaque (2×2 cm²) as counter electrode and a SCE as reference. The electrodepositions of PANi were performed by cyclic voltammetry (CV) at 50 mV/s between –0.2 and +0.8 V versus the SCE using a potentiostat/galvanostat 273A (EG&G/PARC) controlled by the software M270/M352 (CV/corrosion software). The galvanostatic depositions were carried out using 0.5 M H₂C₂O₄ solution containing 0.12 M aniline.

CV in a monomer-free electrolyte was used to test the stability of PANi coatings. The open circuit potentials were recorded in 0.1 M NaCl solutions. Scanning electronic microscopy (SEM) was used to study the morphology of the films. The adhesion of the films on the aluminium coupons was verified by the Sellotape test, which consisted of applying with a thumbnail pressure over the entire surface area, which was removed by slow peeling with pulling back of the tape. The remaining underlying surface of PANi after each removal was characterised by cycling the electrode in monomer-free electrolyte. Films were considered to have good adherence when they remained intact after two operations.

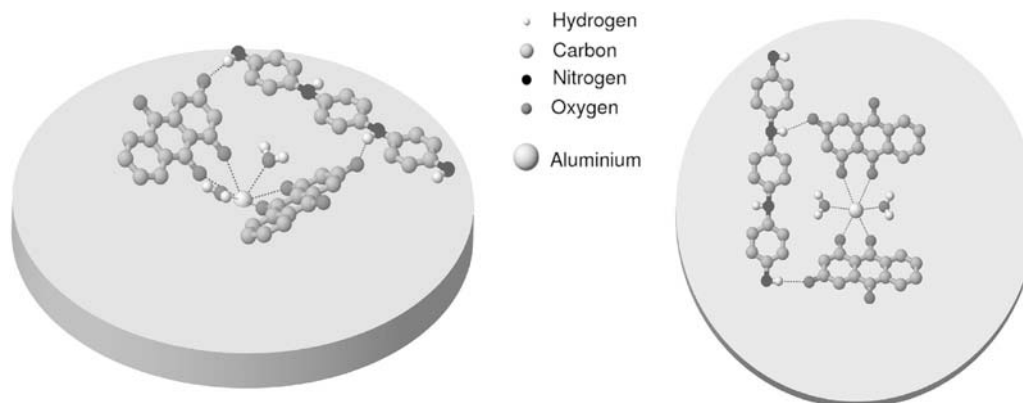
Results and discussion

The role of a chelating agent (alizarin)

Alizarin has the ability to bind chemically to the metal surface and the polyaniline coating. According to the model proposed by Ahmad and MacDiarmid for iron, alizarin is supposed to form more than one coordinate bond with a metal [3]. A two-branch alizarin bond to aluminium cation can be represented as in Fig. 1.

On HER during cyclic voltammetric deposition Figure 2 shows the 40th cyclic voltammogram corresponding to the PANi growth on aluminium with and without previous treatment with alizarin in the potential range of –0.2–0.8 V versus the SCE. Both cyclic voltammograms have the same two peaks corresponding to the oxidation of the polymer from the leucoemeraldine to the emeraldine redox state and from the emeraldine to the pernigraniline state. The effective role of alizarin on the film

Fig. 1 Model (two views) of a chelated aluminium cation bonded to the polyaniline chain



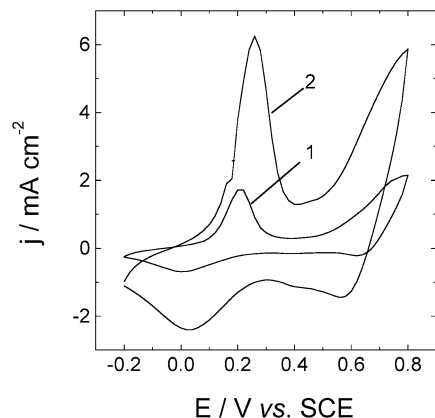


Fig. 2 Cyclic voltammograms recorded during the 40th potentiodynamic scan for deposition of polyaniline (PAni) on aluminium from a solution containing 0.4 M aniline and 0.5 M H_2SO_4 : at a scan rate of 50 mV s^{-1} . 1 Untreated aluminium surface, 2 aluminium surface treated with alizarin

growth is marked by the peak-height of leucoemeraldine/emeraldine oxidation, which increases three times when the surface is previously treated. The peak of emeraldine formation reached up to 24 mA cm^{-2} by deposition with 60 potential cycles, which is 14 times the oxidation peak height observed for the non-treated electrode.

The degradation process of the PAni to hydroquinone is absent during the deposition. Similarly, the overoxidation of the film by polarisation to 0.8 V remained absent up to the 60th cycle. On the non-chelated surface heavy hydrogen evolution was observed, and this effect visually disappeared by using the alizarin treatment. It can, therefore, be stated that alizarin acts as a surface blocker for HER. When hydrogen evolution is reduced to the minimum, the induction time for the film growth is around 50 s and the film already starts to grow during the sixth cycle. In the presence of hydrogen co-evolution that occurs at untreated electrodes, the induction times reach hours and even infinity, as indicated by the surface containing only nuclei over the whole area.

On HER during galvanostatic deposition The galvanostatic deposition of PAni on non-chelated aluminium from 0.12 M aniline dissolved in 0.5 M oxalic acid showed exclusive and copious hydrogen evolution,

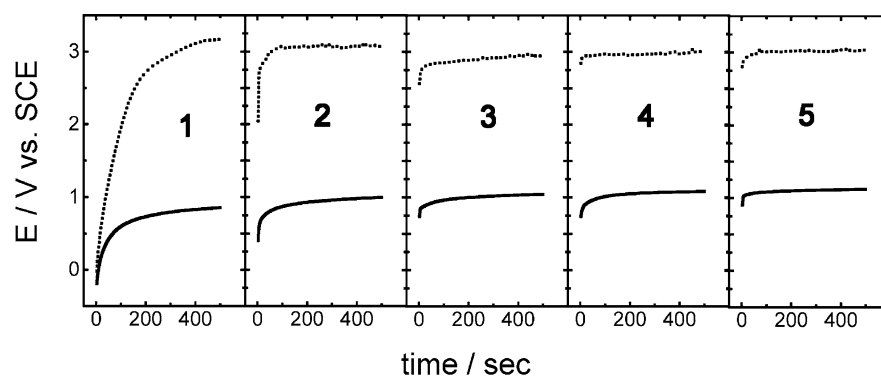
forming bubbles distributed over the entire surface, that is, no film was deposited on the aluminium even after five depositions for 500 s, and the surface presented solely nuclei. It is possible to observe from Fig. 3 that the potential increases during the deposition sequences on non-treated aluminium electrode, attaining steady-state values around 1.0 V that correspond to hydrogen bubble formation.

By contrast, on aluminium pre-treated with alizarin, PAni deposited immediately during the first deposition for 500 s. During the second galvanostatic run a dense film was formed. It was observed that the potential level established for alizarin treated specimens was between 1.9 and 2.2 V higher than at non-treated electrodes, which can be attributed to the electropolymerisation process. Depending on surface preparation and chelation, a great deal of hydrogen evolution can be suppressed by alizarin and the film growth is not much hindered. A compact coverage of the electrode is then attained and the resulting material can be used, for instance, for corrosion protection of aluminium in an aqueous environment.

The role of monomer concentration

When the monomer concentration is too small the induction time becomes too long, especially, for the deposition of PAni by CV. Figure 4 shows the influence of the monomer concentration on the film growth by CV. All CV plots are actually of 30 cycles' deposition. In Fig. 4a–c, where films are not growing, the cyclic voltammograms followed the same path after five cycles. The first oxidation peak during the deposition from 0.1–0.3 M aniline did not appear even after 30 cycles. However, in 0.4 M aniline solutions in 0.5 M H_2SO_4 , this oxidation peak leading to emeraldine followed immediately. The induction time for deposition in the range of 0.1–0.3 M of aniline in sulphuric acid solution is almost infinite. Conroy and Breslin [13] also observed that the delay period prior to the polymer formation is dependent on the applied potential and concentration of the monomer. From analysis of the high induction time situations, it seems evident that the conditions involved

Fig. 3 Galvanostatic deposition of polyaniline on aluminium without pre-treatment (solid lines) and after pre-treatment with alizarin (dashed lines). The aqueous electrolyte solution contained 0.12 M aniline and 0.5 M oxalic acid. Five depositions of 1 mA cm^{-2} for 500 s were performed and the number of each graph (1–5) indicates the deposition sequence



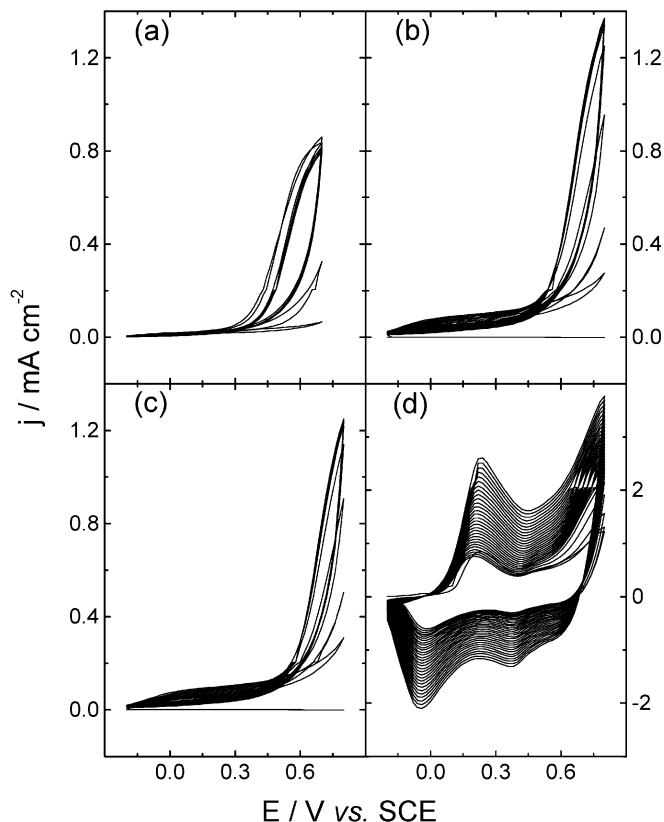


Fig. 4a–d Cyclic voltammograms of PANi deposition on aluminium from 0.5 M H₂SO₄ solution containing **a** 0.1, **b** 0.2, **c** 0.3 and **d** 0.4 M of aniline. Scan rate = 50 mV s⁻¹

generate a low concentration of radical cations, and consequently a slow rate of electropolymerisation.

It is important to note that polymerisation from 0.4 M aniline in 0.5 M H₂SO₄ takes place without any degradation, indicated by the absence of additional oxidation peaks between the two characteristic oxidation peaks of PANi.

Film growth Measuring the cathodic charge of the CV, Q_c , it is possible to monitor the film growth by CV-deposition. Another parameter extracted from the CV is the film growth rate taken as the average difference in charge between the preceding and following cycle number. The film growth on aluminium has been compared to that on platinum. The results for the cathodic charge obtained from the CV deposition on aluminium and on platinum are shown in Fig. 5, and the growth rates are shown in Fig. 6. Independent of the charge, the PANi film on platinum is 25 times thicker than that on aluminium after 20 cycles.

Assuming a 100% Faraday efficiency for the total consumed charge of 22 mC and taking a molecular weight of PANi as 53,000 g/mol with a density of 1.5 g/cm³, the deposited PANi film on 1 cm² aluminium reached a thickness of 8.06 μm. This value was near to that measured with optical microscopy, ca 10 μm.

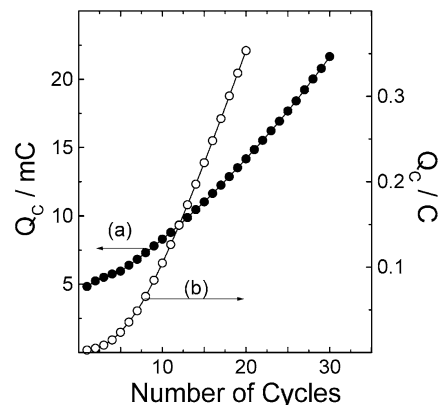


Fig. 5 Cathodic charge for PANi deposition from 0.4 M aniline in 0.5 M H₂SO₄ as a function of number of cycles on Al (a) and Pt (b)

The growth rates increase linearly with the number of cycles. Note that the growth rate on platinum is higher than on aluminium, as indicated by the larger slope. The growth rate on platinum is similar to the result obtained by Stilwell and Park for deposition from 0.328 M aniline in sulphuric acid [16]. On the other hand, the growth rate of PANi on aluminium shows a change in slope at ten deposition cycles, followed by film growth at a lower rate. This can be ascribed to a second outer porous film growing on the first compact film.

The polymerisation rate, dQ/dt , determined from Fig. 6, depends on the electrode surface, and from the calculated values, $(dQ/dt)_{Al} = 0.031 \text{ mC s}^{-1}$ for aluminium and $(dQ/dt)_{Pt} = 1.164 \text{ mC s}^{-1}$ for platinum, it can be concluded that the polymerisation rate on platinum was 37 times greater than on aluminium.

Stability of the film The performance of the electroactivity of those deposits during cycling in the monomer-free electrolyte is shown in Fig. 7. Arrows indicate a decrease in the oxidation and reduction peaks. Both deposited films show loss of activity in 0.5 M H₂SO₄, indicated by the decrease in the oxidation peak to emeraldine (A, A'). The thin film formed by 30 cycles of deposition is more stable than that formed by 40 cycles still showing the second oxidation peak.

Conclusions

In acid solutions, the polymerisation kinetics on aluminium depends on the passivation kinetics of aluminium. If the solution does not contain enough amount of monomer, it is almost impossible to grow a polymer film, because the very few nuclei formed remain very distant from each another on the surface. Therefore, an increase in the monomer concentration results in an increase in the number of nuclei that form very close to each other and the film starts to grow. It can be observed in Fig. 3d that the degradation of the polymer film does not occur, that is, the catalytic reaction of the oxidation

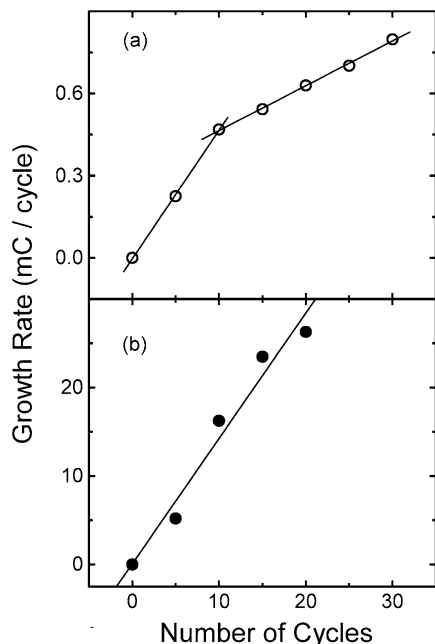


Fig. 6a, b Growth rate of PANi deposition from 0.4 M aniline in 0.5 M H_2SO_4 as a function of number of cycles on **a** Al and **b** Pt

of aniline is predominant. PANi deposition on inert electrodes such as platinum, gold or glassy carbon in sulphuric acid was affected by degradation [16], similarly

to the deposition on stainless steel in perchloric acid [7]. Even the deposits in propylene carbonate with lithium perchlorate and additions of di- and tri-chloroacetic acids were degraded [17]. It is probable that the high catalytic activity of platinum leads to parallel reactions of degradation that occur as discussed in the literature [18, 19].

Thin films prepared by CV of up to 30 cycles presented a little more adherence than those films having a porous outer layer. When the adherence was tested by Sellotape, the outer layer was removed and the first-formed thin layer remained.

In general, the stability tests of PANi films in monomer-free electrolyte showed a loss of electroactivity and an appearance of degradation peaks. This effect was less pronounced for the thin film.

It is noteworthy to stay that, depending on number of cycles by CV and/or time of deposition by potentiostatic and galvanostatic methods, a second compact layer is more prone to grow after drying the first one than growing in one stage for a longer time. This might be due to the low ability of the coagulated centers to grow because they contain soaked electrolyte.

Acknowledgements The financial support of FAPESP (Processes no. 99/11621-7 and 00/02674-9) is gratefully acknowledged.

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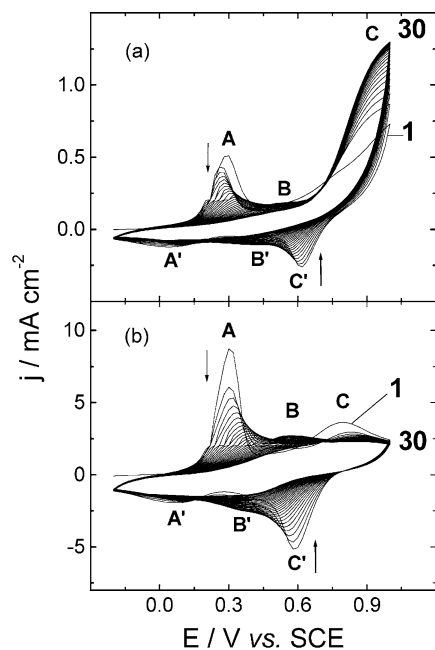


Fig. 7a, b Cyclic voltammograms of PANi in 0.5 M H_2SO_4 . PANi was deposited on Al, after superficial pre-treatment with alizarin, from 0.4 M aniline-containing electrolyte solution by **a** 30 and **b** 40 potential cycles. Scan rate = 50 mV s^{-1} . The first and last cycles are indicated on the corresponding curves. Arrows indicate the decrease of the oxidation and reduction peaks. Peaks: A, A' Oxidation to emeraldine; B, B' degradation process; C, C' oxidation to pernigraniline