



J. Serb. Chem. Soc. 87 (11) 1297–1311 (2022)
JSCS–5595

Corrosion protection properties of polypyrrole coatings formed onto 316 L SS from a solution containing molybdate and salicylate

CAMILA A. RAMOS¹, MARIA B. GONZÁLEZ^{1*}, LORENA I. BRUGNONI²
and SILVANA B. SAIDMAN¹

¹Chemical Engineering Department, Institute of Electrochemical and Corrosion Engineering, National University of the South, CONICET, Bahía Blanca, Argentina and ²Department of Biology, Biochemistry and Pharmacy, Institute of Biological and Biomedical Sciences, National University of the South, CONICET, Bahía Blanca, Argentina

(Received 20 April, revised 11 July, accepted 23 September 2022)

Abstract: The electrosynthesis of PPy films onto 316L stainless steel from nearly neutral and alkaline solutions containing molybdate and salicylate is reported. The corrosion behaviour of the coatings constituted by hollow rectangular microtubes was monitored in Ringer solution using open circuit potential measurements, polarization techniques and electrochemical impedance spectroscopy. The polymer formed in a solution of pH 8 was the most efficient in terms of corrosion protection. The coating significantly reduced the pitting corrosion of the substrate. The results were interpreted taking into consideration the polymer electroactivity, the galvanic interaction polypyrrole/substrate and the nature of dopants. Silver species were effectively immobilized onto the hollow rectangular-sectioned microtubes of PPy. The modified coatings demonstrated that they have a good bactericidal activity against *Escherichia coli* and they were also able to protect the substrate against corrosion in Ringer solution.

Keywords: stainless steel; conducting polymer; microtubes.

INTRODUCTION

Stainless Steel 316L (316 L SS) is the most commonly used alloy in medical implants due to its many features, such as accepted biocompatibility, good mechanical and anticorrosive properties and availability at low cost.¹ It is well known that the presence of a thin “passive film” upon the 316L SS surface is responsible of the corrosion resistance of the substrate. Nevertheless, this passive film can be susceptible to breakdown in the presence of Cl⁻ and as a consequence, pitting corrosion is promoted.² In the surroundings of an implant this localized attack

* Corresponding author. E-mail: belen.gonzalez@uns.edu.ar
<https://doi.org/10.2298/JSC220420077R>

releases metal ions producing a decrease in biocompatibility, and consequently, the implant could be rejected.³ To overcome this problem, surface treatment techniques are used to improve the corrosion properties of the material.⁴ Conducting polymers constitute a physical barrier against corrosive environments, also helps to stabilize the formation of the passive film and, under certain circumstances, they can release corrosion inhibitor anions.⁵ Among all the conducting polymers, polypyrrole (PPy) is the most attractive option to modify the surface of implants because of its eco-friendly synthesis, good stability and satisfactory biocompatibility.⁶ Corrosion protection of the substrate can be improved if the PPy dopant is a corrosion inhibitor.^{7,8} Previously, the electrosynthesis of PPy onto Al from alkaline solution containing MoO_4^{2-} and NO_3^- as dopant anions was reported.⁹ The results obtained showed that MoO_4^{2-} remains entrapped into the polymer matrix, giving greater resistance to pitting corrosion in chloride media. In an earlier study, it was also demonstrated that the electrosynthesis of PPy onto 316L SS from an alkaline solutions containing molybdate and nitrate reduces the pitting corrosion of the substrate. The results are interpreted in terms of the passivating properties of the oxide layer formed in alkaline solution.¹⁰

On the other hand, salicylate (Sa) is considered to be a non-steroidal and anti-inflammatory drug¹¹ and it has also been demonstrated that PPy coatings doped with Sa anions provides corrosion protection for different metallic substrates.¹²⁻¹⁴ Another interesting feature of the Sa anion is that it not only can act as a dopant of PPy, but also is the responsible of the electrosynthesis of rectangular cross-section microtubes of the polymer.^{15,16} The effectiveness of microstructured PPy films doped with Sa anions in protecting 316 L SS from corrosion was studied in a chloride environment. The obtained coating was not enough for the protection of the substrate probably as a consequence of the porous opened structure of the microtubes, allowing the entry of aggressive ions. In order to improve the corrosion protection, a system of two layers was electrodeposited from salicylate solutions of different concentrations. The first layer consisted of granular PPy and the second one, on the top, was constituted by the PPy with microtubes. This bilayered coating exhibited an excellent protective behaviour of 316L SS in chloride solution during considerably long immersion time.¹⁷ A bilayer system onto 316L SS was also studied by our group. A PPy under-layer was electropolymerized in the presence of MoO_4^{2-} and NO_3^- and a microtubular PPy film, from salicylate solution, was formed as a top layer.¹⁸

Implant-related infection is recognized as a tragic problem, and patients with severe infection often require revision surgery.¹⁹ Current strategies to prevent or control implant-related infection include surface coating, modification of surface chemistry, and modification of surface morphology.²⁰

With the objective to provide antibacterial properties, the immobilization of metallic species in polymers has been widely studied in our laboratory. Micro-

structured PPy films were modified with copper species and then were implemented in a laboratory-scale continuous flow system using for disinfection of well water contaminated with *Escherichia coli*. The results indicated that the PPy/Cu-modified electrodes were effective for water disinfection process.²¹ In addition, it was also demonstrated that a PPy film doped with Sa is an effective matrix for the immobilization of Ag species. The PPy-Ag modified electrodes exhibited very good performance toward inhibition of bacteria activity, concluding that the composite is a promising material for biomedical application.²²

According to the revised literature, the protection of 316L SS with PPy microtubular was only attained through the formation of a bilayer system. Hence, the purpose of the present work was to investigate the electroformation of simple and protective PPy films with microtubular morphology on 316L SS. Accordingly, nearly neutral and alkaline solutions containing MoO_4^{2-} and Sa ions were employed during the electrosynthesis PPy film. For the development of an antimicrobial surface, the immobilization of silver species on the microstructured PPy matrix was also studied. The anticorrosive properties of different PPy films in Ringer solutions were determined.

EXPERIMENTAL

Materials and methods

Type 316 L SS rods (wt. % are: 17.47 Cr, 10.32 Ni, 1.88 Mn, 1.90 Mo, 0.39 Si, 0.025C and Fe balance) embedded in a Teflon holder with an exposed area of 0.070 cm^2 were used as working electrodes. Before each experiment, the surface was abraded with a 1200 grit finish using SiC, then degreased with acetone and finally washed with triply distilled water. Following this pre-treatment, the electrode was immediately transferred to the electrochemical cell. Potentials were measured and referred against an Ag/AgCl (3 M) electrode and a platinum sheet was used as the counter electrode. A conventional three electrode system and a 20 cm^3 Metrohm cell were used for the electrochemical experiments. The PPy films were obtained potentiostatically from a solution containing $0.50 \text{ M Py} + 0.50 \text{ M NaSa} + 0.05 \text{ M Na}_2\text{MoO}_4$ at different pH values. The pH of the solution was adjusted by addition of NaOH. The solutions were de-aerated by bubbling N_2 before and during the polymerization. Pyrrole (Sigma-Aldrich) was freshly distilled under reduced pressure before use. Morphological studies of the films metallised with gold were performed by scanning electron microscopy (SEM) LEO 1450 VP coupled using a probe for energy-dispersive scanning (EDS). Electrochemical studies were performed with a potentiostat/galvanostat Autolab/PSTAT 128N with an electrochemical impedance spectroscopy (EIS) module. The anticorrosion properties of the coatings were investigated in 50 mL of Ringer solution (composition per litre was 8.60 g NaCl, 0.30 g KCl and 0.32 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) by open circuit potential as a function of time (OCP-time), potentiostatic measurements, potentiodynamic method and electrochemical impedance spectroscopy. Tafel tests were performed by polarizing from cathodic to anodic potentials with respect to the open circuit potential at 0.001 V s^{-1} . Estimation of corrosion parameters was realized by the Tafel extrapolation method. The extrapolation of anodic and cathodic lines for charge transfer controlled reactions gives the corrosion current density (j_{corr}) at the corrosion potential (E_{corr}). Electrochemical impedance spectra were obtained at the open circuit potential (OCP) in the frequency range from 10 kHz to 100 mHz, and the signal

amplitude was 10 mV. To detect the presence of released ions, an inductively coupled plasma atomic emission spectrometer (ICP-AES) Shimadzu 9000 was used. Electrical conductivity was measured by the two-probe method using a homemade device. Adherence of the electrosynthesized coatings to the substrate was evaluated by using Scotch[®] Magic[™] Tape 810 (3 M). The antibacterial activity against a reference strain of *E. coli* ATCC 25922 was evaluated by a modified Kirby–Bauer technique.²³ The method was previously standardized by adjusting the microbial inoculation rate and the volume of the agar medium layer. A freezing culture of *E. coli* ATCC 25922 (stored at $-70\text{ }^{\circ}\text{C}$ in Trypticase Soy Broth (TSB, BK 046HA, Biokar Diagnostics, Beauvais, France) supplemented with 20 vol. % glycerol (Biopack, Argentina) was used. A loop of frozen cells was cultured in TSB during 24 h at $37\text{ }^{\circ}\text{C}$. Upon appropriate dilution with sterilized phosphate buffer saline solution, a suspension of about 107 cells mL^{-1} was prepared. One millilitre of this suspension was mixed with 25 mL of Trypticase Soy Agar (BK, Biokar Diagnostics, Beauvais, France) melted and cooled at $43\text{ }^{\circ}\text{C}$, and then, placed on a Petri dish. The coated electrodes were pressed onto bacteria-overlaid agar and were incubated at $37\text{ }^{\circ}\text{C}$ for 24 h. Then they were removed from the agar and placed in a fresh one. The data were expressed as growth inhibitory zone diameter (mm) for three replicates.²⁴ Control tests employing unmodified PPy-coated electrodes were also performed.

RESULTS AND DISCUSSION

Polypyrrole coatings

The polymerization solution was prepared from 0.50 M Py + 0.50 M NaSa + 0.05 M Na_2MoO_4 , at two different pH values: 8 and 12. It was previously demonstrated that the solution pH has an influence on the electrosynthesis process.¹⁵ When the solution pH is 8, the oxidation potential of Py was 0.90 V.¹⁰ However, in alkaline solution, there was a competition between the salicylate oxidation and PPy deposition, and as a consequence the electroformation of PPy at pH 12 occurs at potentials equal to or higher than 1.3 V. This value was already determined experimentally in previous work.¹⁵ The *j* vs. *t* transients obtained during the formation of coatings are presented in Fig. 1. As can be seen in the chronoamperometric curves, during the electropolymerization process, after charging the double layer, the current density increases with time until reaching a maximum value. Then *j* decreases and finally rises again at a slower rate. As described in a previous work,¹⁶ the behaviour observed in the curves is associated with the formation of microtubular structures. Under these conditions, the electropolymerization charge was for 4.3 C cm^{-2} for both coatings. A thickness of approximately $11\text{ }\mu\text{m}$ was predicted for the coatings by assuming a film thickness of $1\text{ }\mu\text{m}$ for 0.4 C cm^{-2} charge.²⁵ Under these circumstances, very adherent films were obtained. The morphology of the generated coatings was observed by the SEM technique. For a better understanding, the coatings were named PPy₈ and PPy₁₂. As might be expected, PPy₈ and PPy₁₂ films presented microstructured morphology due to the high salicylate concentrations.¹⁶ As can be seen in Fig. 1, the images reveal that most of the structures have rectangular cross-section with side length changing between 0.5 and $2\text{ }\mu\text{m}$. The external sur-

face of the microtubes was constituted of the typical globular structure of PPy and the inner side was hollow. The same porous morphology had already been obtained for a PPy film electrosynthesized on 316L SS from a solution containing only Sa.¹⁷

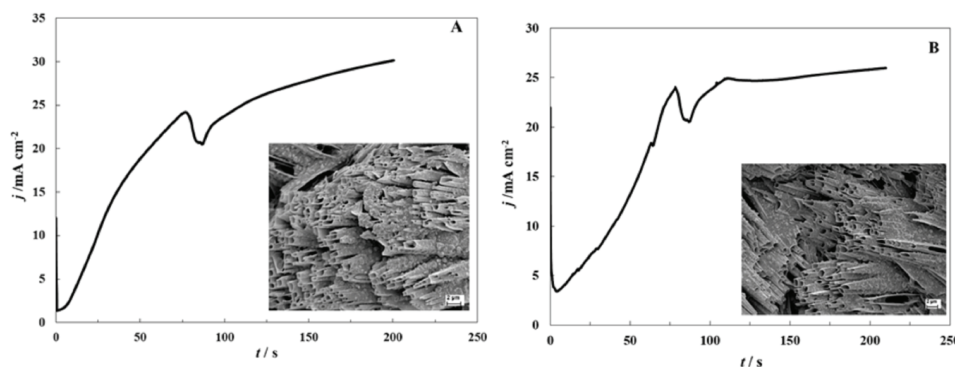


Fig. 1. Chronoamperometric curves obtained during the electrosynthesis of PPy₈ (A) and PPy₁₂ (B) films. SEM images of the films are also presented.

Corrosion test

The variation of *OCP* as a function of time was used to estimate the corrosion protection offered by the polymer coatings. The *OCP* vs. time responses for the different samples after exposure to Ringer solution during 10 days are presented in Fig. 2. For comparison, the curve of the uncoated steel is also showed. For the bare 316L SS sample, the *OCP* value stabilizes after the second day of immersion at a value around -0.15 V (curve c).

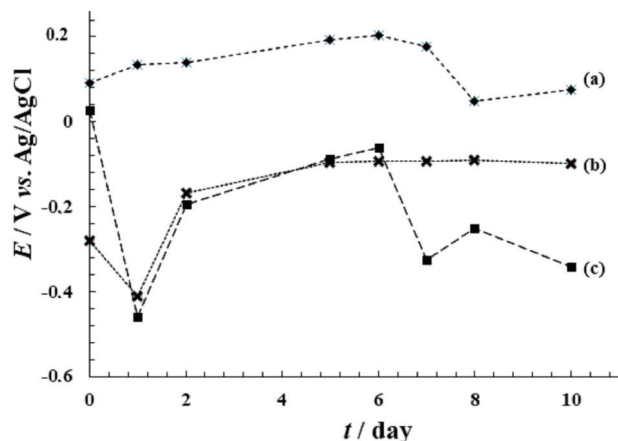


Fig. 2. Time dependence of *OCP* in Ringer solution of 316L SS electrode covered by: PPy₈ (a) and PPy₁₂ (b). The variation for a bare steel electrode is also included (c).

As can be seen in curve a, the presence of the PPy₈ film generates an anodic shift of the corrosion potential even after 10 days of immersion, which is associated with an anodic protection mechanism.^{26,27} However, the *OCP* vs. time curve corresponding to the electrode coated with PPy₁₂ films (curve b), presents values close to the bare steel electrode during the first seven days, and then decreases to -0.40 V. These preliminary results demonstrate that the presence of PPy₁₂ did not improve the corrosion protection of the substrate. The quantity of Fe released after *OCP* experience was <0.005 mg L⁻¹ and 0.084 mg L⁻¹ for the 316L SS electrode covered with PPy₈ and PPy₁₂, respectively. The bare electrode produced a Fe concentration of 1.200 mg L⁻¹. Moreover, the obtained results confirm that the PPy₈ films provided an effective corrosion protection of the substrate.

To acquire more information about the protection level of the PPy films, EIS measurements were performed. The Nyquist plots were recorded during immersion in Ringer solution under *OCP* conditions for a period of 10 days (Fig. 3).

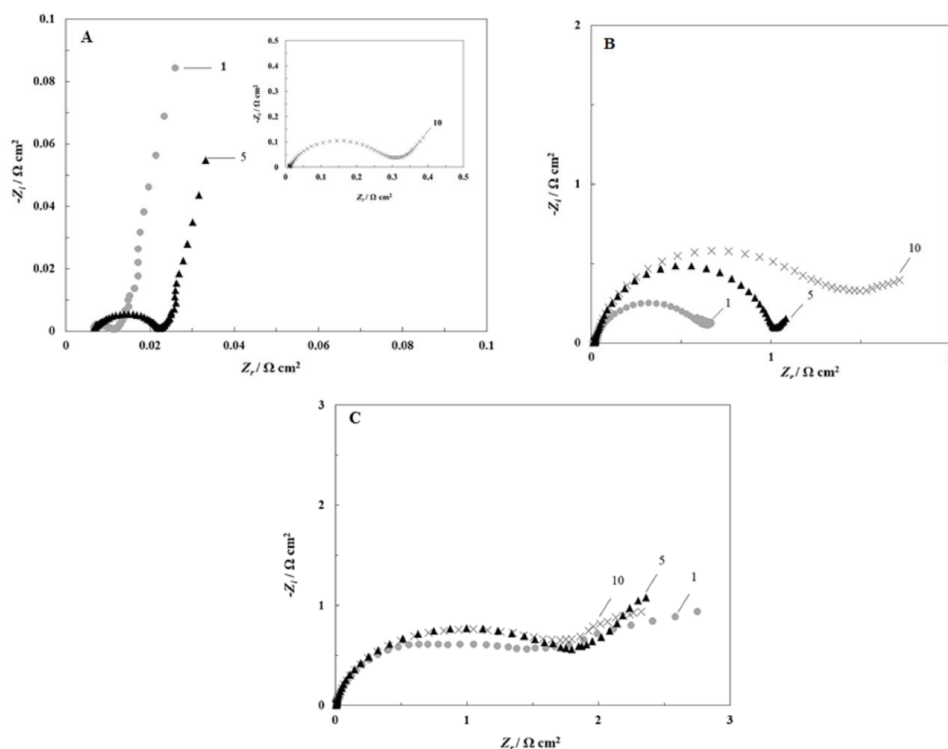


Fig. 3. Nyquist plots registered under *OCP* conditions in Ringer solution during 10 days for a steel electrode covered with: PPy₈ (A) and PPy₁₂ (B). The variation for a bare steel electrode is also included (C). The immersion day is indicated on the curve.

In the high-frequency region, the impedance spectrum all samples showed a depressed semicircle associated with a process at the electrode/electrolyte interface. The semicircle diameter represents R_{CT} , interpreted as the charge transfer resistance of the redox reaction of the polymer.²⁸ In the low-frequency region, a linear response was observed that is associated with the diffusion of ions into the polymer. As can be seen in Fig. 3A, the impedance results show that in the case of the PPy₈ film, the R_{CT} value increases slowly with immersion days. On the contrary, the response of the electrode covered with PPy₁₂ shows that the R_{CT} rises noticeably with the exposure time (see Fig. 3B). The Nyquist response of the uncoated electrode of 316L SS were constituted of a semicircle of $2 \Omega \text{ cm}^{-2}$ in diameter and practically negligible linear part (Fig. 3C). In the case of the PPy₁₂ film, the increment in R_{CT} values suggests that the reaction rate of the redox process of polymer declines over time, probably due to the low conductivity of the film. As was mentioned above, the electrosynthesis of PPy film from a solution of pH 12 begins to occur from 1.3 V. At this potential value, it is expected that the polymer obtained is overoxidized.²⁹ An important characteristic of overoxidized PPy is its poor conductivity and, in terms of corrosion protection, this represents a drawback.

On the other hand, for the electrode coated with PPy₈, the data obtained showed a vertical line in the low frequencies range associated with a semi-infinite Warburg impedance. This behaviour indicates a diffusion-controlled region that involves diffusion of mobile charges in the polymer backbone and mobile ions throughout the PPy coating.³⁰ In contrast, the data for the electrode covered with PPy₁₂ indicates that a contribution of the diffusional process to the total impedance was not observed. Thus, the PPy₈ film presents the best corrosion performance in terms of *OCP*-time and EIS results.

In previous work, the *OCP* response for a 316L SS electrode coated with a PPy film doped with Sa anions (without MoO_4^{2-}) presented a potential value of around 0.15 V during 20 days of immersion in 0.15 M NaCl. The concentration in solution of Fe determined by ICP was $<0.10 \text{ mg L}^{-1}$.¹⁷ Nevertheless, the EIS results demonstrated a marked increase of R_{CT} with time, dominating the impedance behaviour of the covered electrode. The contribution of the diffusional process to the total impedance goes away with exposure time. This EIS response, contrary to the one obtained for PPy₈, indicates that the corrosive species can penetrate the polymer doped only with Sa and reach the substrate. Then, according to these preceding results, it could be concluded that the incorporation of MoO_4^{2-} together with Sa as dopants of PPy film would improve the corrosion protection of the substrate.

Tafel plots were obtained after *OCP* stabilization (3600 s) starting from 0.20 to 0.20 V *vs.* *OCP* with a potential scan rate of 0.001 V s^{-1} . For uncoated 316L SS, the j_{CORR} value was estimated by extrapolation of anodic and cathodic Tafel

lines to the E_{corr} (Fig. 4, curve c). The j_{corr} values of the PPy coated 316L SS were estimated by extrapolation of the cathodic Tafel lines back to the corresponding values of E_{corr} (Fig. 4, curves a and b). According to Fig. 4, the conducting polymer produces a positive shift in the corrosion potential, although the corrosion current densities measured were almost three orders of magnitude higher than those for the uncoated sample (Table I). This result could be interpreted considering that the galvanic interaction between the polymer and the substrate gives rise to oxidation of the substrate and reduction of the polymer, and this mechanism significantly contributes to the total current measured.^{31,32}

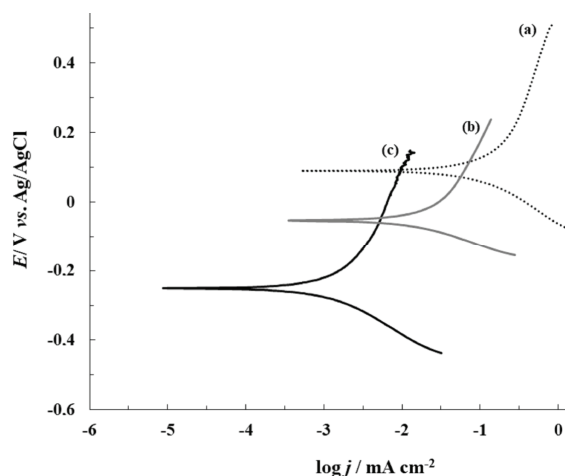


Fig. 4. Tafel curves registered in Ringer solution after OCP measurements for a steel electrode covered with: PPy₈ (curve a) and PPy₁₂ (curve b). Tafel polarization plot for the uncoated steel is also included (curve c). Sweep rate: 0.001 V s⁻¹.

TABLE I. Corrosion parameters calculated from the Tafel polarization plots for the bare 316L SS and the substrate covered with PPy₈ and PPy₁₂

Sample	$E_{\text{corr}} / \text{V}$	$j_{\text{corr}} / \text{mA cm}^{-2}$	$b_{\text{a}} / \text{V dec}^{-1}$	$b_{\text{c}} / \text{V dec}^{-1}$
PPy ₈	0.086	0.933	0.28	-0.14
PPy ₁₂	-0.075	0.017	0.28	-0.07
Bare 316L SS	-0.26	0.001	0.25	-0.13

More information concerning electrochemical behaviour of the covered electrodes could be obtained through linear polarization in Ringer solution (Fig. 5). For comparison purposes, the response of bare steel is also presented. As can be seen in curve c, the current density increases at 0.35 V, denoting the onset of pitting corrosion. In the case of the covered samples, peaks associated with reversible and irreversible oxidation of the PPy were observed at approximately 1.0 V. At more positive potentials, for the electrode covered with PPy₁₂ (curve b), the current density rises abruptly with oscillations denoting the onset of a pitting

corrosion process. On the contrary, the electrode covered with PPy₈ could be polarized to very high positive potentials without any sign of substrate dissolution.

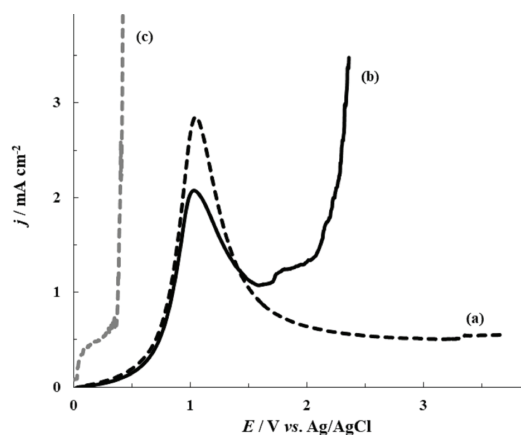


Fig. 5. Polarization curves registered in Ringer solution at 0.001 V s^{-1} for a bare steel electrode covered with: PPy₈ (curve a) and PPy₁₂ (curve b). The data for a bare steel electrode is also included (curve c).

In order to evaluate the protection level under more drastic conditions, the current density-time response was recorded at a potential more positive than the one corresponding to the pitting potential of the bare sample ($1.0 \text{ V vs. Ag/AgCl}$). In Fig. 6, curve c, current density oscillations around a value of 100 mA cm^{-2} were observed. This response could be attributed to pitting corrosion of the substrate. In contrast to this, the measured currents for the electrodes modified with PPy₈ and PPy₁₂ are much lower than that corresponding to the uncoated electrode.

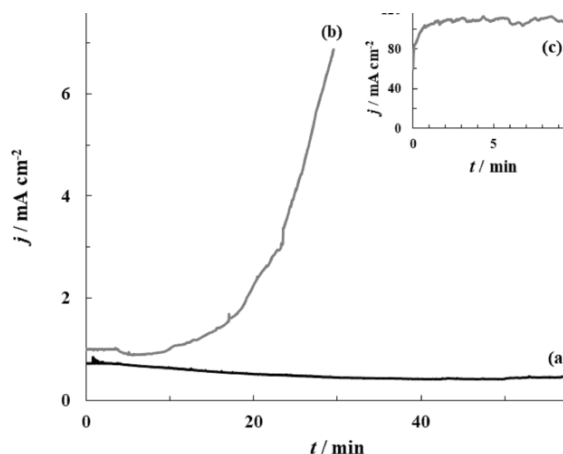


Fig. 6. Chronoamperometric curve obtained at 1 V vs. Ag/AgCl in Ringer solution for a bare steel electrode covered with: PPy₈ (curve a) and PPy₁₂ (curve b). The figure inset is the result for a bare steel electrode (curve c).

As could be seen in curve b), the response for the electrode covered with PPy₁₂ shows that the current density remained at 0.7 mA cm⁻² for 17 min, but an abrupt increase is observed later, probably due to the attack of Cl⁻ ions on the 316L SS. However, in the data presented in Fig. 6, curve a, the current density measured for the electrode covered with PPy₈ remained low even after 60 min of applying a constant potential value of 1.0 V (*vs.* Ag/AgCl), which indicates that the polymer electrosynthesized at pH 8 onto 316L SS is a protective film. The ICP-AES analysis indicated that the amount of Fe released during the chronoamperometric experience in Ringer solution was <0.005 and 0.039 mg L⁻¹ for 316L SS electrode covered with PPy₈ and PPy₁₂, respectively. The uncoated 316L SS electrode released an amount of Fe of 2.760 mg L⁻¹. The data confirmed that the dissolution of the substrate was significantly reduced in the presence of the PPy₈ film.

When the anticorrosion performance of the polypyrrole films were compared, it could be concluded that the coating electrosynthesized in a solution containing MoO₄²⁻ and Sa ions at pH 8 exhibits the best protection performance. These results could be explained in terms of the conductivity of coatings. The conductivity values obtained were 27.2 and 6.6 S m⁻¹ for PPy₈ and PPy₁₂ films, respectively; and they are within the interval already reported for PPy doped films.³³ These values were estimated considering a film thickness of 11 μm.²⁵ The difference between the obtained values could be associated with the potential of electrosynthesis. An increase in the electropolymerization potential results in a decrease in the conductivity of the studied PPy films. As was mentioned previously, the PPy₁₂ film was electroformed at 1.3 V and at this potential value, it is expected that the polymer obtained is overoxidized, probably due to the formation of a carboxyl group on the pyrrole ring that disrupts the conjugation of the PPy chain.²⁹ In addition, galvanic coupling is the most usual corrosion protection mechanism of conductive polymers. The cathodic reaction implicates the reduction of the coating accompanied with the release of the doping anions, whereas the anodic reaction includes the oxidation of the substrate. Then, the O₂ reduction occurs on both the conductive polymer and metal surfaces, promoting the re-oxidation of the polymer film. At least this interaction led to the formation of a protective layer at the metal–film interface.^{34,35} This proposed protection mechanism requires an electroactive polymer. Hence, it can be stated that the PPy film obtained at pH 8 gives the best corrosion protection of 316L SS in comparison with PPy₁₂ due to the higher conductivity in the film. In addition, the effective corrosion inhibition provided by the PPy₈ could be explained by considering, in the first instance, the galvanic interaction between the electroactive polymer and the substrate. Under these circumstances, the preservation of a passive protective oxide film is promoted. Additionally, due to its large size and negative charge, MoO₄²⁻ remains trapped in the polymer matrix, avoiding the entrance of chloride

ions. Nevertheless, the inhibitors might be released eventually and contribute to the corrosion protection of the alloy.

Silver immobilization

With the aim of providing bactericidal properties to the obtained films, the capacity of the polymer matrix to immobilize metallic species was studied. As commented previously, the electrode covered with PPy₈ presented the best corrosion behaviour in Ringer solution and those, it was selected for metallic immobilization experiments. The immobilization procedure was already described in a previous work²² and consisted in dipping the electrode covered with PPy₈ film in 0.05 M AgNO₃ during 5 h in the dark under *OCP* conditions. The modified polymer was named PPy₈Ag. The analysis by SEM shows the existence of rectangular structures coexisting with rosette-like deposits of 1 μm of diameter. As could be seen in Fig. 7A, the deposits present a highly rough surface and this type of morphology was previously observed in silver microstructures.³⁶ An EDS analysis (Fig. 7B) demonstrates that the deposits were constituted of silver and the signal of Mo confirms that molybdate is entrapped into the PPy₈ matrix. It was proposed that the salicylate anion fulfils an important function in the immobilization of silver species onto the coating. Metallic cations present in the solution were concentrated in the film as a result of the interaction between Sa⁻ and Ag⁺. Metallic silver was then deposited as a result of a redox reaction between non oxidized segments of the polymer and Ag⁺.

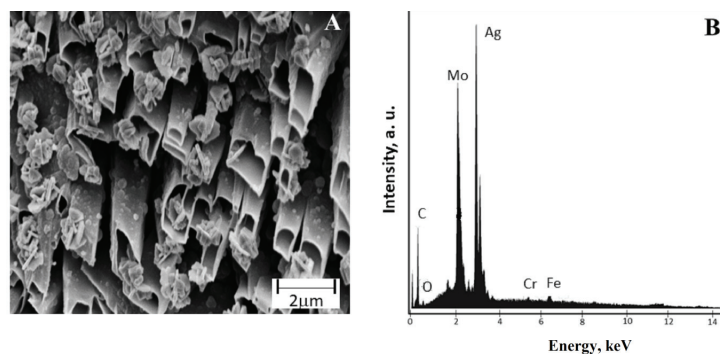


Fig. 7. SEM image (A) and EDS examination (B) of the 316 L SS electrode covered with PPy₈Ag.

The antibacterial activity of PPy₈Ag films against the Gram-negative bacterium *E. coli* was investigated by determining the width of the inhibition zone around the modified electrode. Antibacterial activity of unmodified PPy₈ film against *E. coli* ATCC 25922 consisted of an inhibition zone of approximately 4 mm surrounding the sample. Previously, it was shown that salicylate has notable antibacterial activity and it was also shown that this inhibitory effect is

concentration dependent.²² Nevertheless, the inhibition area is notoriously increased (12 mm) when PPy₈Ag was analysed. The antibacterial properties of PPy₈Ag film could be described by the insertion of the released Ag⁺ and colloid silver particles through the bacteria cell wall.³⁷

In order to determine the corrosion properties of the 316L SS electrode covered with PPy₈Ag film, the *OCP*-time dependence and the polarization curve at 1.0 V *vs.* Ag/AgCl were registered in Ringer solution. The obtained curves are shown in Fig. 8. In the first sight, the measured potentials were nobler than the potential of bare steel electrode (−0.15V) even after 10 days of immersion, suggesting that the film was an effective protective coating (Fig. 8A). The result is supported by the determination of the amount of iron released in Ringer solution. A concentration less than 0.005 mg L^{−1} was obtained after 10 days of immersion; this value is identical to the one previously reported for the unmodified PPy₈. The amount of Fe released from PPy₈Ag and PPy₈ during the immersion is much lower than that found for the bare electrode (1.200 mg L^{−1}). The data would confirm that the corrosion protection properties of PPy₈ are not altered by the presence of silver species. In addition, the *j vs. t* transient shown in Fig. 8B denotes that the density current values remained well below the values obtained for the bare electrode (see Fig. 6, curve c), even after 60 min of experience. The ICP-AES analysis of the amount of Fe released into the Ringer solution gave a value of 0.132 mg L^{−1}. Although this concentration is greater than that obtained previously for the unmodified PPy₈, the data confirms that the dissolution of the alloy was reduced by the presence of PPy₈Ag film, taking into account the measured Fe concentration for the bare electrode (2.76 mg L^{−1}).

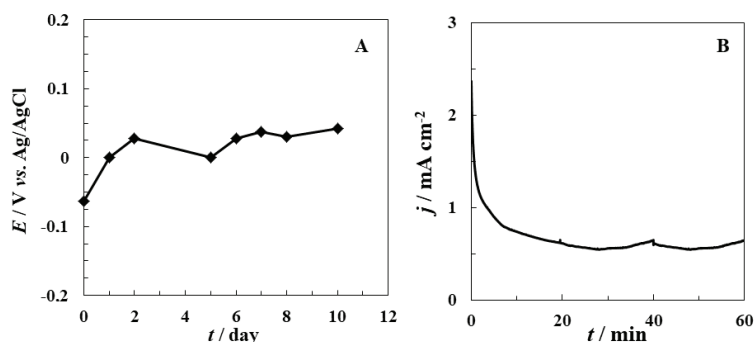


Fig. 8. A) Time dependence of *OCP* in Ringer solution of a 316L SS electrode covered by PPy₈Ag. B) Chronoamperometric curve obtained at 1.0 V *vs.* Ag/AgCl in Ringer solution of a 316L SS electrode covered by PPy₈Ag.

CONCLUSIONS

Single-layer polypyrrole coatings with microtubular morphology were obtained from solutions containing molybdate and salicylate at two different pH

values by a potentiostatic technique on 316L SS. All the corrosion procedures performed were to evaluate the degree of protection of AI 316L SS coated with polypyrrole films electrosynthesized from salicylate and molybdate solutions at different pH values demonstrated that a PPy₈ coating could completely protect the substrate against pitting corrosion in Ringer solution, even when the coated sample is polarized to a potential higher than the breakdown potential of the bare substrate (1 V (Ag/AgCl 3M)). One possible reason for the best corrosion protection properties of PPy₈ is the electroactive polymer ability and the galvanic interaction with the substrate. In addition, the fixed negative charge of MoO₄²⁻ avoids the entrance of chloride into the polymer matrix and also the release of corrosion inhibitor anions from the polypyrrole matrix helps with the protection of the substrate. Silver species were effectively immobilized onto the hollow rectangular-sectioned microtubes of PPy. The antibacterial test against *E. coli* for PPy₈Ag samples demonstrated that they have good bactericidal activity and were also able to protect 316L SS against corrosion in Ringer solution. Thus, this film has potential applications as a biomaterial with antibacterial properties.

Acknowledgements. The financial support of the Secretaría de Ciencia y Técnica – UNS (PGI 24/M159), the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET – PIP 112-20150-100147) and the Agencia Nacional de Promoción Científica y Tecnológica (ANPCYT PICT-2019-02758) is gratefully acknowledged.

ИЗВОД

АНТИКОРОЗИВНЕ ОСОБИНЕ ПРЕВЛАКА ПОЛИПИРОЛА ФОРМИРАНИХ НА НЕРЂАЈУЋЕМ ЧЕЛИКУ 316 L ИЗ РАСТВОРА КОЈИ ЈЕ САДРЖАО МОЛИБДАТЕ И САЛИЦИЛАТЕ

CAMILA A. RAMOS¹, MARIA B. GONZÁLEZ¹, LORENA I. BRUGNONI² и SILVANA B. SAIDMAN¹

¹Chemical Engineering Department, Institute of Electrochemical and Corrosion Engineering, National University of the South, CONICET, Bahía Blanca, Argentina u ²Department of Biology, Biochemistry and Pharmacy, Institute of Biological and Biomedical Sciences, National University of the South, CONICET, Bahía Blanca, Argentina

У раду је описана електрохемијска синтеза филмова полипиброла на нерђајућем челику 316L из раствора блиских неутралним и алкалних који су садржали молибдате и салицилате. Корозионо понашање превлака које су биле сачињене од шупљих правоугаоних микроцеви је праћено у Рингеровом раствору мерењем потенцијала отвореног кола, поларизационим мерењима и спектроскопијом електрохемијске импеданције. Полимер који је формиран у раствору рН 8 је био најефикаснији у заштити од корозије. Превлака је значајно смањила питинг корозију подлоге. Резултати су дискутовани узимајући у обзир електрохемијску активност полимера, галванску интеракцију између полипиброла и подлоге и природу допанта. Хемијске врсте сребра су ефикасно имобилисане у шупљим правоугаоним цевима полипиброла. Модификоване превлаке су показале добра бактерицидна својства према *Escherichia coli* и такође заштиту подлоге од корозије у Рингеровом раствору.

(Примљено 20. априла, ревидирано 11. јула, прихваћено 23. септембра 2022)

REFERENCES

1. M. Z. Ibrahim, A. A. D. Sarhan, F. Y. M. Hamdi, *J. Alloys Compd.* **714** (2017) 636 (<https://doi.org/10.1016/j.jallcom.2017.04.231>)
2. M. J. K. Lodhi, K. M. Deen, M. C. Greenlee-Wacker, Waseem Haider, *Addit. Manuf.* **27** (2019) 8 (<https://doi.org/10.1016/j.addma.2019.02.005>)
3. N. S. Manam, W. S. W. Harun, D. N. A. Shri, S. A. C. Ghani, T. Kurniawan, M. H. Ismail, M. H. I. Ibrahim, *J. Alloys Compd.* **701** (2017) 698 (<https://doi.org/10.1016/j.jallcom.2017.01.196>)
4. R. K. Gupta, N. Birbilis, *Corros. Sci.* **92** (2015) 1 (<https://doi.org/10.1016/j.corsci.2014.11.041>)
5. C. Garcia-Cabezon, C. Garcia-Hernandez, M. L. Rodriguez-Mendez, F. Martin-Pedrosa, *J. Mat. Sci. Tech.* **37** (2020) 85 (<https://doi.org/10.1016/j.jmst.2019.05.071>)
6. W. A. El-Said, M. Abdelshakour, Jin-Ha Choi, Jeong-Woo Choi, *Molecules* **25** (2020) 307 (<https://doi.org/10.3390/molecules25020307>)
7. Z. Chen, W. Yang, B. Xu, Y. Guo, Y. Chen, X. Yin, Y. Liu, *Prog. Org. Coat.* **122** (2018) 159 (<https://doi.org/10.1016/j.porgcoat.2018.05.022>)
8. H. M. Hung, D. K. Linh, N. T. Chinh, L. M. Duc, V. Q. Trung, *Prog. Org. Coat.* **131** (2019) 407 (<https://doi.org/10.1016/j.porgcoat.2019.03.006>)
9. I. L. Lehr, S.B. Saidman, *Electrochim. Acta* **51** (2006) 3249 (<https://doi.org/10.1016/j.electacta.2005.09.017>)
10. M. B. González, S. B. Saidman, *Corr. Sci.* **53** (2011) 276 (<https://doi.org/10.1016/j.corsci.2010.09.021>)
11. R. Amann, B. A. Peskar, *Eur. J. Pharmacol.* **447** (2002) 1 ([https://doi.org/10.1016/S0014-2999\(02\)01828-9](https://doi.org/10.1016/S0014-2999(02)01828-9))
12. K. Cysewska, M. Gazda, P. Jasiński, *Surf. Coat. Technol.* **328** (2017) 248 (<https://doi.org/10.1016/j.surfcoat.2017.08.055>)
13. D. O. Flamini, M. I. Valle, M. J. Sandoval, V. L. Massheimer, S. B. Saidman, *Mater. Chem. Phys.* **209** (2018) 76 (<https://doi.org/10.1016/j.matchemphys.2018.01.065>)
14. A. D. Forero López, I. L. Lehr, L. I. Brugnoli, S. B. Saidman, *J. Magnes. Alloys* **6** (2018) 15 (<https://doi.org/10.1016/j.jma.2017.12.005>)
15. M. B. González, S. B. Saidman, *Electrochem. Comm.* **13** (2011) 513 (<https://doi.org/10.1016/j.elecom.2011.02.037>)
16. M. B. González, O. V. Quinzani, M. E. Vela, A. A. Rubert, G. Benítez, S. B. Saidman, *Synth. Met.* **162** (2012) 1133 (<https://doi.org/10.1016/j.synthmet.2012.05.013>)
17. M. B. González, S. B. Saidman, *Prog. Org. Coat.* **75** (2012) 178 (<https://doi.org/10.1016/j.porgcoat.2012.04.015>)
18. M. B. González, S. B. Saidman, *Prog. Org. Coat.* **78** (2015) 21 (<http://dx.doi.org/10.1016/j.porgcoat.2014.10.012>)
19. J. M. Brown, J. B. Mistry, J. J. Cherian, R. K. Elmallah, M. Chughtai, S. F. Harwin, *Orthopedics* **39** (2016) 1129 (<https://doi.org/10.3928/01477447-20160819-06>)
20. M. Wang, T. Tang, *J. Orthop. Transl.* **17** (2019) 42 (<https://doi.org/10.1016/j.jot.2018.09.001>)
21. M. B. González, D. O. Flamini, L. I. Brugnoli, L. M. Quinzani S. B. Saidman, *J. Water Health* **16** (2018) 921 (<https://doi.org/10.2166/wh.2018.072>)
22. M. B. González, L. I. Brugnoli, M. E. Vela, S. B. Saidman, *Electrochim. Acta* **102** (2013) 66 (<https://doi.org/10.1016/j.electacta.2013.03.116>)

23. V. Maquet, D. Martin, B. Malgrange, R. Franzen, J. Schoenen, G. Moonen, R. Jérôme, *J. Biomed. Mater. Res.* **52** (2000) 639 ([https://doi.org/10.1002/10974636\(20001215\)52:4<639::AID-JBM8>3.0.CO;2-G](https://doi.org/10.1002/10974636(20001215)52:4<639::AID-JBM8>3.0.CO;2-G))
24. P. T. Sudheesh Kumar, S. Abhilash, K. Manzoor, S.V. Nair, H. Tamura, R. Jayakumar, *Carbohydr. Polym.* **80** (2010) 761 (<https://doi.org/10.1016/j.carbpol.2009.12.024>)
25. Q. Pei, R. Qian, *Electrochim. Acta* **37** (1992) 1075 ([https://doi.org/10.1016/0013-4686\(92\)85225-A](https://doi.org/10.1016/0013-4686(92)85225-A))
26. S. Biallozor, A. Kupniewska, *Synth. Met.* **155** (2005) 443 (<https://doi.org/10.1016/j.synthmet.2005.09.002>)
27. A. A. Hermas, *Corros. Sci.* **50** (2008) 2498 (<https://doi.org/10.1016/j.corsci.2008.06.019>)
28. C. M. Chang, C. S. Song, H. J. Huang, *J. Chin. Chem. Soc.* **41** (1994) 693 (<https://doi.org/10.1002/jccs.199400098>)
29. T. Patois, B. Lakard, N. Martin, P. Fievet, *Synth. Met.* **160** (2010) 2180 (<https://doi.org/10.1016/j.synthmet.2010.08.005>)
30. [A. El Jaouhari](#), [A. Chennah](#), [S. Ben Jaddi](#), [H. Ait Ahsaine](#), [Z. Anfar](#), [Y. Tahiri Alaoui](#), [Y. Naciri](#), [A. Benlhachemi](#), [M. Bazzaoui](#), *Surf. Interfaces* **15** (2019) 224 (<https://doi.org/10.1016/j.surfin.2019.02.011>)
31. E. Machnikova, M. Pazderova, M. Bazzaoui, N. Hackerman, *Surf. Coat. Technol.* **202** (2008) 1543 (<https://doi.org/10.1016/j.surfcoat.2007.07.006>)
32. D. O. Flamini, M. I. Valle, M. J. Sandoval, V. L. Massheimer, S. B. Saidman, *Mater. Chem. Phys.* **209** (2018) 76e85 (<https://doi.org/10.1016/j.matchemphys.2018.01.065>)
33. A. Kaynak, L. Rintoul, G. A. George, *Mater. Res. Bull.* **35** (2000) 813 ([https://doi.org/10.1016/S0025-5408\(00\)00280-4](https://doi.org/10.1016/S0025-5408(00)00280-4))
34. M. K. Zadeh, M. Yeganeh, M. T. Shoushtari, A. Esmailkhanian, *Synth. Met.* **274** (2021) 116723 (<https://doi.org/10.1016/j.synthmet.2021.116723>)
35. P. P. Deshpande, N. G. Jadhav, V. J. Gelling, D. Sazou, *J. Coat. Technol. Res.* **11** (2014) 473 (<https://doi.org/10.1016/j.surfcoat.2007.07.006>)
36. K. A. M. Eid, H. M. E. Azzazy, *Int. J. Nanomed.* **7** (2012) 1543 (<https://doi.org/10.2147/IJN.S26524>)
37. S.A. Ahmad, S. S. Das, A. Khatoun, M. T. Ansari, M. Afzal, M. S. Hasnain, A. K. Nayak, *Mater. Sci. Energy Technol.* **3** (2020) 756 (<https://doi.org/10.1016/j.mset.2020.09.002>).