



Silver deposition on polypyrrole films electrosynthesized in salicylate solutions



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ARTICLE INFO

Article history:

Received 16 October 2012

Received in revised form 13 March 2013

Accepted 15 March 2013

Available online xxx

Keywords:

Silver

Polypyrrole

Electropolymerization

Salicylate

Antibacterial

ABSTRACT

This work is a study of the immobilization of silver species in polypyrrole films electrosynthesized in salicylate solutions. The obtained coatings were characterized by electrochemical and surface analysis techniques. It is proposed that the presence of salicylate in the polymer plays a crucial role in allowing the immobilization of silver species. The modified electrode presents antibacterial activity against Gram-positive bacteria *Staphylococcus aureus*.

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1. Introduction

The incorporation of silver species in different matrix has attracted great attention due to applications in several fields such as electrocatalysis [1], electroanalysis [2], medical devices [3] and SERS detection [4]. The antibacterial activity of silver ions is very well known but the unique properties of silver nanoparticles make them also useful in bactericide agents [5]. Silver nanoparticles in polymers can constitute effective antimicrobial biomaterials for a variety of promising applications [6]. It was postulated that nanoparticles release silver ions, which will have an additional contribution to the bactericidal effect of the silver nanoparticles [5]. The much better antimicrobial efficacy of the nanocomposites was explained by a more efficient silver release due to the larger surface to volume ratios and crystallographic surface structure of the silver nanoparticles [5,6]. Recently an explanation of toxicity based on Ag(0) oxidation and Ag⁺ release was proposed considering the lack of toxicity when silver nanoparticles were synthesized and tested under strictly anaerobic conditions [7].

Polypyrrole (PPy) has been found suitable to incorporate Ag. The polymer is particularly attractive due to its high stability,

relatively simple preparation in aqueous solutions and good biocompatibility [8]. The synthesis of several Ag-PPy composites has been reported. Two main processes can occur when the polymer matrix is in contact with a silver ions solution: silver ions uptake and/or silver ions reduction. Silver uptake was reported for PPy modified electrodes containing complexing or precipitating agents such as ethylenediamine tetra-acetic acid, 2,6-pyridine dicarboxylic acid and chloride [9]. Uptake of silver ions was also performed by employing PPy films doped with polyanions, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) and poly(2-hydroxy-4-*N*-methacrylamidobenzoic acid), which are complexing agents for these cations [10]. The formed films have antibacterial activity against the Gram-negative bacteria *Escherichia coli* and Gram-positive bacteria *Staphylococcus aureus*. Contrary to these results, it was reported that silver species could be extracted onto a PPy film with no incorporated precipitants or complexing ligands. The incorporation of silver species in the film can occur by a complex formation between silver ions and the amine groups present in PPy film [11].

With respect to silver ions reduction, in some works it was reported that the polymer should have certain properties in order to promote silver deposition. It was postulated that deposition of metallic Ag on a PPy matrix occurs as a result of an electroless reduction of silver ions at a reduced PPy film [11]. Silver species present at the oxidized film were found to be in the +1 valence state. A redox reaction between silver ions and PPy films dedoped

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in 0.5 M NaOH [12] or in 0.1 M ammonia [13] solutions has also been postulated. Aggregates of silver particles were observed in a PPy film loaded with silver ions upon light exposure [10]. In another work it has been postulated that the PPy is in the oxidized state after electropolymerization but a semi-oxidized state is developed under open circuit conditions [14]. This polymer can be further oxidized by Ag^+ in solution. Other works reported Ag deposition on non-pretreated PPy. It was postulated that metallic silver was deposited as a result of a redox reaction between nonoxidized segments of the polymer and the silver ions [15]. In this case a PPy powder synthesized in the presence of nitrate was impregnated in silver salt solution. It was also found that Ag nanoparticles were spontaneously adsorbed on the surface of PPy nanofibers when the polymeric material was in contact with a silver ions solution [16].

Our previous work on the electrodeposition of PPy has shown that hollow rectangular-sectioned microtubes can be generated by electropolymerization of pyrrole (Py) in aqueous solutions of salicylate (Sa) [17]. The anion acts as a dopant and as a promoter of the formation of the rectangular microtubes. In addition it plays an important role in protecting the steel surface from corrosion [18]. On the other hand Ag^+ was known to form a complex with Sa through an interaction with the carboxylate group [19,20]. Thus, the uptake of silver ions could be performed by the combination of the precipitation and/or complexation interactions due to the presence of these dopant ions in the polymer. The high specific area of these coated electrodes combined with antibacterial activity of silver species may envisage applications where bactericidal action is required. In the present paper we study the anchoring of silver ions by PPy films doped with salicylate as well as their antibacterial activity against the Gram positive bacteria *Staphylococcus aureus* (*S. aureus*), one of the most common pathogens isolated from tissue and the environment around implant infections.

2. Experimental

The electrode was prepared from stainless steel 316 L (SS 316 L) rod sample which was embedded in a Teflon holder with an exposed area of 0.070 cm^2 . Before each experiment, the exposed surface was abraded to a 1200 grit finish using SiC, then degreased with acetone and washed with triply distilled water. Following this pretreatment, the electrode was immediately transferred to the electrochemical cell. Potentials were measured against a Ag/AgCl (3M) electrode and a platinum sheet was used as a counter electrode. The aqueous solutions used for electropolymerization contain 0.25 M pyrrole (Py) and 0.5 M sodium salicylate (Sa), in a purified nitrogen gas saturated atmosphere at 25°C . Freshly prepared solutions of pyrrole (Sigma–Aldrich, distilled under reduced pressure) were used for each electropolymerization experiment. Electrosynthesis of PPy films on steel electrodes was carried out at 0.8 V. After deposition the electrode was intensively washed with distilled water and dipped in a 0.05 M AgNO_3 solution under dark conditions and open circuit potential during 2 or 5 h.

Electrochemical experiments were carried out with a potentiostat–galvanostat Autolab/PGSTAT128N. A dual stage ISI DS 130 SEM and an EDAX 9600 quantitative energy dispersive X-ray analyser were used to examine the electrode surface characteristics. X-ray diffraction (XRD) analysis was made using a Rigaku X-ray diffractometer (model D max III C) equipment, with CuK radiation and a graphite monochromator.

The antibacterial activity against the Gram-positive bacteria *S. aureus* was evaluated by a modified Kirby–Bauer technique [21]. The method was previously standardized by adjusting the microbial inoculation rate and the volume of the agar medium layer.

A freezing culture of *S. aureus* ATCC 25923 (stored at -70°C in Trypticase Soy Broth (TSB) (BK 046HA, Biokar Diagnostics, Beauvais,

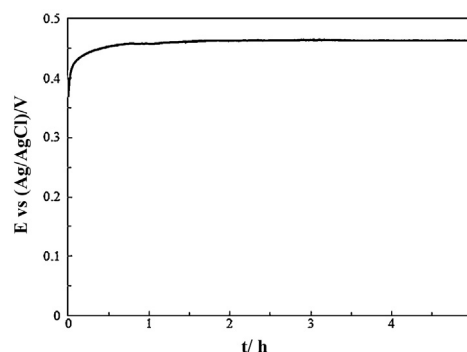


Fig. 1. Time dependence of the open circuit potential of a PPy-coated steel electrode in 0.05 M AgNO_3 . The polymer was synthesized at $E = 0.80 \text{ V}$ vs. Ag/AgCl for 600 s in 0.5 M Sa and 0.25 M Py.

France) supplemented with 20% (v/v) glycerol (Biopack, Argentina) was used. A loop of frozen cells was cultured in TSB during 24 h at 37°C . Upon appropriate dilution with sterilized phosphate buffer saline solution, a suspension of about 10^7 cells/mL was prepared. One milliliter of this suspension was mixed with 25 ml of Trypticase Soy Agar (BK, Biokar Diagnostics, Beauvais, France) melted and cooled at 43°C , and then, placed on a Petri dish. The coated electrodes were pressed onto bacteria-overlaid agar and were incubated at 37°C for 24 h. Then they were removed from the agar and placed in a fresh one. In order to determine the antibacterial performance this was done once a day during five consecutive days. The data were expressed as growth inhibitory zone diameter (mm) for three replicates [22]. Control tests employing unmodified PPy-coated electrodes were also performed.

3. Results and discussion

The PPy electrosynthesis was performed at 0.80 V during 600 s in a solution containing 0.50 M salicylate and 0.25 M pyrrole. The consumed charge was $10.00 \pm 0.01 \text{ C cm}^{-2}$. For each electropolymerization experiment we checked that the shape of the j - t curve has almost the same that the typical response obtained for micro-tube formation [17].

Then, the covered electrode was left in an AgNO_3 solution during 5 h under open circuit conditions. After 10 min of immersion the open circuit potential reaches 0.46 V which corresponds to the potential of the Ag^+/Ag -redox pair for a 0.05 M AgNO_3 solution (Fig. 1). In an attempt to evaluate the chemical state of silver in the coating, anodic and cathodic stripping sweeps starting at 0.46 V were recorded in 0.50 M Sa solution. The incorporation of metallic Ag is evidenced by the presence of a strong well-defined anodic peak at 0.50 V (Fig. 2, curve a), which is attributable to the oxidation of the deposited metal. No peak within this potential range is discerned when the polymer without incorporated silver was tested (Fig. 2, curve d). In this case a current rise associated with the overoxidation of the polymer and Sa oxidation is observed at more positive potentials. Analyzing the reduction process obtained after immersion in AgNO_3 solution, a new cathodic peak appears at 0.21 V which represents the reduction of silver ions (Fig. 2, curve b).

After immersion in the AgNO_3 solution the electrode surface appears silvery white at the macroscopic level. The deposit could only be removed by mechanical polishing. A SEM micrograph reveals the presence of rosette-like aggregates with a highly rough surface deposited on the PPy microtubes (Fig. 3). This type of morphology was recently reported for silver nanostructures synthesized by chemical reduction of AgNO_3 in aqueous solution [23]. EDX analysis indicates that the deposit was constituted by Ag particles (Fig. 4).

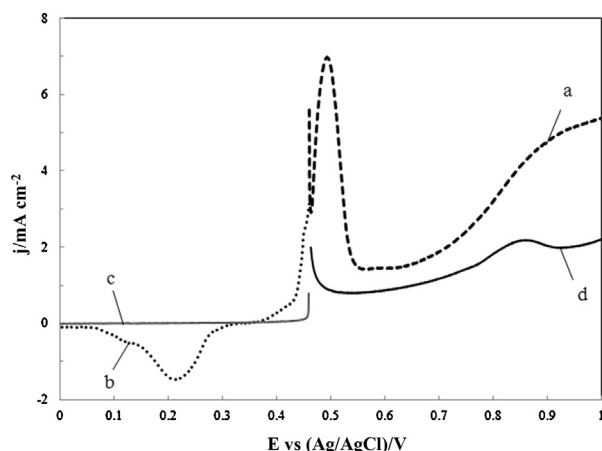


Fig. 2. Anodic and cathodic polarization curves registered in 0.5 M Sa at 0.001 V s⁻¹ for: (a) and (b) PPy-coated steel electrode after immersion during 5 h in AgNO₃ under open circuit conditions, (c) and (d) PPy-coated electrode. The polymer was synthesized at $E = 0.80$ V vs. Ag/AgCl for 600 s in 0.5 M Sa and 0.25 M Py.

The deposition of metallic silver was confirmed by XRD (Fig. 5). It was found that the polymer with rectangular morphology is amorphous [24,25]. Two intense diffraction peaks detected at 2θ values of 38.2° and 44.4° were observed corresponding to Bragg's reflections from the (1 1 1) and (2 0 0) planes of Ag [26]. The signal of salicylic acid was also detected at 29.07°.

One may raise the question about which is the oxidation reaction that occurs simultaneously with Ag⁺ ions reduction. Considering the porous structure of the polymer it is possible a displacement of silver from solution by iron which is itself oxidizing. This option was discarded because we found that silver was also deposited on hollow rectangular microtubes of PPy grown on a vitreous carbon electrode, proving that no influence can be attributed to the substrate.

No silver deposition was detected for those PPy coatings obtained by electropolymerization in nitrate solution with all other conditions remaining the same as those performed in salicylate solutions. It was reported a successful deposition of Ag on PPy doped with NO₃⁻ but when the film was previously conditioned under open circuit conditions in order to obtain a semi-oxidized polymer [14].

The morphology of the polymer electrosynthesized in Sa solution was shown to be Sa concentration dependent [27]. Preparing

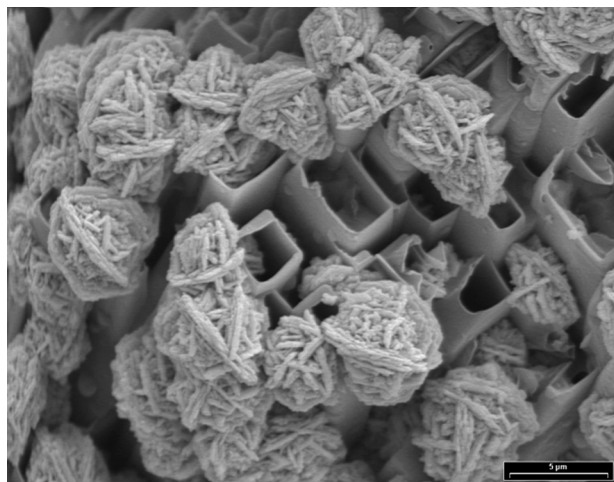


Fig. 3. SEM image of a PPy-coated steel electrode after immersion during 5 h in 0.05 M AgNO₃ under open circuit conditions. The film was formed potentiostatically at 0.8 V vs. Ag/AgCl during 600 s in 0.5 M salicylate solution containing 0.25 M Py.

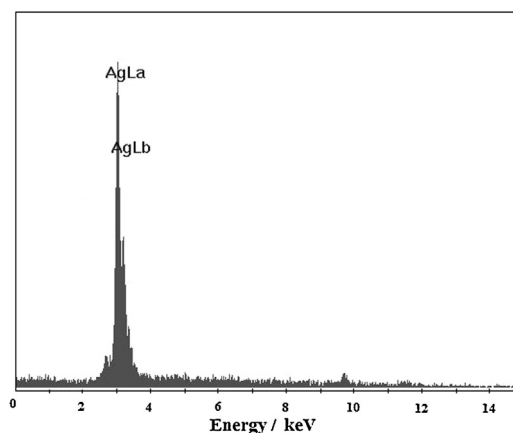


Fig. 4. EDX examination of a PPy-coated steel electrode after immersion during 5 h in 0.05 M AgNO₃ under open circuit conditions. The film was formed potentiostatically at 0.8 V vs. Ag/AgCl during 600 s in 0.5 M salicylate solution containing 0.25 M Py.

the PPy film in 0.1 M Sa solution results in the typical PPy globular morphology with a flatter surface. No silver deposits were observed when the steel electrode covered with this film was exposed to the AgNO₃ solution. The unsuccessful incorporation can be explained considering a decreased surface area of the polymer in contact with the AgNO₃ solution but also by considering a lesser amount of Sa anions available.

In order to check if Sa anions play a key role in the incorporation of Ag species in the coating, they were partially replaced by NO₃⁻ anions. The exchange was achieved by cycling the electrode potential between -1.00 and 0.60 V at 0.001 V s⁻¹ in a 1.0 M NaNO₃ solution. As a control experiment the covered electrode was subjected to cyclic voltammetry under the same experimental conditions but in a 0.50 M Sa solution. Two films with different electropolymerization charges were prepared (1.80 and 10.00 C cm⁻²). The waves in Fig. 6 are due to the switching between the oxidized and neutral PPy forms [28]. When the PPy-coated electrode was transferred and potentiodynamically polarized in the NO₃⁻ solution, oxidation and reduction waves appear at more positive potentials (Fig. 6, curve a). This redox couple is associated with the exchange of nitrate. Finally the prepared samples were dipped into the AgNO₃ solution and later polarized in a Sa solution. For the thicker film cycled in Sa, the peak associated with Ag oxidation appears broader and placed at more positive potentials,

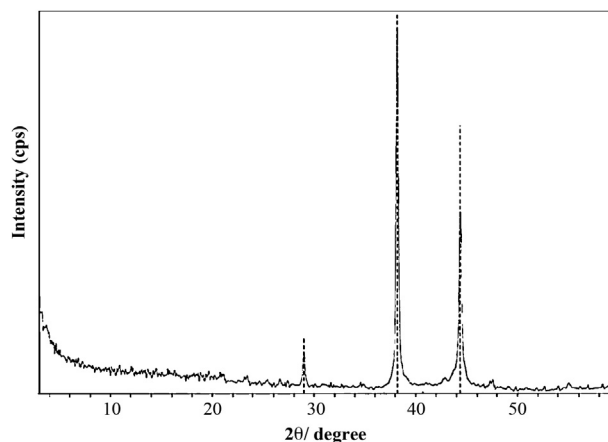


Fig. 5. X-ray spectra of a PPy-coated steel electrode after immersion during 5 h in 0.05 M AgNO₃ under open circuit conditions. The film was formed potentiostatically at 0.8 V vs. Ag/AgCl during 600 s in 0.5 M salicylate solution containing 0.25 M Py.

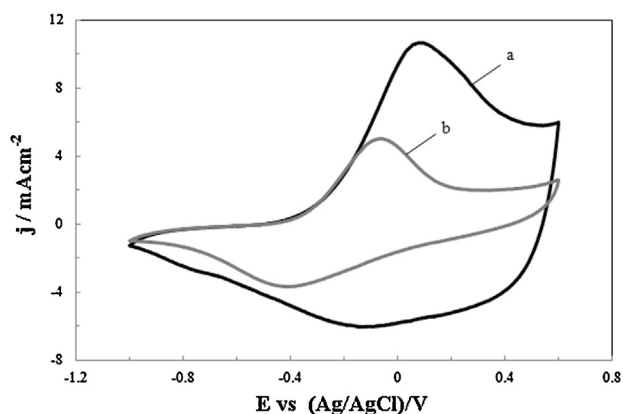


Fig. 6. Cyclic voltammograms of a PPy-covered steel electrode at 0.05 V s^{-1} in (a) 1 M NaNO_3 and (b) 0.5 M salicylate solution. The film was formed potentiostatically at $0.8 \text{ V vs. Ag/AgCl}$ during 120 s in 0.5 M salicylate solution containing 0.25 M Py . The 160th cycle is displayed.

being its charge more than fivefold higher than that cycled in NO_3^- (Fig. 7, curves a and c). When the PPy films were prepared with a lower electropolymerization charge the extent of anion exchange is expected to be higher. For the electrode subjected to potential cycles in Sa there was a decrease in the peak charge corresponding to Ag oxidation with respect to the thicker film (Fig. 7, curve b), whereas for the film cycled in NO_3^- there was no signal in this potential range (Fig. 7, curve d). The results demonstrate that the capacity of the film for immobilizing Ag species is strongly related to the presence of Sa anions.

Another possible oxidation reaction coupled to the Ag^+ reduction might be Sa oxidation, but this process is expected to start at more positive potentials. A linear potential scan was applied at 0.0001 V s^{-1} from 0 V in 0.50 M Sa solution using a bare stainless steel electrode as a substrate. The onset potential for Sa oxidation was observed at 0.65 V .

According to the obtained results the film not bearing Sa did not incorporate Ag species. Then, the anion plays a key role in the immobilization of silver species into the coating. It can be proposed that Ag^+ ions are concentrated in the film as a result of the interaction between Sa with Ag^+ . At the same time, NO_3^- ions of the

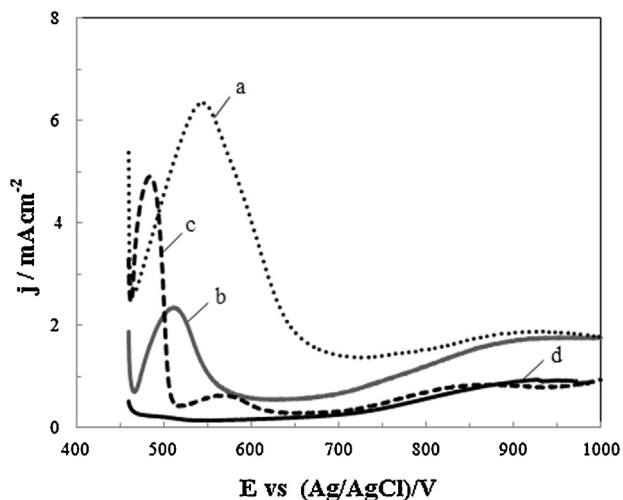


Fig. 7. Anodic polarization curves registered in 0.5 M Sa at 0.001 V s^{-1} for PPy-coated steel electrode after immersion during 5 h in 0.05 M AgNO_3 under open circuit conditions. The PPy films were formed at $0.8 \text{ V vs. Ag/AgCl}$ in 0.5 M salicylate solution containing 0.25 M Py during 600 s (curves a and c) and 120 s (curves b and d) and then were cycled in 0.5 M Sa (curves a and b) or in 1 M NaNO_3 solutions (curves c and d).

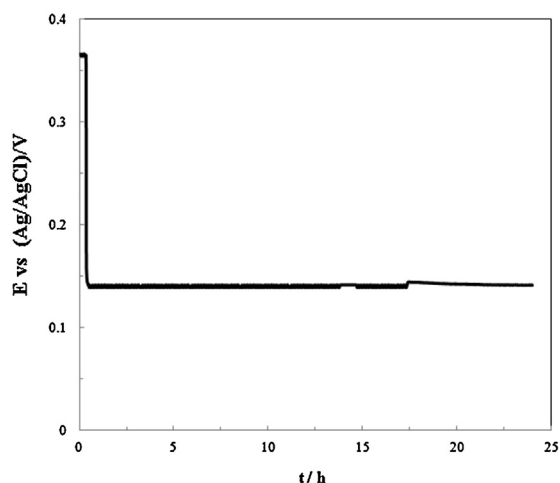


Fig. 8. Time dependence of the open circuit potential in Ringer's solution of the steel electrode covered with Ag-modified PPy. The polymer was synthesized at $E = 0.80 \text{ V vs. Ag/AgCl}$ for 600 s in 0.5 M Sa and 0.25 M Py and then was immersed during 5 h in 0.05 M AgNO_3 under open circuit conditions.

electrolyte are incorporated into the polymer matrix for maintaining charge neutrality. Metallic silver can be formed assuming a redox reaction between the polymer and silver ions which involves an interaction with nonoxidized segments within the polymer [15,29]. In other words, the role of Sa is to increase silver ions concentration at the PPy surface. Under these conditions the redox reaction between the nonoxidized segments of the polymer and silver ions anchored by Sa produces an increased amount of Ag particles.

With the purpose to check the stability of the coating, the steel electrode covered with Ag-modified PPy was left in Ringer solution at open circuit condition during 24 h . The potential is maintained at 0.38 V during the first 20 min and then declined to a value of 0.15 V (Fig. 8). This potential coincides with that measured for the substrate covered with PPy without Ag^0 species [18].

SEM examination after immersion shows that the polymer remains unaltered in the corrosive medium (Fig. 9). The EDX analysis of the deposits observed over the microtubes gave a Ag:Cl ratio of 3 indicating that the material is composed of a mixture of Ag and AgCl (Fig. 10). These results are consistent with the obtained X-ray

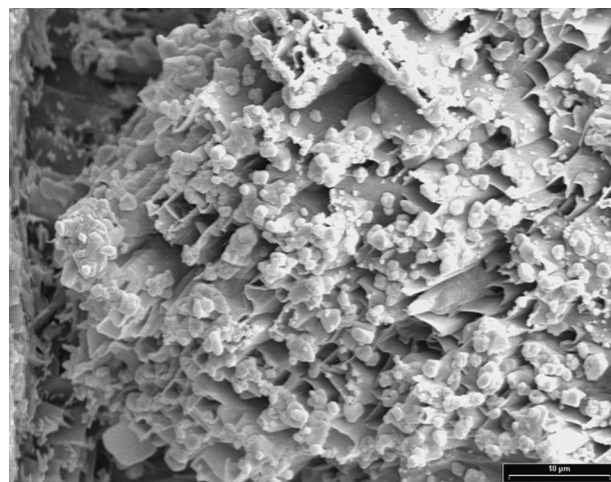


Fig. 9. SEM image of the steel electrode covered with Ag-modified PPy after immersion during 24 h in Ringer's solution under open circuit conditions. The film was formed potentiostatically at $0.8 \text{ V vs. Ag/AgCl}$ during 600 s in 0.5 M salicylate solution containing 0.25 M Py and then was immersed during 5 h in 0.05 M AgNO_3 under open circuit conditions.

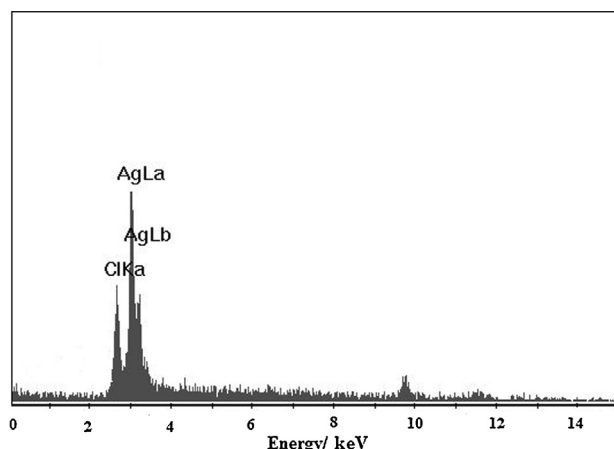


Fig. 10. EDX examination of the steel electrode covered with Ag-modified PPy after immersion during 24 h in Ringer's solution under open circuit conditions. The film was formed potentiostatically at 0.8 V vs. Ag/AgCl during 600 s in 0.5 M salicylate solution containing 0.25 M Py and then was immersed during 5 h in 0.05 M AgNO₃ under open circuit conditions.

spectrum of the sample after immersion in Ringer solution where the diffraction peaks related to Ag ($2\theta = 38.159$ and 44.326) and AgCl ($2\theta = 27.876$, 32.281 and 46.249) are observed (Fig. 11). Deposits morphology resembles that of AgCl-coated electrodes [30]. Then, it could be inferred that Ag particles were covered by AgCl after immersion in Ringer solution.

We investigated the antibacterial activity of immobilized silver against the Gram positive bacteria *S. aureus* by determine the width of the inhibition zone around the coated surfaces. Because it has been shown that salicylate itself has remarkable antibacterial activity and this inhibitory effect was found to be concentration dependent [31], PPy films electrosynthesized in 0.1 and 0.5 M Sa solutions were tested. The PPy film formed in 0.1 M Sa solution does not inhibit the growth of *S. aureus*, but an inhibition zone of 4 mm was observed in the case of the film formed in 0.5 M Sa solution. The results indicate that the inhibitory activity of coated electrodes is practically independent of the immersion time in the AgNO₃ solution during the coating preparation.

Table 1 shows the dimensions of the inhibition halos for steel electrodes covered with Ag-modified PPy measured during five consecutive days for two different dipping times in the AgNO₃

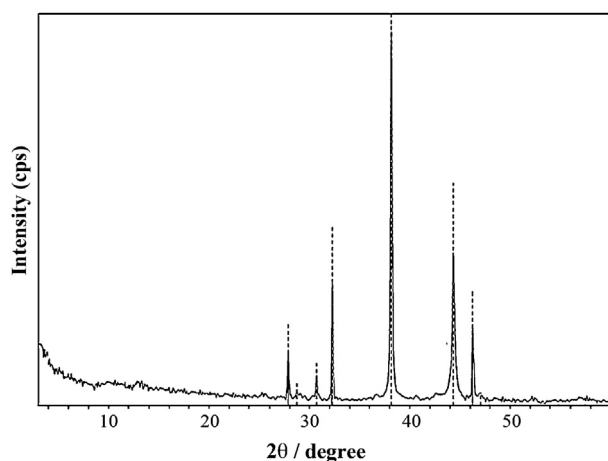


Fig. 11. X-ray spectra of the steel electrode covered with Ag-modified PPy after immersion during 24 h in Ringer's solution under open circuit conditions. The film was formed potentiostatically at 0.8 V vs. Ag/AgCl during 600 s in 0.5 M salicylate solution containing 0.25 M Py and then was immersed during 5 h in 0.05 M AgNO₃ under open circuit conditions.

Table 1

Average inhibition zones for steel electrodes covered with Ag-modified PPy pressed onto *Staphylococcus aureus*-overlaid agar and replicated to fresh cultures every 24 h for five consecutive days. First, the larger and then the smaller diameter are indicated. The immersion time in AgNO₃ was: 2 h (Ag-PPy 2 h) and 5 h (Ag-PPy 5 h).

	Incubation time (h)				
	24	48	72	96	120
Halo dimensions	13.5–10.0	13.0–9.0	11.5–7.0	10.0–6.5	10.0–6.5
Ag-PPy 2 h					
(mm) Ag-PPy 5 h	13.0–10.0	13.0–9.0	12.0–8.0	10.0–7.0	9.0–6.5

solution. Due to the shape of the samples, the major and minor diameters of the inhibition halos were measured. The presence of inhibition zones indicates the release of silver to the surrounding environment and subsequent antimicrobial effect, which was more pronounced than that produced by the PPy without silver species.

The antibacterial activity of Ag-PPy films could be explained by the penetration of the released Ag⁺ ions and colloid silver particles through the bacteria cell wall. Their complexation with enzymes in the cell membrane results in the inhibition of the enzymatic activity and the bacteria death [32].

The antibacterial capacity of these coatings was challenged by the daily exchange of nutrient medium. According to this, PPy matrices effectively allow Ag dissemination during for at least five consecutive days. These results allow us to envisage the applicability of the Ag-modified PPy coatings in biomedical applications.

4. Conclusions

The present work demonstrates that a PPy film doped with Sa is an effective substrate for Ag species immobilization. The high content of Sa in the hollow rectangular-sectioned microtubes of PPy allows Ag⁺ species to be concentrated at the polymer surface. Then these cations can be reduced while nonoxidized segments within the polymer are oxidized. Under these conditions deposits of metallic silver with an unusual morphology were observed, which present a highly rough surface. No secondary components which promote Ag⁺ reduction were needed to obtain silver deposits in the microtubes.

The modified polymer has good stability in Ringer solution and protects the substrate from corrosion. The high specific area of these silver coated electrodes combined with the very good performance of the coating toward inhibition of bacteria activity indicates that the composite is a promising material for biomedical applications.

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