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Corrosion Science 49 (2007) 2210-2225

CORROSION SCIENCE

www.elsevier.com/locate/corsci

# Corrosion protection of iron by polypyrrole coatings electrosynthesised from a surfactant solution

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> Received 8 March 2006; accepted 17 October 2006 Available online 22 December 2006

#### Abstract

This work is a study of the electropolymerisation of pyrrole onto iron electrodes in the presence of sodium bis(2-ethylhexyl) sulfosuccinate in a wide pH interval. The characterisation of the films was done using electrochemical techniques, SEM/EDX and IR spectroscopy. We show that it is possible to synthesise homogeneous, adherent and very compact films in the pH range between 7 and 12 under potentiodynamic, galvanostatic and potentiostatic conditions without substrate dissolution. The effects of various parameters on electrodeposition were investigated. The new procedure for the electrochemical synthesis of polypyrrole results in improved anticorrosion properties. The inhibition is proposed to be due to the sum of a repulsion of chloride ions because AOT remains entrapped in the polymer matrix and the presence of the iron oxide. Advantages of the use of surfactants in the electropolymerisation solution are discussed.

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Keywords: A. Iron; A. Surfactant; C. Electrodeposited polypyrrole; C. Corrosion inhibition

## 1. Introduction

Conducting polymers are interesting materials for fundamental research and for technological applications. There has been an increasing interest in the use of these polymers for protection of oxidisable metals against corrosion. The electropolymerisation is very

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difficult when a strong dissolution of the substrate initiates at potentials more negative than that corresponding to the oxidation of the monomer. Thus, it is necessary to find the appropriate experimental conditions to diminish the dissolution rate of the metal without blocking the monomer oxidation and further polymerisation.

Due to the technological importance of iron and ferrous alloys there is a great interest in finding new surface coatings to improve their corrosion protection. Significant results have been reached in the electropolymerisation of conducting polymers, polypyrrole (PPy) and polyaniline (PANI) in particular, on these materials. It is well known that the process can be done in a few media [1]. The formation of the coatings from aqueous solutions containing oxalate ions has been investigated by several groups because this medium inhibits iron dissolution [2–8]. Other electrolytes such as nitrate [2,9], phosphate [10] and sulphate [2,11] have also been employed for the electrosynthesis.

A noticeable enhancement of protection of ferrous materials against corrosion using conducting polymers as coatings has been demonstrated [11-14] and several mechanisms have been described to explain this protection [15]. It has been proposed an anodic galvanic protection mechanism which considers that the film in its conductive state acts as an efficient oxidiser to maintain the metal in the passive state [16]. It has also been proposed that the conducting polymer serves to mediate the anodic current between the passivated surface and oxygen reduction on the polymer film. The Fe<sup>2+</sup> reacts with the doped anion released as a consequence of polymer reduction and the formed insoluble iron-dopant salt passivates the pinhole [17,18]. The release of anions as a result of polymer reduction for PPy doped with molybdate or phosphomolybdate has been consider to explain the improved protection of the coating [14]. The presence of molybdate allows to passivate the substrate.

The incorporation of different anions in the polymer matrix may result in new possibilities for the modification of the properties of conducting polymers. It has been demonstrated that surfactants influence the morphology and redox behaviour of conducting polymers [19–21]. In a previous work it was reported that Al electrodes covered by PPy electrodeposited in the presence of sodium bis(2-ethylhexyl) sulfosuccinate exhibit significant corrosion protection properties in highly aggressive electrolytes such as chloride solutions or very alkaline media [22]. This compound, also known as AOT, is a bulky anionic surfactant with a sulfonate group in its polar head and two large and branching hydrocarbon tails (Fig. 1) and it is widely used for forming reverse inverse micelles. The incorporation of a large and immobile anion like AOT conditions the ion-exchange behaviour of the polymer matrix. In this work results are presented and discussed on the electropolymerisation process of Py onto iron in AOT solutions with different pH values. Another objective of the present work is to examine the protection of iron against corrosion by using the electrodeposited coatings.



Fig. 1. Structural formula of sodium bis(2-ethylhexyl) sulfosuccinate (AOT).

# 2. Experimental

Electrodes were prepared from pure iron rod samples. The rods were embedded in a Teflon holder with an exposed area of  $0.070 \text{ cm}^2$ . Before each experiment, the exposed surfaces were polished to a 1000 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. The covered electrodes subjected to corrosion tests were pretreated during 15 s in HNO<sub>3</sub> 10% to improve adhesion of the films. 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<sup>3</sup> 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 pyrrole (Py) and 0.05 M AOT in a purified nitrogen gas saturated atmosphere at 25 °C. The pH of the solution was adjusted by addition of NaOH. In order to avoid the slow hydrolysis of AOT all the measurements were done with freshly prepared samples. All chemicals were reagent grade and solutions were made in twice distilled water. Pyrrole was purchased from Acros Organics and it was freshly distilled under reduced pressure before use.

# 3. Results

# 3.1. Electrosynthesis of PPy

## 3.1.1. Potentiodynamic polymerisation

The potentiodynamic curves for iron between -1.40 and 1.10 V in 0.05 M AOT solution of different pH values with and without Py are presented in Fig. 2. The addition of Py to the AOT solution with pH 3 does not lead to any significant change in the shape of the voltammograms. No polymer film formation occurred at this pH where a continuous dissolution of iron takes place in the potential range analysed (Fig. 2A). A different response is obtained as the pH is raised. A sharp current increase starting at about 0.60 V is observed at pH 7 and 12 which is associated with Py oxidation. New reduction-oxidation waves appear at potentials more negative than the potential corresponding to the oxidation of the monomer which are associated with electroactive polymeric products (Fig. 2B and C). After recording the curves, the presence of a polymer film on the electrode surface was observed. For comparison, the curves obtained in monomer-free solutions are also presented. In neutral media the response is characterised by an anodic peak at approximately 0.20 V (small insert in Fig. 2B), which is related with the presence of AOT since the peak charge increases as the surfactant concentration increases. This peak disappears when adding Py, probing that Py is adsorbed on the iron surface and slows down its oxidation. In the alkaline solution the voltammetric peaks in the potential range between -1.0 and -0.5 V (small insert in Fig. 2C) basically can be attributed to ferrous and ferric species formation and their reduction [23]. A dissolution process takes place at the most positive potentials [5]. The voltammetric behaviour at pH 13 in the presence of Py is very close to that observed without the monomer (Fig. 2D), indicating that this medium is unsuitable for the electropolymerisation of Py on iron.

#### 3.1.2. Galvanostatic polymerisation

Galvanostatic deposition also conducted to very homogeneous and thick PPy films in the pH interval between 7 and 12. The E/t curves during deposition show that the potential very rapidly reaches a constant value of 0.59 V (Fig. 3). The greater the applied current, the plateau potential in the E/t curve is raised and thicker the film homogeneous black films covering the whole electrode surface were obtained for values of applied current higher than 5 mA cm<sup>-2</sup>, while for lower values of current only a partially PPy-covered electrode were observed. In the absence of pyrrole the basic curve displays a constant potential plateau at very positive potentials (curves c and d). A thick gel-like product



Fig. 2. Cyclic voltammograms obtained with an iron electrode in 0.05 M AOT solution containing 0.25 M Py at pH: (A) 3; (B) 7; (C) 12 and (D) 13. Scan rate:  $0.05 \text{ V s}^{-1}$ . Scans 1 (full line) and 10 (discontinuous line) are displayed. Small inserts in (B) and (C): stabilised cyclic voltammograms in the same AOT solutions without Py.



Fig. 2 (continued)

around the polymer was observed during electropolymerisation. This product was more clearly seen using an iron wire as working electrode and longer deposition times.

## 3.1.3. Potentiostatic polymerisation

Ppy films can also be formed on iron at a constant potential. Fig. 4 displays an example of the transient obtained in 0.05 M AOT, pH 12 without Py by applying a potential of 0.9 V, where a continuously decreasing current associated with oxide growth is observed. The chronoamperometric curves obtained with the monomer at different pH values are shown in the same figure. Interestingly, the i-t transients are practically independent of



Fig. 3. Chronopotentiometric curves obtained at  $5 \text{ mA cm}^{-2}$  on iron electrodes in 0.05 M AOT with 0.25 M Py (a and b) and without Py (c and d). Solution pH: 7 (a and c) and 12 (b and d).



Fig. 4. Chronoamperometric curves obtained on iron electrodes in 0.05 M AOT containing 0.25 M Py, in response to a potential steps from 0.0 to 0.90 V. Solution pH: (a) 7; (b) 10 and (c) 12. The chronoamperometric curve obtained in 0.05 M AOT, pH 12 without Py, in response to the same potential step is also included (curve d).

solution pH. The electrodes were covered by an homogeneous and thick deposit at the end of the electropolymerisation period. The current measured during the transient increases as the potential is made more positive (not shown in the figure). No film could be obtained when the polarisation was carried out with 0.0025 M AOT, independently of solution pH. If the AOT concentration was raised to 0.005 M the obtained film was only partially covering at pH 7 while no deposition occurred at pH 12.

# 3.2. PPy characterisation

### 3.2.1. SEM/EDX analysis

PPy films electrosynthesised on an iron electrode by applying 5 mA cm<sup>-2</sup> have been analysed by SEM/EDX. Compact and homogeneous coatings were obtained at pH 7 and 12 (Figs. 5 and 6). The film grown at pH 12 appears smoother but SEM examination at higher magnification reveals that a more regular film with very low porosity coating was synthesised at the lower pH. In both cases the images indicates the presence of a granular structure with very small grains of about 0.2  $\mu$ m diameter. The obtained samples were then



Fig. 5. SEM micrograph at different magnifications of PPy-coated iron. The film was formed at 5 mA cm<sup>-2</sup> in 0.05 M AOT, pH 7 solution containing 0.25 M Py.



Fig. 6. SEM micrograph at different magnifications of PPy-coated iron. The film was formed at  $5 \text{ mA cm}^{-2}$  in 0.05 M AOT, pH 12 solution containing 0.25 M Py.

investigated by EDX technique and the results are shown in Fig. 7. The presence of sulphur indicates that AOT is incorporated into the polymer matrix. No signal for Fe was detected confirming the formation of homogeneous and thick films.

# 3.2.2. IR analysis

The FTIR spectrum of the PPy film shown in Fig. 8 was obtained in a KBr pressed pellet after its deposition at pH 12 by applying 5 mA cm<sup>-2</sup>. For comparison the spectrum of pure AOT is also included. It can be observed bands between 1130 and 1310 cm<sup>-1</sup> and a peak at 1050 cm<sup>-1</sup> attributed to the asymmetric and symmetric stretching vibrations of the SO<sub>3</sub> group, respectively, and a peak at 1736 cm<sup>-1</sup> attributed to C=O stretching vibration



Fig. 7. EDX examination of PPy-coated iron. The film was formed at  $5 \text{ mA cm}^{-2}$  in 0.05 M AOT containing 0.25 M Py. Solution pH: (A) 7 and (B) 12.

in the AOT molecule [24]. This result shows a clear sign of the incorporation of AOT as dopant in the polymer film.

#### 3.2.3. Redox behaviour

The redox behaviour of the PPy-coated iron formed at  $5 \text{ mA cm}^{-2}$  in AOT solutions with pH values of 7 and 12 were examined in monomer-free solutions (Fig. 9). The current response is characterised by broad oxidation peaks and the back sweep exhibits a single reduction peak which was attributed to the compensation of the polymer charge by Na<sup>+</sup> insertion [25]. The films are quite stable and can be cycled for 5 h without evidence of decomposition. The redox curve was not altered when the covered electrode was cycled in the presence of small inorganic anions such as nitrate.



Fig. 8. Infrared spectra of (a) PPy deposited on iron at 5 mA cm<sup>-2</sup> in 0.05 M AOT, pH 12 solution containing 0.25 M Py; (b) pure AOT. Arrows indicate bands associated with stretching vibrations of SO<sub>3</sub><sup>-</sup> and C=O groups.

# 3.3. Anticorrosion behaviour

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 polymer. When the coating is not sufficiently protective the pitting potential of the uncovered electrode is inevitably reached in chloride solutions. Once formed, the poly-



Fig. 9. Cyclic voltammograms of PPy-coated iron electrode at  $0.05 \text{ V s}^{-1}$  in 0.05 M AOT at pH: (A) 7 and (B) 12. The PPy films were made galvanostatically ( $i = 5 \text{ mA cm}^{-2}$ , t = 1 min) in the same solutions containing 0.25 M Py. Scans 1 (full line) and 10 (discontinuous line) are displayed. Initial potential: 0.60 V.

mer-coated electrodes were washed with distilled water and subjected to tests in chloride solution. The electropolymerisation was carried out at 5 mA cm<sup>-2</sup> for a period 30 min in order to assure the formation of a thick film. Assuming a film thickness of 1  $\mu$ m for 0.4 C cm<sup>-2</sup> charge [26], a thickness of approximately 23  $\mu$ m is predicted. For comparative purpose, the response obtained for the iron electrode subjected to the same galvanostatic programme but in a monomer-free AOT solution was also included (Fig. 10, small insert). The initial OCP value was 0.16 V (Fig. 10). Then, the OCP decreases until around -0.20 V where it remains for a long period. This potential value was still nobler than that for the uncoated electrode and it is independent of the NaCl concentration. Finally, the corrosion



Fig. 10. Time dependence of the OCP in 0.5 M NaCl of PPy-coated iron electrode. The polymer was synthesised at  $i = 5 \text{ mA cm}^{-2}$  for 30 min in 0.05 M AOT solution containing 0.25 M Py at pH: (a) 7 and (b) 12. The dependence for an iron electrode polarized at 5 mA cm<sup>-2</sup> for 30 min in 0.05 M AOT solution at pH 12 is also included (small insert).

potential of bare iron is reached. At this stage the chloride solution do not present the typical yellow coloration indicative of iron dissolution. As a rough test to detect Fe(II), ferricyanide was added to the solution after removal of the Ppy-coated sample from the cell. No visible formation of the precipitate Prussian blue was detected indicating no signs of considerable corrosion. The protection time is shorter when the film is formed under potentiostatic conditions. The potential corresponding to the bare electrode is attained in this case after around a day of immersion in the chloride solution.

The polarisation behaviour in NaCl solution of the electrode covered by PPy synthesised at pH 12 is presented in Fig. 11 in comparison for the uncoated iron. As can be seen a significant decrease of the current is observed for the coated sample, indicating corrosion retardation. An extensive passive region is acquired and at more positive potentials, a current peak is observed followed by the oxidation of the medium.

## 4. Discussion

It is well known that the pH of the solution conditions the electrochemical behaviour of iron. A high pH promotes the passivation of iron as predicted by the Pourbaix diagram [27]. Although there is no consensus about the complex mechanism of iron oxidation, the majority of authors proposed the initial formation of an intermediate transient species  $Fe(OH)_{ads}$  [28]. Above the Fe/Fe(II) reversible potential, dissolution or passivation may occur depending on the solution composition. In acid solution dissolution of iron conducts to the formation of Fe(II) species, while in slightly acidic solution it has been postulated the formation of Fe(OH)<sub>2</sub> via a dissolution/precipitation mechanism. In alkaline media



Fig. 11. The polarisation behaviour in 0.5 M NaCl at 0.001 V s<sup>-1</sup> of: (a) PPy-coated iron electrode. The polymer was synthesised at 5 mA cm<sup>-2</sup> for 30 min in 0.05 M AOT, pH 12 solution containing 0.25 M Py; (b) iron electrode polarised at 5 mA cm<sup>-2</sup> for 30 min in 0.05 M AOT, pH 12.

passivation via the formation of  $Fe(OH)_2$  by a solid state mechanism has been proposed, while dissolution of  $Fe(OH)_2$  occurs in highly alkaline media. The Fe(II) species are oxidised to Fe(III) species soluble or insoluble at more anodic potentials. The formation of several oxidation products such as FeOOH,  $Fe_3O_4$ ,  $Fe_2O_3$  and  $FeO_2^-$  has been proposed.

Thus, according to the above discussion, high dissolution rate of iron substrate, probably via the formation of a complex with AOT hinders the electropolymerisation process in acidic solutions. As the solution pH is raised a protective iron oxide is formed, allowing the electropolymerisation process at pH values between 7 and 12. The formed passive film does not block the electron transfer in such an extent that Py oxidation is not inhibited. It was demonstrated that PPy films can be synthesised in alkaline solutions and that they can be cycled in acid or alkaline solutions without loosing electrochemical activity [25]. Further increase in pH results in a suppression of electrodeposition because the strong passivation of the iron surface.

When dilute AOT solution was used (0.005 M), partially covering coatings were obtained at pH 7 while no film was deposited at pH 12. This was interpreted in terms of the more protective film formation at the higher pH.

The chronopotentiometric curves for galvanostatic deposition of PPy onto ferrous materials typically show a first stage associated with iron dissolution [1,3,6]. After this stage, when the electrode potential remains constant, the pyrrole oxidation potential is reached. It has been reported that when the electropolymerisation of Py was done at pH 8.5 at a constant current there is no induction period and the oxidation potential

was much higher than that in acid media [3,6]. The absence of induction period was attributed to the readily formed passive film at the application of anodic potentials in alkaline solutions. In the present work the E/t curves also indicate that there is no iron dissolution before the electropolymerisation starts but the polymerisation potential in 0.05 M AOT, pH 12 solution was not higher than that obtained for the same applied current in neutral media (Fig. 3) or in acid electrolytes according to literature data. This type of response was also described for PPy electrosynthesis in the presence of neutral salts (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and KNO<sub>3</sub>) [1]. In the absence of Py the basic curve shows a constant potential plateau at very positive potentials associated with oxide growth.

Considering the potentiostatic synthesis, well-formed rising *i*-t transients were obtained with increased current densities as the applied potential is more positive. These observations are those expected for a phase-formation process involving nucleation and growth. Another possible way for the formation of the film is the precipitation of soluble intermediates from a supersaturated solution, which are generated during Py oxidation [29]. The magnitude of the deposition charge is practically independent of solution pH in the range between 7 and 12 (Fig. 4). The same behaviour was found for the electrodeposition onto aluminium [22]. The current-time response for the electropolymerisation of Py onto noble material is affected by the solution pH [30]. Working with an oxidisable metal like iron, the pH independence of the transients implies that the process is not affected by the nature of the surface oxide, which is pH-dependent. This independence and the development of a gel-like structure in contact with the produced polymer suggest that the rate of the film growth is controlled by the diffusion of the monomer through the viscous phase. This is in accordance with the proposition of Hien et al. [12] which considers that the transport of Py units to the surface could be the rate determined step because the diffusivity of a micelle is much lower than that of the Py unit in solution. The gel-like material is probably related with a multiple-layered self-assembled surfactant structure. Investigations to elucidate the nature of this material are now in progress.

Concerning the corrosion studies, a high degree of corrosion protection was attained when the iron electrode is covered with the PPy film. It was found that, for a long period of immersion in chloride solution, the OCP remains at a practically constant value, which is higher than that of the bare iron (Fig. 10), with no visible signs of corrosion. On polarising anodically the covered electrode no iron dissolution occurs even at very positive potentials (Fig. 11). After the extensive passive region an oxidation peak, probably associated with overoxidation of PPy, was obtained followed by the oxidation of the medium.

It was postulated that low carbon steel is covered by a composite coating comprised of a passive film and PPy coatings [3]. It was also found that the corrosion rate of steel is reduced when the electrode is covered by a PANI film in the emeraldine base form. The result was explained considering the coating produces a highly alkaline environment that is conducive to passive oxide formation [31]. On the other hand, it was postulated that the redox capability of PANI maintained the oxide layer sufficient enough to prevent pitting corrosion of iron [15]. When the polymer is formed in neutral and still more in alkaline media the presence of a stable oxide in the first stages of oxidation is guaranteed. Thus, given the more protective oxide film formed at high pH an improvement in the corrosion protection might be expected. One can conclude that the degree of protection attained is due in part to the initial formation of a stable oxide layer.

The present results demonstrate that AOT is incorporated into the polymer matrix to maintain electroneutrality. The redox behaviour of the polymer indicates that the AOT

molecule remains entrapped into the film due to its large size (Fig. 9). Then, the anticorrosion properties are also due to the presence of immobile AOT as dopant which strongly inhibits the ion exchange between polymer and chloride solution. On the other hand, it was found that AOT slightly inhibits dissolution of bare iron in chloride media.

The redox transition of PPy is accompanied by cation exchange because the large organic dopant remains entrapped in the polymer matrix. Assuming that the doping level of the PPy is approximately constant, it is expected a linear dependence with a positive slope between the OCP and the electrolyte concentration. But the OCP measured for protected iron is independent of the NaCl concentration. One can conclude that in this case the rest potential is not a result of the ion-exchange properties of the polymer itself. Instead this potential represents the equilibrium value of the galvanic coupling of iron and the more noble PPy coating, in agreement with the proposition of various authors [15].

It is known that surfactants act not only as doping agents. Surfactants form bilayers or multilayers structures on surfaces at or near the cmc [32]. 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. The electropolymerisation process is dependent of the distribution of reactants between the micellar and aqueous phase [20]. Since pyrrole is solubilised and concentrated into the inner part of the bilayer or multilayer, the electropolymerisation process is facilitated. The modifications of the surface conditions increase the deposition rate and the coating are formed by very small grains. SEM examination demonstrates that films with smoother and more compact morphologies are obtained compared to those synthesised with inorganic anions (Figs. 5 and 6).

## 5. Conclusions

It has been demonstrated that Ppy can be electrodeposited into iron in a wide pH interval between 7 and 12. Homogeneous and adherent films were deposited under potentiodynamic, galvanostatic and potentiostatic conditions. The presence of AOT allows the electrosynthesis of very compact films, being the rate determined step the diffusion of the monomer through the micellar assembly. AOT becomes part of the synthesised material and this large organic anion has a very low mobility in the polymer matrix.

The use of neutral and still more alkaline solutions as electrolyte medium for electropolymerisation promotes the formation of a highly protective oxide layers onto iron, allowing electropolymerisarion to occur without substrate dissolution. Iron is highly corroded in acid aqueous solutions and the possibility of coating formation at higher solution pH where the passive oxide film is stabilised constitutes a large advantage. Films deposited under galvanostatic control are more stable against corrosion in chloride media.

The anticorrosion properties of the deposits is a combination of the following: (a) Ppy containing a fixed negative charge; (b) a passive film is formed at the initial stages of electropolymerisation.

# Acknowledgements

Consejo Nacional de Investigaciones Científicas y Técnicas and Universidad Nacional del Sur, Bahía Blanca, Argentina are acknowledged for financial support.

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