

# Characterisation and corrosion protection properties of polypyrrole electropolymerised onto aluminium in the presence of molybdate and nitrate

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## Abstract

This paper describes the first attempts for the electrosynthesis of polypyrrole films containing molybdate onto aluminium electrodes. Electrogeneration was carried out in an alkaline solution in the presence of molybdate, nitrate and the monomer. The optimum concentrations for electropolymerisation were chosen in order to improve the corrosion protection of the substrate. The coatings were characterised by SEM/EDX and IR spectroscopy and the cyclic voltammetric response of the film is discussed. Pitting corrosion resistance was studied by means of open circuit potential and potentiodynamic measurements. The results presented below show that molybdate remains entrapped into the polymer matrix, providing greater resistance to breakdown of passivity in chloride media.

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**Keywords:** Aluminium; Polypyrrole; Electrodeposition; Molybdate; Corrosion

## 1. Introduction

A great deal of research has been devoted to the electrodeposition of conducting polymers onto active metals due principally to their use as anti-corrosion coatings [1]. The synthesis of polypyrrole (PPy) onto reactive metals such as Al has been the subject of several papers [2–10]. The electrodeposition from a  $\text{NO}_3^-$  containing solution of pH 12 results in conductive and adherent PPy films [8], which can be cycled in acid solution without losing its redox behaviour.

It is expected an improvement in the corrosion protection of the substrate if the dopant of the polymer is a corrosion inhibitor. Molybdate is widely used as a corrosion inhibitor. It reduces the passivity current and increases the pitting potential of Al and its alloys in chloride media [11–13]. It has been proposed that a molybdate-rich region on the film surface inhibits the ingress of  $\text{Cl}^-$  to the metallic/film interface [11]. A competitive adsorption of chloride and molybdate at the flawed regions followed by oxidation/reduction reactions was also proposed [13]. The pitting corrosion resistance is also improved with molybdenum as

an alloy component [14–16]. The behaviour of the passive film formed on stainless steel containing molybdenum in acid media was explained considering that the incorporation of oxygen ligands from the  $\text{MoO}_4^{2-}$  molecule provide a source of strong negative charge that repel  $\text{Cl}^-$  and  $\text{OH}^-$  anions passing through an unblocked channel [14]. The inhibiting  $\text{Cl}^-$  ion adsorption when an Al alloy was implanted with molybdenum has been explained considering that Mo oxide has a lower isoelectric pH than Al oxide [16].

Studies of the incorporation of molybdate into the PPy films electrogenerated onto Al in alkaline solution are presented in this work.

## 2. Experimental

Aluminium (99.999%, Aldrich Chemical Company) rods embedded in a Teflon holder with an exposed area of  $0.070 \text{ cm}^2$  were used as working electrodes. Before each experiment, the electrode was polished successively with 200, 600 and 1000 emery paper, then degreased with acetone and washed with triply distilled water. Following this pretreatment, the electrode was immediately transferred to the electrochemical cell. All the potentials were measured against a saturated calomel electrode (SCE) and a platinum sheet was used as

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a counter electrode. The experiments were conducted in a 20 cm<sup>3</sup> Metrohm measuring cell and measurements were done in a purified nitrogen gas saturated atmosphere at 25 °C. The solutions were not deaerated during open circuit potential measurements.

Solutions of different salts as NaNO<sub>3</sub>, Na<sub>2</sub>MoO<sub>4</sub>, NaCl were used. All chemicals were reagent grade and solutions were freshly made in twice distilled water. The pH of the solutions was adjusted by addition of NaOH. Pyrrole was purchased from Acros Organics and it was freshly distilled under reduced pressure before use.

Electrochemical measurements were done using a potentiostat–galvanostat PAR Model 273A. 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. Infrared spectra were recorded with a Nicolet Nexus FTIR spectrophotometer, using the KBr pellet technique.

### 3. Results and discussion

#### 3.1. Electrochemical synthesis

It was not possible to obtain deposition of PPy in a molybdate solution at pH 12. Molybdate is a nucleophile that attacks the radical cations, hindering the electropolymerisation process. On the other hand, it has been demonstrated that NO<sub>3</sub><sup>−</sup> is a good choice of anion for electropolymerisation [7,8]. Then, the possibility of electropolymerisation in the presence of both, nitrate and molybdate anions was considered. In order to choose the most favourable electrolyte composition, solutions with different nitrate and molybdate concentrations were tested. The best results were obtained with 0.7 M NO<sub>3</sub><sup>−</sup> + 0.25 M MoO<sub>4</sub><sup>2−</sup> + 0.5 M Py, pH 12 solution. This optimum electrolyte composition represents the result of the following effects: (i) as the nitrate concentration increases the amount of electrosynthesised polymer increases, (ii) for a fixed nitrate concentration, as the molybdate concentration increases, the amount of electrosynthesised polymer first increases and thereafter decreases and (iii) the protection attained increases as the molybdate concentration increases.

As occurred with the alkaline solution containing only nitrate, the best quality PPy films are produced potentiostatically (Fig. 1, curve a). Thick, uniform and adherent films were deposited on the electrode under these conditions. The rapid initial decrease in the anodic current is associated with the formation of the oxide layer [8]. At longer times of anodic polarisation ( $t = 20$  s) a chronoamperometric maximum is reached and then the current follows a  $I-t^{-1/2}$  relationship, which can be attributed to a diffusion controlled process. Lower consumed charge are measured from the chronoamperometric curve when the solution containing only NO<sub>3</sub><sup>−</sup> (Fig. 1, curve b). Solution anions participate in the electropolymerisation of Py and the increase in the anion concentration benefits the polymerisation reaction. Considering the solution pH, the dominant species is MoO<sub>4</sub><sup>2−</sup> [17]. At the working electrolyte concentration employed the capture of the radical cation by the molybdate nucleophilic

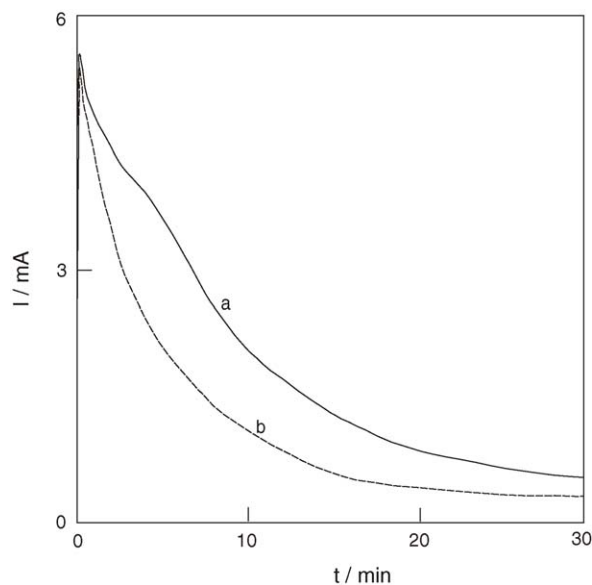


Fig. 1. Chronoamperograms obtained on Al at 0.90 V: (a) 0.7 M NO<sub>3</sub><sup>−</sup> + 0.25 M MoO<sub>4</sub><sup>2−</sup> + 0.5 M Py and (b) 0.7 M NO<sub>3</sub><sup>−</sup> + 0.5 M Py.

attack becomes reduced in favour of electropolymerisation reaction. Thus, electrodeposition in the presence of nitrate and molybdate may lead to an insertion of both anions into the polymer.

Addition of molybdate did not lead to significant change in the voltammetric response of bare Al in 0.01 M NaOH [8]. The oxide formed in this electrolyte consists of a relatively compact inner barrier film covered with an outer crystalline layer. The compact inner film thickness is representative of the balance between chemical dissolution at the oxide film/solution interface and oxide film growth at the metal/oxide film interface. Hence, the properties of the oxide layer in controlling current flow are not significantly influenced by the presence of molybdate in solution.

The IR spectrum of a KBr pellet of the doped PPy is presented in Fig. 2. For comparison, the spectrum of a coating synthesised in nitrate solution under similar conditions is included in the same figure. The bands at 900 and 837 cm<sup>−1</sup> correspond to stretching vibrations of the MoO<sub>4</sub><sup>2−</sup> anion,  $\nu_1$ (MoO<sub>4</sub><sup>2−</sup>) and  $\nu_3$ (MoO<sub>2</sub><sup>4−</sup>), respectively [18]. The sharp band at 1386 cm<sup>−1</sup> attributed to stretching vibrations of the NO<sub>3</sub><sup>−</sup> anion [18] also appears but its relative intensity is clearly diminished compared to that obtained for the film formed in nitrate solution. Thus, these results indicate that both anions are incorporated as dopants into the polymer matrix. Likewise, the presence of MoO<sub>4</sub><sup>2−</sup> produces modifications in the PPy structure considering the changes observable in the range between 1390 and 1650 cm<sup>−1</sup>, where the peaks are due to C=C and C=N in plane vibrations.

SEM micrographs show the morphology of the PPy coating on Al substrate formed at 0.9 V for 30 s and 30 min (Fig. 3). The polymer presents a fine-grained structure with the formation of aggregates. The structure is less compact than that formed in a solution containing only nitrate. The presence of Mo in the film is evidenced by EDAX spectra.

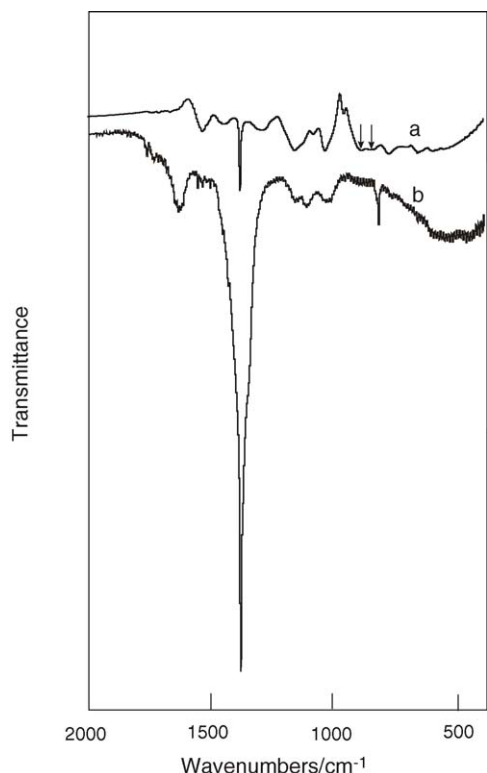


Fig. 2. Infrared spectra of PPy deposited on Al (a) at 0.90 V in 0.7 M  $\text{NO}_3^-$  + 0.25 M  $\text{MoO}_4^{2-}$  + 0.5 M Py and (b) at 0.90 V in 0.7 M  $\text{NO}_3^-$ , pH 12 solution containing 0.5 M Py. Arrows indicate bands at 900 and 837  $\text{cm}^{-1}$ .

### 3.2. Redox behaviour of PPy

To have a better understanding of the processes that occur at the electrode, the redox response of the film formed under low deposition charge was analysed in a monomer-free solution. When PPy was electrodeposited under high deposition charges such as those employed in Fig. 1, the  $I/E$  curve is practically a straight line, indicating an increased polymer resistance. A PPy-coated Al electrode was prepared at 0.9 V for 30 s from a solution containing molybdate and nitrate. The modified electrode was then subjected to potential cycling between 0.60 and  $-1.40$  V at  $0.050$   $\text{V s}^{-1}$  (Fig. 4). The total charge diminishes progressively until a stabilised response is achieved. The film can be cycled over a period of time of 5 h without evidence of decomposition. The polymerisation efficiency, evaluated through the charge consumed during the oxidation of the film and that consumed during the electropolymerisation process is slightly higher compared with that obtained using nitrate alone for electropolymerisation. Likewise, the redox conversion is less reversible.

In view of previous reports, the voltammetric peaks at about 0.30 and  $-0.20$  V are due to the exchange of nitrate [8]. By comparing with the response of the film formed in nitrate, an additional peak appears at 0.45 V, whose height increases with the increase of molybdate in the electropolymerisation solution. This peak was also found when the polymer is formed in acid media containing Mo(VI) [19]. Cyclic voltammetry performed in 0.25 M  $\text{MoO}_4^{2-}$ , pH 12 solution using vitreous carbon as

a substrate allows to conclude that there is no electrochemical response of the anion itself in the potential range analysed. Thus, the oxidation peak may be attributed to a response of the polymer, in accordance with the results reported for PPy formed in acid media [19]. The reduction peak at the more negative potentials, which is absent when only nitrate is used in the electropolymerisation solution, was attributed to the insertion of the cation from the electrolyte [20]. This assignment was tested by cycling the film in  $\text{NaNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  solutions. While the reduction peak is observed in  $\text{NaNO}_3$ , it is absent in  $\text{Ca}(\text{NO}_3)_2$  because the calcium ion is expected to be less easily incorporated into the polymer matrix. Therefore, it can be proposed that there is no exchange of molybdate in the first redox cycles and ingress of  $\text{Na}^+$  equilibrates the polymer charge. With increasing the number of scans, the current of the peak associated with the exchange of the cation and the current of the peak at 0.45 V decrease, and finally both peaks disappear. This result is probably related to the incorporation of  $\text{Al}^{3+}$  in the polymeric matrix. This explanation is supported by the fact that the response of PPy deposited on vitreous carbon under the same polymerisation charge used for the Al substrate shows that the cathodic peak associated with  $\text{Na}^+$  insertion remains during cycling (Fig. 5). Likewise, the peak was not found when a smaller scan rate was used (Fig. 6). In this case, the elapsed time during the first cathodic sweep allows the  $\text{Al}^{3+}$  ion to penetrate into the polymer matrix.

Sulphate is a weaker nucleophile than molybdate and it allows PPy electropolymerisation to proceed [20]. But considering that both anions have the same molecular structure and charge and that their sizes are not very different, their behaviour as a dopant should be similar. As in the case of sulphate, it is expected a small ionic conductivity of molybdate in the polymer film due to a strong ion–ion interaction between the divalent ion and the charged polymer [21]. Thus, upon the reduction of PPy, molybdate remains in the matrix so that the cation penetrates into the film in order to equilibrate the charge.

### 3.3. Response of PPy/Al electrodes in chloride media

The corrosion protection properties of the covered electrode were investigated in chloride solutions. The variation of the open circuit potential (OCP) as a function of time can be used to evaluate the passivation of oxidisable metal surface covered with a polymer. The OCP in 0.5 M  $\text{Cl}^-$  for PPy formed in 0.7 M  $\text{NO}_3^-$ , pH 12 solution drops to  $-0.74$  V, the pitting potential of Al, indicating that the presence of the film is not sufficient to keep chloride ions away from the metal surface (Fig. 7, curve a). A more positive potential is obtained when the film is formed by passing the same charge in a solution containing both,  $\text{NO}_3^-$  and  $\text{MoO}_4^{2-}$  (Fig. 7, curve b). The presence of both anions in the solution caused a less significant displacement of the OCP of bare Al towards positive values (Fig. 7, curve c). These results indicate that molybdate not only serves the purpose of maintaining the electroneutrality of the polymer matrix, but it also plays an important role in the corrosion protection of Al. Likewise, it can be inferred from the

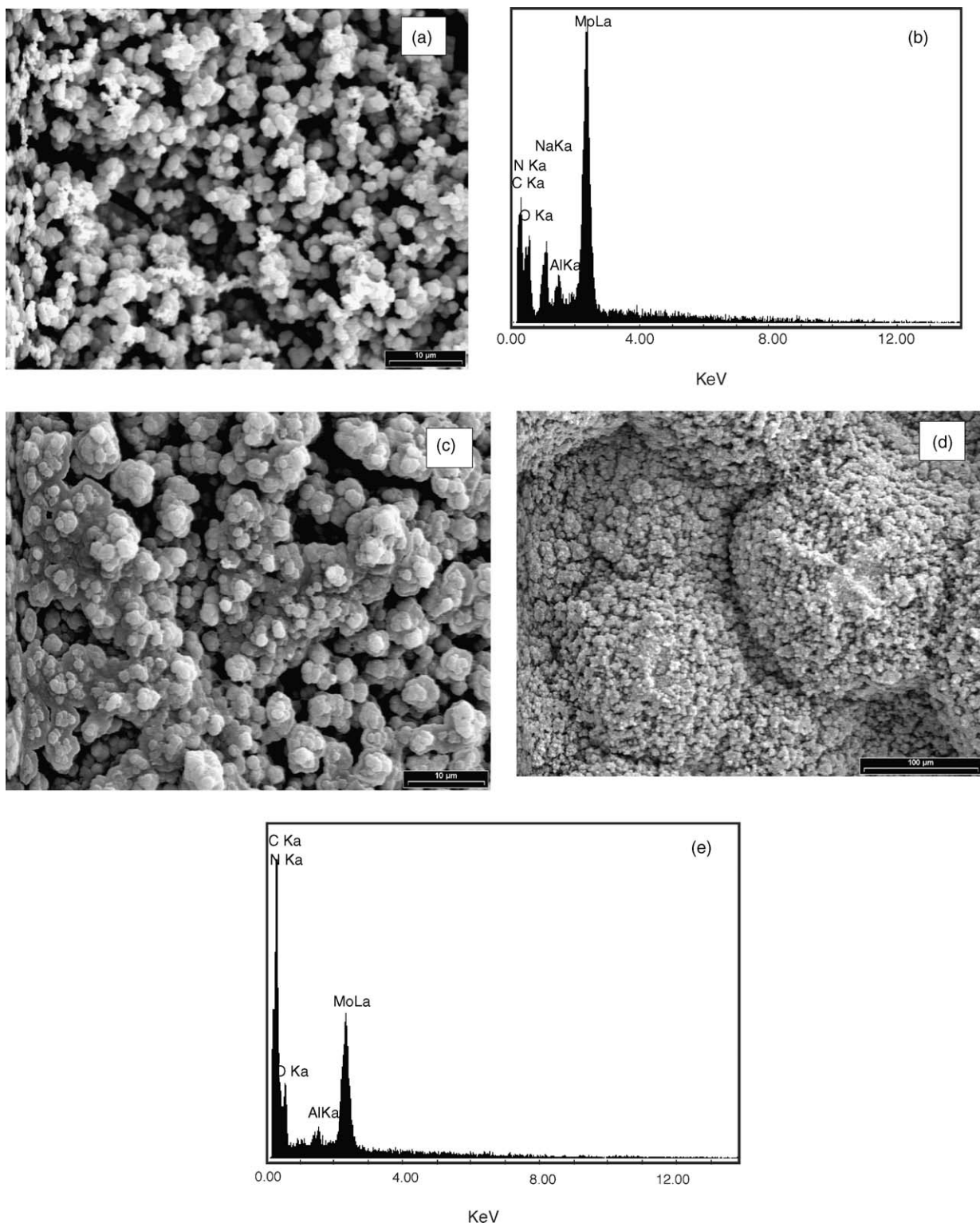


Fig. 3. SEM/EDX examination of PPy-coated Al. The film was formed at 0.90 V in 0.7 M  $\text{NO}_3^-$  + 0.25 M  $\text{MoO}_4^{2-}$  + 0.5 M Py, pH 12 for: (a and b) 30 s and (c–e) 30 min.

OCP measurements that molybdate do not leave the film by an ion exchange process in the time interval analysed. When lesser electropolymerisation charges were employed, the OCP variation showed that the films have not proved adequate protection.

The improved corrosion resistance of PPy formed in the presence of molybdate can also be evaluated by comparing the polarisation curves in chloride solution.

The polarisation behaviours of Al samples covered with PPy formed in nitrate solution with (Fig. 8a) and without molybdate

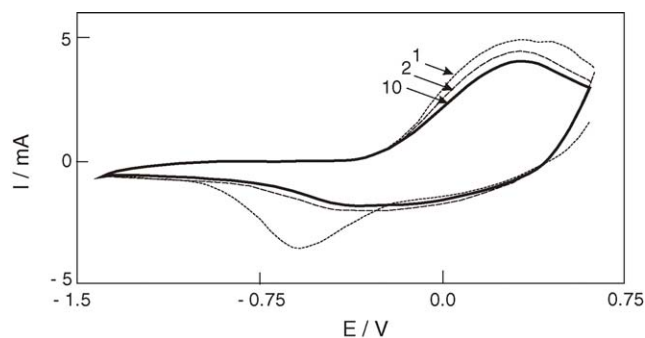


Fig. 4. Cyclic voltammograms of PPy-coated Al electrode in 0.7 M  $\text{NO}_3^- + 0.25 \text{ M MoO}_4^{2-}$ , pH 12 solution at  $0.05 \text{ V s}^{-1}$ . The PPy films was made potentiostatically ( $E = 0.90 \text{ V}$ ,  $t = 30 \text{ s}$ ) in  $0.7 \text{ M NO}_3^- + 0.25 \text{ M MoO}_4^{2-} + 0.5 \text{ M Py}$ , pH 12. The cycle numbers are indicated. Initial potential: 0.60 V.

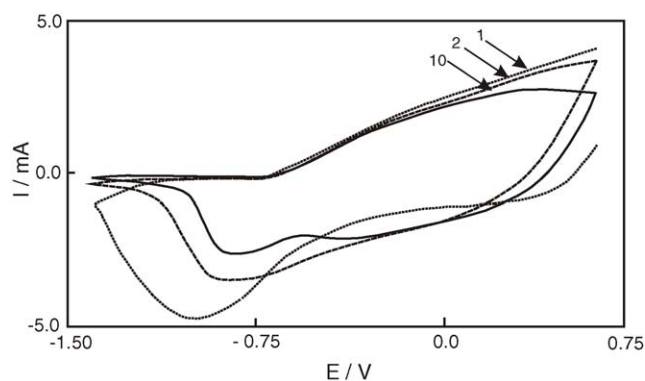


Fig. 5. Cyclic voltammograms of PPy-coated vitreous carbon electrode in 0.7 M  $\text{NO}_3^- + 0.25 \text{ M MoO}_4^{2-}$ , pH 12 solution at  $0.05 \text{ V s}^{-1}$ . The PPy films was made potentiostatically ( $E = 0.90 \text{ V}$ ,  $t = 18 \text{ s}$ ) in  $0.7 \text{ M NO}_3^- + 0.25 \text{ M MoO}_4^{2-} + 0.5 \text{ M Py}$ , pH 12. The cycle numbers are indicated. Initial potential: 0.60 V.

(Fig. 8b) are presented, being the consumed charge the same in the two cases. The potentiodynamic run for the film formed in the presence of both anions shows a broad anodic peak. The polymer deposited onto vitreous carbon under the same experimental conditions gives rise to a similar voltammetric wave. Thus, this anodic peak can be associated with the polymer film.

The potentiodynamic run for the film formed in nitrate shows that the current rises continually while oscillations appear, denoting the onset of pitting corrosion (Fig. 8b). The improved of

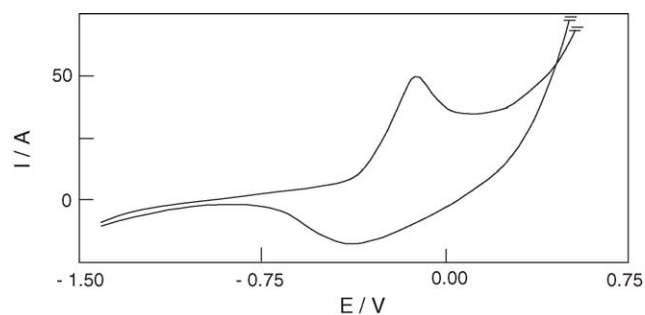


Fig. 6. Cyclic voltammogram of PPy-Al electrode in 0.7 M  $\text{NO}_3^- + 0.25 \text{ M MoO}_4^{2-}$ , pH 12 solution at  $0.001 \text{ V s}^{-1}$ . The PPy films was made potentiostatically ( $E = 0.90 \text{ V}$ ,  $t = 30 \text{ s}$ ) in  $0.7 \text{ M NO}_3^- + 0.25 \text{ M MoO}_4^{2-} + 0.5 \text{ M Py}$ , pH 12. Initial potential: 0.60 V.

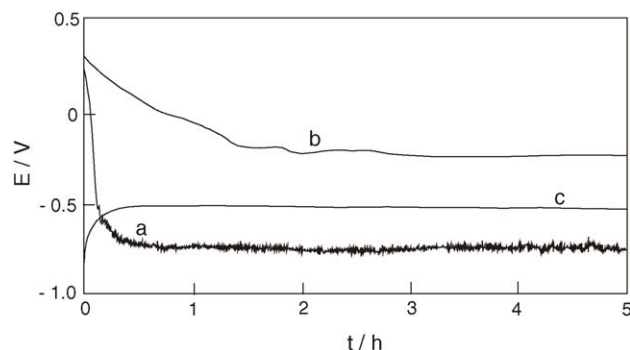


Fig. 7. Time dependence of the OCP in 0.5 M NaCl of: (a) PPy-coated Al electrode. The polymer was synthesised potentiostatically at 0.90 V for 70 min in  $0.7 \text{ M NO}_3^- + 0.5 \text{ M Py}$ , pH 12; (b) PPy-coated Al electrode. The polymer was synthesised potentiostatically at 0.90 V for 30 min in  $0.7 \text{ M NO}_3^- + 0.25 \text{ M MoO}_4^{2-} + 0.5 \text{ M Py}$ , pH 12; (c) bare Al. The solution also contains  $0.7 \text{ M NO}_3^- + 0.25 \text{ M MoO}_4^{2-}$ .

passivation is seen in the significantly higher breakdown potential by comparing curves in Fig. 8a and b. For comparison, the curve of bare Al in a chloride solution containing nitrate and molybdate is also presented (Fig. 8c). The peak at  $-1.1 \text{ V}$  is probably due to oxidation of Mo(III) formed by reduction of Mo(VI) at the more negative potentials [12,13]. The effect of molybdate and nitrate in the solution is to lead a significantly increase in the pitting potential by comparison to the uninhibited solution. But the better pitting inhibition is achieved with PPy electrodeposited in the presence of both anions.

The behaviour in NaCl solution of the PPy-coated electrode after different treatments was analysed. First, the polymer transition from oxidised to neutral state was performed by polarising the electrode at  $-1.0 \text{ V}$  during 15 min in a solution without the monomer. The OCP variation showed that the film was not protective enough in presence of chloride ions after this treatment. This result is probably related with the reduction of molybdate. The response of overoxidised polymer was also checked. The PPy covered electrode was polarised at  $1.2 \text{ V}$  during 15 min in a solution without the monomer. In this case, the films have not proved adequate protection either. It was postulated that chloride penetration is favoured because the films were dedoped during overoxidation.

A chemical polymerisation takes place when the same molybdate and nitrate concentrations used in alkaline solution were used for PPy formation in acid solutions (pH 1). It is well known that the polymeric anion  $\text{Mo}_6\text{O}_{21}^{6-}$  is the dominant species in acid solutions [17]. This anion oxidises the monomer, initiating the polymerisation process [22]. The incorporation of heteropolymolybdate anions on Ppy film generated onto noble metals has been reported [22,23]. Anyway, the aluminium electrode was covered by a film by applying 0.9 V in this solution but the obtained coating can be easily be peeled off from the electrode. The protection properties of the obtained films were not satisfactory. This result can be explained considering that chemical polymerisation and electropolymerisation proceed simultaneously. Further work on this issue is presently being carried out.

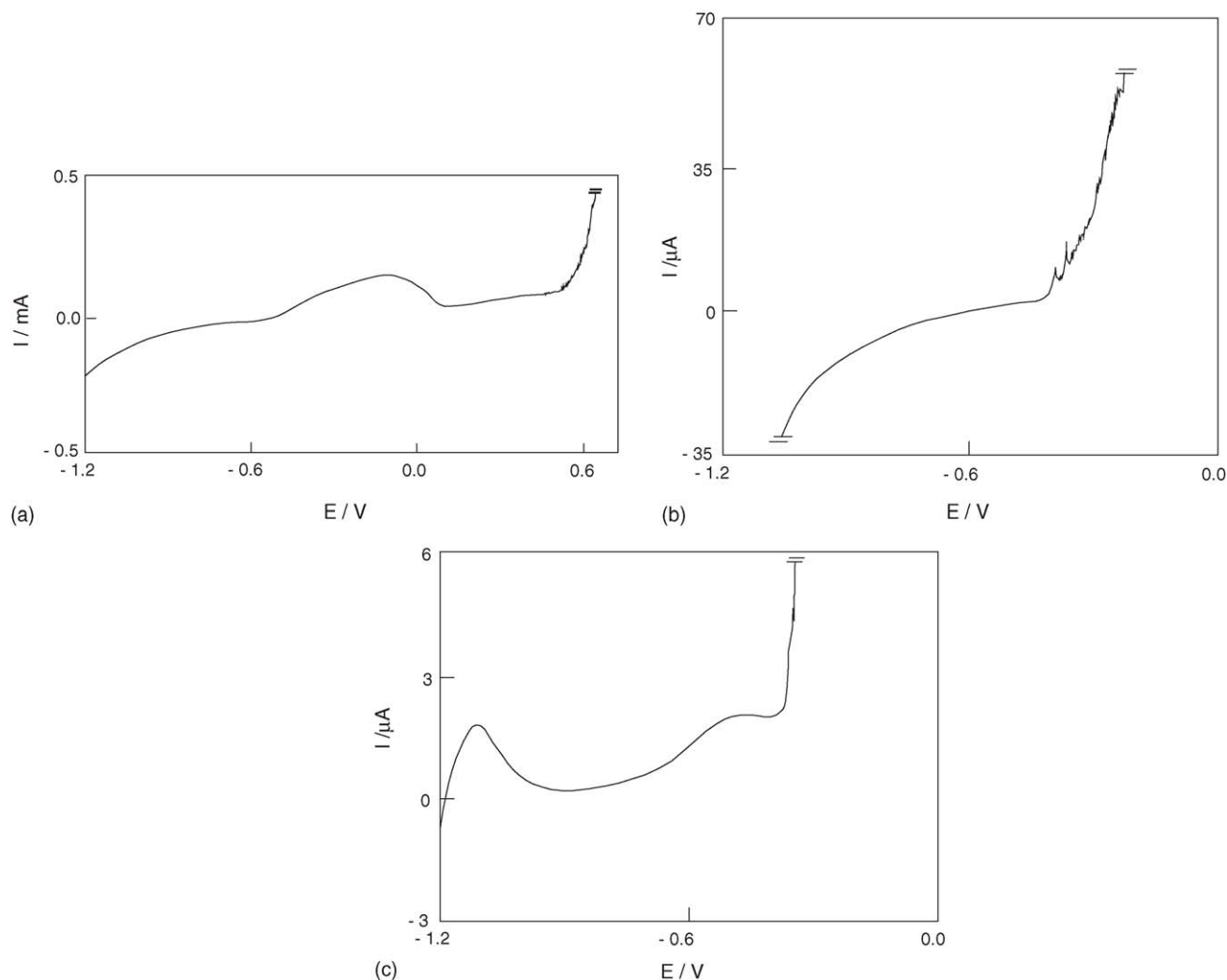


Fig. 8. The polarisation behaviour in 0.5 M NaCl at  $0.001 \text{ V s}^{-1}$  of: (a) PPY-coated Al electrode. The polymer was synthesised potentiostatically at 0.90 V for 30 min in  $0.7 \text{ M NO}_3^- + 0.25 \text{ M MoO}_4^{2-} + 0.5 \text{ M Py}$ , pH 12; (b) PPY-coated Al electrode. The polymer was synthesised potentiostatically at 0.90 V for 70 min in  $0.7 \text{ M NO}_3^- + 0.5 \text{ M Py}$ , pH 12; (c) bare Al. The solution also contains  $0.7 \text{ M NO}_3^- + 0.25 \text{ M MoO}_4^{2-}$ .

#### 4. Conclusions

The present electrochemical results demonstrate that molybdate can be accumulated into the positive charged PPY during electrochemical preparation of the film. The best films were electropolymerised in  $0.70 \text{ M NO}_3^- + 0.25 \text{ M MoO}_4^{2-} + 0.5 \text{ M Py}$  at pH 12. The method offers the advantage of working in alkaline solution where the molybdate is the dominant species. The presence of both, molybdate and nitrate in the polymer matrix increases the pitting potential in neutral chloride solutions compared to the results obtained for: (a) bare Al in the chloride solution containing molybdate and nitrate and (b) Ppy covered Al electrode formed in  $\text{NO}_3^-$  solution. Molybdate remains entrapped into the PPY during the oxidation/reduction of the film, being the cation involved in charge compensation. Thus, PPY acts as a reservoir of molybdate, which functions as both, dopant and inhibitor anion.

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