

Electrodeposition of polypyrrole on aluminium in the presence of sodium bis(2-ethylhexyl) sulfosuccinate

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Abstract

Stable and adherent polypyrrole films have been successfully electrodeposited onto aluminium electrode over a wide solution pH interval by using sodium bis(2-ethylhexyl) sulfosuccinate as dopant. The redox behaviour of the deposited coating was studied by cyclic voltammetry in different electrolytes and the corrosion protection properties were examined in chloride solution by polarisation studies and open circuit measurements. The polymer film was characterised by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX). The obtained results are explained considering the surfactant remains entrapped into the polymer matrix. The coatings inhibit the oxidation of the aluminium substrate even on polarisation to high anodic potentials.

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1. Introduction

The electrodeposition of conducting polymers onto active metals has been a subject of a great number of studies due principally to the corrosion protection properties of these coatings. A successful electropolymerisation requires the formation of a passive layer, which might be able to inhibit the dissolution of the oxidisable metal without blocking the access of the monomer and its further oxidation. Polypyrrole and its derivatives have been widely described because the low potential for polymer formation, easy preparation and stability of the formed films.

There is an extensive literature on the electrodeposition of polypyrrole in the presence of surfactants onto non-oxidisable [1–6] and oxidisable metals [7–14]. The chemical formation of PPy using surfactants has also been widely studied [15–18]. It has been demonstrated that surfactants influence the morphology and the electrical, thermal and oxidative stability of the polymers.

Sodium bis(2-ethylhexyl) sulfosuccinate, also known as AOT, is a bulky anionic surfactant with a sulfonate group in its

polar head and two large and branching hydrocarbon tails and its principal use is related to the formation of reverse micelles. It has been reported that the chemical synthesis of PPy in the presence of AOT results in the formation of films with improved mechanical and electrical properties [17–18]. The surfactant acts as a co-dopant because it is incorporated into the polymer together with the anion of the oxidising agent employed for the chemical polymerisation. The electrodeposition of PPy onto stainless steel in a mixed solvent of acetonitrile and dichloromethane containing AOT for the construction of a single-layer actuator has also been reported [19].

It is well known that the incorporation of large and immobile anions like surfactants conditions the ion-exchange behaviour of the polymer matrix. In a previous paper the electrosynthesis of PPy on Al electrodes in alkaline solutions containing sodium dodecyl sulphate (SDS) or sodium dodecylbenzene sulfonate (SDBS) was reported [20]. The presence of surfactants produces smoother films and the exchange of OH^- and Na^+ occur during the redox process.

In this paper results are presented on the electropolymerisation of Py from an AOT solution. The characterisation of the films was done using electrochemical techniques and SEM/EDX. The study is also focused on the examination of the corrosion protection properties of the formed films by a potentiodynamic technique and open circuit potential measurements.

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2. Experimental

Aluminium (99.999%, Aldrich Chemical Company) rods embedded in a Teflon holder with an exposed area of 0.070 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 a counter electrode. The cell was a 20 cm^3 Metrohm measuring cell. 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.

Measurements were performed in solutions containing 0.5 M Py and 0.05 M AOT in a purified nitrogen gas saturated atmosphere at 25°C . The solution containing was briefly stirred before use.

The pH of the solution was adjusted by addition of NaOH. All chemicals were reagent grade and solutions were freshly made in twice distilled water. Pyrrole was purchased from Acros Organics and it was freshly distilled under reduced pressure before use.

3. Results and discussion

3.1. Electrosynthesis of polypyrrole

The current–time responses during deposition of PPy at 0.9 V in 0.05 M AOT solutions with different pH values are presented in Fig. 1. Thick and adherent deposits were formed that could only be removed on mechanical polishing. Although the electrosynthesis can also be performed by potentiodynamic or galvanostatic techniques, the best films were obtained potentiostatically. The shape of the curve obtained in alkaline solution is very similar to that found in the presence of SDBS or SDS [20], although with AOT the consumed charge decreases to 40%. It has been reported a retardation in the chemical oxidative polymerisation of aniline in the presence of AOT and this fact was attributed the limited miscibility of monomer and surfactant solution [15].

No film formation was observed in neutral or weakly alkaline solutions containing nitrate or sulfate [21]. On the other hand,

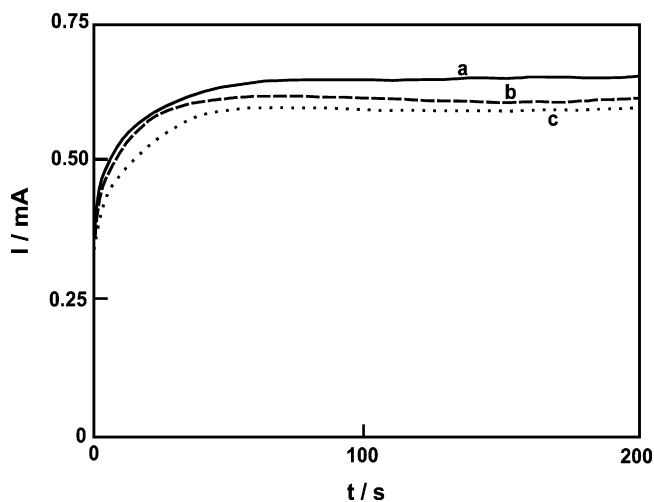


Fig. 1. Chronoamperometric curves obtained on Al in response to potential steps from -1.0 to 0.90 V in 0.05 M AOT containing 0.5 M Py at pH: (a) 12, (b) 7 and (c) 3.2.

PPy films have been successfully electrodeposited from SDBS or SDS solutions at pH 9.5, but the charge measured during deposition of the film is smaller than that measured at pH 12 for the same polymerisation time [20]. These results are related to the formation of a more stable and passive oxide film in neutral solution, which hinders the electropolymerisation process. Thus, PPy electrosynthesis can be performed in a wide pH interval using AOT. Likewise it is interesting to note that the magnitude of the deposition charge is practically independent of the solution pH.

It has been postulated that surfactants act not only as dopants but they also modify the surface conditions, affecting the electropolymerisation process. The cmc of AOT in water is 2.2 mM and this value is generally reduced with additions of electrolytes. Then, it is expected that at the working conditions, the concentration of AOT is above the cmc. It is known that surfactants form layers or bilayers on surfaces at or near the cmc [22], and the monomer is considered to be preferentially dissolved and concentrated into this micellar assembly [8]. Taking into account the hydrophilic nature of the Al oxide it is expected that the hydrophobic group of the surfactant is adsorbed on its surface with the polar group and the hydrophobic group facing the solution [8]. The great hydrophobic tails volume in the AOT molecule probably favours a better organisation of the bilayer enhancing the amount of Py inside micelles. Thus, the highly concentrated pyrrole in surface areas where the oxide presents flaws and defects allows electropolymerisation to start, even at neutral pH. Moreover, the adsorption of the hydrophobic tails on the PPy film facilitates the polymer growth [15].

The SEM pictures for the PPy films formed on Al in 0.05 M AOT at pH 12 and 7 are shown in Figs. 2a and 3a, respectively. The morphology of the polymer is characterised by the formation of aggregates. The grains are smaller and the coatings are smoother and more compact than those formed in 0.1 M NO_3^- , pH 12 solution, as was previously found using SDBS or SDS [20]. It was inferred that surfactants produce homogeneously distributed nucleus of growth that produce a higher deposition rate of the polymer. The grains appear more polyhedral in shape in the presence of AOT. SEM pictures show that at pH 7 synthesised film has a more irregular surface. EDX analysis indicated a content of S (Figs. 2b and 3b), confirming AOT is entrapped into the polymer to maintain electrical neutrality.

The lack of features in the X-ray diffraction pattern spectrum of the samples indicated a highly disordered structure.

3.2. Redox behaviour of PPy

In order to study the redox switching behaviour of the films, the coated electrodes prepared under potentiostatic condition were examined in monomer-free solutions containing different anions and cations. First, the responses obtained in 0.05 M AOT solutions at different pH values are presented (Fig. 4). The reduction scans for the three pH values tested exhibit only very low currents until a reduction peak is obtained at very negative potentials (ca. -1 V). This peak was attributed to the compensation

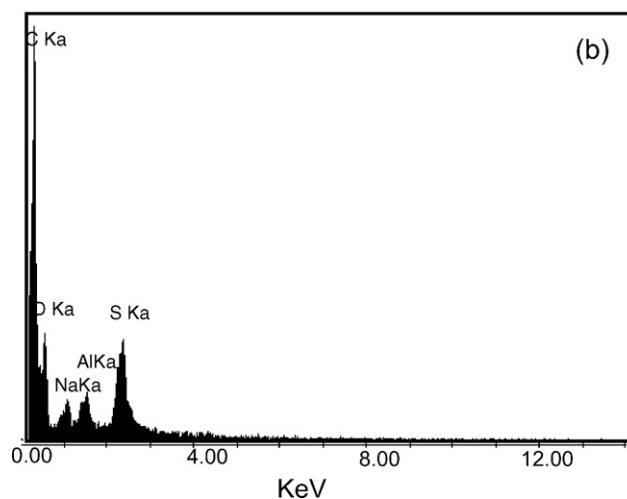
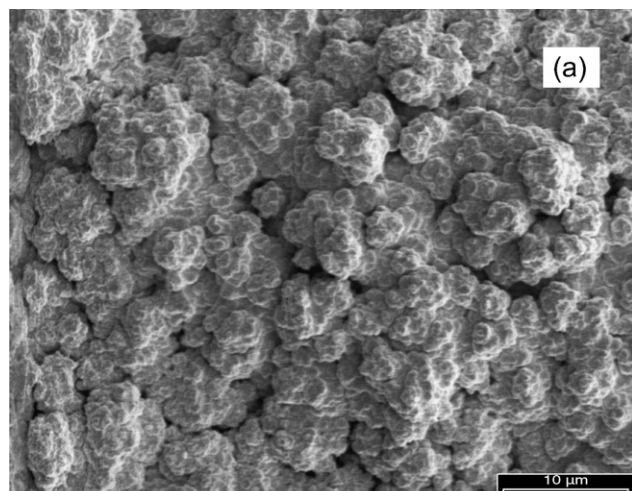


Fig. 2. (a) SEM micrograph and (b) EDX spectrum of PPy-coated Al. The film was formed at 0.90 V in 0.05 M AOT, pH 12 solution containing 0.5 M Py.

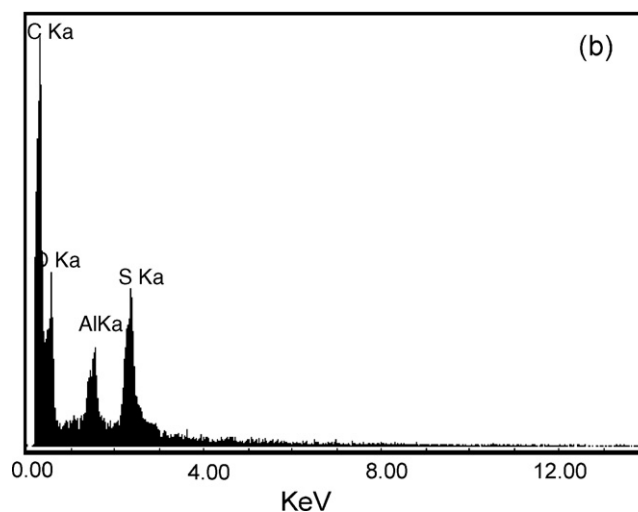
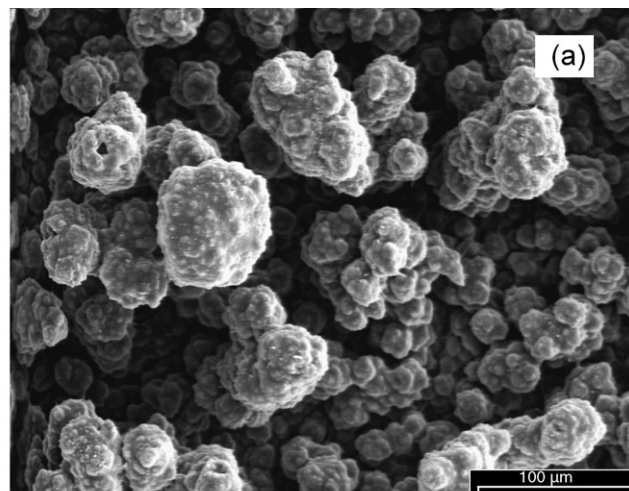


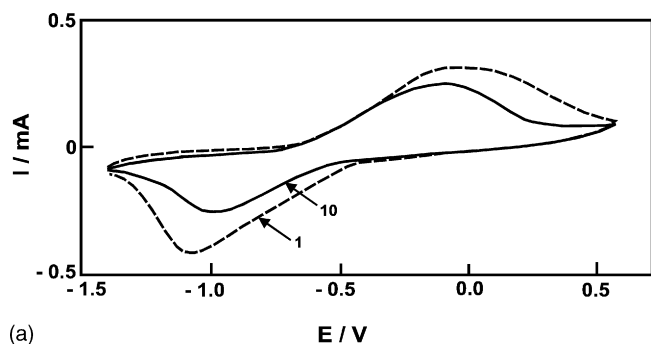
Fig. 3. (a) SEM micrograph and (b) EDX spectrum of PPy-coated Al. The film was formed at 0.90 V in 0.05 M AOT, pH 7 solution containing 0.5 M Py.

of the polymer charge by Na^+ insertion [23]. On reversing the potential scan, a very broad oxidation peak is observed. The films can be cycled for 5 h from the conducting to the insulating state without evidence of decomposition. The charge passed in film oxidation and reduction are nearly equal. These charges correspond to 10.0 and 4.7% of the charge passed on deposition for pH values of 12 and 7, respectively. For the film formed in acid solution the integrated charge is only 1.4% of the deposition charge. The redox peaks associated with the release and incorporation of small anions into the polymer film occur at more positive potentials. Thus, the shapes of the voltammetric curves suggest that there is no release of AOT from the polymer during the negative sweep due to its large size and then, no intercalation of OH^- takes place to conserve the electroneutrality of the film. The immobilisation of the dopant might be also related to the compatibility of the polar end of the surfactant with the charged matrix and the unpolar end with the neutral matrix [4].

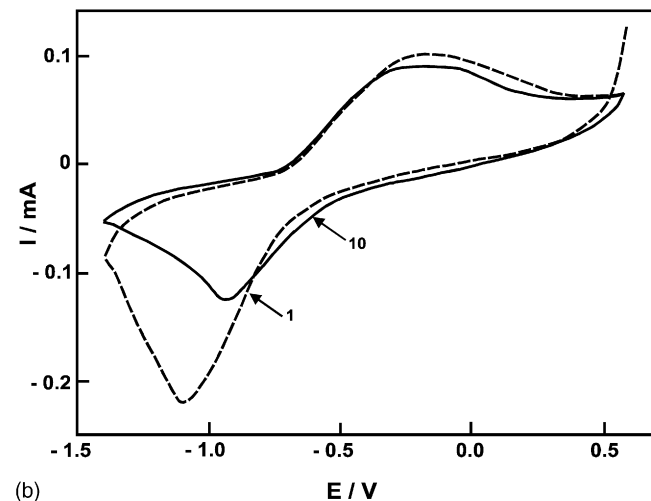
The cyclic voltammogram of the PPy film in NaNO_3 solution shows a pair of reduction and oxidation peaks, which is

associated with the exchange of Na^+ (Fig. 5). Considering again that the redox peaks associated with the exchange of small-size anions such as nitrate would occur at more positive potentials, the cyclic voltammetric response indicates that the transport of nitrate does not contribute to the redox process. Cycling in $\text{Ca}(\text{NO}_3)_2$ gives a response with practically the same shape. The cathodic peak was not observed when the film formed in nitrate solution was cycled in CaCl_2 , being the charge exclusively compensated by anions [23]. These results are consistent with the fact that cations are mainly involved in the redox process of the film when large surfactant anions remain immobilised in the polymer matrix.

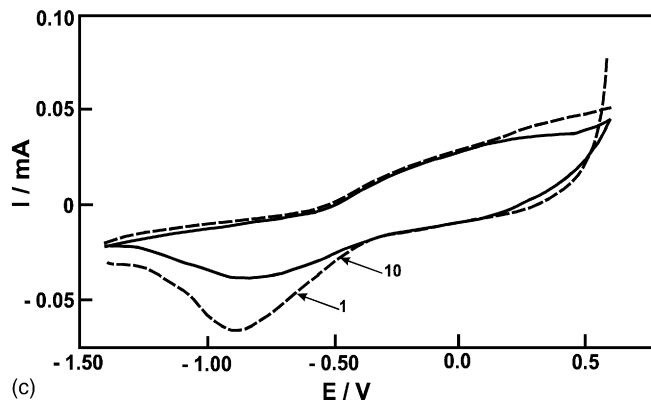
A high oxidation current was measured immediately after the PPy-covered electrode formed in 0.05 M AOT for 1 min was immersed in 0.5 M NaCl solution, indicating pitting attack. This response might be explained considering that the film is thin enough to allow chloride to penetrate or that uncovered areas of the substrate are exposed to the solution. However, for a polymerisation time of 5 min, the film can be reversibly switched



(a)



(b)



(c)

Fig. 4. Cyclic voltammograms of PPY-coated Al electrode at 0.05 V s^{-1} in 0.05 M AOT at pH: (a) 12, (b) 7 and (c) 3. The PPY films were made potentiostatically ($E = 0.90 \text{ V}$, $t = 1 \text{ min}$) in the same solutions containing 0.5 M Py . The cycle numbers are indicated. Initial potential: 0.60 V .

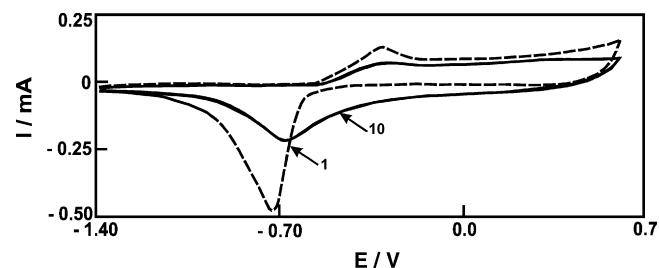


Fig. 5. Cyclic voltammograms of PPY-coated Al electrode in 0.5 M NaNO_3 solution at 0.05 V s^{-1} . The film was made potentiostatically ($E = 0.90 \text{ V}$, $t = 1 \text{ min}$) in 0.05 M AOT , pH 12 solution containing 0.5 M Py . The cycle numbers are indicated. Initial potential: 0.60 V .

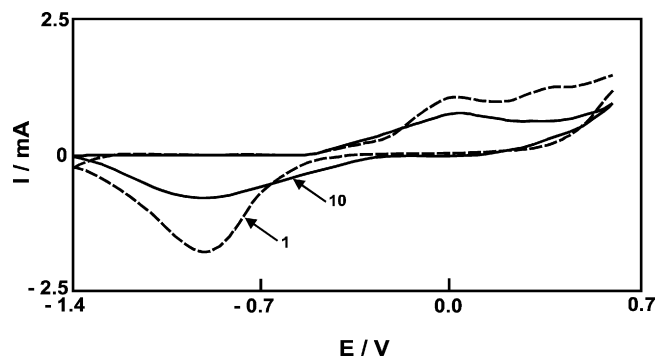


Fig. 6. Cyclic voltammograms of PPY-coated Al electrode in 0.5 M NaCl solution at 0.05 V s^{-1} . The film was made potentiostatically ($E = 0.90 \text{ V}$, $t = 5 \text{ min}$) in 0.05 M AOT , pH 12 solution containing 0.5 M Py . The cycle numbers are indicated. Initial potential: 0.60 V .

between the oxidised and neutral state in the chloride solution (Fig. 6).

The redox switching behaviour in a strong alkaline solution was also analysed. The redox ability of the PPY disappears at pH 13 when the film is doped with nitrate. Immediately after immersing the PPY-covered Al electrode in solution of pH 13, a high oxidation current was measured, being the oxidation of the substrate the main reaction at the electrode surface [24]. On the contrary, the cyclic voltammogram for the polymer doped with AOT is characterised by defined oxidation and reduction waves, which appear superimposed on an anodic current (Fig. 7). This background current is due to the simultaneous dissolution of the substrate and it is smaller than that obtained for the bare Al. Thus, the stability of the film differs markedly when the film is doped with AOT. Tafel polarisation measurements of bare Al in alkaline solution containing AOT reveal that the surfactant slightly inhibits the formation of aluminates, which is the slow step in the anodic reaction [25]. The improved stability with AOT can be explained considering the dual roll of the molecule as immobilised dopant and as inhibitor.

3.3. Response of PPY/Al electrodes in chloride media

The variation of the open circuit potential (OCP) as a function of time can be used to evaluate the degree of corrosion protection attained after covering the substrate with the conducting

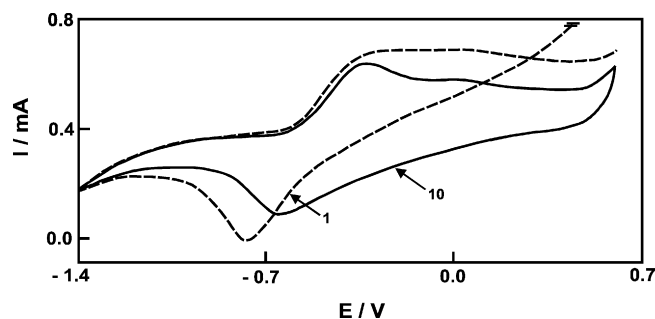


Fig. 7. Cyclic voltammograms of PPY-coated Al electrode in 0.1 M NaOH solution at 0.05 V s^{-1} . The film was made potentiostatically ($E = 0.90 \text{ V}$, $t = 1 \text{ min}$) in 0.05 M AOT , pH 12 solution containing 0.5 M Py . The cycle numbers are indicated. Initial potential: 0.60 V .

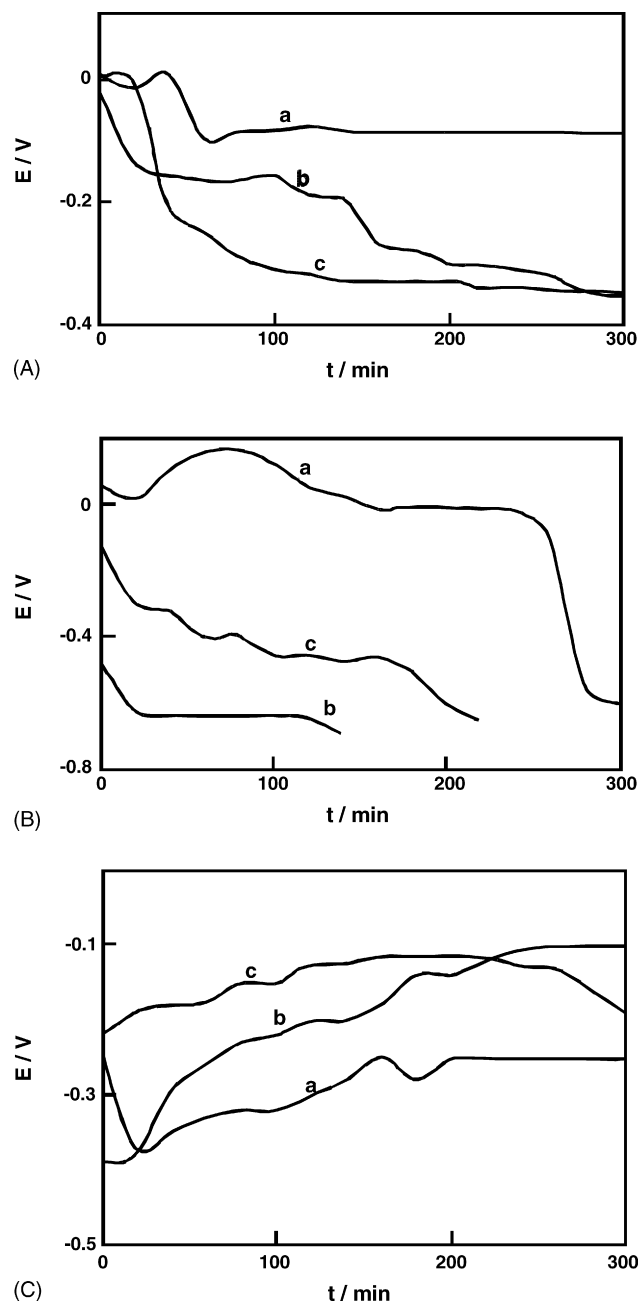


Fig. 8. Time dependence of the OCP in 0.5 M NaCl of: (A) PPY-coated Al electrode. The polymer was synthesised potentiostatically at 0.90 V for 30 min in 0.05 M AOT solution at pH: (a) 12, (b) 7 and (c) 3; (B) PPY-coated Al electrode formed as in (A) and then polarised at 1.2 V during 15 min in a solution without the monomer; (C) PPY-coated Al electrode formed as in (A) and then polarised at -1.0 V during 15 min in a solution without the monomer.

polymer. When the coating is not sufficiently protective the pitting potential of the uncovered electrode (-0.74 V) is inevitably reached in chloride solutions. The OCP was monitored in 0.5 M NaCl for PPY films obtained from 0.05 M AOT solution at different pH. In order to assure the formation of a thick film the electropolymerisation time chosen was 30 min. There is a clear ennoblement in the OCP for the coated electrodes (Fig. 8A). The pitting potential of the uncovered Al electrode in 0.5 M NaCl remains unchanged when AOT is added to the solution. Thus,

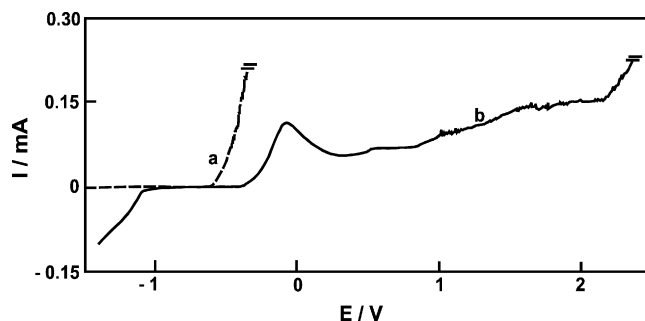


Fig. 9. The polarisation behaviour in 0.5 M NaCl at 0.001 V s^{-1} of PPY-coated Al electrode. The polymer was synthesised potentiostatically at 0.90 V in 0.05 M AOT solution, pH 12 for 30 s (curve a) and 10 min (curve b).

the ingress of chloride is hindered mainly because AOT remains entrapped into the polymer matrix. Covering the Al electrode with PPY films doped with SDS or SDBS did not give the same response. In these cases, the OCP drops to a value corresponding to the occurrence of the pitting process after 15 min [20].

The behaviour in NaCl solution of the PPY-coated electrode after different treatments was analysed. It is well known that PPY films can be overoxidised at high positive potentials. In order to overoxidise the polymer, the PPY-covered electrode was polarised at 1.2 V during 15 min in a 0.05 M AOT solution without the monomer. Fig. 8B compares the responses for the coatings formed at the three pH. It can be seen that OCP values shift to more negative values until the initiation of pitting occurs, indicating that the films are not protective enough in presence of chloride ions after this treatment. A release of the inserted anions may occur in the course of overoxidation. But the PPY doped with small anions also presented less protective properties after overoxidation [26], suggesting that the effect is due to changes in the polymer backbone.

The response of the polymer after its transition from oxidised to neutral state was also analysed. The coated electrode was polarised at -1.0 V for 15 min in a solution without the monomer and then OCP measurements in chloride solution were performed (Fig. 8C). The film also proved adequate protection suggesting that AOT do not leave the film under this extremely reduction condition.

Anodic polarisation data for Al-coated with PPY films formed for 30 s and 10 min are presented in Fig. 9. For the thinner film, the pitting process initiates at a potential nearly identical to that obtained for bare Al, indicating that the coating is not sufficiently protective. An anodic peak is observed in the case of films formed for higher polarisation times. The same peak was obtained using vitreous carbon as a substrate, leading to the conclusion that the signal is associated with polymer oxidation. On polarising further in the anodic direction, current oscillations and significant current increase are observed at very positive potentials, denoting the onset of pitting corrosion. Although it is not possible to know exactly at which potential the pitting process begins, the low currents measured even at very high potentials provide evidence for pitting inhibition. A SEM micrograph for the polarised sample shows a few holes in the polymer where pitting probably started (Fig. 10). The results indicate that the presence of immobilised AOT prevents chloride ingress into the

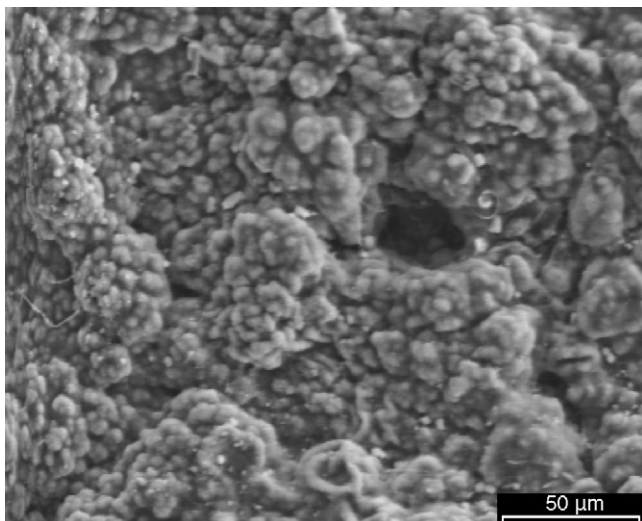


Fig. 10. SEM micrograph of PPY-coated Al obtained by removing the electrode at 3 V after the potentiodynamic polarisation in 0.5 M NaCl at 0.001 V s^{-1} presented in Fig. 9 (curve b).

matrix and then breakdown occurs at extreme potential values. While similar corrosion-protection degree was obtained for PPY formed in a neutral AOT solution, the breakdown initiated at less positive potentials when the film was electrosynthesised in acid solution.

4. Conclusions

The results of the present work indicate that adherent and homogeneous PPY coatings can be deposited onto Al in the presence of AOT in a wide pH interval. The oxidation of the monomer and its further oxidation are not blocked even at pH 7. The films formed in alkaline solution provide the best redox cycling and corrosion protection properties. The coated electrodes exhibit significant corrosion protection properties in highly aggressive electrolytes such as chloride solution or very alkaline media. AOT plays several roles: it acts as an immobilised dopant, passivating agent and surfactant. Because AOT remains entrapped into the polymer matrix it difficulties the ingress of chloride or hydroxide ions.

Acknowledgements

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