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Corrosion protection of iron by polystyrenesulfonate-doped polypyrrole films

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Abstract

Electropolymerized polypyrrole (PPy) has been studied as a protective coating for iron in NaCl 3% corrosive medium. The protection mechanism is of the galvanic type, and the main cause for the loss of protection is the progressive invasion of the film by chloride anions. To reduce exchanges between PPy counter-ions and chloride anions, a composite polyanions/PPy film was used. Polystyrenesulfonate was chosen as a large size counter-ion which could be trapped in the polymer matrix. Due to the negligible mobility of these anions, the film permselectivity changed from anionic to cationic. A significant improvement in PPy film protection efficiency was obtained.

1. Introduction

Since the pioneering work of DeBerry in 1985 [1] on corrosion protection by conducting polymers, there have been many attempts both to propose a comprehensive mechanism and to optimize the protection efficiency of these films against corrosion. Two classes of compounds, belonging to the Polyaniline (PANI) [2–12] and polypyrrole (PPy) families (for example PPy on iron or steel [13–20] or aluminium [21] or zinc [22] or nickel [23] or magnesium [24]), have received most attention, owing to their long-term stability and efficiency. Anodic galvanic protection in the case of metals possessing a passive range or barrier effect have been envisaged.

This study focussed on PPy rather than on PANI because PPy can be electropolymerized as thick films and maintains good conductivity up to pH 10. For practical application, PPy is therefore more suited for use as a protective coating for iron in 3% NaCl corrosive medium and hence for steels having a similar electrochemical behaviour as iron. Our previous results support an anodic galvanic protection mechanism, which implies that the film, being in its conductive state (doped) may act as an efficient oxidizer to maintain the metal in the passivity domain. The loss in protection efficiency was mainly ascribed to interchange between the counter-ion of the film and chloride ions of the solution and therefore, the nature of the counter-ion inside the film determines the efficiency of the coating. It was suggested that a significant improvement to the protective characteristics could be gained by preventing the chloride ingress in the film.

In this work, a modified composite PPy film is investigated. PPy is doped with large size anions with weak mobility so as to change the nature of the film permselectivity from anionic to cationic. In fact, ionic transport in PPy doped with poly(styrenesulfonate) anions (PSS) has been intensively studied and has revealed cation movement [25–30]. This paper presents results on iron protection by PSS-doped PPy coating.

2. Experimental conditions

An iron rod (dia. 5 mm) from Goodfellow (99.99% pure) was coated with an insulating cataphoretic lacquer and embedded in an epoxy resin. Prior to the electrosynthesis, the iron sample was ground with emery paper down to 2400 grit, rinsed with demineralized water and finally dried in pulsed warm air.

The electrochemical set-up consisted of an electrochemical interface Solartron 1286. The electrosyntheses were carried out with a three-electrode cell arrangement: a platinum grid as counter electrode, a saturated sulfate reference electrode (SSE), and the iron samples as working electrodes. The pyrrole was distilled prior to coating synthesis. After the coating synthesis, the samples were rinsed in demineralized water and then dipped at open circuit in a 3% NaCl aqueous solution as corrosive medium.

Corrosion tests were performed by following the time dependence of the open-circuit potential (o.c.p.) with a saturated calomel reference electrode (SCE). For better comparison, all further potentials are referred to a SSE.

The morphology of the films was examined with a Leica S440 scanning electron microscope (SEM) with a tungsten filament.

3. Results and discussion

3.1. *Polypyrrole electrodeposition*

Polypyrrole can be prepared on various conducting substrates by anodic electropolymerization from either non-aqueous or aqueous solution containing the monomer and a supporting electrolyte [31, 32]. During the electropolymerization, the anion of the electrolyte is incorporated as the counterion of oxidized polypyrrole. From a practical point of view, aqueous electrolytes were preferred.

Direct electrosynthesis of PSS-doped PPy on iron, attempted as a first step, failed. The most likely reason was that iron passivity is incomplete with a significant dissolution current while PPy electrosynthesis proceeds. These are obviously not satisfactory conditions for the achievement of an adherent and well-structured film.

Therefore, electrosynthesis was performed in two steps. PSS-doped PPy films were electrosynthesized after electrodeposition of a first oxalate-doped PPy film. In a previous paper, we showed that the dissolution behaviour of iron in potassium tetraoxalate (PTO) media produces adherent and conductive PPy films [33–35]. The mechanism for this system is strongly influenced by the chemistry of oxalates [36, 37]. The passivating potential corresponds to a dissolution–precipitation process due to the low solubility of ferrous oxalate, and has a value near −0.65 V/SSE, owing to the interfacial concentration of Fe^{2+}. When $E = 0$ V vs SSE, the anodic current in the passive domain increases slightly, which marks the Fe^{2+} oxidation, and then three valent iron forms an oxide film. The normal potential for pyrrole oxidation starts around +0.23 V vs SSE, corresponding to the existence of the passive film which must be formed prior to the onset of PPy film growth. Thus, the potassium tetraoxalate yielding the most appropriate potential characteristics was chosen as the best medium for the first step synthesis. Furthermore, oxalate plays an important role in the protection mechanism, as shown below.

Potentiostatic or galvanostatic conditions were applied for PPy electrodeposition and both were found to ensure films of reproducible quality. The optimum galvanostatic electrodeposition conditions were obtained at 1 mA cm^{-2} [33, 35]. The current transient obtained for a typical potentiostatic PPy electrodeposition is presented in Figure 1. In 0.05 M pyrrole and 0.05 M PTO solution, the polymer was electrosynthesized in two potential steps, the first to obtain the passive film formation, the second the PPy electrodeposition.

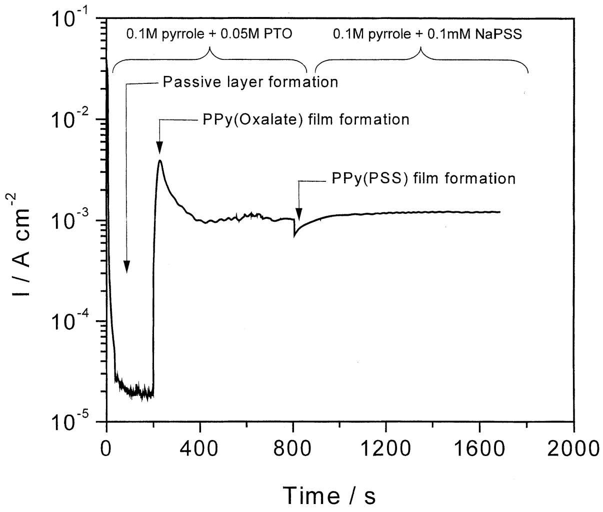

Fig. 1. Chronoamperometric curves during potentiostatic electrodeposition of PPy on iron for a given charge of 1 C cm^{-2} in 0.1 M pyrrole and 0.05 M potassium tetraoxalate and of 1 C cm^{-2} in 0.1 M pyrrole and 0.1 mM potassium poly(styrene)sulphonate.

The first applied potential was $E = -0.3$ V vs SSE leading to iron dissolution with a very high critical passivation current which rapidly decreased to a small value around 20 μA cm^{-2} indicating passive film formation. The second applied potential $E = 0.23$ V vs SSE, at $t = 800$ s, corresponds to pyrrole electropolymerization with a stable current of 1 mA cm^{-2}. The electrode was then moved to a 0.1 mM NaPSS and pyrrole 0.1 M solution to form the PSS-doped PPy film at $E = 0.23$ V vs SSE. In this paper, this duplex layer coating will be referred to as being a mixed oxalate/PSS-doped PPy film.

3.2. *Scanning electron microscopy*

Micrograghs of oxalate-doped PPy and mixed oxalate/PSS-doped PPy films are presented in Figure 2. The samples display the same homogeneous cauliflower type structure. However, the mixed oxalate/PSS-doped PPy film surface which, in fact, corresponds to the upper PSS-doped PPy film, presents smaller spots and less roughness than does the oxalate-doped PPy film. Indeed, roughness could be estimated by comparing the photo color contrast. On the oxalate-doped PPy micrograph, white spots indicate more protruding PPy amounts while the mixed oxalate/PSS-doped PPy micrograph presents a uniform black color. Mixed oxalate/PSS-doped PPy appears to be more homogeneous with fewer defects, which might initiate corrosion.

SEM micrographs show a compact structure of the films, corresponding to a low porosity. An estimate of the void fraction in the film was calculated by comparing the oxygen reduction current on the Au electrode and on the PPy coated electrode at the same potential of −1.3 V vs SSE. This potential corresponds both to a

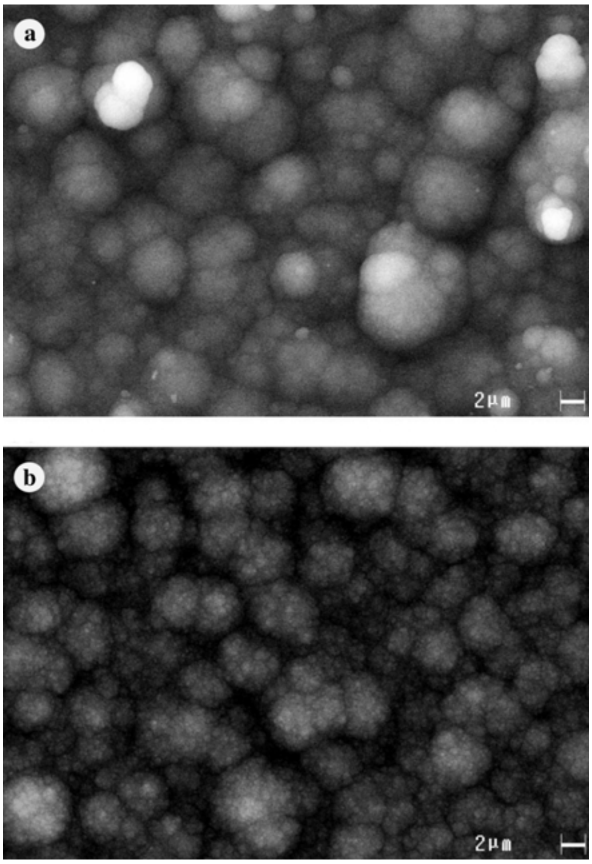

Fig. 2. (a) SEM photo of oxalate-doped PPy film. (b) SEM photo of mixed oxalate/PSS-doped PPy film.

diffusion-controlled current and to conditions where PPy is de-doped and therefore insulating. Koutecky–Levich behaviour was observed in the latter case, from which the oxygen diffusivity D_f in the de-doped film was obtained as $D_\mathrm{f} = 5.63 \times 10^{-7}$ cm^2 s^{-1}.

This value was compared to the value of 1.3×10^{-5} cm^2 s^{-1} for oxygen diffusivity D_s in solution.

The porosity, ε, can then be calculated as [38]: $\varepsilon = (D_\mathrm{f}/D_\mathrm{s})^{2/3}$, leading to $\varepsilon \approx 0.1$. This value is likely to be an upper limit due to the fact that a parasitic mediated current might still exist on PPy.

3.3. *Corrosion tests*

3.3.1. *Open circuit potential curves*

A typical time dependance of the open circuit potential for PPy coated iron electrodes in 3% NaCl solution is presented in Figure 3. The curves corresponding to different counter-ions used as synthesis media have a similar form featuring two potential plateaus before the potential drops to the iron corrosion potential.

In the early stages, the potential increases slightly between −0.25 V vs SSE and −0.2 V vs SSE, which confirms that iron is in the passive state. This plateau, also existing for a PPy coated Pt electrode, is close to the formal polymer potential and represents changes in the polymer doping during equilibration in 3% NaCl solution. At this stage, solvent exchange and also exchange between PPy counter-ions and chloride ions take place. The potential evolution related to these exchanges is less significant with PSS-doped PPy.

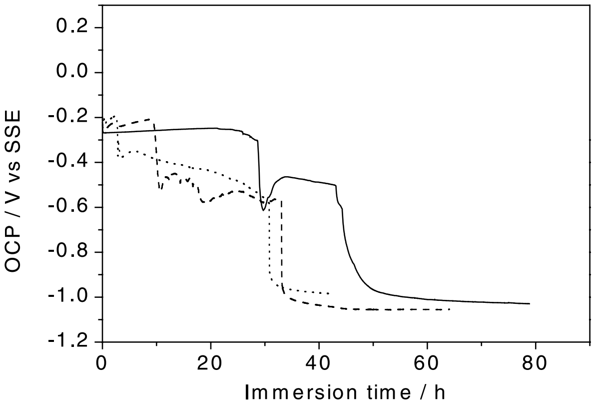

Fig. 3. Dependence of the open circuit potential (OCP) on immersion time in NaCl 3%: for oxalate-doped PPy (- - -, 2 C cm^{-2}), mixed oxalate/tosylate-doped PPy (— — —, 1 C cm^{-2}) and mixed oxalate/PPS-doped PPy coated iron electrodes (—, 1 C cm^{-2}) ($Q_\mathrm{total} = 2$ C cm^{-2}).

The potential decreases until a second plateau is seen around −0.4 ~ −0.5 V vs SSE. This last value is close to the reactivation potential previously assigned, in the absence of PPy, to the reduction of the passivating oxide to a two-valent iron form [33, 35]. It has been shown that, at this stage, chloride ions have reached the metal, involving its oxidation and then partial polymer reduction. This reduction releases oxalate anions which ensures repair of the passive layer. Furthermore, during the second step, one can eventually see sharp decreases of potential down to a value close to the uncoated iron corrosion potential and followed by a fast return to the previous value corresponding to the second plateau: this means that the film has some ability to self-repair. An equilibrium between the polymer and the iron system is reached and the potential around −0.4 ~ −0.5 V vs SSE ensures a passive iron state and consequent its protection. In this potential range, oxygen reduction would be more effective to reoxidize the film and investigations in this direction are now under way to confirm this.

Finally, when the chloride anion concentration is too large at the polymer–iron interface, or when oxalate anions are no longer available, the second plateau is finally followed by a sharp decrease towards the corrosion potential of uncoated iron. The metal is then no longer protected.

3.3.2. *Counter-ion effect*

The protection efficiency achieved by PPy films-doped with different counter-ions can be deduced from Figure 3. This efficiency was defined in a previous paper as the total time for the OCP to reach the normal corrosion potential of unprotected iron [35]. Oxalate, para-toluenesulphonate (tosylate) and PSS were compared. For each coating, the total electrodeposition charge was

2 C cm^{-2}. For mixed PPy films, the electrosynthesis charges of the oxalate-doped PPy film (first layer) and of the tosylate or PSS-doped PPy film (second layer) were 1 C cm^{-2} each. Corrosion tests show an increase in the total protection time when the counter-ions size increases, that is, Ox < tosylate < PSS. This improvement is mostly due to the longer duration of the first plateau where exchange between chloride ions and counter-ions occurs. The protection on the first plateau corresponds to effective passive conditions, and therefore, the improvement provided by the large size anions is much more substantial than that reflected by the total protection time only. This effect is illustrated in Figure 4 where the mixed oxalate/PSS-doped PPy film efficiency is compared to that of a oxalate-doped PPy film, both obtained with a synthesis charge of 4 C cm^{-2}. The duration of the first plateau (o.c.p. > −0.45 V vs SSE) is twenty times longer with the mixed film. The protection time of iron, evaluated from Figure 4, varies between 50 and 170 h, depending on the film. This time is significant in view of the use of PPy coating as a primer coating for metal. For comparison, a chromatation layer used as primer would give much shorter protection times.

Large size anions are surrounded by PPy and become trapped in the polymeric matrix during synthesis. PSS represents a specific situation as it is a linear polyelectrolyte containing negatively charged sulfonate groups. This type of linear polymer is known to form statistical coils in good solvent conditions and in dilute conditions [39]. The gyration radius of the coil increases as $M^{3/5}$, i.e. faster than $M^{1/3}$ which would correspond to a constant number of monomers per unit volume for any M value (where M is the polymer molecular weight); thus, high molecular weight chains are very expanded and ions or small neutral molecules can diffuse freely through them as in the solvent.

The molecular weight used here for PSS was an intermediate one, and, in addition, the concentration was large $-c \sim 7$ g L^{-1}. The solution, therefore, behaved as a gel. In this case, entanglements may occur which reduce the monomer mobility. It may also be assumed that oligomers formed during the first steps of the polymerization mechanism are able to remain close to the interface due to their low mobility in this entanglement network.

Due to the presence of the sulfonate groups, which change the film permselectivity, the co-ions, here sodium, penetrate the film when PPy is reduced, and are expelled when PPy is oxidized, thus preventing chloride exchange [25–30].

Even if the total protection time is better, the duration of the second plateau is smaller with mixed oxalate/tosylate or PSS-doped PPy films than with ‘pure’ oxalate-doped PPy film. In fact, oxalate anions allowing autorepair of the passive layer are in lower quantity in the mixed film (electrodeposition charge for oxalate-doped PPy is 1 C cm^{-2} for mixed films and 2 C cm^{-2} in pure film), which reduces the efficiency of the film during the second potential step.

3.3.3. *Electrodeposition charge effect*

The protection time is reported in Figure 5 as a function of charge instead of the thickness, because there is so far no clear relation between the charge and the film thickness. In fact, it can be assumed that the faradaic yield should remain approximately constant because the electrodeposition current does not vary substantially after the initial peak following passivation (see the chronoamperometric curves of Figure 1). Results obtained with ‘pure’ oxalate-doped PPy films and with ‘mixed’ oxalate/PSS-doped PPy films are given. For the mixed films, electrosynthesis charges of 0.5 and 1.5 C cm^{-2} of the first oxalate-doped PPy film were chosen.

The protection time increases with a quasi linear dependence on the total electrosynthesis charge, up to 4 C cm^{-2}, which appears to be very encouraging from the application point of view. The slope is larger when the iron coating is a composite polyanion PPy film, indicating better protection with this film due to weak mobility of the PSS as mentioned above.

Figure 5 (compare (●) and (□) symbols) shows a significant protection time improvement when the oxa-

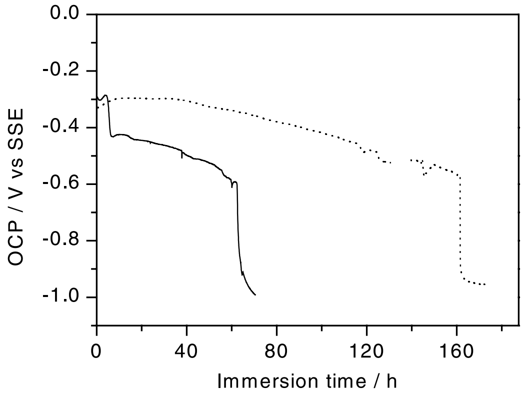

Fig. 4. Comparison of the open circuit potential (OCP) in NaCl 3% of (——) an oxalate-doped PPy coated iron electrode ($Q_{total} = 4$ C cm^{-2}), and (- - -) a mixed oxalate/PSS-doped PPy coated iron electrode ($Q = 1.5$ and 2.5 C cm^{-2}, respectively, for each layer).

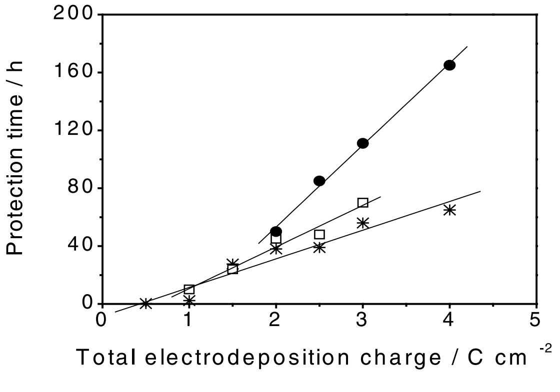

Fig. 5. Dependence of the protection time on the total electrodeposition synthesis charge for oxalate-doped PPy coated iron (∗) and mixed oxalate/PSS-doped PPy coated iron (● at 1.5 C cm^{-2}; □ at 0.5 C cm^{-2}) electrodes.

late-doped PPy film (first layer) synthesis charge increases. This result confirms the protection mechanism suggested involving the ability of oxalate anions to repair the passive layer during the second potential plateau.

3.4. *Cyclic voltammetry*

Cyclic voltammograms obtained in 3% NaCl solution are compared in Figure 6 for an oxalate-doped PPy-film-coated iron electrode and a mixed oxalate/PSS-doped PPy-film-coated iron electrode at a sweep rate of 10 mV s^{-1}. A voltammogram obtained with chloride-doped PPy-film synthesized on a Pt substrate is also presented.

During the first cycle (Figure 6(a) and (b), solid line), the oxalate-doped PPy reduction wave presents one large peak around $-1 \sim -1.1$ V vs SSE while two peaks are observed in the same potential domain in the case of mixed oxalate/PSS-doped PPy. This behaviour is also found with a Pt substrate (not shown here). These observations were interpreted as being caused by cation incorporation in the film instead of anion release, due to low mobility of the counter-ions [40]. Indeed, the first reduction of a Cl^--doped PPy in 3% NaCl presents two peaks (Figure 6(c), solid line), the first peak around $-0.5 \sim -0.6$ V vs SSE and usually ascribed to mobile Cl^- release and a second peak, more cathodic, situated around $-1.2 \sim -1.3$ V vs SSE and attributed to cation incorporation [28]. Furthermore, as can be seen in Figure 6, during the second and the following cycles, a reduction peak appeared which is attributable to release of Cl^- anions, which were previously inserted in the film during the first oxidation [41]. In the case of mixed oxalate/PSS-doped PPy films, the two cathodic peaks observed in the first cycle correspond to reduction of each film. The decrease of the more cathodic peak after several cycles may be attributed to reduction of the residual water entrapped in the film during synthesis [42].

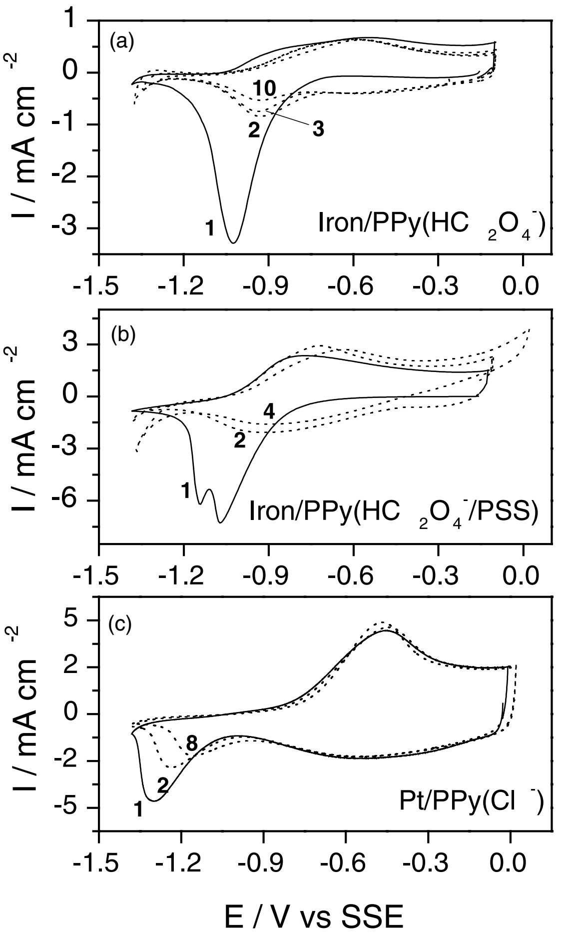

Fig. 6. Cyclic voltammetry in a NaCl 3% solution of (a) oxalate-doped PPy coated iron electrode, (b) mixed oxalate/PSS-doped PPy coated iron electrode and (c) chloride-doped PPy film synthesized on Pt substrate.

Cyclic voltammetry results show that the first reduction of the composite polyanions/PPy films mainly involves a cationic process, behaviour which explains the longer duration of the first potential plateau and the corresponding improvement in iron protection.

5. Conclusion

In this work, composite Polyanion/PPy electrodeposition on iron using polystyrenesulfonate has been described to prepare efficient pretreatment films for protective coatings against iron corrosion. An initial oxalate-doped PPy film must be electrosynthesized prior to PSS-doped PPy electrodeposition, to allow adherent PSS-doped PPy film and also to use the ability of the oxalate to repair the passive iron layer. Corrosion tests by following the open circuit potential of these systems with time in 3% NaCl corrosive medium have shown an improvement in the iron protection time. Polyanions, used as PPy counter-ions, reduce chloride diffusion in the protective coating, due to their low mobility involving a cationic redox PPy process. Corrosion tests on samples consisting of paint coatings on iron and/or steel pretreated with PPy coating are under way.

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