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Characterization of polypyrrole films electrosynthesized onto titanium in the presence of sodium bis(2-ethylhexyl) sulfosuccinate (AOT)

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ABSTRACT

Films of polypyrrole (PPy) were successfully electrosynthesized onto titanium in neutral and alkaline solutions of sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT) by potentiodynamic, galvanostatic and potentiostatic techniques. Results of the characterization of the films by cyclic voltammetry, scanning electron microscopy (SEM) and adhesion measurements are presented. It was found that the AOT molecule remains entrapped within the polymer matrix. The initial growth of the polymer produces electroactive toroidal deposits whereas for electropolymerization of longer duration the typical globular structure is developed. Adherence to Ti increases with deposition time and this result is interpreted as a consequence of the growth of a composite PPy/Ti oxide.

1. Introduction

Titanium exhibits an excellent corrosion resistance for long periods in physiological fluids due to the spontaneous formation of a protective and stable oxide film. This property, plus its good biocompatibility and its mechanical resistance, make Ti the most important material for use in clinical applications.

On the other hand, the unique physical and chemical properties of various conducting polymers allow for a wide range of applications in the biological field such as their use in biosensors, tissue-engineering, neural probes, artificial muscles and drug delivery systems [1–4]. Electropolymerization offers the advantage of generating polymer coatings with controlled thickness on irregular surfaces. Polypyrrole is one of the most studied conducting polymers due to the ease with which the polymer may be electrosynthesized and the high stability and conductivity of the formed films. By selecting appropriate electropolymerization conditions, films with desired properties can be produced. Nowadays polypyrrole is considered as the most promising conducting polymer for biomedical applications due to its biocompatibility and corrosion protection properties [2,5].

One of the frequent problems connected with conducting polymers is adhesion. Unfortunately adherence between the polymer and the Ti-based material is not good enough for biological applications. Several pretreatments are described in the literature in order to improve adherence of PPy films electrosynthesized on Ti. One pretreatment involves oxidation of Ti in a boiling solution containing NH_3 and H_2O_2 [6], and another one involving a chemical etching in an alkaline peroxide solution has also been reported [7]. Authors assumed that one of the possible reasons of improved adhesion is an increase in the number of nucleation sites for electropolymerization. Another method to enhance adhesion of the coating to the substrate was through PPy deposition on different silanized Ti substrates [8]. The monolayer of silane-bearing pyrrole molecules in the surface was reported as the most suitable.

Previous results indicate that an AOT-containing solution is an effective electrolyte for obtaining conductive PPy films on Al, Fe and nickel–titanium alloy (Nitinol) without any preliminary treatment [9–11]. It was found that all the polymer coatings inhibit substrate corrosion in aggressive chloride media. The compound AOT, which is widely used for forming inverse micelles, is a bulky anionic surfactant with a sulfonate group in its polar head and two large and branching hydrocarbon tails (Fig. 1). The incorporation of a large and immobile anion like AOT conditions the ion-exchange behaviour of the polymer matrix. The AOT molecule plays the dual role of dopant and surfactant. Under the working conditions used in this work, the AOT concentration is above the critical micelle concentration (cmc) (2 mM in water). Therefore, the formation of aggregate structures on the electrode surface is expected.

In this study, results on the electropolymerization process of Py onto Ti in neutral and alkaline AOT solutions are presented and discussed. One of the aims of this study is to find the experimental conditions for obtaining an adherent coating. Other properties of the electrodeposited films such as morphology and redox behaviour are also analyzed.

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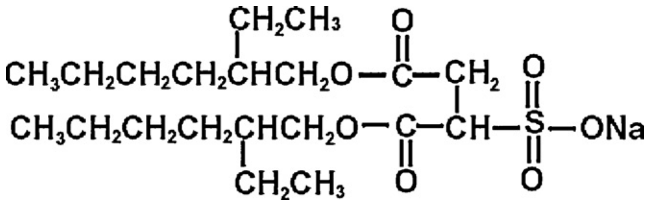

Fig. 1. Structural formula of sodium bis(2-ethylhexyl) sulfosuccinate (AOT).

2. Experimental

The electrode used in the experiments was a pure Ti rod (99.99%, Alfa Aesar) embedded in a Teflon holder with an exposed area of 0.070 cm^2. The exposed surface area was polished with 1000 emery paper, then degreased with acetone and cleaned with triply distilled water. After this, the electrode was immediately transferred to the electrochemical cell. All the potentials were measured against a saturated calomel electrode (SCE) and a platinum sheet was used as a counter electrode. The cell was a 20 cm^3 Metrohm measuring cell. Electrochemical measurements were carried out using a potentiostat–galvanostat PAR Model 273A. A dual stage ISI DS 130 SEM and an EDAX 9600 quantitative energy dispersive X-ray analyzer were used to characterize the synthesized film. Film adhesion was tested using the 3 M scotch tape.

Measurements were performed in neutral and alkaline solutions containing 0.25 M pyrrole (Py) and 0.05 M AOT in a purified nitrogen gas saturated atmosphere at 25 °C. The pH of the solution was adjusted by addition of NaOH. All chemicals were reagent grade and solutions were made in triply distilled water. The surfactant AOT was supplied from Alfa Aesar. In order to avoid the slow hydrolysis of AOT all the measurements were done with freshly prepared samples. Pyrrole was purchased from Sigma–Aldrich and it was freshly distilled under reduced pressure before use.

3. Results and discussion

3.1. Electrochemical synthesis

The voltammetric responses of Ti in a 0.05 M AOT solution of pH 7 and 12 with and without monomer addition are presented in Figs. 2 and 3. The response in the monomer-free pH 7 solution is the usual polarization behaviour of Ti [12,13]. That is, an active/transition process followed by an essentially potential-independent current. Oxidation in alkaline media occurs without a previous electrodissolution/precipitation step [14]. The potential-independent current is associated with passivation of Ti by a thin film that consists essentially of Ti(IV) oxide. It was reported that the passive current is independent of the solution anion and practically independent of solution pH for pH values higher than 4 [12]. In accordance with this, we found that the *i* vs. *E* curves presented in Figs. 2A and 3A are practically independent of the AOT concentration in the range 0.01–0.1 M. Moreover, the passive current measured in neutral media is practically the same as that observed in alkaline media (Figs. 2A and 3A). This can be explained by taking into account that the range of pH values considered here leads to the same thermodynamically stable species [15,16]. The cathodic polarization curve exhibits a peak in the hydrogen evolution potential range. It has been suggested that Ti(IV) oxide is partially reduced followed by its chemical dissolution during potential cycles in this potential zone [17]. Thus, the small anodic charge registered in the stabilized voltammogram at pH 7 is consistent with the replacement of the dissolved oxide. The stabilized response in alkaline medium indicates a more passive state.

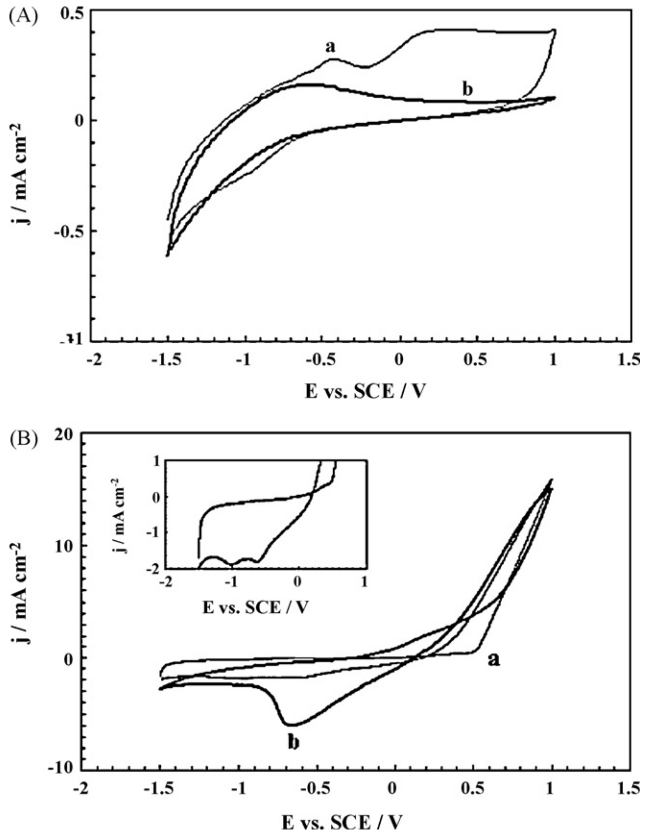

Fig. 2. Cyclic voltammograms obtained for a titanium electrode in a 0.05 M AOT, pH 7 solution: (A) without Py and (B) with 0.25 M Py. Small insert in (B): amplified zone of the first cycle. The first (curve a) and tenth (curve b) cycle are displayed. Scan rate: 0.05 V s^{-1}.

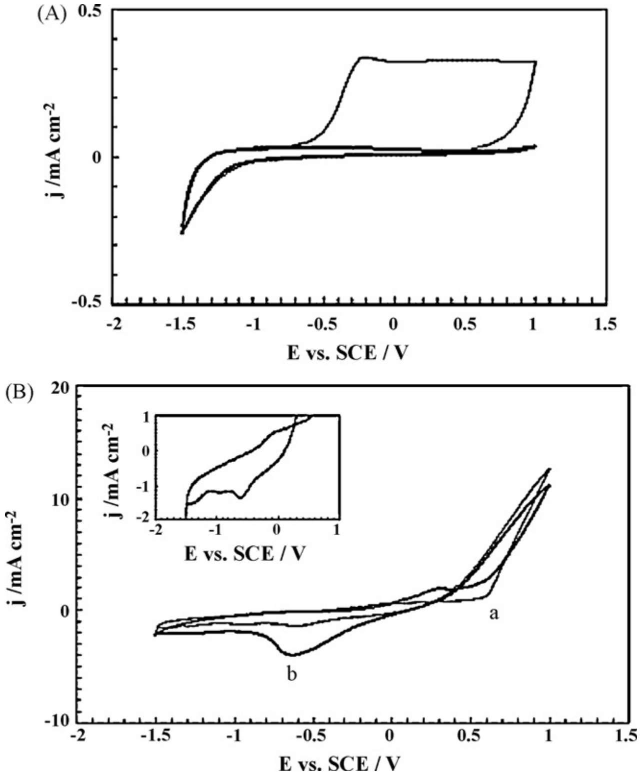

Fig. 3. Cyclic voltammograms obtained for a titanium electrode in a 0.05 M AOT, pH 12 solution: (A) without Py and (B) with 0.25 M Py. Small insert in (B): amplified zone of the first cycle. The first (curve a) and tenth (curve b) cycle are displayed. Scan rate: 0.05 V s^{-1}.

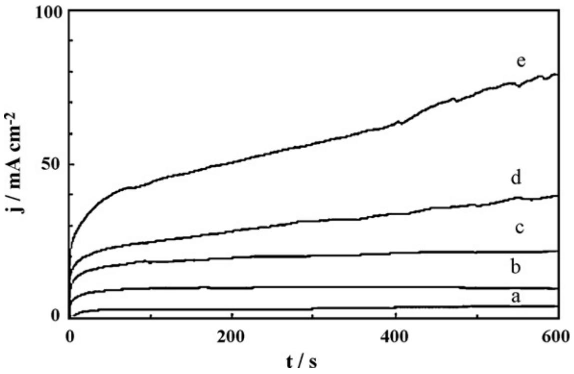

Fig. 4. Chronoamperometric curves obtained for a titanium electrode in a 0.05 M AOT, pH 7 solution containing 0.25 M Py, in response to a different potential step from 0.0 V to: (a) 0.5 V, (b) 0.7 V, (c) 0.9 V, (d) 1.1 V and (e) 1.3 V.

The first cycle of a freshly polished electrode in an AOT solution of pH 7 containing the monomer only presents a very small anodic current at the lower potentials, indicating that Py is adsorbed on the titanium surface and slows down its oxidation (insert in Fig. 2B). This is not observed in alkaline medium (insert in Fig. 3B) probably due to a competitive adsorption of OH^-. An increase in the anodic current is observed at about 0.6 V, which corresponds to Py oxidation. New oxidation–reduction waves associated with the redox process of the deposited polymer can also be observed. The absence of these waves in the cyclic voltammogram obtained in the monomer-free solution indicates that they cannot be related to the oxide film. At the end of the experiment, the formation of a black PPy film on the surface of the electrode could visually be observed.

Current–time transients recorded for different potential steps are shown in Figs. 4 and 5. There is an initial steep increase in current which is characteristic of a nucleation a growth mechanism. A current decay associated with the formation of the oxide layer was observed in the absence of the monomer. Thus, the electropolymerization process occurs almost instantaneously. A film thickness of 80 μm was estimated by SEM for the coating obtained at 0.9 V during 600 s (Fig. 6).

The polymer is not overoxidized under the conditions used in the present work (Figs. 4 and 5). The current density increased during potentiostatic electropolymerization even at 1.3 V and the resulting films exhibit redox activity. Similar results were obtained by other authors working with other substrates [18].

The electropolymerization current for the highest applied potentials decreases with solution pH. Since, as was earlier discussed, the stable species of Ti formed on the electrode surface are

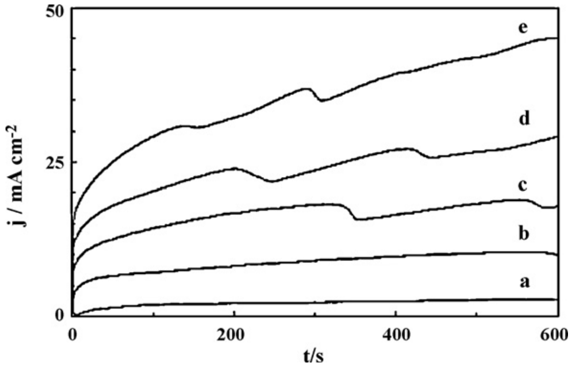

Fig. 5. Chronoamperometric curves obtained for a titanium electrode in a 0.05 M AOT, pH 12 solution containing 0.25 M Py, in response to a different potential step from 0.0 V to: (a) 0.5 V, (b) 0.7 V, (c) 0.9 V, (d) 1.1 V and (e) 1.3 V.

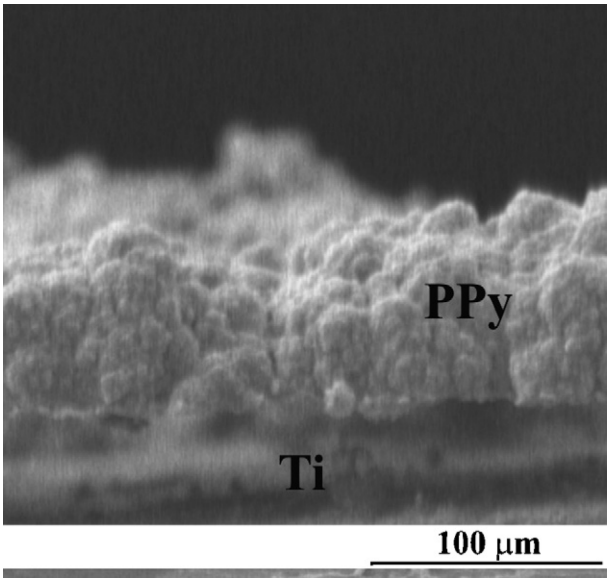

Fig. 6. SEM image of the PPy film potentiostatically formed at 0.9 V during 600 s onto a titanium electrode in a 0.05 M AOT, pH 7 solution containing 0.25 M Py.

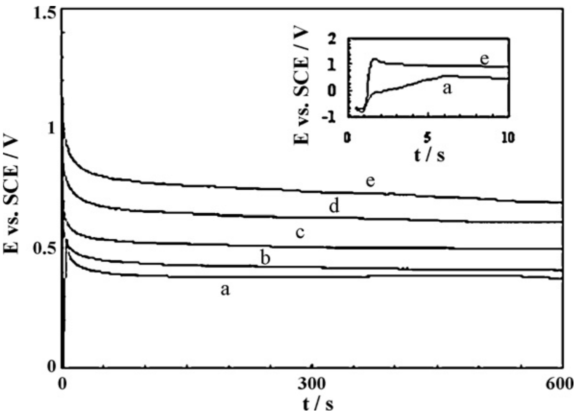

Fig. 7. Chronopotentiometric curves obtained for a titanium electrode in a 0.05 M AOT, pH 7 solution containing 0.25 M Py at different current densities: (a) 1 mA cm^{-2}, (b) 2.5 mA cm^{-2}, (c) 5 mA cm^{-2}, (d) 10 mA cm^{-2} (e) 15 mA cm^{-2}. Small insert: first stages of polarization at 1 and 15 mA cm^{-2}.

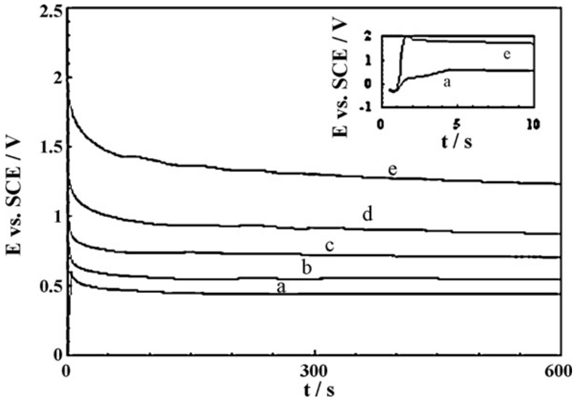

Fig. 8. Chronopotentiometric curves obtained for a titanium electrode in a 0.05 M AOT, pH 12 solution containing 0.25 M Py at different current densities: (a) 1 mA cm^{-2}, (b) 2.5 mA cm^{-2}, (c) 5 mA cm^{-2}, (d) 10 mA cm^{-2} and (e) 15 mA cm^{-2}. Small insert: first stages of polarization at 1 and 15 mA cm^{-2}.

the same in both solutions, the result can be explained by considering a decreased conjugation along the polymer backbone when the film is electrosynthesized in alkaline solutions [19]. It was proposed that the electrosynthesis in a solution of increased basicity results in PPy chains with an increased proportion of saturated C—C bridges and of fully unsaturated pyrrolic rings.

The constant current method was also used to electropolymerize Py (Figs. 7 and 8). The applied current density was varied from 1 to 15 mA cm^{-2}. In the absence of pyrrole the potential increased to values higher than 10 V leading to the growth of a blue-violet film, probably Ti_2O_3 or Ti_3O_5 [15]. The response obtained with Py for the lower applied current showed a slow potential increase in the first seconds which was related to the dissolution and passivation of Ti. During this time the insoluble oligomers concentration required to initiate polymer nucleation was reached. After this period the electrode potential attained a stable plateau associated with PPy electrodeposition. Deposition of the film also occurred on the substrate when the higher current densities were employed although in this case the potential was still slowly decaying at the end of the experiment.

3.2. Morphology of the PPy films

The evolution of the polymer morphology obtained at 0.9 V in a neutral solution was followed by SEM measurements (Fig. 9). In the initial stage toroidal deposits with a diameter of 1 μm are formed on the bare electrode surface (Fig. 9a). Preferential polymer growth on scratches produced during mechanical polishing is observed. With increasing deposition time toroids grow up to ca. 2.5 μm in diameter, the majority of them being oriented parallel to the electrode

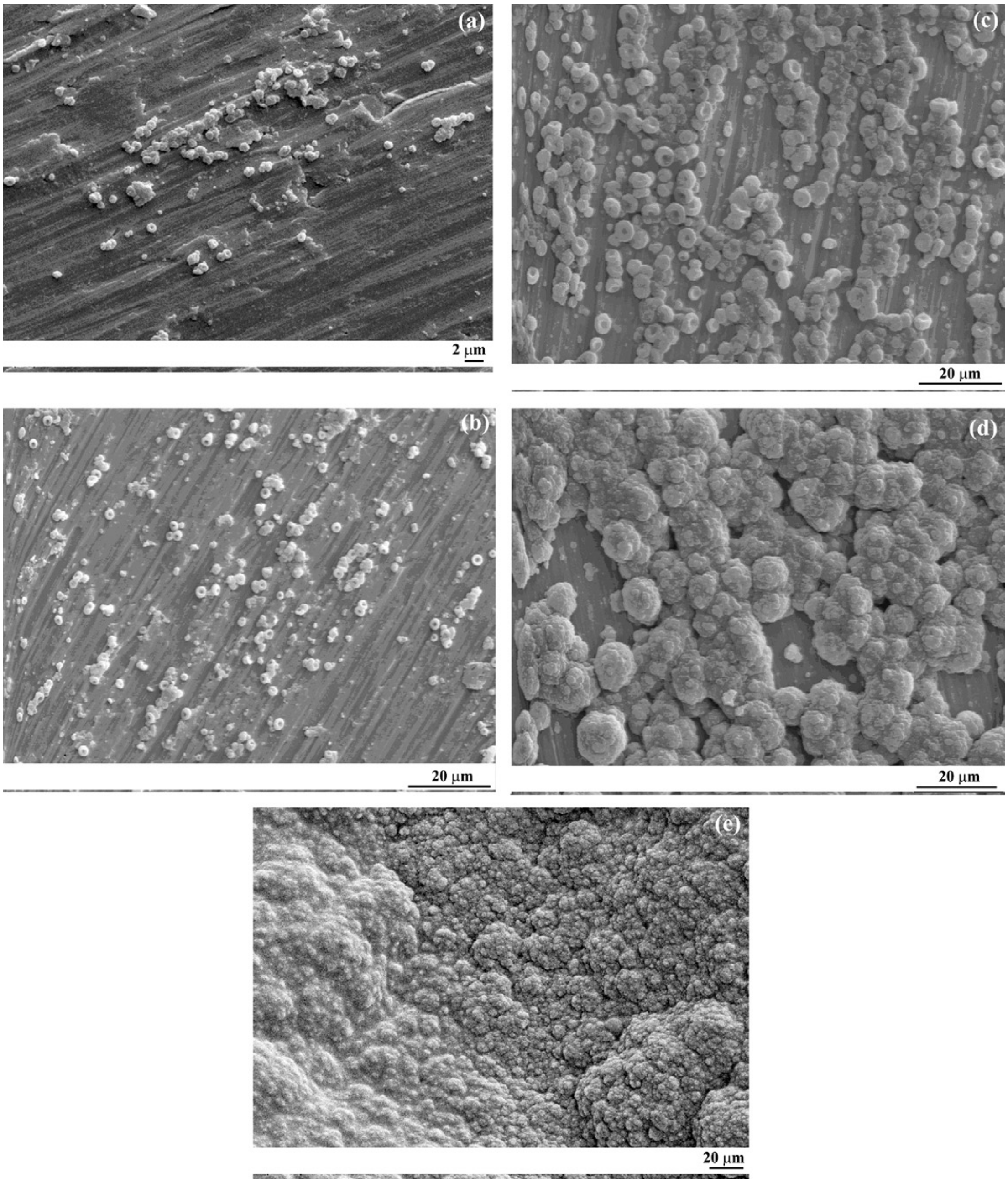

Fig. 9. SEM images of the PPy electrosynthesized onto titanium electrode in a 0.05 M AOT, pH 7 solution containing 0.25 M Py. The film was formed at 0.9 V for different times of polarization: (a) 1 s, (b) 5 s, (c) 25 s, (d) 45 s and (e) 600 s.

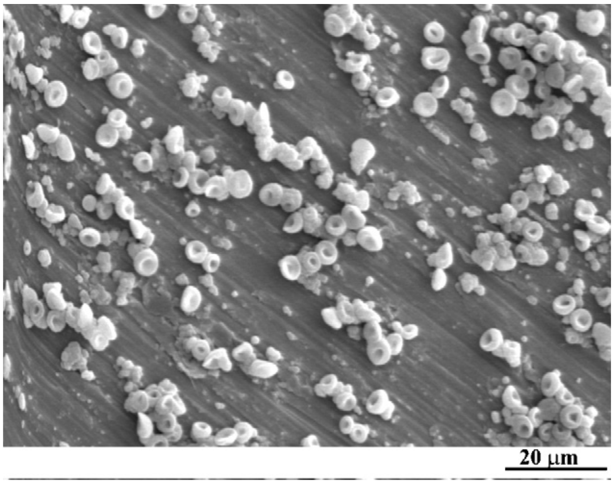

Fig. 10. SEM image of the PPy electrosynthesized onto titanium electrode in a 0.05 M AOT, pH 7 solution containing 0.25 M Py. The film was formed at 0.6 V for 45 s.

surface (Fig. 9b). The number of toroids also increases as electropolymerization advances. This means that structures already formed continue to grow simultaneously with the growth of new toroids. When the deposition time approaches 25 s the toroidal structures have a mean size of 4 μm (Fig. 9c). The electrode surface was covered almost completely after 45 s (Fig. 9d). The structures, with an average size of 7 μm, are fused to each other. It can be observed that at this time the hole of toroids is sealed by additional growth. Finally, as the polymerization proceeds further the polymer morphology conforms to the typical cauliflower structure (Fig. 9e).

SEM micrograph of the sample prepared in a neutral solution but at 0.6 V reveals the presence of toroids of the same size as those obtained at 0.9 V for 25 s (Fig. 10) (electropolymerization charges are the same). However, the amount of polymer deposited at the less positive potential is lower, probably due to the competitive growth of Ti oxide.

On average, toroids formed at pH 12 are more variable in size and shape than those synthesized in a neutral solution employing the same charge for deposition. The structures are more agglomerated and several of them appear as deformed toroids (Fig. 11).

When the polymer obtained after 300 s in neutral solution is peeled off, the SEM image of the coating side in contact with the electrode indicates that porosity of the film is very low.

Due to the great variety of synthesis conditions, a large variety of PPy morphologies was reported. Toroidal deposits of PPy were obtained on iron from an AOT solution, although in this case the structures grew after the initial formation of PPy grains [20]. This type of deposit has the potentiality of biomaterial immobilization on the surface [21] and particularly the possibility of its formation onto Ti materials may offer significant advantages in the field of biological applications. Although toroids are common for DNA and other biological macromolecules, there is no complete agreement about the mechanism of their growth. Polymer chain flexibility plays an important role in their formation [20].

3.3. Redox behaviour of the PPy films

The redox response in neutral and alkaline monomer-free solutions of Ti electrodes covered with PPy films deposited at different electropolymerization times are shown in Figs. 12 and 13, respectively. The oxidation and reduction charges are nearly equal. A reduction process appears at very negative potentials, which can be attributed to Na^+ insertion [22]. Thus, the obtained voltammetric curves seem to indicate that there is no release of AOT from the polymer during the negative sweep due to its large size and then cations are the dominant mobile species during switching.

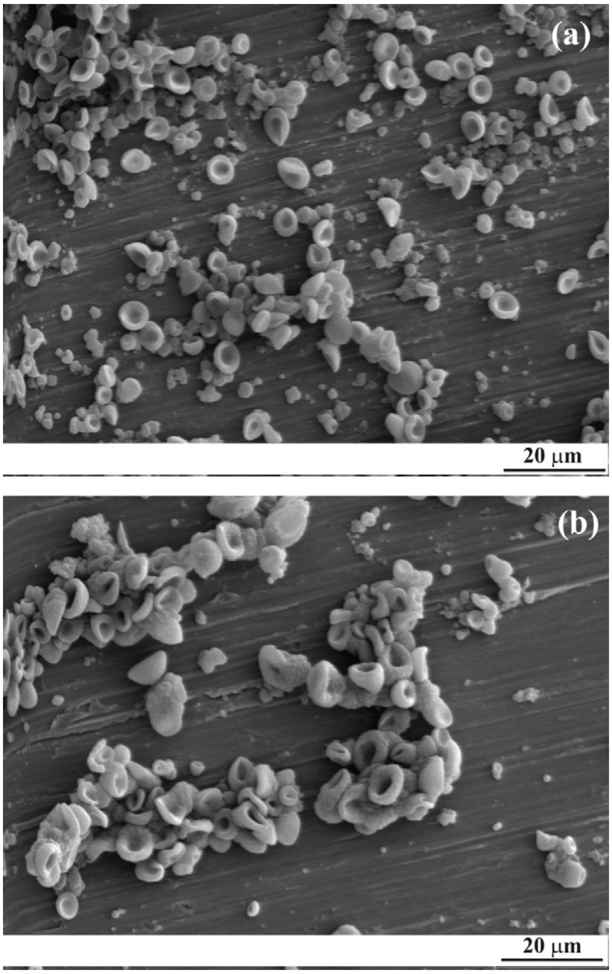

Fig. 11. SEM images of the PPy electrosynthesized onto titanium electrode in 0.05 M AOT, pH 12 solution containing 0.25 M Py. The film was formed: (a) at 0.6 V for 60 s and (b) at 0.9 V for 30 s.

In order to check that the AOT molecules remain entrapped within the polymer matrix, the covered electrode was also cycled in a chloride solution. The doping/undoping curve is presented in Fig. 14, curve a. For comparative purposes, the *i* vs. *E* profile corresponding to the film grown in the presence of a small anion (nitrate), but consuming the same electropolymerization charge, is also included (Fig. 14, curve b). In the latter curve it can be seen that the redox peaks associated with the release and incorporation of small anions into the polymer film occur at more positive potentials [23]. According to the literature [24–26], the shift of the redox peaks towards negative potentials (Fig. 14, curve a) is expected in the case of immobilized dopants, being the cation involved in the charge compensation.

It should be remarked that well-defined redox responses were obtained when toroidal-shaped structures were preferentially deposited on the Ti surface. This observation points out that these structures have good electroactivity. In addition, the ratio between the redox charge per cycle in the monomer-free solution and the charge used for polymerization is greater for the polymer formed at the first stages of electropolymerization (Fig. 15), although it should be taken into account that the substrate can have a significant contribution to the measured current at these stages.

Increasing the electropolymerization time resulted in an increased separation and broadness of the peaks in the cyclic

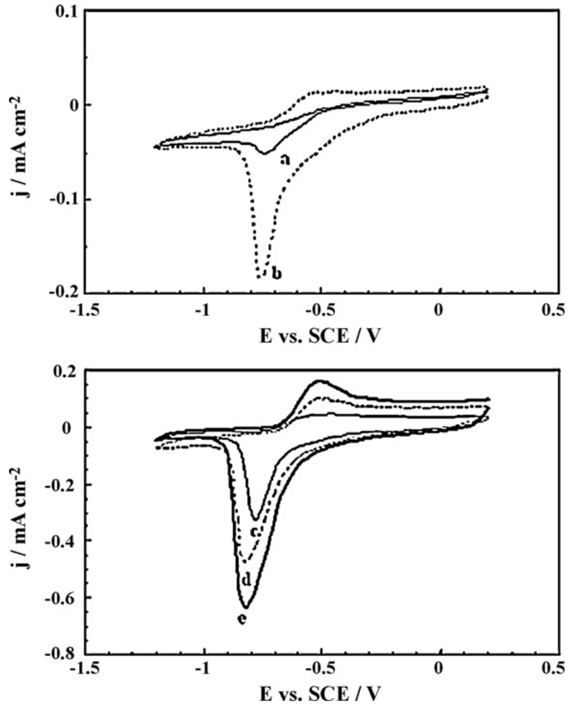

Fig. 12. Cyclic voltammograms of a PPy-covered titanium electrode at 0.001 V s^{-1} in a 0.05 M AOT, pH 7 solution. The PPy films were made potentiostatically at 0.9 V in the same solution containing 0.25 M Py for different polarization times: (a) 5 s, (b) 25 s, (c) 45 s, (d) 90 s and (e) 120 s; corresponding to charge densities of: 0.039, 0.321, 0.645, 1.435 and 1.984 C cm^{-2}, respectively.

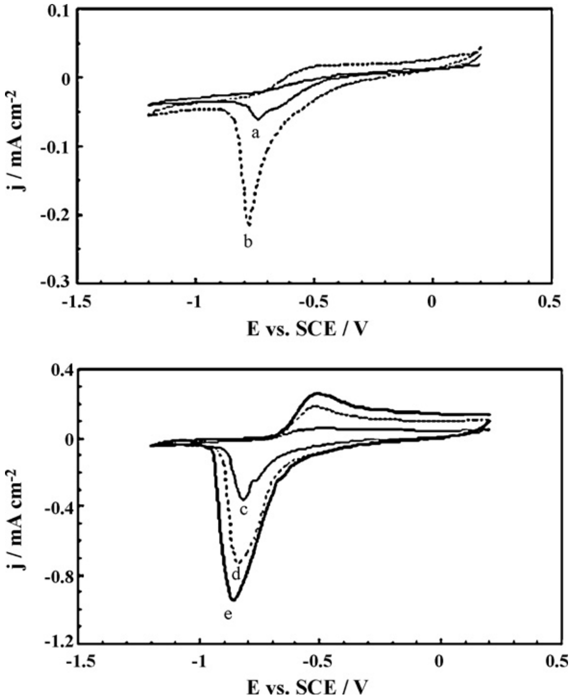

Fig. 13. Cyclic voltammograms of a PPy-covered titanium electrode at 0.001 V s^{-1} in 0.05 M AOT, pH 12 solution. The PPy films were made potentiostatically at 0.9 V in the same solution containing 0.25 M Py for different polarization times: (a) 5 s, (b) 25 s, (c) 45 s, (d) 90 s and (e) 120 s; corresponding to charge densities of: 0.029, 0.232, 0.467, 1.060 and 1.490 C cm^{-2}, respectively.

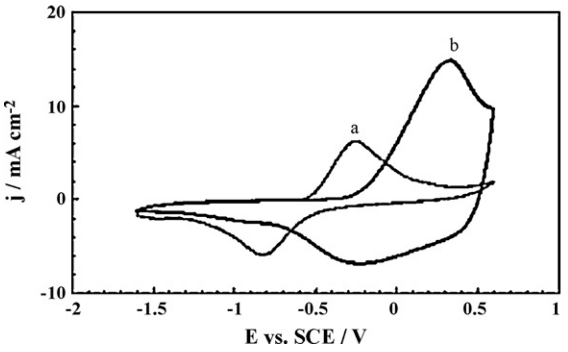

Fig. 14. Cyclic voltammograms of a PPy-covered titanium electrode at 0.05 V s^{-1} in a 0.15 M NaCl, pH 7 solution. The PPy films were made potentiostatically at 0.9 V during 60 s in a different solution containing 0.25 M Py: (a) 0.05 M AOT and (b) 0.05 M $NaNO_3$. The tenth cycle (stabilized) is displayed.

voltammograms. This indicates a higher migration resistance of ions and/or an increase in the value of ohmic drop due to oxide growth as the thickness of the film increases.

3.4. Adherence of the PPy films

Concerning the coating adherence, electropolymerization time plays an important role in the adhesion of the films for both, potentiostatic and galvanostatic methods. PPy films with poor adherence were obtained at 0.9 V for electropolymerization times shorter than 60 s. Under these conditions the electrode surface was not completely covered with the polymer film. But the percentage of the polymer that remained attached to the electrode increased with deposition time until no polymer was peeled off for 600 s. That is, the higher the deposition charge, the better its adhesion to the substrate. The coating synthesized for 600 s remains adherent even after potential cycling between −1.50 and 0.60 V in a monomer-free AOT solution.

Adhesion to the substrate also depends on the applied potential. Polypyrrole films were prepared at different potentials but employing the same charge consumed during deposition at 0.9 V for 600 s. In the case of electropolymerization at less positive potentials, i.e. 0.6 V, homogeneous films covered the substrate entirely but they were easily detached from the electrode. Adhesion was also poor when very positive potentials such as 1.3 V were used for electrosynthesis.

Under galvanostatic conditions, good adherent PPy films were obtained when current densities higher than 15 mA cm^{-2} were applied during 600 s.

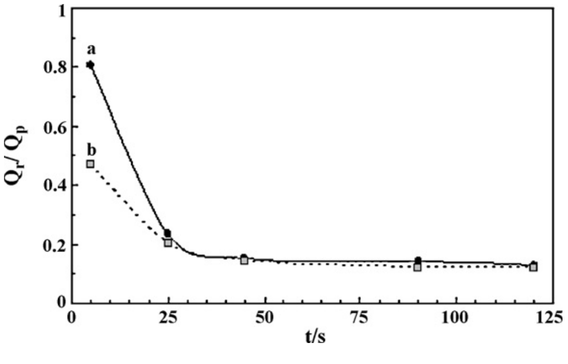

Fig. 15. Graph of the ratio between the redox charge per cycle in a monomer-free solution (Q_r) and the charge used for polymerization (Q_p) as a function of electropolymerization time. The films were obtained and cycled at different pH values: (a) 7 and (b) 12.

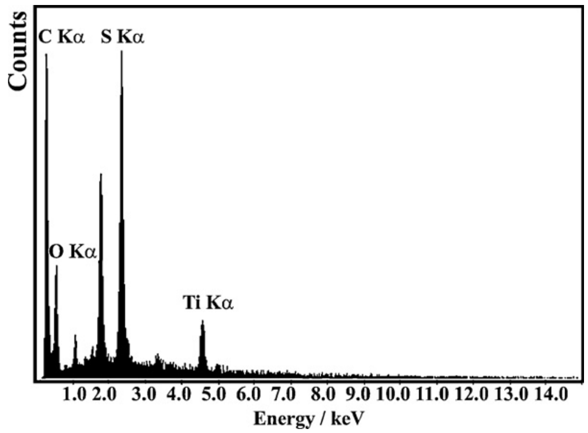

Fig. 16. EDAX analysis of the polymer cross-section in the bottom zone near the substrate surface (Fig. 6).

Table 1
Average atomic percentage of C and Ti obtained from the EDAX analysis.

Sample	C (at.%)	Ti (at.%)
Ppy film formed at 0.9 V during 120 s	34.78	0.79
Ppy film formed at 0.9 V during 600 s	24.69	3.41

Although uniform deposits were visually observed after potentiodynamic polarization, the scotch tape test was unsuccessful even for the films formed after 40 successive cycles.

In contrast with the polymer grown on Ti, the PPy film electrosynthesized on NiTi can easily be removed from the substrate, independently of thickness [11]. The PPy-coated electrode was submitted to an anodic polarization in a monomer-free solution in order to achieve adherent films.

It was proposed by Idla et al. [6] and later by Earley et al. [7] that an increase in the number of the nucleation sites for electropolymerization extends the substrate area that PPy is attached to, improving adhesion. It has been also proposed that surfactants improve the film-substrate adhesion [23,27]. It is expected that above the cmc, the monomer is solubilized and concentrated inside the micelle assembly formed on the electrode surface. As a consequence the presence of AOT allows a more homogeneous distribution of nucleus and a higher deposition rate of the polymer [23]. Improved adhesion is then expected. However, this is not enough to promote the formation of a very adherent coating onto Ti.

In an attempt to evaluate if the improvement in adhesion was due to a transformation of the passive oxide layer during polymerization, the electrode was first polarized at 0.9 V for 600 s in a monomer-free solution prior to electrosynthesis, and then PPy was deposited on the oxidized Ti surface. There was no observable increase in the adhesion of the polymer subsequently formed at the oxidized surface.

It was found that adhesion was lost when, after polymerization at 0.9 V for 600 s, the coated electrode was polarized at −0.8 V during 1800 s. At this potential, polymer and Ti oxide could be reduced.

EDAX analysis of the polymer cross-section in the bottom zone near the substrate surface is presented in Fig. 16. A Ti signal can be detected which would be indicative of the presence of titanium oxide. The percentage of elements (Table 1) reveals that the Ti content in this zone increases with electropolymerization time, while the C signal became smaller.

In the light of the above results, it is plausible to consider the growth of a composite structure PPy/TiO(IV) as was suggested by Idla et al. [6]. The development of this structure during electropolymerization would be responsible for the improved adhesion attained as the deposition charge increases.

4. Conclusions

In this work we show that it is possible to synthesize PPy films onto Ti from AOT solutions by employing different methods. Homogeneous PPy films can be formed on electrode surfaces covered by an oxide film in neutral and alkaline solutions. Electropolymerization efficiency is practically independent of solution pH. The AOT molecule remains immobilized in the polymer structure.

Considering the adherence of the films, the best results are obtained for the polymer synthesized at 0.9 V. Under this condition, adhesion of the films to the Ti surface increases with deposition time. While thin films are easily detached from the substrate, adherence to Ti is observed for electrodeposition times longer than 600 s. This behaviour is attributed to the development of a composite structure PPy/Ti oxide at the substrate/PPy interface.

The polymer morphology changes in time from toroidal-shaped structures to the typical globular PPy morphology. Optimal conditions for formation of toroidal deposits are found to be at neutral pH and an applied potential of 0.9 V. Toroids are electroactive and they are promising structures for further developments of clinical applications.

Acknowledgments

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