



Corrosion protection properties of polypyrrole electropolymerized onto steel in the presence of salicylate

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ABSTRACT

The corrosion performance of a polypyrrole coating constituted by hollow rectangular microtubes was monitored in chloride solutions using open circuit potential measurements, potentiostatic polarization and electrochemical impedance spectroscopy. The coating was electrosynthesized onto 316 L stainless steel from a salicylate solution and it provided a very good corrosion resistance to the substrate. It was found that polypyrrole films with granular morphology electrodeposited from a salicylate solution with lower concentration behave better in terms of protective behavior. In order to improve the corrosion protection imparted by the polypyrrole coating formed by the microtubes a system of two layers was electrodeposited, the first one consisted of polypyrrole with a granular morphology and the second one, on the top, was constituted by the microtubes. This bilayered system exhibited an excellent protective behavior during considerably long immersion time.

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1. Introduction

Since the works by Mengoli et al. [1] and DeBerry [2], who observed effective passivation of stainless steels and iron by polyaniline, conducting polymers are intensively investigated for their use in corrosion protection applications. It is generally accepted that the polymer helps to stabilize the passive layer as a result of a galvanic coupling between the coating and the metallic substrate. Reoxidation of the polymer coating through oxygen reduction at the polymer/electrolyte interface has been proposed [3]. On the other hand anion dopants are usually released from the polymer during its reduction [4]. If dopants are corrosion inhibitors it is expected an improvement in corrosion protection. The release of anions from a PPy film doped with molybdate or phosphomolybdate has been considered to explain the corrosion protection imparted by the coating [5]. The presence of molybdate allows passivating the substrate. An improved corrosion protection was also achieved by depositing a duplex film where the underlying PPy was doped with tetraoxalate anions and the outer one with dodecyl sulfate anions [6]. Oxalate anions were necessary for self-healing of the damaged passive film. More recently, a bilayered PPy film consisted of an inner layer doped with phosphomolybdate ion and an outer layer doped with dodecylsulfate ion was designed to protect a steel substrate [7]. It was found that the coating had the ability to repair the

passive oxide at a defect site, where an insoluble iron molybdate salt was detected.

Among corrosion inhibitor anions, salicylate (Sa) was found to be a good electrolyte for the electrosynthesis of conducting polymers and it has been demonstrated that the formed coatings provide corrosion protection of different metallic substrates [8–11].

On the other hand 316 L stainless steel (316 L SS) is one of the most common materials suitable for biomedical applications. However it is susceptible to localized attack in body fluids with the risk that harmful metallic ions may be released into the environment. Surface modifications techniques have been applied to improve the corrosion resistance of the steel. The biocompatibility and conductive properties of polypyrrole (PPy) make it an useful material for controlling corrosion [12]. In addition PPy can also be used to load and release drugs with therapeutic activity like Sa [13].

Conducting polymers are also investigated due to their interesting morphologies such as fibers, rods and tubes [14]. Hollow rectangular microtubes are particularly interesting due to their multiple applications in the fields of electronics, optics, catalysis, and energy storage [15]. Their synthesis by a chemical route has been reported [16,17]. We have observed for the first time the electroformation of hollow rectangular microtubes of PPy using a salicylate aqueous solution [18]. It was found that the typical granular morphology of PPy is obtained when the polymer is electrosynthesized with a low concentration of Sa, while the microtubes growth was observed when the amount of Sa is raised. It was proposed that microtubes growth is templated by salicylic acid (H₂SA) crystals which crystallize on the electrode surface as a result of the decrease in pH that accompanies the electrodeposition.

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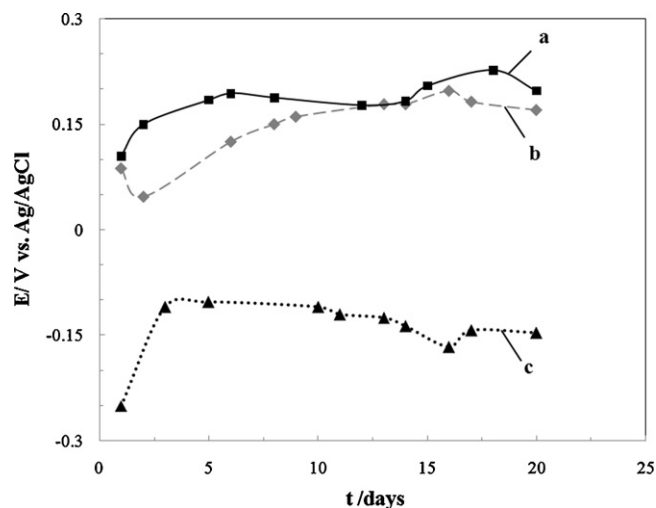


Fig. 1. Time dependence of the OCP in 0.15 M NaCl of 316 L SS electrode covered by: PPy_{0.15Sa} (curve a) and PPy_{0.55Sa} (curve b). The variation for a bare steel electrode is also included (curve c).

Thus, according to previous studies, Sa plays several roles in the electrosynthesis of PPy coatings. It acts as a dopant and as a promoter of rectangular cross-section microtubes. In addition, under determinate experimental conditions the anion can be released from the film. In this contribution we evaluate the effectiveness of PPy films doped with Sa anions in protecting 316 L SS from corrosion in a chloride environment.

2. Experimental

Type 316 L SS rods (wt.% is: 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 cm² were used as working electrodes. Before each experiment, the exposed surfaces were abraded with 200, 600 and 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 an Ag/AgCl (3 M) electrode and a platinum sheet was used as a counter electrode. The experiments were conducted in a 20 cm³ Metrohm measuring cell and measurements were carried out in a purified nitrogen gas saturated atmosphere at 25 °C. The solutions were not deaerated during open circuit potential measurements.

The aqueous solutions used for electropolymerization contain 0.25 M pyrrole (Py) and sodium salicylate 0.1 M and 0.5 M. Pyrrole (Sigma–Aldrich) was freshly distilled under reduced pressure before use.

Electrosynthesis of PPy films on steel electrodes was carried out by potentiostatic techniques. The anticorrosion properties of the coatings was investigated by open circuit potential (OCP)–time curves, potentiostatic measurements and electrochemical impedance spectroscopy (EIS) in 0.15 M NaCl, an electrolyte solution that is frequently used to simulate the biological environment.

Electrochemical experiments were performed with a potentiostat–galvanostat Autolab/PGSTAT128N. A dual stage ISI DS 130 SEM was used to examine the morphology of the deposits. EIS measurements were performed using a VoltaLab 40 Potentiostat PGZ301. The frequency used for the impedance measurements was changed 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.

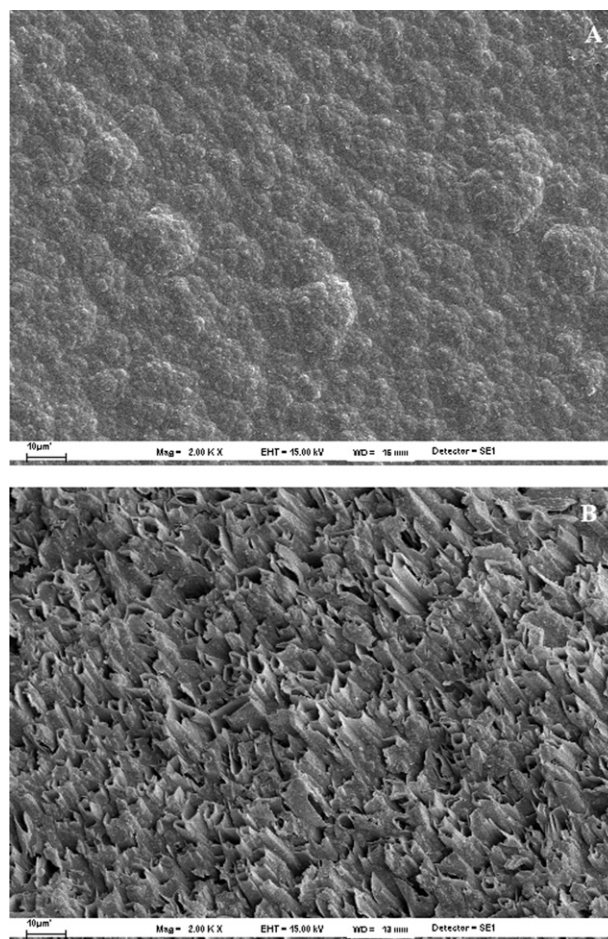


Fig. 2. SEM images obtained after 20 days at OCP in 0.15 M NaCl solution of 316 L SS electrode covered by: (A) PPy_{0.15Sa}; and (B) PPy_{0.55Sa}.

3. Results and discussion

3.1. Single layers of polypyrrole

The coatings were electrosynthesized at 0.8 V in 0.1 M and 0.5 M Sa solutions. For simplification they were named PPy_{0.15Sa} and PPy_{0.55Sa}, respectively. The electropolymerization charge was approximately 10 C/cm² for both coatings. A thickness of approximately 25 μm is predicted for the coatings by assuming a film thickness of 1 μm for 0.4 C/cm² charge [19]. Under these conditions, very adherent films were obtained. The granular morphology was obtained for the more diluted solution while the microtubes were generated for the more concentrated one.

The variation of OCP as a function of time was used to evaluate the corrosion protection realized by the polymer coatings. Fig. 1 shows the OCP–time curves for the different samples when exposed to NaCl solution for 20 days. For comparative purposes the response of the uncoated steel is also presented. The presence of the coatings causes an anodic shift of the corrosion potential which is associated with an anodic protection mechanism. The corrosion potentials of the PPy-coated steel are higher than that of the bare steel even after 20 days of immersion for both samples, demonstrating that the polymers are effective corrosion resistant coatings in chloride solutions.

After the OCP measurements, the chloride solution was analyzed to detect the presence of released ions. The concentrations of Fe, Ni and Cr in solution were all less than 0.10 mg/L. On the contrary the quantity released of Fe, Ni and Cr in the case of the uncovered steel

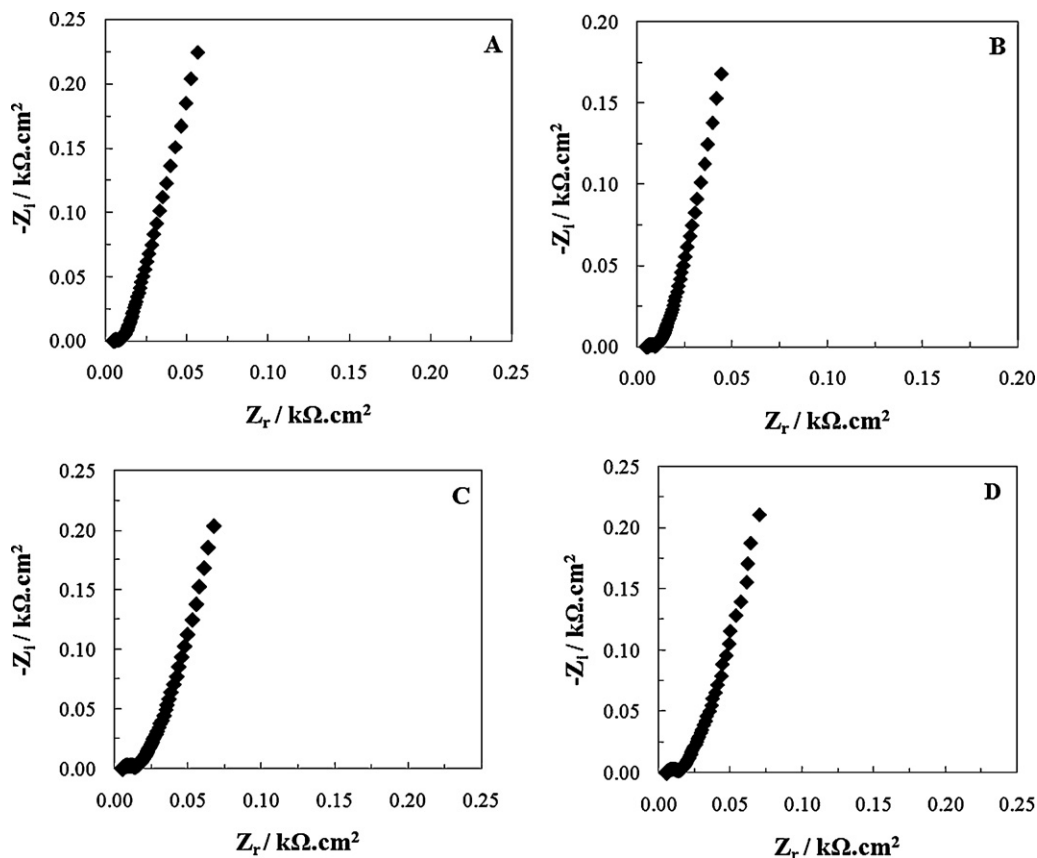


Fig. 3. Nyquist plots registered at OCP in 0.15 M NaCl solution of 316 L SS electrode covered by PPY_{0.15a} after: (A) 1; (B) 8; (C) 13 and (D) 20 immersion days.

exposed during 20 days were 1.20, 1.12 and 1.09 mg/L, respectively. The results corroborate that the presence of the coating substantially decreases the corrosion of the substrate.

The SEM pictures for PPY-coated steel samples after exposure to chloride solution under open circuit conditions during 20 days are presented in Fig. 2. In the case of the PPY_{0.15a} it can be observed the globular structure of the polymer without any sign of damage. The image of the sample PPY_{0.55a} shows that the rectangular-sectioned PPY microtubes remain intact except that several tips appear broken. Thus, there are no detectable changes associated with corrosion of the substrate.

For a better assessment of the protection performance of the coatings additional information was obtained by EIS. The analysis was performed during immersion in the chloride solution. The shape of the curves was a depressed semicircle at high frequencies and a linear part at low frequencies (Figs. 3 and 4). Interpretation of the measurements was done by fitting the data to the equivalent circuit shown in Fig. 5, which has been proposed by Koene et al. [20] for explaining the corrosion protective properties of PPY films electropolymerized on mild steel electrodes. The model assumes that the reduction process of the coating promotes the oxidation of the substrate. R_s represent the solution resistance and R_{ct} is the charge transfer resistance of the redox reaction of the polymer. CPE is associated to a non-ideal double layer capacitance of the PPY/solution interface and it is defined as:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (1)$$

where j is the imaginary unit, n has the meaning of a phase shift with values between 0 and 1 and Y_0 is a constant with the dimension $F\text{ cm}^{-2}\text{ s}^{n-1}$.

Finally, W is the finite-length Warburg impedance which accounts for a diffusional process throughout the PPY coating. It can be expressed as following:

$$W_0 = R_w \frac{\coth(j\omega s)^\alpha}{(j\omega s)^\alpha} \quad (2)$$

R_w represents the diffusion resistance and $s = \lambda^2/D$, where λ is the effective diffusion thickness and D is the effective diffusion coefficient of involved species. The results of the fitting are presented in Table 1. The model simulates the experimental data well, considering that the errors of fitting are lower than 3% for all the parameters.

In the case of PPY_{0.15a} the R_{ct} increases slowly with exposure time. On the contrary, the response of PPY_{0.55a} shows that R_{ct} markedly increases with time dominating the impedance behavior of the covered electrode. The increase in R_{ct} values implies that the reaction rate of the redox process of the polymer decreases with time probably due to a loss of film conductivity.

On the other hand the data indicate that diffusional impedance controls the response of the electrode covered with PPY_{0.15a} while for the PPY_{0.55a} the contribution of the diffusional process to the total impedance decreases with exposure time. A transition from finite-length Warburg to semi-infinite Warburg behavior can be explained on the basis that ion diffusion in solution replaces diffusion throughout the PPY coating. This is indicative that corrosive species can penetrate into the coating and reach the substrate [20]. This transition does not take place in the steel covered by PPY_{0.15a} providing evidence of a high stability of the coating. Thus, taking into account the OCP variation with time, the above-described electrical circuit is an appropriate model for describing the impedance response. EIS results indicate that although both films were effective anticorrosion coatings for steel, PPY_{0.15a} exhibits better protection behavior than PPY_{0.55a}.

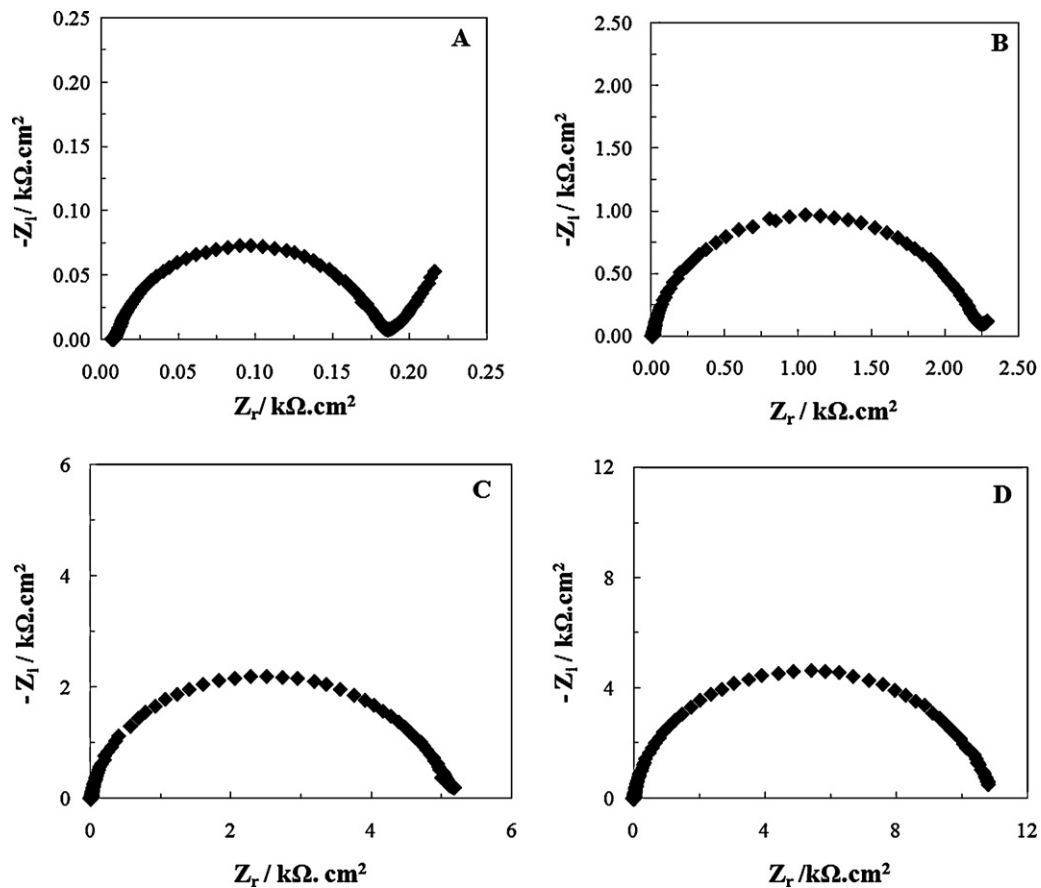


Fig. 4. Nyquist plots registered at OCP in 0.15 M NaCl solution of 316 L SS electrode covered by PPY_{0.55a} after: (A) 1; (B) 8; (C) 13 and (D) 20 immersion days.

Table 1

Values for the parameters of the equivalent circuit obtained from the best fit to the impedance data.

	<i>t</i> (days)	<i>R_s</i> (Ω cm ²)	<i>Y₀</i> (μF cm ⁻²)	<i>n</i>	<i>R_{ct}</i> (Ω cm ²)	<i>R_w</i> (Ω cm ²)	<i>s</i> (Ω cm ²)	<i>α</i>
PPY _{0.15a}	1	5.074	2.96E-4	0.805	2.70	9.15	0.495	0.420
	8	5.21	2.40E-4	0.810	2.79	8.86	0.535	0.426
	13	5.235	1.62E-4	0.855	3.32	10.3	0.576	0.421
	20	5.617	7.9E-9	0.910	5.97	20.07	0.850	0.404
PPY _{0.55a}	1	8.284	7.03E-5	0.851	173.6	9	0.850	0.315
	8	10.21	3.91E-5	0.896	2218	0.001	2.5E-6	0.372
	13	11.13	3.63E-5	0.903	5100	8E-6	1E-8	0.395
	20	11.48	3.51E-5	0.902	10,834	1E-9	3E-9	0.586

Both coatings show a different behavior when they are polarized at 0.6 V (Fig. 6). In the case of PPY_{0.15a} the current remains low even after 6 h of polarization. In contrast for PPY_{0.55a} the current rises approximately after 200 min of polarization denoting the onset of pitting corrosion, which was corroborated by surface examination of the sample after immersion. Considering that the PPy microtubes are hollow, this shorter protection time is connected with a relative easier penetration of the electrolyte through the film.

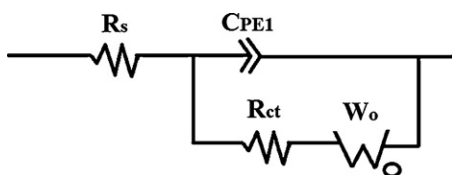


Fig. 5. Equivalent circuit proposed to simulate EIS results of coated samples. The significance of the parameters is given in the text.

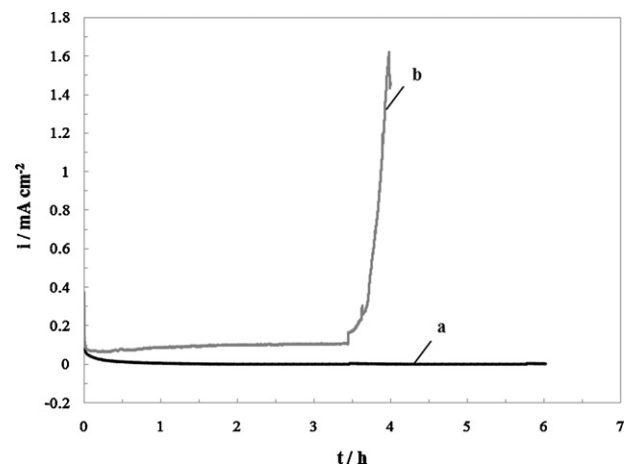


Fig. 6. Chronoamperometric curves obtained at 0.60 V vs. Ag/AgCl in 0.15 M NaCl solution for 316 L SS covered electrode by: (a) PPY_{0.15a} and (b) PPY_{0.55a}.

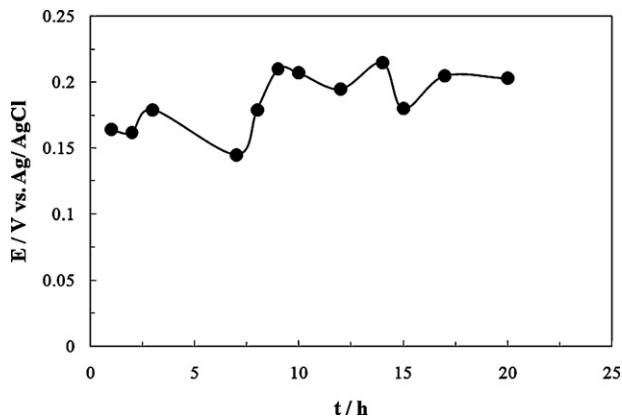


Fig. 7. Time dependence of the OCP in 0.15 M NaCl of bilayer-coated 316 L SS electrode.

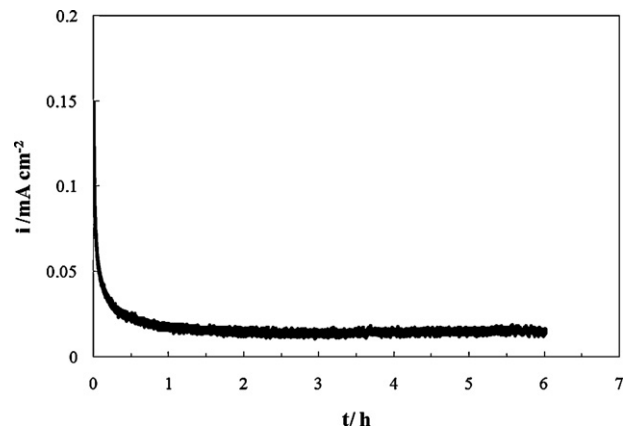


Fig. 8. Chronoamperometric curve obtained at 0.60 V vs. Ag/AgCl in 0.15 M NaCl solution for a bilayer-coated 316 L SS electrode.

3.2. Bilayered polypyrrole

With the aim to combine the best properties of both coatings that are the morphological characteristics of the PPY_{0.5Sa} film and the degree of anticorrosive protection of PPY_{0.1Sa} layer, we decided to electrodeposit a bilayer of the polymers. The system consists of PPY_{0.1Sa} as the inner layer and PPY_{0.5Sa} as the top layer. Both films were electrosynthesized under the same conditions described above except that the electropolymerization charges were 10 C/cm² and 2 C/cm² for PPY_{0.1Sa} and PPY_{0.5Sa}, respectively. The estimated thickness for the outer layer was 5 μm. The first deposit is sufficiently conductive to allow deposition of the second layer. On the other hand the result confirms that the formation of the microtubes is independent of the substrate material [18].

The OCP of the bilayer-coated electrode in chloride solution remains around a value of 0.2 V vs. Ag/AgCl (Fig. 7) which is more noble than that of the bare steel (Fig. 1). The positive shift in OCP indicates the protection of the steel by the bilayer. The morphology remained globally invariant proving that the coating remains stable and protective after 20 days of immersion. Moreover, the amounts of Fe, Ni and Cr released during immersion were all less than 0.10 mg/L.

The protection against corrosion was also tested under polarization at 0.6 V in 0.15 M NaCl. The chronoamperometric curve shows very low currents indicating that chloride anions have not reached the steel surface (Fig. 8). Moreover, the absence of any detectable change in the polymer surface indicates no occurrence of pitting

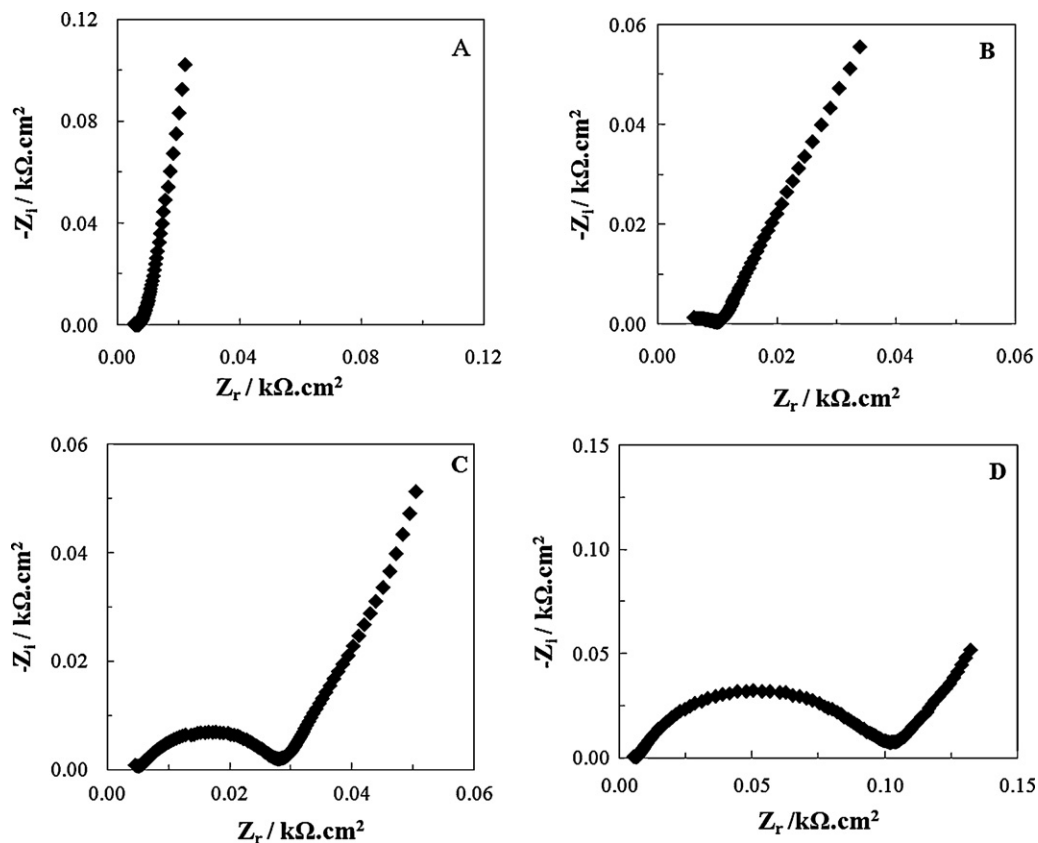


Fig. 9. Nyquist plots registered at OCP in 0.15 M NaCl solution of bilayer-coated 316 L SS electrode after (A) 1; (B) 8; (C) 13 and (D) 20 immersion days.

Table 2

Values for the parameters of the equivalent circuit obtained from the best fit to the impedance data.

	t (days)	R_s ($\Omega \text{ cm}^2$)	Y_0 ($\mu\text{F cm}^{-2}$)	n	R_{ct} ($\Omega \text{ cm}^2$)	R_w ($\Omega \text{ cm}^2$)	s ($\Omega \text{ cm}^2$)	α
Bilayer	1	5.29	4E-6	0.93	1.13	4.57	0.463	0.463
	8	4.21	2.70E-4	0.51	5.34	3.43	0.331	0.372
	13	4.98	2.3E-4	0.65	23.5	0.09	1.1E-3	0.35
	20	6.26	1.2E-4	0.74	91.9	10.4	0.98	0.31

corrosion after polarization. Thus, there is no difference between the behavior of the bilayer and PPY_{0.1Sa}.

Fig. 9 shows the EIS spectra of the covered electrode corresponding to different immersion times in chloride media. At the beginning of immersion the spectra has a resemblance with that of PPY_{0.1Sa}. That is, a small semicircle and a linear part are obtained. But in the case of the bilayered film, the diameter of the semicircle increases with time, as was observed for PPY_{0.5Sa}. The simulated data were generated using the equivalent circuit previously described (Fig. 5) and they are presented in Table 2. The increase in R_{ct} during immersion would indicate that the redox reaction of the polymer is not produced rapidly enough which is detrimental for maintaining the steel in the passive state. However the R_{ct} values are much smaller than those for PPY_{0.5Sa}. On the other hand a diffusional process throughout the coating contributes to the total impedance even for extended periods of immersion. EIS data suggest that the bilayered PPY provides slightly inferior corrosion protection than PPY_{0.1Sa}.

4. Conclusions

Open circuit potential measurements in chloride solution and the analysis of the electrolyte showed that the three PPY coatings synthesized in this work remained stable and protective during 20 days. However EIS results indicated that the coating with granular morphology had better protective properties than the film constituted by the microtubes.

On the other hand the passivating effect of PPY_{0.1Sa} was also demonstrated by polarization at 0.6V while the presence of the PPY_{0.5Sa} was not enough to protect the steel for a long period at this high positive potential. These results can be explained considering the porous opened structure of the microtubes. So we decided to propose a bilayered coating to enhance the protection performance of the coating with microtubes morphology. The film was applied

as a topcoat onto a previously deposited PPY_{0.1Sa}. Its anti-corrosion behavior, although slightly poorer than that of PPY_{0.1Sa}, is excellent. The coating remained protecting, stable and adherent during prolonged exposure times.

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