Electrodeposition of polypyrrole on Nitinol alloy in the presence of inhibitor ions for corrosion protection

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ABSTRACT

The electrosynthesis of polypyrrole (PPy) films on Nitinol (NiTi) from solutions containing different corrosion inhibitors is reported. The corrosion behaviour of the coated samples was investigated in 0.15 M NaCl solution. The presence of molybdate ions in the polymer matrix confers to the substrate a greater resistance to pitting corrosion. The polymer formed potentiostatically in a solution at pH 12 containing nitrate and molybdate is the most efficient in terms of adhesion and corrosion protection. Results are interpreted in terms of the nature of the dopants, the good electroactivity of the polymer and passive properties of the oxide layer.

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1. Introduction

Nitinol (an acronym for the Nickel–Titanium Naval Ordnance Laboratory) alloy has been extensively studied as an implant material for biomedical applications (orthodontic wires, self-expanding cardiovascular and urological stents, bone implants and tiny surgery tools) [1,2]. Its good corrosion resistance and biocompatibility with the human body can be attributed to a layer comprised mainly of TiO_2, with a small amount of NiO on the outermost surface layer [3]. Whereas pure titanium shows a wide range of passive state (up to 10 V(SCE)) in physiological solution, NiTi alloy has a smaller range of passivity and is susceptible to localised corrosion (pitting or crevice) at relatively low anodic potentials (between 0.0 and 1.0 V(SCE)) [3–6]. The main issue related to the use of NiTi alloy as a biomaterial is the release of carcinogenic Ni^{2+} and Ti^{2+} ions into the human body [3,7,8]. Finding a solution to this problem has motivated many researchers to study surface modifications and the use of different coatings. Chemical and thermal passivation [3,9,10], laser welding [11], laser melting surface [12], ion implantation [13] and cathodic electrophoretic deposition of functional materials [14] have been used as surface modification treatments to improve the corrosion resistance of NiTi alloy. What is more, different coating treatments for NiTi alloy such as nitride treatment [7], using

different silane coupling agents as adhesion promoter of polymer matrix [15], polymerisation of styrene on self assembled monolayer of carboxylic acid [16] and the formation of nanocomposite polymers [17] were also employed to enhance the corrosion performance of NiTi alloy.

It has been demonstrated that PPy is capable of providing corrosion protection. The polymer can be deposited in different ways such as a single film [18,19], as part of a multilayered coating [20,21] or it can be incorporated as an additive in a matrix [22]. PPy is also an attractive organic coating for a large number of biological and biomedical applications due to its biocompatibility with the human body [23]. Moreover, a PPy coating can act as a remarkable corrosion inhibitor for metal substrates although the adhesion of the polymer to the metallic substrate is frequently poor [24]. In a previous paper, we have demonstrated that a PPy film presented the ability to protect NiTi alloy against localised corrosion when it was synthesised in a neutral solution of sodium bis(2-ethylhexyl) sulfosuccinate (AOT) containing the monomer (pyrrole (Py)) [25].

Several corrosion inhibitor ions such as molybdate and citrate have been used to passivate the surface of Ti and Ti6Al4V alloy [26–30]. Furthermore, molybdate ion was used as a corrosion inhibitor of NiTi alloy over a wide range of chloride ion concentrations [31]. In this case, potentiodynamic curves of the NiTi alloy passivated in molybdate solution show a positive displacement of 0.4 V(SCE) in the breakdown potential value when is compared to the non-passivated sample. This result was explained by an increase in TiO_2 content on the outermost surface.

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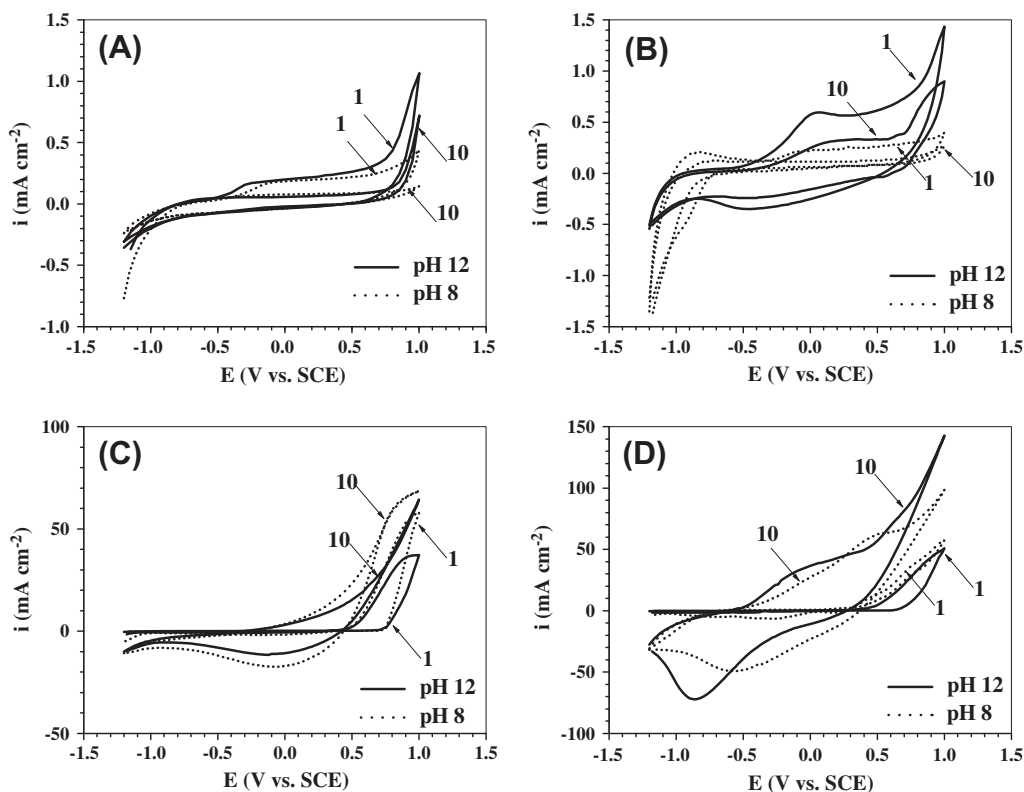 *E-mail address:* dflamini@uns.edu.ar (D.O. Flamini).

Fig. 1. Cyclic voltammograms obtained for NiTi alloy in 0.35 M NO_3^- solutions at different pH values (8 and 12) containing: (A) 0.12 M $C_3H_5O(COO)_3^{3-}$, (B) 0.12 M MoO_4^{2-}, (C) 0.12 M $C_3H_5O(COO)_3^{3-}$ + 0.50 M Py and (D) 0.12 M MoO_4^{2-} + 0.50 M Py. The first and tenth cycle are displayed. Scan rate: 0.05 V s^{-1}.

The presence of different ions in the electrolyte solution during the electrochemical synthesis of conducting polymers produces coatings with certain characteristics and properties. An improvement of the corrosion protection of 55% Al–Zn-coated steels when molybdate is doped into a PPy layer was found [32]. A recent investigation demonstrated that PPy films electrosynthesised from an alkaline solution of pH 12 containing nitrate and molybdate onto 316L stainless steel have good adhesion and can completely protect the substrate against pitting corrosion in chloride solutions,

even when the sample has been polarised at very positive potentials during a considerable period of time [33].

The goal of the present research work was to obtain adherent and protective PPy coatings on NiTi alloy. For this purpose, nearly neutral and alkaline solutions containing different combinations of corrosion inhibitor ions (nitrate and citrate or nitrate and molybdate) were employed during PPy film electrodeposition. To the best of our knowledge, it is the first time that polypyrrole is electrosynthesised on NiTi alloy using inorganic corrosion inhibitor ions. The
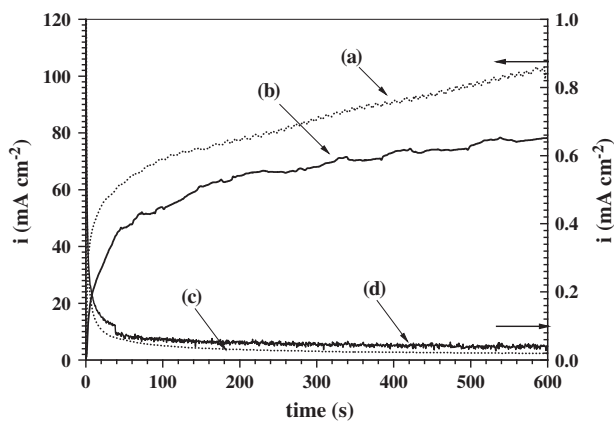

Fig. 2. Chronoamperometric curves obtained for NiTi alloy in 0.35 M NO_3^- + 0.12 M $C_3H_5O(COO)_3^{3-}$ solution containing 0.5 M Py at pH 8 (curve a) and at 12 (curve b), in response to a potential step from 0.0 to 0.80 V(SCE). The chronoamperometric curves obtained in 0.35 M NO_3^- + 0.12 M $C_3H_5O(COO)_3^{3-}$ solution at pH 8 (curve c) and at pH 12 (curve d) without Py, in response to the same potential step are also included.
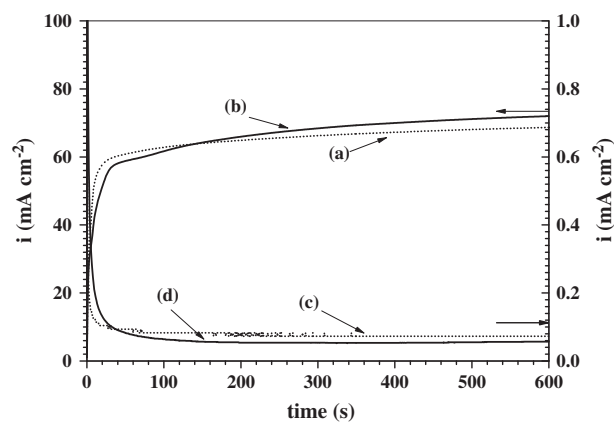

Fig. 3. Chronoamperometric curves obtained for NiTi alloy in 0.35 M NO_3^- + 0.12 M MoO_4^{2-} solution containing 0.5 M Py at pH 8 (curve a) and at 12 (curve b), in response to a potential step from 0.0 to 0.80 V(SCE). The chronoamperometric curves obtained in 0.35 M NO_3^- + 0.12 M MoO_4^{2-} solution at pH 8 (curve c) and at pH 12 (curve d) without Py, in response to the same potential step are also included.

Table 1
Adherence force obtained for different PPy-coated NiTi alloy using the peel-off test.

Sample	Adherence force (N)
NiTi/PPy-NC8	11.70
NiTi/PPy-NC12	12.45
NiTi/PPy-NM8	16.25
NiTi/PPy-NM12	19.90

role played by each dopant anion in the adherence and corrosion protection performance of the coating will be analysed.

2. Material and methods

NiTi rods in the form of discs axially mounted in a Teflon holder were used as working electrodes (WE). The apparent area of the WE is 0.096 cm^2 and its chemical composition (in wt.%) is: 55.8 Ni, 0.05 O, 0.02 C and Ti balance. Before each experiment, the exposed surface area of the WE was abraded with SiC papers down to 1200 grit finish, then degreased with acetone and finally washed with triply distilled water. Following this pretreatment, the WE was immediately transferred to an electrochemical cell. The counter electrode (CE) was a large Pt sheet and a saturated calomel electrode (SCE) was used as a reference electrode (RE). All the potential values in this work are referred to SCE. A Metrohm cell of 20 cm^3 was employed for electrochemical experiments.

PPy films were electrosynthesised on bare NiTi alloy using solutions containing 0.50 M Py as monomer and different corrosion inhibitors: (a) 0.35 M NaNO$_3$ + 0.12 M Na$_3$C$_3$HO$_5$(COO)$_3$ and (b) 0.35 M NaNO$_3$ + 0.12 M Na$_2$MoO$_4$. The pH of solutions was adjusted to 8 and 12 by adding concentrated sodium hydroxide (NaOH) solution. Solutions were purified with a saturated atmosphere of nitrogen gas at 25 °C. All chemicals were reagent grade and solutions were made with triply distilled water. Pyrrole (Sigma–Aldrich) was freshly distilled under reduced pressure before use.

Electrosynthesis of PPy films on NiTi electrodes was carried out by means of potentiodynamic and potentiostatic techniques. The corrosion performance of the coatings was evaluated by open
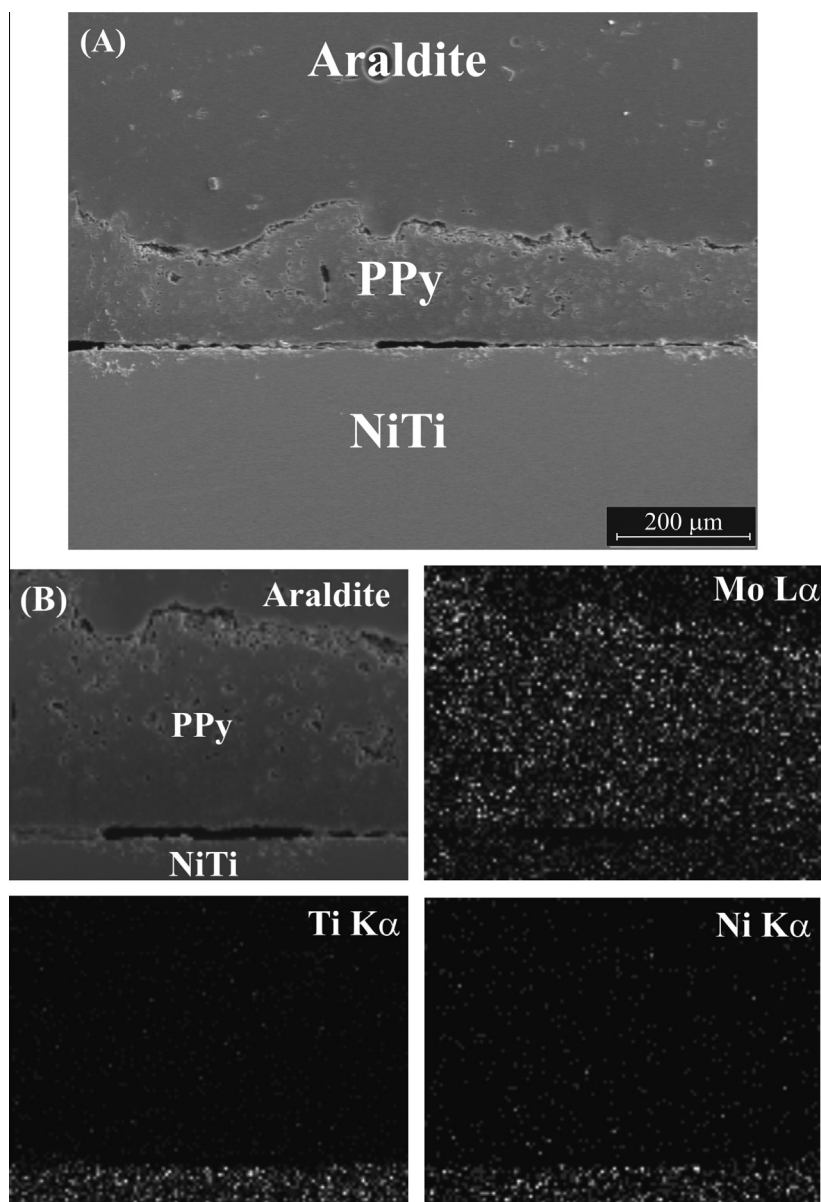

Fig. 4. (A) Cross-section SEM image of NiTi/PPy-NM12 electrode and (B) X-ray maps (Mo Lα, Ti Kα and Ti Kα) of the cross-section.

circuit potential (OCP) value variation with time, linear polarisation, potentiostatic measurements and electrochemical impedance spectroscopy (EIS) in 0.15 M NaCl solution, which is frequently used to simulate the biological environment.

Electrochemical experiments were performed utilising a potentiostat–galvanostat PAR Model 273A. EIS measurements were made using a potentiostat VoltaLab 40 Model PGZ301. The frequency used for impedance measurements was changed from 10 kHz to 100 mHz and the signal amplitude was 10 mV.

A dual stage ISI DS 130 scanning electron microscopy (SEM) and an EDAX 9600 quantitative energy dispersive X-ray (EDX) analyser were used to examine the characteristics of the electrode surface. Ni and Ti released concentrations in chloride solution from bare NiTi and PPy-coated NiTi samples were determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).

Adhesion of PPy coatings to NiTi surface was tested measuring the force necessary to peel-off the film using a Scotch® Magic™ double coated Tape 810 (3 M) and a Mecmesin basic force gauge (BFG 50 N).

3. Results and discussion

3.1. Electrochemical synthesis of PPy film

Potentiodynamic polarisation curves in monomer-free solutions containing corrosion inhibitor ions will provide general information about the electrochemical behaviour of bare NiTi alloy.

The voltammetric responses of NiTi alloy in nitrate solutions at pH 8 and 12 containing citrate or molybdate are presented in Fig. 1(A) and (B), respectively. The WE potential was cycled repetitively between −1.20 and 1.00 V(SCE) at a scan rate of 0.05 V s^{-1}. In both monomer-free solutions at pH 8, there is an active process beginning at −0.50 V(SCE) associated with the oxidation of Ni to NiO [34]. It is then followed by a current increase, related to the formation of NiO_2 on top of the previously formed film and a subsequent transpassive dissolution of NiTi alloy (Fig. 1(A) and (B)) [35]. On the other hand, the redox couple observed at −0.85 V(SCE) in solution containing molybdate at pH 8 (Fig. 1(B)), corresponding to redox reactions between MoO_4^{2-} and Mo^{3+} species [36,37].

The voltamperometric response of NiTi alloy in citrate solution at pH 12 does not change significantly compared to the one obtained at pH 8, except that the transpassive dissolution is increased (Fig. 1(A)). In the case of monomer-free solution containing molybdate at pH 12 (Fig. 1(B)) there is a current shoulder, at about −1.00 V(SCE), attributed to the oxidation of Ti to TiO_2 [34,38]. The anodic current peak has a higher charge compared to that observed in citrate solutions at pH 12. When the scan is reversed, the cathodic peaks, observed at 0.50 and −0.50 V(SCE), are related to the electroreduction of NiO_2 and NiO to Ni, respectively [39]. In the following cycles the anodic current decreases indicating a complete stabilisation of NiTi alloy.

The voltammetric responses in the presence of the monomer were obtained under the same experimental condition described above. For both pH values, the anodic process starting at approximately 0.50 V(SCE), is attributed to Py oxidation (Fig. 1(C) and (D)). Repetitive cycling of the potential results in a progressive increase in the charge of the reduction and oxidation waves. When the number of cycles increases, the oxidation potential of the monomer turns more negative. A black and uniform polymeric film covering the substrate completely after the potential sweeps was observed. The adherence of these coatings was not good and the films could be easily peeled-off the substrate.

The voltammograms obtained in solutions containing nitrate and molybdate (Fig. 1(D)) exhibit better-defined peaks with higher current densities compared with the ones obtained in citrate
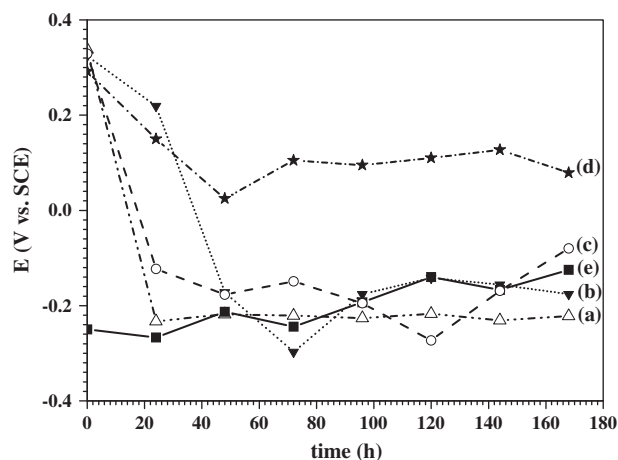
Fig. 5. Time dependence of the OCP in 0.15 M NaCl of the different PPy-coated NiTi alloy: (a) NiTi/PPy-NC8, (b) NiTi/PPy-NC12, (c) NiTi/PPy-NM8 and (d) NiTi/PPy-NM12. The dependency for bare NiTi alloy (curve e) is also included.

solution (Fig. 1(C)), indicating an easier electropolymerisation process in these solution. A low mobility of molybdate through the polymer matrix is expected due to its size and charge [40]. As a
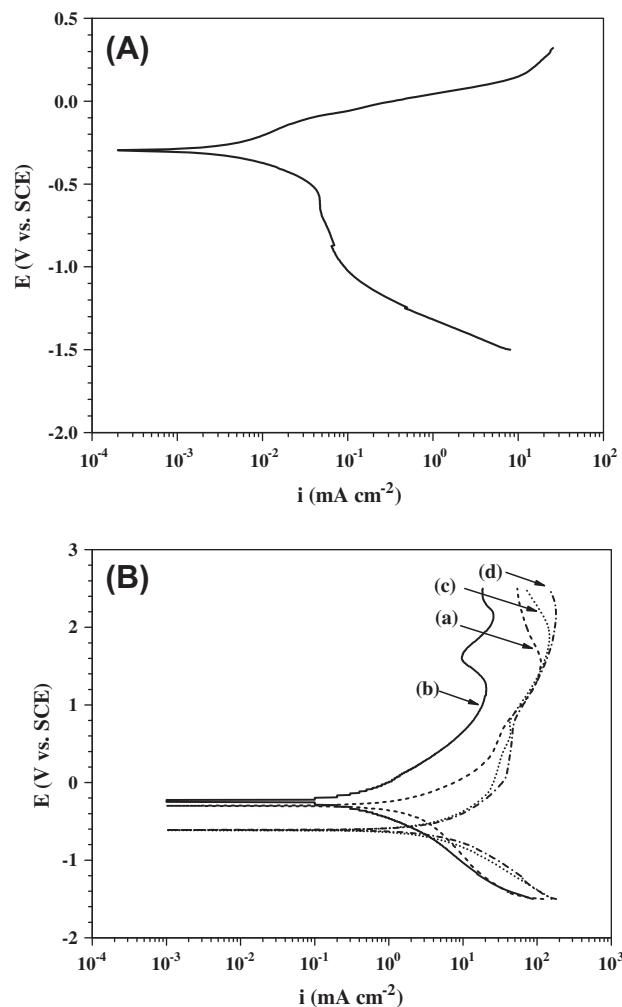
Fig. 6. Polarisation curves registered in 0.15 M NaCl solution at 0.005 V s^{-1} for: (A) bare NiTi alloy and (B) different PPy-coated NiTi alloy: (a) NiTi/PPy-NC8, (b) NiTi/PPy-NC12, (c) NiTi/PPy-NM8 and (d) NiTi/PPy-NM12.

consequence, the reduction peak at very negative potentials is attributed to Na^+ insertion to compensate the polymer charge.

Polypyrrole films can also be synthesised on NiTi alloy at a constant potential (0.8 V(SCE)). Well-formed rising i/t transients were obtained (Figs. 2 and 3, curve a and b). For this applied potential the response obtained for monomer-free solutions exhibits a continuously decreasing current associated with oxide growth (Figs. 2 and 3, curve c and d).

For simplification the films synthesised in solutions containing nitrate and citrate at pH 8 and 12 will be named PPy-NC8 and PPy-NC12, respectively; and those formed in solutions containing nitrate and molybdate, PPy-NM8 and PPy-NM12.

In order to investigate the role played by each anion, the electropolymerisation process was carried out in solutions containing only one corrosion inhibitor. PPy films were successfully electrosynthesised in solutions containing 0.35 M NO_3^- at pH 8 and at 12, but the polymer can be easily removed from the NiTi surface. The electropolymerisation can proceed in solutions containing only molybdate or citrate but under certain conditions. This is related to the fact that molybdate and citrate are nucleophiles that attack the radical cations formed during the electropolymerisation, in consequence a high molar ratio between Py and the anion is needed. For a monomer concentration of 0.5 M, the electropolymerisation takes place in a 0.01 M citrate solution at pH 8, while no deposition occurs for higher citrate concentrations. In the case of molybdate, successful electrosynthesis is attained at pH 8 for concentrations between 0.01 and 0.15 M. In spite of both anions having similar nucleophilicity according to the pK_a values of molybdic and citric acids (3.6 and 3.1, respectively) [41], it seems that molybdate is more suitable for polymer deposition. But, in all the cases described above, the coatings were not adherent. On the other hand, no film could be obtained when the polarisation was carried out at pH 12 for either molybdate or citrate solutions. After polarisation in molybdate solution the NiTi sample shows a

golden surface due to the formation of an oxide layer composed of TiO_2 on the outermost surface, as was previously reported by other authors [31,42].

In order to comparatively evaluate the adhesion force property of the different coatings, the necessary force to peel-off the films was measured (Table 1). All coatings appear to be of good quality in terms of adhesion, being PPy-NM12 the most adherent. This film can be removed only by mechanical abrading.

Considering the good adhesion between the PPy-NM12 coating and the substrate, the NiTi/PPy-NM12 interface was analysed using SEM and EDX techniques. A SEM micrograph showing a cross-sectional view of the electrodeposited polymer is presented in Fig 4(A), where an average film thickness of 150 μm can be measured. Molybdate signal detected by the X-ray map (Fig. 4(B)) indicates that the anion is homogeneously distributed in the PPy coating.

3.2. Corrosion tests

The variation of OCP value as a function of time in an aggressive medium can be use to evaluate the protection degree of the substrate covered with the coating (Fig. 5). For the bare NiTi sample, the initial OCP value is −0.25 V(SCE) and then moves smoothly in the positive direction. In the early stages of immersion the presence of the coatings causes an anodic shift in the corrosion potential which is related to an anodic protection mechanism. But later and for all covered samples, except for PPy-NM12, the OCP drops to values close to the potential corresponding to the bare electrode. The OCP of the NiTi/PPy-NM12 sample is higher than that of the bare NiTi alloy even after 7 days of immersion, indicating that the film is an effective protective coating.

To address the protective properties of the coatings, we have also recorded potentiodynamic polarisation curves in 0.15 M NaCl solution (Fig. 6). The bare sample remains passivated until 0.05 V(SCE), when the current increases indicating the onset of
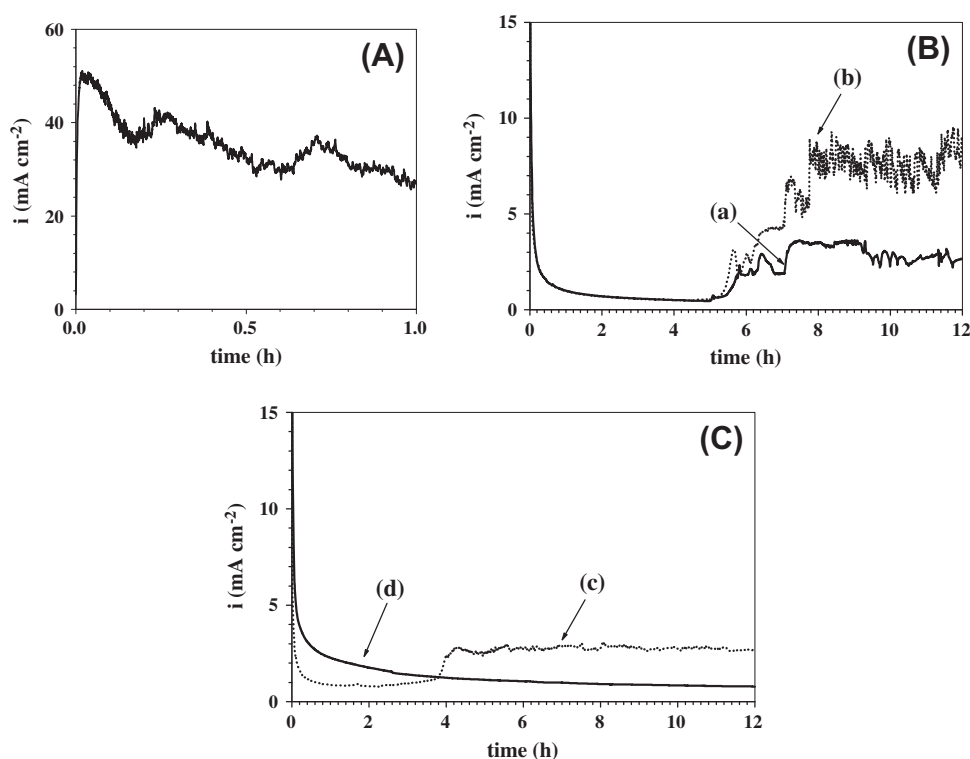

Fig. 7. Potentiostatic response obtained at 0.65 V(SCE) in 0.15 M NaCl solution for: (A) bare NiTi alloy, (B) and (C) different PPy-coated NiTi alloy: (a) NiTi/PPy-NC8, (b) NiTi/PPy-NC12, (c) NiTi/PPy-NM8 and (d) NiTi/PPy-NM12.

pitting corrosion (Fig. 6(A)). The curves corresponding to the coated electrodes present anodic peaks associated with oxidation and overoxidation of the polymers (Fig. 6(B)). The oxygen evolution reaction takes place simultaneously with the overoxidation reaction at about 1.80 V(SCE) [43]. The absence of current oscillations reveals that all the coatings remain protective at very positive potentials without evidence of pitting corrosion.

To get an insight into the pitting corrosion protection, chrono-amperometric measurements were made at 0.65 V(SCE), a potential that is higher than that necessary to initiate the localised attack of the bare sample (Fig. 7). Thus, uncovered NiTi alloy is characterised by high oscillating anodic currents which indicate localised corrosion (Fig. 7(A)). In the first hours, all polymers covering the samples act as good protective coatings considering the low currents registered (Fig. 7(B) and (C)). After a certain period of polarisation the current increases exhibiting oscillations due to the development of pitting corrosion (Fig. 7 curves a, b and c). Only the sample covered with PPy-NM12 exhibits low and stable currents during all the experiment (Fig. 7 curve d).

SEM micrograph of the surface of bare NiTi alloy after 1800 s of polarisation at 0.65 V(SCE) confirms that localised corrosion has occurred since several pits can be observed (Fig. 8(A)). Moreover, SEM analysis of the sample covered with PPy-NC12 after 12 h of polarisation shows a completely deteriorated coating in several zones (Fig. 8(B)). EDX analysis performed in these areas detected the presence of Ti, Ni and Cl (Table 2). On the contrary, SEM micrograph of the sample covered with PPy-NM12 reveals that the surface morphology of the film remains intact after anodic polarisation (Fig. 8(C)). Neither Ti nor Ni is detected in the EDX analysis, which indicates that an homogeneous and thick film has been formed (Table 2). The signal of Mo reveals that molybdate is entrapped into the polymer matrix. Thus, the presence of this coating hinders the pitting corrosion process even after 12 h of polarisation. Further evidence in support of this was obtained by monitoring the released concentrations of Ni and Ti in chloride solution after anodic polarisation (Table 3). The results are consistent with a decrease of the alloy dissolution rate due to its modification with PPy-NM12 film.

Additional information about the resistance of the bare NiTi alloy and the PPy-NM12 coated substrate to pitting corrosion can be obtained from EIS measurements performed at 0.65 V(SCE) in chloride solution at different polarisation times. Measurements were taken three times for each sample and the values turned out to be reproducible.

The Nyquist plot of the bare NiTi alloy is shown in Fig. 9(A). The electrochemical impedance spectrum presents a depressed semicircle and low magnitude of impedance associated with the breakdown of the passive oxide film [44]. The latter was also observed in the Bode plot (Fig. 10(A)). A different result was obtained for the sample coated with PPy-NM12 (Fig. 9(B)), where the Nyquist plot presents a depressed semicircle at high frequencies values related to the resistance of the PPy-NM12 film itself and the corresponding oxide passive layer, followed by a straight line with a slope of 45° in the low frequency region attributed to a mechanism controlled by diffusion. This kind of response has also been reported by other authors for PPy films electrodeposited onto oxidised metals [19,45,18,46,47]. Bode plot of the NiTi/PPy-NM12 sample (Fig. 10(B)) shows that the magnitude of the impedance increases with increasing polarisation time, which indicates qualitatively the stability and good anticorrosion properties of the coating in an aggressive solution.

It is possible to estimate the double layer capacitance and charge transfer resistance from Bode plots [48]. Capacitance was estimated using the following equation: $C = -1/2\pi f Z_i$, where f is the frequency corresponding to the maximum phase angle value and Z_i is the imaginary part of the impedance at this frequency.
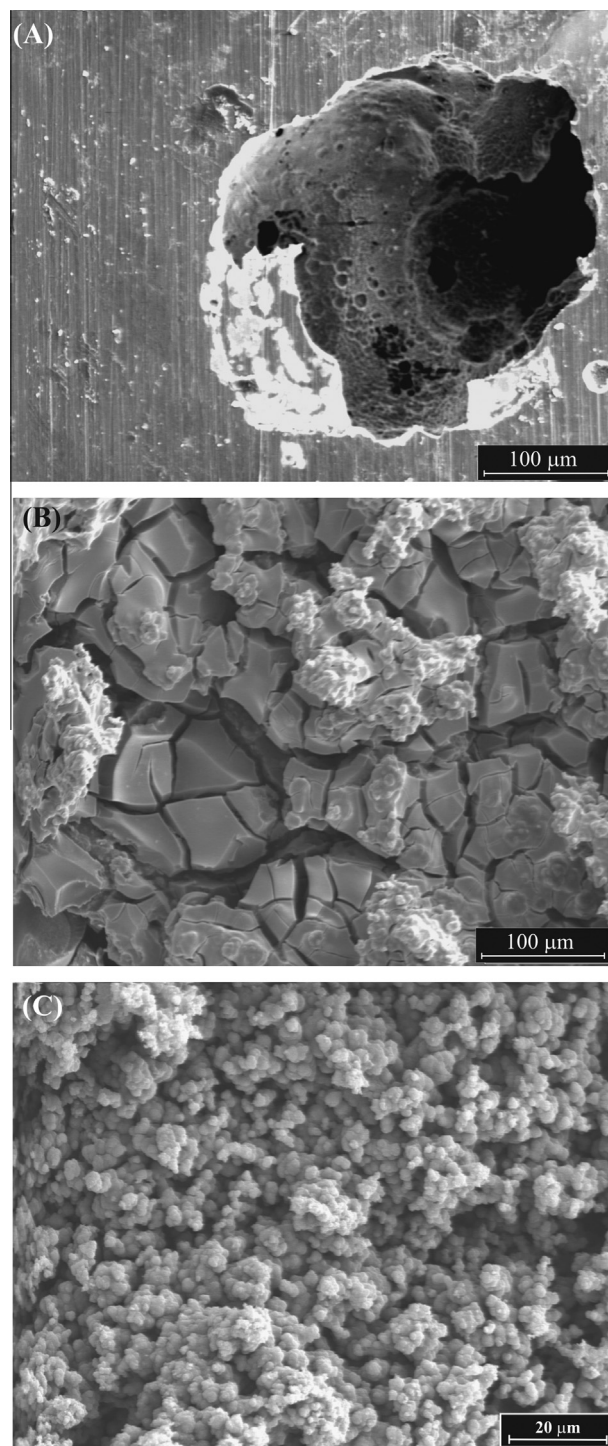

Fig. 8. SEM micrograph of: (A) bare NiTi alloy after 1800 s of polarisation at 0.65 V(SCE) in 0.15 M NaCl solution, (B) NiTi/PPy-NC12 and (C) NiTi/PPy-NM12 electrodes after 12 h of polarisation at 0.65 V(SCE) in 0.15 M NaCl solution.

Table 2
Elemental composition (in wt.%) obtained by EDX of: NiTi/PPy-NC12 attacked areas (Fig. 8(B)) and NiTi/PPy-NM12 (Fig. 8(C)) after 12 h of polarisation at 0.65 V(SCE) in 0.15 M NaCl solution.

Film	C	O	Mo	Cl	Ti	Ni
PPy-NC12	12.18	–	–	9.97	29.8	48.05
PPy-NM12	6.67	39.87	53.46	–	–	–

Table 3
Concentration of Ni and Ti released after anodic polarisation in 0.15 M NaCl solution for bare NiTi and the different PPy-coated NiTi alloy.

Sample	Applied potential (V(SCE))	Time (h)	Ni concentration (mg L^{-1})	Ti concentration (mg L^{-1})
Blank	–	–	0.015	<0.002
Bare NiTi	0.65	0.5	14.96	4.41
NiTi/PPy-NC8	0.65	12	19.5	0.002
NiTi/PPy-NC12	0.65	12	23.4	0.046
NiTi/PPy-NM8	0.65	12	5.8	<0.002
NiTi/PPy-NM12	0.65	12	3.6	<0.002
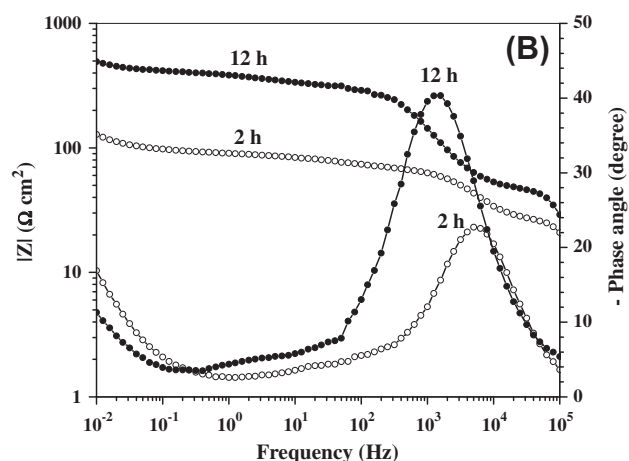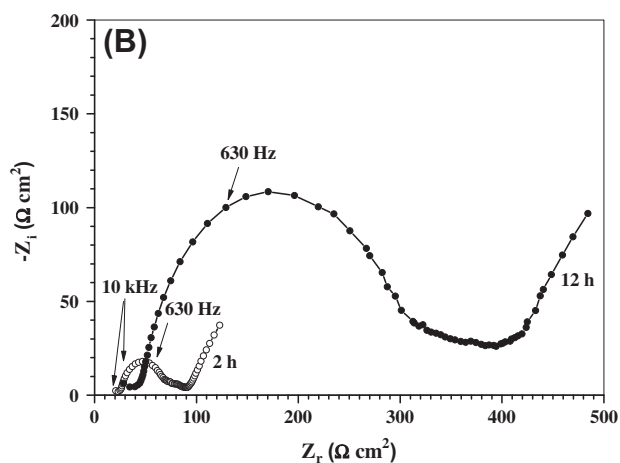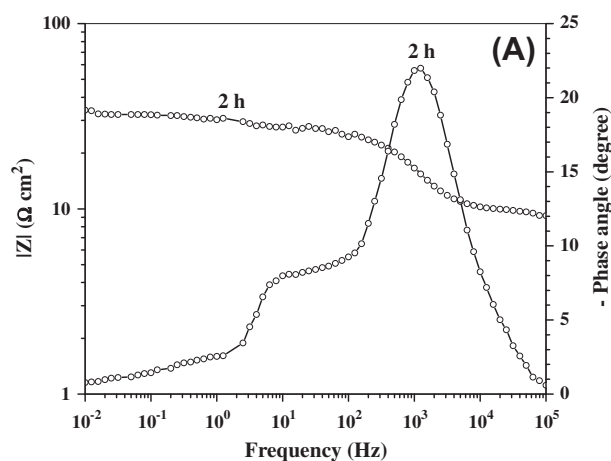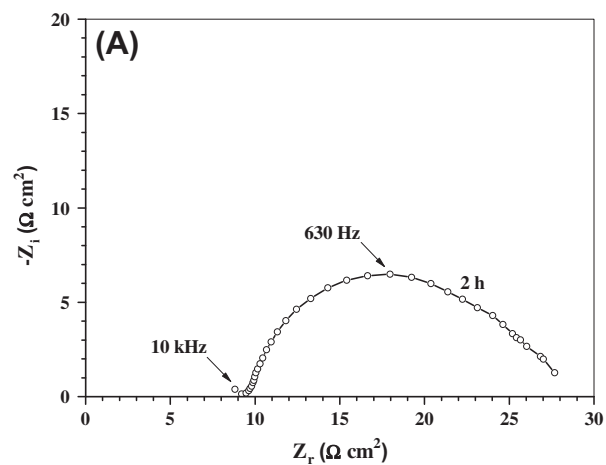
Fig. 9. Nyquist plots registered at 0.65 V(SCE) in 0.15 M NaCl solution for: (A) bare NiTi alloy and (B) NiTi/PPy-NM12 electrode. Polarisation times are indicated.

Fig. 10. Bode plots registered at 0.65 V(SCE) in 0.15 M NaCl solution for: (A) bare NiTi alloy and (B) NiTi/PPy-NM12 electrode. Polarisation times are indicated.

For the resistance estimation, equation $R = Z_r$ was used, where Z_r is the real part of the impedance at the frequency corresponding to the minimum phase angle value. The capacitance and resistance values obtained for PPy-NM12 coated alloy indicate a decrease in the capacitance and an increase in the resistance values with polarisation time, which can be associated with an effective corrosion protection performance of the film (Table 4).

The obtained results confirm that the anodic current measured for the NiTi/PPy-NM12 sample polarised at potentials where the bare sample suffers pitting corrosion is related to the response of the PPy film and not to a breakdown of the passive oxide film (Fig. 7(C), curve d). The protection for localised corrosion is a consequence of the incorporation of anodic inhibitor ions (MoO_4^{2-}) in the polymer matrix. Previous results obtained in our laboratory indicate that MoO_4^{2-} ions can act as an immobilised dopant when the PPy film is synthesised onto 316L stainless steel and Al

Table 4
Double layer capacitance and resistance values calculated for bare NiTi alloy and NiTi/PPy-NM12 electrode after polarisation at 0.65 V(SCE) in 0.15 M NaCl solution.

Sample	Polarisation time (h)	C (μF cm^{-2})	R (Ω cm^2)
Bare NiTi	2	22.07	26.85
NiTi/PPy-NM12	2	1.90	90.42
NiTi/PPy-NM12	12	1.41	398.85

electrodes [33,49]. In these works it has been demonstrated that molybdate ions are retained in the polypyrrole backbone and they are not easily exchanged with chloride, in concordance with the results showed above (Table 2). As was suggested by other authors, when a galvanic interaction between coating and substrate is produced, an eventual release of molybdate anion from the polymer matrix during its reduction can provide protection [50,51].

When the anticorrosion performance of the coatings was compared, it can be concluded that the coating electrosynthesised in solution containing nitrate and molybdate ions at pH 12 exhibits a very good protection performance. The coated alloy exhibits the most positive OCP values (Fig. 5, curve d), the lowest current density registered at 0.65 V (SCE) (Fig. 7(C), curve d) and the smallest concentrations of Ni and Ti released in chloride solution (Table 3). In addition, its SEM image obtained after anodic polarisation indicates that the coating remains intact (Fig. 8(C)).

As was previously stated, during electrochemical polymerisation of Py in solution containing molybdate ion at pH 12 a simultaneous growth of a Ti-oxide is produced, which leads to the formation of a composite structure of TiO$_2$/PPy as was proposed by Idla et al. for pure Ti [52]. The development of this structure during electropolymerisation could be responsible for the improved adhesion and for the improved corrosion protection performance attained by the coated alloy.

4. Conclusions

Polypyrrole films could be electrodeposited on NiTi alloy in nearly neutral and alkaline solutions containing different inhibitor anions. Only the coatings electrosynthesised potentiostatically in an alkaline solution containing nitrate and molybdate are strongly adherent to the NiTi alloy surface. The coating can completely protect the substrate against pitting corrosion in 0.15 M NaCl solution, even when the coated sample is polarised during a prolonged period of time to a potential higher than the breakdown potential of the bare substrate (0.65 V(SCE)). The possible causes of the corrosion protection properties of the coating are: (i) the presence of the molybdate anion as corrosion inhibitor modifies the properties of the passive oxide layer giving the substrate a greater adherence to the polymer due to the formation of a composite structure of TiO$_2$/PPy; (ii) the synthesised PPy film is an electroactive polymer and there is a galvanic interaction with the substrate; (iii) the fixed negative charge of molybdate prevents the ingress of chloride into the polymer matrix and (iv) the release of the corrosion inhibitor anions from the polymer matrix also contributes to the protection of the alloy

Acknowledgments

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