

Design of a new bilayer polypyrrole–xerogel hybrid coating for corrosion protection

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In order to improve the anticorrosion protection properties of polypyrrole (PPy) films deposited on iron or mild steel, the organic conductive polymer was covered by a thermally and mechanically resistant xerogel layer. The anticorrosion protective effect of such a bilayered coating was evaluated by electrochemical measurements ($i=f(E)$; $E=f(t)$; polarization resistance (R_p)) in NaCl (30 g L⁻¹) and in HCl (1 M) aqueous solutions and by analysis of NaCl and HCl aqueous solutions in which samples coated by PPy and the xerogel were immersed for one and seven days. The results were compared with those obtained, in the same conditions, for naked mild steel plates, PPy or xerogel coated mild steel plates. The bilayer coating ensures a very efficient protection of mild steel against corrosion. A synergy between PPy and the xerogel was revealed. Moreover, the weak adherence of the xerogel on PPy was improved by the incorporation in the organic polymer of carboxylic acid-functionalized pyrrole units, and the corrosion protection of these modified layers was still increased.

Introduction

The protection of oxidizable metals through the use of organic coatings is a quite ancient field of research. Among them, conducting polymer, particularly polypyrrole (PPy), films are very attractive since their use against corrosion in the case of iron, zinc, aluminium and magnesium has been investigated with some success.^{1–6} Several formulations containing chemically prepared PPy are already commercially available.⁶ Moreover, Truong *et al.* propose to disperse PPy powder in acrylic paint in order to enhance the anticorrosion protection.⁵ But the deposition of these coating formulations does not derive benefit from the electrical properties of the conducting polymers which allow the electrochemical formation of films on conductive substrates. Indeed, the electrodeposition of an organic film is quite attractive, since a homogeneous film can be deposited on a complex shape. Most often, conductive polymers have been used since the electrodeposition can be carried out beyond a few monolayers, due to the conducting character of the film which allows continuous deposition of a thick film. Besides, the redox character of conducting polymer confers a free potential to the layer much higher than the bare metal, usually protecting it against corrosion processes. The main difficulty encountered in most cases comes from the high deposition potential of polypyrrole which lies far above the oxidation of non noble metals such as copper, zinc or iron.⁷

In the case of iron, a few strategies have been used to overcome this problem. A first method consists of having in the electrolytic solution an anion able to complex the first Fe²⁺ cations coming from the electrodisolution of the first Fe layers, and upon this, produce a film inhibiting Fe dissolution but conducting enough to allow the polypyrrole deposition.^{8–10} However, the induction time necessary can be long, and contamination of the solution by Fe²⁺ ions is a major drawback

and cannot be avoided. Another way described by Lacaze *et al.* consists of passivating the metal with nitric acid, and electropolymerization of the pyrrole onto the passivated surface.¹¹ This is a quite effective process, although the same group developed a still more efficient method, which consists of using sodium salicylate as the electrolyte salt.¹² The salicylate is a good iron ion complexant and totally inhibits iron oxidation, and a resistant and very adhesive polypyrrole film can be instantaneously deposited. The authors as well as other teams have tested the efficiency of polypyrrole layers against iron corrosion, which is good.^{1,2} However, the debate is still not closed if the protection is anodic (due to the redox active character of polypyrrole) or if the polymer acts mainly as a physical barrier.^{6,13,14} In fact, it is clear anyway that most conducting polymers, and especially polypyrrole, are more or less porous (otherwise they would not be wholly electroactive). Therefore, whatever the main reason why they protect the oxidisable metal, this protection is expected to be better upon improving the quality of the physical barrier provided by the coating.

On the other hand, sol–gel deposits are known to be effective for corrosion protection.^{15,16} This protection comes only from the physical barrier provided by the tight gel layer, but this class of polymers (in the form of xerogels, that is, dried gels) are known to display a better thermal and mechanical resistance.^{17,18}

In this work we describe the preparation of deposits associating a PPy and a xerogel (XG) layer. Such a realization is not obvious, because the mechanical qualities of the polypyrrole layers are very average, and other coatings are usually poorly adherent on polypyrrole layers, resulting in brittle films and poor corrosion protection. Therefore, we have developed a polypyrrole copolymer possessing anchoring groups which allows the deposition of a tailored tight, resistant and strongly

adherent hybrid xerogel layer. The structure and the mechanical properties of the layers have been investigated through several characterization techniques. The anticorrosion properties of the deposits on mild steel have been studied through free potential measurements, electrochemical cycling and dipping into aggressive saline or acidic solutions, and have been found to be superior to most materials reported to date.

Experimental

Polypyrrole electrodeposition

The polypyrrole has been deposited from an aqueous 0.5 M pyrrole solution containing 1 M of sodium salicylate. In the case of copolymers the solution contained 0.5 M of pyrrole and 0.1 M of 3-(pyrrol-1-yl)propanoic acid (CAPy). A classical three compartment electrochemical cell has been used, with a working electrode made of a 2 cm² polished mild steel plate (%C=0.057; %Cr=0.024) and a 5 cm² platinum electrode as counter-electrode. Saturated calomel electrode (SCE) was used as the reference electrode. All potentials are referred to SCE. The mild steel plate was ultrasonically treated in acetone, then rinsed twice in ethanol. All syntheses were realized applying a constant current density of 2 mA cm⁻² for a given time (according to the desired thickness) without stirring.

Preparation and deposition of the hybrid gel layer

The sol precursor of the gel layer was prepared at 22–24 °C as follows: to 1.5 mL of diethoxydimethylsilane (DEDMS) in 3 mL of propanol were slowly added 0.5 mL water under vigorous stirring. The stirring was maintained for 1 h, after which 2.5 mL of triethoxymethylsilane (TEOMS) were added, and the stirring continued for 3 h. Finally 0.5 mL of zirconium propoxide was added and the solution was still stirred for 15 min. The molar ratios are reported in Table 1 and will be discussed in the section focusing on XG layers. The resulting viscous sol was highly stable and could be kept up to three weeks at room temperature (and much longer if stored in the cold). When the sol was deposited on a flat surface, it gelled in about one hour, then it was hardened by thermal treatment at a moderate temperature (70 °C) at reduced pressure (15 mmHg) for 14 hours, which eliminated all volatile compounds to leave a smooth xerogel. On polypyrrole layers the viscous sol was coated with the help of a flat lancet before the conversion process into the xerogel.

Characterization of the deposits

The thickness of the deposits was evaluated with Scanning Electron Microscopy (SEM). The PPy thickness is 5 µm (±0.2 µm). The XG layer has a thickness of 20 µm (±0.5 µm); however the uncertainty on it is more important due to the deposition process. At each step of a process (for example before and after a corrosion test), the deposit was examined using an optical microscope (OM) (Zeiss AxioTech, fitted with a Sony DXC 107AP CCD camera) and SEM (JEOL JSM 5600). Similarly X-Ray Fluorescence experiments were also carried out using a Fisherscope XRAY 1600 instrument. IR spectra (Bruker Spectrospin IFS-45) of the coatings, which were crushed and mixed to KBr pellets, were also recorded. XG, PPy, copolymer films and the bilayer copolymer/xerogel

Table 1 Molar ratios of the main components used for the preparation of the sol

$n_{\text{H}_2\text{O}}/n_{\text{EtO}} = n_{\text{H}_2\text{O}} / (2n_{\text{DEDMS}} + 3n_{\text{TEOMS}})^a$	$n_{\text{DEDMS}}/n_{\text{TEOMS}}$	$n_{\text{Zr}}/n_{\text{Si}}$
0.40	0.73	0.04

^aIn respect of the stoichiometry, $n_{\text{H}_2\text{O}}/n_{\text{EtO}} = 0.5$.

(PPy_cXG) interface were studied by X-ray Photoelectron Spectroscopy (XPS). The XPS analysis apparatus was a Riber SIA 200, using the Al K α X-ray line (1486.6 eV). EDS, Energy Dispersive Spectroscopy (JEOL JSM 5600-FODIS), was carried out after adhesion tests of bilayer systems (PPyXG or PPy_cXG) in order to confirm the possible detachment of XG from the organic polymer. The concentrations of iron ions in the solution in which samples were immersed were determined by atomic absorption (Perkin Elmer 3100).

Adhesion tests

The adhesion tests on the coatings were performed before and after various treatments according to the French standard (T30-038), in order to estimate the adherence of the polypyrrole layer on the mild steel, and of the xerogel on the polypyrrole.

Incisions were made with a cutter, and a calibrated adhesive tape was then stuck on the deposit. The tape was pulled off, and according to what remained on the metal and on the tape, the adherence was estimated on a 0 to 5 scale (0 corresponds to nothing on the tape, the best possible adherence, and 5 to more than 35% of the coating on the tape).

Results and discussion

Characterization and properties of the deposits

a) Conducting polymer layer. Two types of PPy layers were prepared, either using pure pyrrole or a mixture of pyrrole and a functionalized pyrrole (CAPy). In both cases, PPy as well as the copolymer are uniform, black coatings. The OM and SEM views (Fig. 1) show the presence of a homogeneous, regular polymer layer, which becomes more and more granular as the thickness increases (see the difference between Fig. 1a and d), as is often encountered with electrodeposited conducting polymers.^{9,19,20} There is absolutely no morphology change when changing from PPy to the copolymer (Fig. 1c and e). Adhesion tests were performed on both types of layer, and confirm the excellent adherence of these organic coatings on steel, as suggested by previous studies.¹²

b) XG layers. They are fully transparent and therefore it is difficult to observe them by OM. They present no defects at the submicrometric scale according to the SEM micrographs. The absence of cracks in the thick xerogel layers results probably from the presence of polydimethylsiloxane (PDMS) chains in the xerogel coating. Hybrid materials containing PDMS rarely exhibit cracking problems and are characterized by good flexibility because of their excellent relaxation properties.^{21,22}

The synthesis of hybrid siloxane–oxide materials from hydrolysis–condensation of DEDMS with cross-linking reagents such as Si(OR)₄ or transition metal alkoxides (Ti, Zr) has been thoroughly described.^{21,23,24,25} In our case, we use as cross-linking agents TEOMS and Zr(OPr)₄. According to the previous studies, the gel we prepared is constituted by a dense interconnected network of difunctional and trifunctional units because of the high content of TEOMS ($n_{\text{DEDMS}}/n_{\text{TEOMS}} = 0.73$). Indeed, Babonneau²³ showed in the case of the hydrolysis–condensation of DEDMS and tetraethoxysilane (TEOS) that PDMS chains are shorter and the polysiloxane network more cross-linked when $n_{\text{DEDMS}}/n_{\text{TEOS}} \leq 2$.

Moreover, zirconium oxopolymer domains are dispersed in the cross-linked PDMS network. The dimensions of these domains do not exceed the nanometer scale according to the study of Sanchez *et al.*²¹ The transparency of the xerogel confirms the absence of aggregates of the zirconium oxopolymers. At the interface between the polysiloxane network and the zirconium oxopolymer domains, Si–O–Zr bonds were likely to be established but they are not detected by FTIR because the absorption band of Si–O–Zr stretching vibrations (in the region

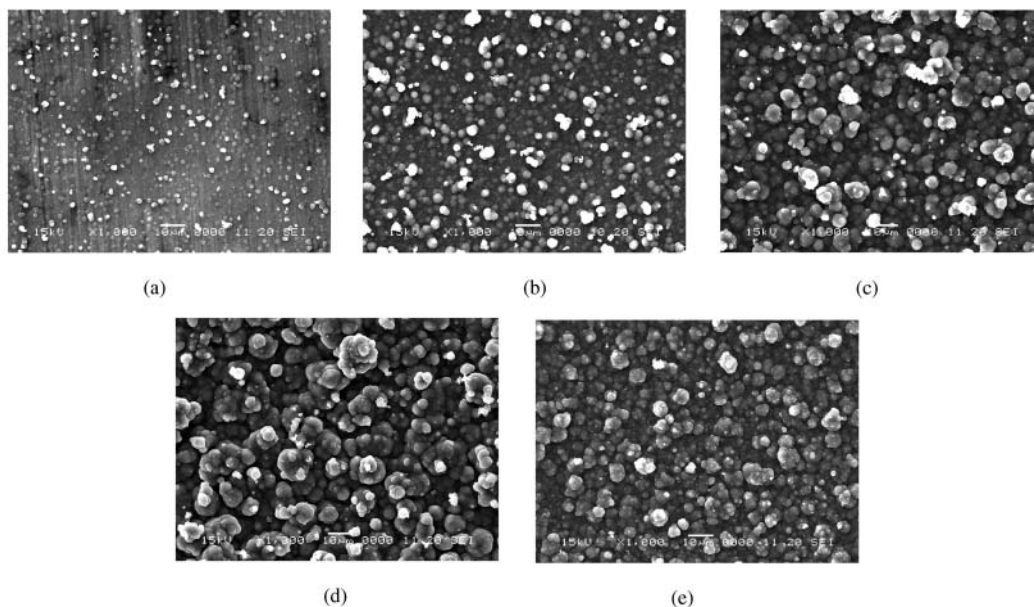


Fig. 1 SEM micrographs of mild steel coated by PPy electrodeposited during (a) 200 s; (b) 400 s; (c) 800 s; (d) 1600 s, and of (e) a coating electrogenerated from a mixture of 0.5 M pyrrole and 0.1 M CAPy during 800 s ($\times 1000$).

970–980 cm^{-1}) is masked by those of Si–O–Si. Indeed, Si–O–Zr band is observed only when the Zr/Si molar ratio is greater than 0.30²¹ (*i.e.* noticeably larger than in the xerogels we prepared (Table 1)).

The amount of added water is slightly less than the stoichiometric amount ($n_{\text{H}_2\text{O}}/n_{\text{EtO}} = 0.40$ instead of 0.50): the amount of water is also not sufficient to fully hydrolyze and condense the DEDMS and TEOMS species. However C/Si values extracted from XPS data of the xerogel (Table 2) reveal that almost all the ethoxy (EtO) groups were removed, *i.e.* the hydrolysis–condensation is complete. The small carbon excess observed could also arise from the presence of propanol or ethanol entrapped in the xerogel, and/or from contamination of the samples. The fact that the hydrolysis is nearly complete whereas the water amount is not sufficient, arises from the air moisture which provides the missing water for the hydrolysis–condensation. This protocol limits considerably the problem of precipitation when adding Zr(OPr)₄.

c) PPy–XG bilayers. A XG layer can be deposited on polypyrrole and hardened by soft thermal treatment (see Experimental). Immediately after deposition, the XG surface is perfectly smooth and mechanically resistant. However, adhesion tests performed on the composite layer show that the XG is peeled from the PPy layer: the adherence of the xerogel onto the polypyrrole is relatively weak (Fig. 2, inserts 1a and 1b). In order to improve the anchorage of the xerogel onto the PPy layer, an attractive way seemed to functionalize the PPy by carboxylic groups, since they are known to strongly chelate zirconium oxo species^{26,27} and therefore we prepared a copolymer containing carboxylic groups.

We had shown in a previous work that copolymerization of pyrrole in acetonitrile with CAPy gives copolymers where the

number of functionalized pyrrole units is always lower than the proportion of functionalized pyrrole in the polymerization feed.²⁸ Nevertheless, the electropolymerization of a mixture of pyrrole and CAPy (with a ratio $[\text{Py}]/[\text{CAPy}] = 1$) in 0.1 M LiClO₄/CH₃CN provides a conducting film which contains CAPy in a ratio $[\text{Py}]/[\text{CAPy}] \approx 5$. Copolymers can be prepared in aqueous electrolytic solution containing 0.1 M LiClO₄ and a mixture of pyrrole and CAPy. Solutions are stable (no precipitation was observed) for $[\text{Py}]/[\text{CAPy}]$ ratios at least equal to 0.5 while CAPy is insoluble in water at neutral pH. But for the same relative proportion of CAPy in solution, the relative proportion of CAPy units in the copolymer film is smaller when the electropolymerization is carried out in aqueous solution (Table 3).

In order to deposit a copolymer film on mild steel, LiClO₄ (electrolytic salt) must be replaced by sodium salicylate: no PPy films could be deposited on steel when using LiClO₄ as doping species (see Introduction). Whereas LiClO₄ seems to be indifferent to the presence of CAPy, sodium salicylate reacts with CAPy according to a classical acido–basic equilibrium. The protonation of the salicylate produces salicylic acid (isolated and identified by ¹H NMR) which precipitates in water. Whereas the highest COOH group concentration was the most desirable, we were limited by the fact that the polymerization reaction had to be conducted in the presence of sodium salicylate in water. In such conditions, the highest achievable proportion of functionalized pyrrole which did not lead to a phase separation in the electrolyte was 0.1 M of CAPy (along with 0.5 M of pyrrole). The determination by IR of the COOH group content in the copolymers was not feasible, because the relative proportion of CAPy in the copolymer film is too small and probably will not be detected. However, from the result of our former study²⁸ conducted in LiClO₄ and acetonitrile we can estimate that the proportion of functionalized rings in the copolymer is less than 5%. The presence of CAPy units in the copolymer film was revealed by XPS. The organic films were deposited on a gold anode from electrolytic solutions containing LiClO₄ instead of sodium salicylate. This allows us to eliminate the contribution of its carbonyl group to the spectra and then simplify the interpretation of the XPS spectra. Indeed the comparison between the C1s peaks of PPy, poly(CAPy) and copolymer films exhibit marked differences (Fig. 3). The presence of carbonyl groups generates a modification of the peak of the C1s core in the XPS spectra: an

Table 2 XPS data for C1s and Si2p cores of the xerogel layer: binding energy, FWHM, C/Si ratios

	Binding energy/eV	FWHM/eV	C/Si calculated ^a	C/Si measured
C1s	284.5	2.45		
Si2p	102.8	2.50	1.37	1.74

^aWe suppose that all the ethoxy groups of DEDMS and TEOMS were removed by hydrolysis.

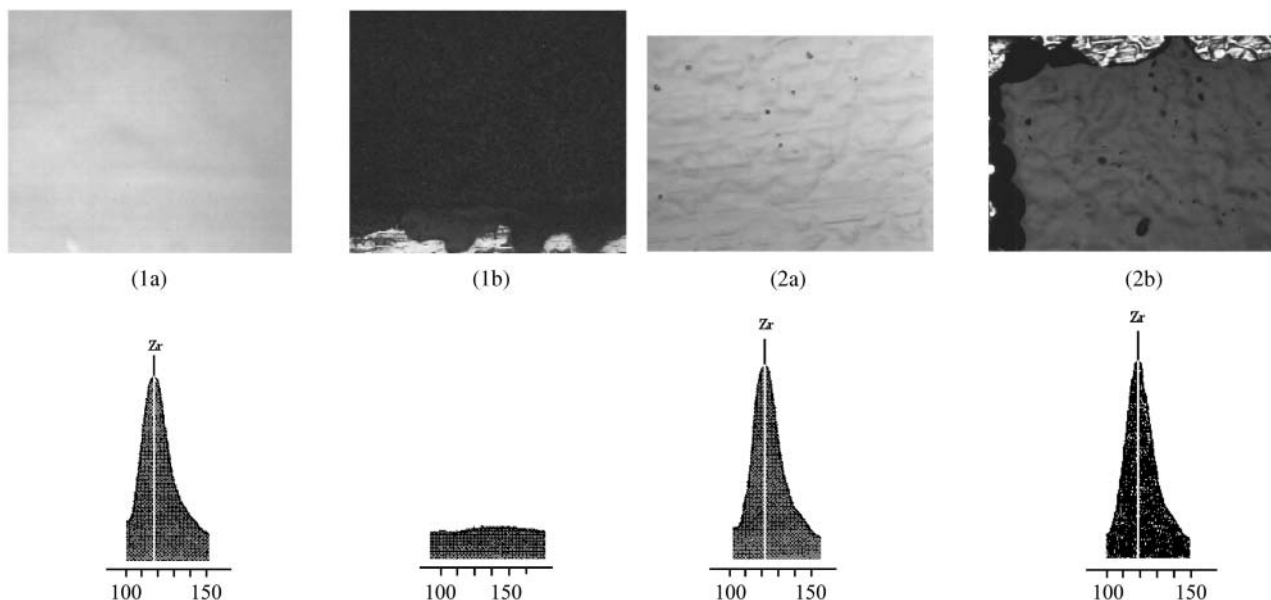


Fig. 2 Optical micrographs ($\times 20$) and X-ray fluorescence spectra before (a) and after (b) adhesion tests of (1) PPy/XG and (2) copolymer/XG films.

Table 3 Relative proportions p of CAPy in the copolymer *versus* its relative proportion x in aqueous or organic solution

x	p (aqueous solution)	p (acetonitrile solution)
0.50	0.05	0.17
0.67	0.14	0.29

additional peak appears at higher energy binding values. Indeed, in the case of poly(CAPy) which contains only CAPy units, such a peak is observable (Table 4 and Fig. 3) whereas the C1s core peak of PPy should not exhibit it. However, there is a smaller shoulder in this peak due to the presence of carbonyl groups at the end of the polymer chains.¹⁹ In the case of the copolymer, the characteristic carbonyl peak is not visible in XPS spectra but the C1s peak becomes larger towards high binding energy (Table 4 and Fig. 3). This phenomenon features the presence of the carbonyl groups in the copolymer. XPS is thus able to detect the presence of CAPy units.

The striking feature of the presence of CAPy in the copolymer is the considerable improvement of the adherence of the

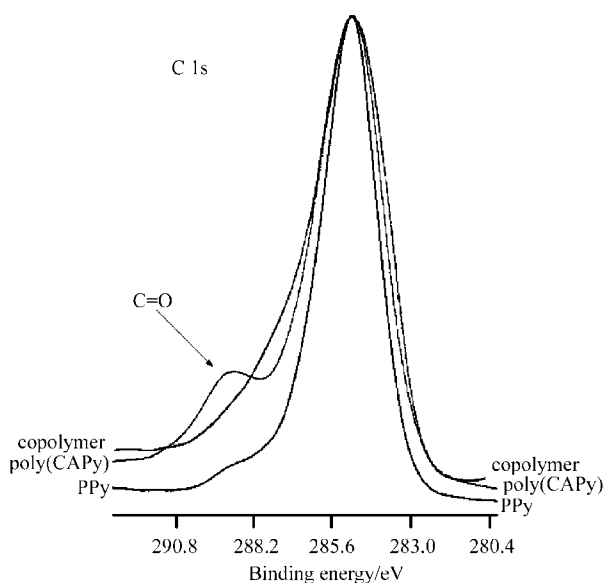


Fig. 3 C 1s XPS spectra of the copolymer, poly(CAPy) and PPy films.

XG layer on the conducting polymer. From the worst mark, 5, obtained for XG adhesion on pure PPy, the mark shifts to 0 in the case of the copolymer. The fact that the XG layer remains totally unchanged on the copolymer has been confirmed by SEM, OM, X-ray fluorescence and EDS. The OM micrographs reveal that XG is always present on the copolymer film after the adhesion test, whereas it is totally removed by the adhesion test when deposited on a PPy film (Fig. 2). Moreover, the spectra obtained by X-ray fluorescence and by EDS exhibit a Zr peak (which characterizes the xerogel) only when XG covers the copolymer layer (Fig. 2). It has been similarly verified that no zirconium at all was present on the adhesive tape after the test. This shows: i) that in the copolymer anchoring COOH groups are clearly present, and ii) that the proportion of carboxylic groups present, although it is small relatively compared to the number of pyrrolic rings, greatly improves the mechanical resistance of the bilayer coating and therefore makes it an attractive material for metal protection.

The large improvement of the adhesion of XG on the copolymer (compared to pure PPy) arises probably from the interaction between COOH groups present in the copolymer and the metallic centers of XG. This interaction causes a shift of the zirconium peak preferentially. Therefore, we studied the interface between the copolymer and XG layers. However, the analysis of the copolymer/XG interface did not allow us to extract reliable data. On the one hand, such an analysis is possible only if the thickness of the XG is smaller than 4–5 nm. The preparation of such a thin film is quite difficult because the organic layer is rough. The roughness of the polymer film prevents the deposition of a uniform XG layer. Nevertheless, we succeeded in the preparation of such a bilayered coating by

Table 4 XPS data for the C1s core of poly(CAPy), PPy and the “copolymer”: binding energy, FWHM

	C1s	
	Binding energy/eV	FWHM/eV
poly(CAPy)	288.95	—
	285.05	2.60
copolymer	288.95	—
	285.00	2.35
PPy	285.00	2.10

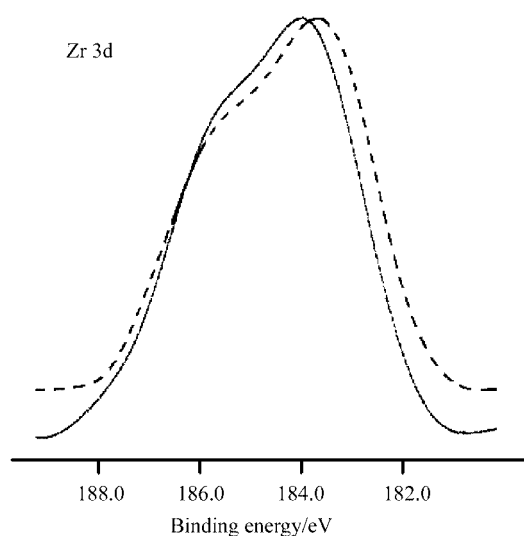


Fig. 4 XPS spectra: Zr 3d_{3/2} and Zr 3d_{5/2} peaks observed for a copolymer film coated by a xerogel thin layer (solid line) and for a xerogel thick layer (dashed line).

Table 5 XPS data for Zr3d core of poly(CAPy)/XG, XG and the “copolymer”/XG: binding energy, FWHM

		Binding energy/eV	FWHM/eV
Zr3d _{5/2}	poly(CAPy)/XG	184.0	4.35
	XG	183.6	4.50
	copolymer/XG	184.0	4.35

100-fold dilution of the corresponding sol. Indeed, the N1s peak characteristic of the organic polymer is observed in the XPS spectrum of the copolymer/XG coating. The main obstacle of this study lies in the fact that the response from the interface is “diluted” by that of the rest of the coating. However, the comparison of the Zr peaks between the spectra of XG and copolymer/XG (Fig. 4, Table 5) shows a shift (0.4 eV) and a shortening (0.15 eV) at full width at half maximum (FWHM) of the Zr peak of the copolymer/XG spectrum. The variations are weak but sufficient to signify a change in the zirconium surroundings. FTIR investigations have been shown to be helpful in determining carboxylate coordination modes^{29–31} (monodentate, bidentate chelating or bidentate bridging coordination). Unfortunately, as we mentioned previously, in our materials, the amount of CAPy units in the organic film is too low to be detected by IR.

Electrochemical behavior of the coatings

Since the main application of our coatings was corrosion protection, rather than working in an organic solvent, we have chosen to investigate the electrochemical behavior of various types of coatings in either salted (NaCl) or acidic (HCl) water. The choice of the chloride ions was justified by the fact that it is well known that corrosion processes are generally accelerated by aggressive chloride ions.³² Fig. 5 displays the low scan rate voltammograms of naked mild steel (Fe), mild steel–copolymer (FePPy_c), mild steel–xerogel (FeXG), and finally mild steel coated by the bilayer copolymer–xerogel (FePPy_cXG) in aqueous sodium chloride solution. It is clear that, while the naked mild steel is very quickly oxidized, both polypyrrole and the xerogel provide protection. In the case of FePPy_c, the electroactivity of the polymer is clearly distinguishable, along with Fe protection. In both cases, the oxidation of mild steel begins relatively high, up to 1 V. The presence of the xerogel does not affect the electroactivity of the conducting polymer, but considerably decreases, by about three orders of magnitude,

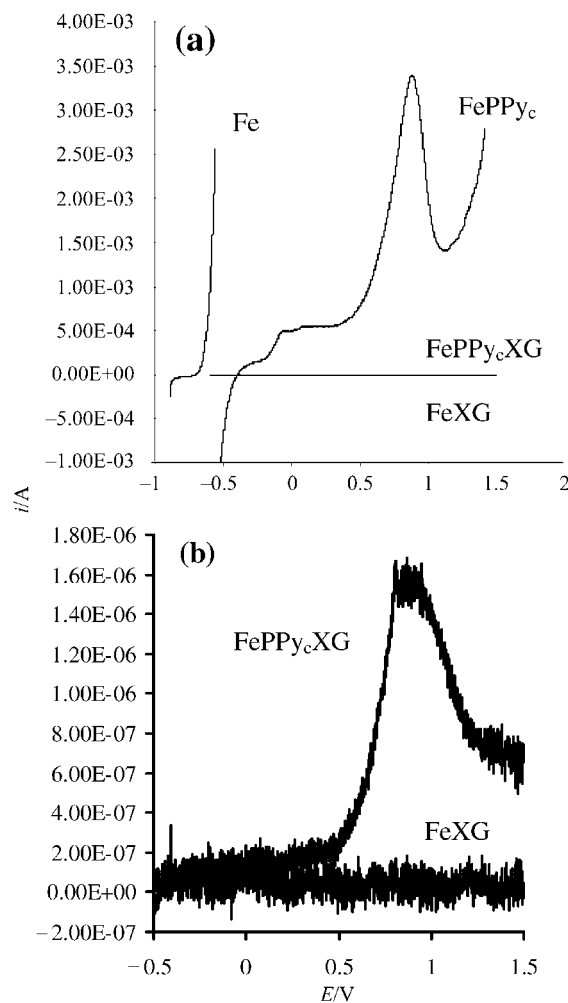


Fig. 5 Voltamperometric curves ($i=f(E)$) obtained in NaCl (30 g L⁻¹) aqueous solution of (a) various coated mild steel plates; (b) magnification of the curves corresponding to FePPy_cXG and FeXG. $v=10$ mV s⁻¹.

the currents. It is very probable that the xerogel layer acts as a transport barrier for the mobile species (counter ions, solvent, etc.) implied in the electrochemical reaction and therefore leads to an overall strong diminution of the kinetics of the reaction. The presence of the xerogel does not affect the redox potential of the copolymer as could be expected. Similar features are observed in the presence of HCl as supporting electrolyte, as could be expected. In fact it is known that protons, although they enhance the corrosion processes in general, have almost no effect on polypyrrole electroactivity.³³

The stability of the protection is still much more evidenced when one looks at the free potential of each sample. In the NaCl medium (Fig. 6), when only the XG layer is present, the potential is higher than that of the metal alone, although there is no straightforward explanation for this; this contradicts somewhat our formal hypothesis that the XG layer behaves only as a physical barrier. However, one cannot exclude the existence of a junction potential between the sol–gel layer and the metal. In any case this is quite stable since it does not change with time. On the other hand, one can see that both PPy_c and PPy_cXG layers offer good protection, as indicated by a high free potential. However, in the case of PPy_c alone, after about 1000 s the potential begins to drop sharply, which shows that the PPy_c coating has lost its protection properties. It should be moreover noted that the protection offered by the PPy_cXG layer is better than that of PPy alone, even at short times.

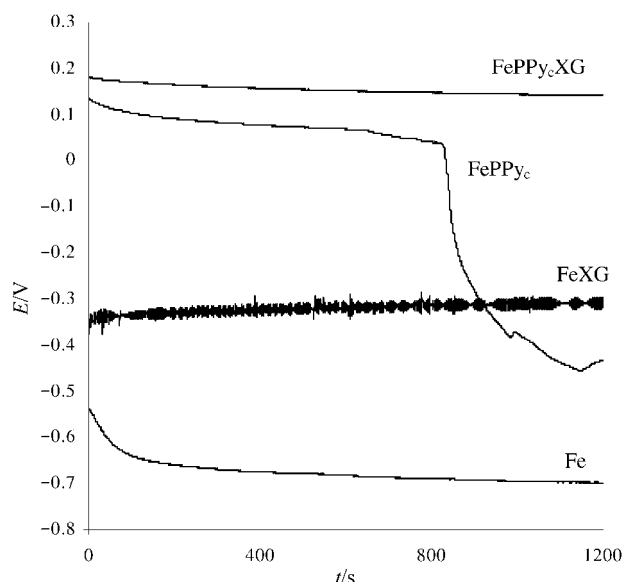


Fig. 6 Variation of free potential as a function of time for various samples in NaCl (30 g L⁻¹) aqueous solution.

The features are even more enhanced when the same study is carried out in 1 M HCl (Fig. 7). In such conditions one can notice that not even the PPy_c alone or the XG alone give any protection, since in both cases the free potential is quite close to that of the metal alone. It may look surprising that, in the presence of HCl the naked metal and the XG protected metal exhibit the same free potential, while in the absence of the acid they are different. However, the protons certainly should diffuse through the oxide film, which is so much more wetted by the ambient solution in this case and this probably reduces strongly its efficiency as physical barrier. Only in the case of the composite PPy_cXG is a high free potential obtained, showing that the corrosion processes are blocked by this protection. Again this tends to show, even more clearly than in the previous set of experiments with NaCl, that there is a synergy between the protective action of the PPy_c and the XG. In fact, if the XG layer had only a physical protection role, one would have expected a corrosion potential similar to the one obtained with PPy_c alone.

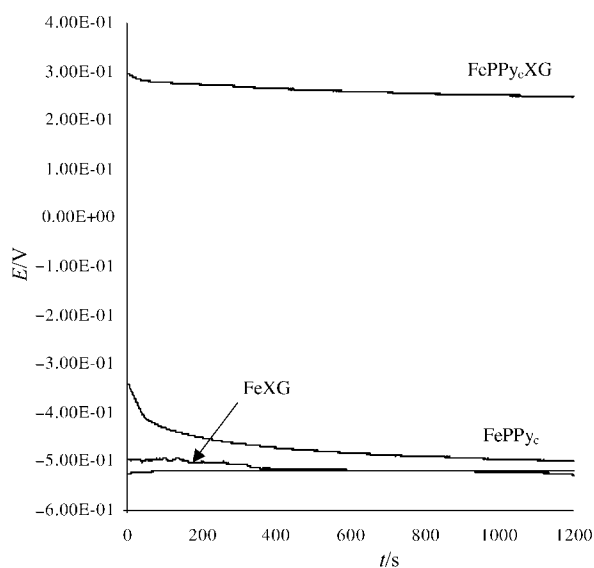


Fig. 7 Same as Fig. 6 but experiments were carried out in HCl (1 M) solution.

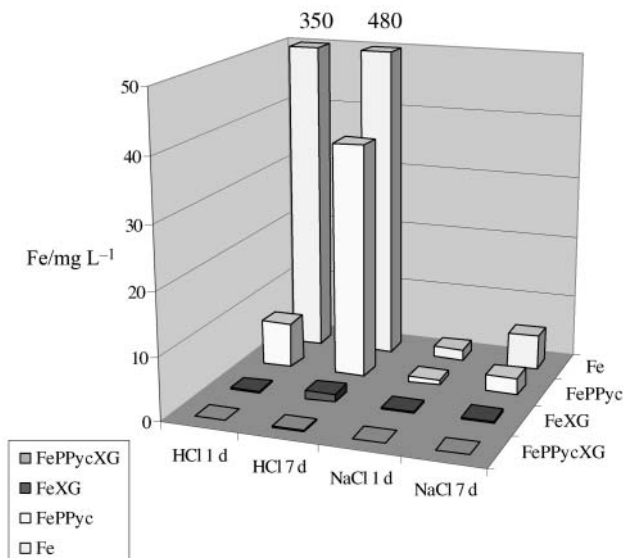


Fig. 8 Determination of iron concentration (mg L⁻¹) in solution after immersion of various samples in HCl (1 M) and NaCl (30 g L⁻¹) solutions during one and seven days.

Corrosion investigations

a) Determination of the metal dissolution rate. In order to confirm the results of the electrochemical study, experiments were performed in order to determine quantitatively the corrosion processes. For this we determined the quantity of Fe ions set free in solution from the corrosion of the metallic substrate of each sample, both in the case of NaCl (30 g L⁻¹) and in the case of HCl (1 M). The results are represented in Fig. 8, and summarized in Table 6. It can be observed that in the case of NaCl, the corrosion processes are always slow, especially when a protecting layer is present. It is somewhat surprising that better protection is offered by the xerogel than by the conducting polymer, probably because of the very high porosity of the latter. It is clear that the composite layer offers absolute protection in this case, since no iron at all is detected in solution, even after 7 days.

In the case of HCl, perfect protection is not possible. Here again XG layers are more protective than PPy_c layers. However, the most striking feature is that the protection offered by the composite layer is 10 to 20 times better than that offered by the xerogel alone, and 200 to 700 times better than that offered by the polypyrrole. Again a synergy between the XG and PPy_c layers is obvious, and results in excellent protection of the oxidizable metal, even in harsh conditions.

b) Microscopy study. The layers were characterized by both optical microscopy (OM) and scanning electron microscopy (SEM), both before and after corrosion tests. It is clear that in the case of the PPy_c or of the XG layers alone, the coatings are very degraded by the corrosion tests (Fig. 9a and b). In both cases the originally smooth and adherent coatings undergo visible changes. In the case of the XG coatings, scattered stains appear as the result of steel corrosion. In the case of PPy_c coatings, the difference is even more striking. The polymer has

Table 6 Summary of the results shown in Fig. 8

	HCl 1 day	HCl 7 days	NaCl 1 day	NaCl 7 days
FePPy _c XG	0.01	0.15	0.00	0.00
FeXG	0.23	1.27	0.23	0.37
FePPy _c	7.23	37.45	0.80	2.68
Fe	350.00	480.00	1.76	5.49

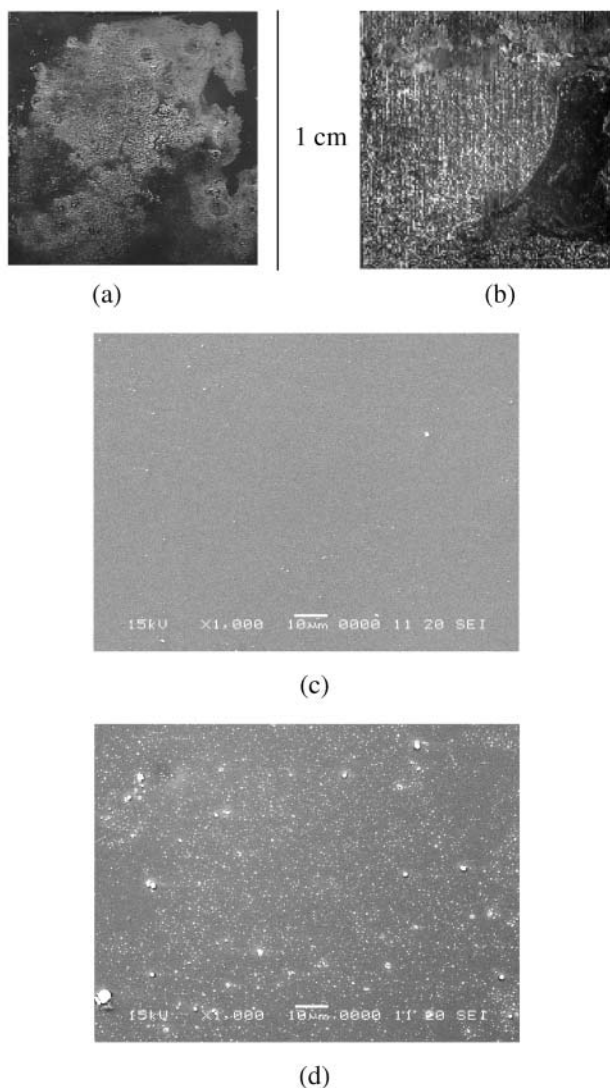


Fig. 9 Optical micrographs after immersion of (a) FePPyc in HCl (1 M) $S = 1 \text{ cm}^2$ for seven days; (b) FeXG in HCl (1 M) for seven days; SEM micrographs of FePPycXG (c) before and (d) after immersion in HCl (1 M) for seven days ($\times 1000$).

its color change in the process (from black to brownish grey), and rusty stains appear. In addition this is accompanied by a complete loss of the adherence of the PPyc, originally excellent (see Discussion section 1).

In contrast, there is no apparent degradation of the composite PPycXG layers (Fig. 9c and d), and in addition, the mechanical properties of the layers are unaffected. This was finally confirmed by X-ray fluorescence experiments, which show that the ratio Zr/Fe remains unchanged, as a result of the fact that neither the XG nor the metal are appreciably attacked through the corrosion attempt.

Conclusion

We have described that smooth, mechanically resistant composite polypyrrole-xerogel deposits can be realized on mild steel. This is probably extendable to most other oxidizable metals, for which protection against corrosion is required. Such

coatings have been shown to display excellent corrosion protection, and the most striking feature is that the composite layers offer protection which is always considerably superior to the simple addition of the protection offered by each layer separately. This is a remarkable and unprecedented fact which should stimulate work in the field of conducting polymer-sol-gel hybrid composites. To our knowledge, our materials are actually excellent hybrid organic-inorganic coatings in relation to the corrosion protection of mild steel.

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