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Surface & Coatings Technology 190 (2005) 264–270

SURFACE & COATINGS TECHNOLOGY

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Polyaniline-coated iron: studies on the dissolution and electrochemical activity as a function of pH

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Received 14 August 2003; accepted in revised form 30 April 2004
Available online 8 July 2004

Abstract

Polyaniline coatings were electrodeposited from an oxalic acid solution onto iron and their electrochemical activity and corrosion protection properties studied as a function of pH. It was found that the coating (emeraldine salt) had a limited effect on the corrosion protection of iron in acidic solutions. However, in an alkaline borate solution, where the conducting polyaniline was converted to the emeraldine base, the coating had a clear beneficial effect on the local breakdown of iron by chloride anions; much higher pitting potentials were recorded following a 2 h immersion period for the polyaniline-coated substrate relative to the uncoated electrode. Relatively small anions, such as acetates, nitrates and borates, were transported readily across the polymer interface. However, the emeraldine base inhibited the transport of the much larger ethylenediamine tetraacetate (EDTA) species to the iron interface, preventing complexation of the iron by EDTA.

Keywords: Polyaniline; Iron; Corrosion; Emeraldine base; Emeraldine salt

1. Introduction

In recent years, there has been much interest in the possibility of using polyaniline coatings as a new corrosion-control technology [1–6]. Polyaniline can be synthesized chemically and then coated onto the metal surface, or deposited at the metal through the electropolymerization of aniline from a suitable medium that limits the dissolution of the substrate. For example, polyaniline has been electrodeposited at iron from an oxalic acid medium [7,8]. In this case, dissolution of the iron is inhibited by the formation of an oxalate/oxide layer.

Most of the studies devoted to the corrosion protection properties of polyaniline have been carried out in acidic or near acidic solutions. Under these conditions, polyaniline resides in the doped, conducting state as the emeraldine salt. These conducting properties enable oxidation and passivation of the substrate. Indeed, Kinlen et al. [9] have shown, using a scanning vibrating reference electrode technique that doped polyaniline induces the passivation of steel at pinhole defects in the coating, while Gašparac and Martin [10] have concluded that polyaniline coatings induce passivation of a stainless steel surface even though the surface is not completely coated with the polymer.

There are much fewer studies devoted to the corrosion protection properties of polyaniline in the undoped emeraldine base form. Furthermore, there is some controversy on whether the conducting or nonconducting form of polyaniline exhibits the best corrosion protection properties. For example, Spinks et al. [3] concluded from a comparison of emeraldine salt and emeraldine base coatings for the corrosion protection of steel that the emeraldine base was superior. This was explained in terms of the production of a highly alkaline environment with the emeraldine base, which is conducive to passive oxide formation, while the emeraldine salt produced a mildly acidic environment in which formation of the passive oxide phase was less likely. However, Gašparac and Martin [5] found that the corrosion protection properties of polyaniline were independent of the doping level and that the totally undoped emeraldine base was equally capable of maintaining the potential of the stainless steel substrate in the passive region. On the other

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doi:10.1016/j.surfcoat.2004.04.083

hand, Martyak et al.[11] have shown that polyaniline-coated steel panels protect steel from corrosion in high pH solutions even in the presence of chloride ions, while Morales et al. [12] concluded that the doped polyaniline coating was the more beneficial system.

In light of the limited number of studies conducted on the corrosion protection properties of polyaniline in nonacidic media, polyaniline coatings were electrodeposited at pure iron and their electrochemical activity and corrosion protection properties explored in both acidic and alkaline solutions in the presence of various anions. Results are presented and discussed on the protective properties of these polyaniline coatings deposited at pure iron in a range of solutions with different pH values.

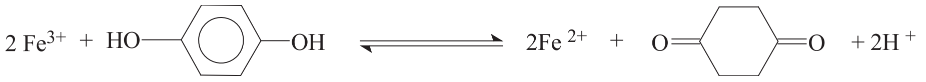
2. Experimental

Electrodes were prepared from rods of pure iron (99.995%, 0.5 cm in diameter) and platinum (99.99%, 0.4 cm in diameter). These rods were embedded in epoxy resin in a Teflon holder with electrical contact being achieved by means of a copper wire threaded into the base of the metal sample. Prior to each test, the exposed sample surface was polished to a smooth surface finish, using 1200 grit SiC and rinsed with distilled water and dried. High-density graphite rods were used as the auxiliary electrodes and a saturated calomel electrode (SCE) was used as the reference electrode, with all potentials represented relative to this electrode.

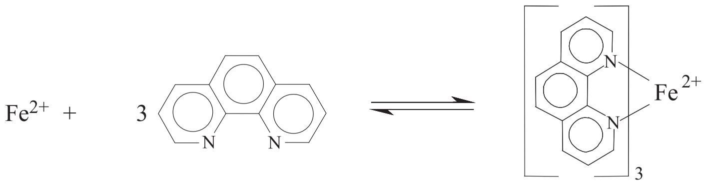
Solutions were prepared using analytical grade reagents and distilled water. The electropolymerization solutions consisted of 0.1 mol dm^{-3} aniline added to either a 0.1 mol dm^{-3} oxalic acid solution or a 1.0 mol dm^{-3} sulphuric acid solution. The aniline was distilled and stored under a nitrogen atmosphere before use. The oxalate system was used to electrodeposit polyaniline at iron, while the sulphate medium was used in the electroformation of the polymer at the platinum electrodes. The electrochemical activity and anodic polarization measurements were carried out in alkaline pH 10.5 solutions (a borate buffer solution with 0.015 mol dm^{-3} NaCl, an acetate solution comprising 0.05 mol dm^{-3} CH_3CO_2Na and 0.015 mol dm^{-3} NaCl, a complexing solution consisting of 0.05 mol dm^{-3} EDTA and 0.015 mol dm^{-3} NaCl solution) and acidic pH 3.5 solutions (0.05 mol dm^{-3} CH_3CO_2Na and 0.015 mol dm^{-3} NaCl). The pH of the solutions was adjusted to the required values using either HCl or NaOH.

Electrochemical experiments were carried out using an EG&G Potentiostat, Model 263, a Solartron 1250 frequency response analyser and a Solartron EI 1287 electrochemical interface. The polymers were formed using potential cycling at a scan rate of 10 mV s^{-1}. Anodic polarization measurements were recorded in chloride containing solutions from the open-circuit potential at a scan rate of 0.5 mV s^{-1} until breakdown occurred. Cyclic voltammograms were recorded at a rate of 50 mV s^{-1}. Electrochemical impedance measurements were recorded at the open-circuit potential following different immersion periods. An excitation voltage of 10 mV was used in all tests. The frequency of the potential perturbation was varied between 65 kHz and 2 mHz. All impedance data were fit to appropriate equivalent circuits using a complex nonlinear least squares fitting routine, using both the real and imaginary components.

A spectrophotometric analysis was used to determine the amount of iron released on immersion of the coated and uncoated electrodes in acidic solutions. This two-step analysis involved reduction of any Fe^{3+} to Fe^{2+}, Eq. (1), and complexation of the Fe^{2+} to a phenanthroline ligand, resulting in a coloured complex with λ_{max} at 508 nm.



(1)



(2)

Scanning electron micrographs and energy dispersive X-ray analyses were recorded on a Hitachi S-4700 cold cathode field emission SEM using a secondary electron detector at an accelerating voltage of 15 kV. The samples were gold coated prior to imaging using an Emitech K550 sputter coater.

3. Results and discussion

3.1. Deposition of polyaniline at iron

The deposition of polyaniline at iron was carried out in 0.1 mol dm^{-3} oxalic acid and 0.1 mol dm^{-3} aniline by cycling the electrode between -0.6 and 1.5 V (SCE) at a scan rate of 10 mV s^{-1} for a total of 10 cycles. This method of electropolymerization is similar to that used previously [7,8,13] and leads to the deposition of adherent and homogenous green coloured polyaniline layers, characteristic of polyaniline in the conducting emeraldine salt state. There is considerable evidence in the literature to suggest that polyaniline films deposited from phosphoric acid give rise to enhanced corrosion protection properties because of the presence of a phosphate layer [14]. However, this method was not used in this study so that information on the polyaniline film in the absence of a corrosion resistant interface could be obtained.

Typical SEM micrographs of the polyaniline deposits formed during the very early stages of deposition and at the end of the deposition process are shown in Fig. 1a and b, respectively. In Fig. 1a, the characteristic iron oxalate crystals [15–17] are clearly evident. These crystals differ in size and dimension and are oriented in a random fashion on the iron substrate. There are also regions on the iron surface that are free of these crystals and these regions probably consist of iron oxides. These observations agree well with previous studies in which it is proposed that the oxidized iron, Fe^{2+}, produced during dissolution of the iron, reacts with the oxalate species producing the iron(II) oxalate dihydrate. This compound has a low solubility and is precipitated on the iron substrate, Eq. (3) [7,17–19].

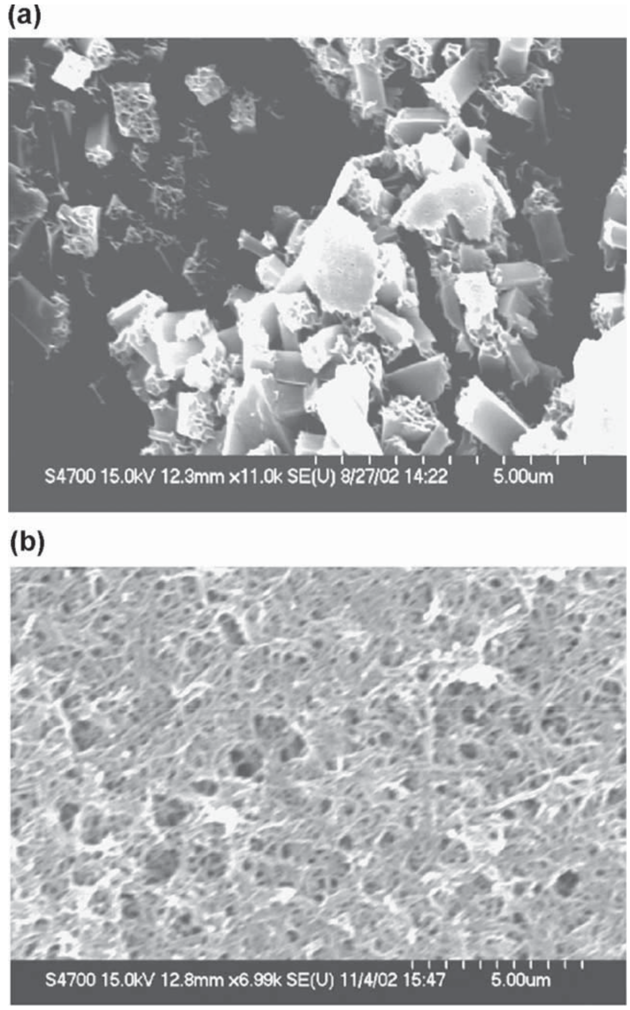


Fig. 1. (a) SEM micrograph recorded during the early stages of polymer deposition; (b) SEM micrograph of polyaniline deposition on iron.

$$Fe^{2+} + C_2O_4^{2-} + 2H_2O \rightarrow FeC_2O_4 \cdot 2H_2O \tag{3}$$

It is generally accepted that as the potential is increased above 0.6 V this Fe(II) oxalate is oxidized to the Fe(III) species (which is considerably more soluble) and dissolves giving rise to the formation of iron oxides [19]. It is interesting to note that traces of polyaniline can be seen on the faces of some of these crystals, Fig. 1a. This suggests that some of the Fe(II) oxalate species remain stable as the electrode is polarized to the higher potentials where oxidation of aniline occurs and the polymer is formed. However, partial dissolution of this oxalate layer must occur in order to maintain the surface electrochemically active. The morphology of the final polymer, which is shown in Fig. 1b, consists of an intertwined network of fibres, each with a diameter of 0.6 μm. This agrees well with the morphology of polyaniline deposited at platinum [20]. These SEM analyses show that the polymers formed on the iron surface are homogenous and free from any defects that may limit the corrosion protection properties of the coatings.

In order to assess the corrosion protection properties of these polymers, the electrochemical behaviour of the polyaniline-coated iron substrate was studied in solutions with pH values between 3.5 and 10.5. Under the acidic conditions, the polymer will exist as the emeraldine or leucoemeraldine salt, depending on the degree of oxidation; but, as the solution is made more alkaline, the equilibrium will shift to the corresponding base, as shown in Fig. 2. In this figure, charge neutrality is maintained by the dopant anions in the solution phase.

3.2. Electrochemical behaviour of polyaniline-coated iron in acidic media

The open-circuit potentials adopted by the polyaniline-coated iron electrode on immersion in the acidified solutions were in the region of 200 mV. However, with continued immersion this potential dropped to values similar to the corrosion potential of iron in the acidic solution, signifying a loss in the corrosion protection properties of the coating [14]. Direct information on the extent of corrosion was obtained by analysis of the solution for oxidized iron. Representative data obtained on immersion of the coated and uncoated iron electrodes in an acidified chloride containing acetate and borate solution are shown in Fig. 3a and b, respectively. These data clearly show that the polymer offers some degree of corrosion protection during the early stages, but with continued immersion, particularly after 80 h, nearly identical amounts of iron are detected in the

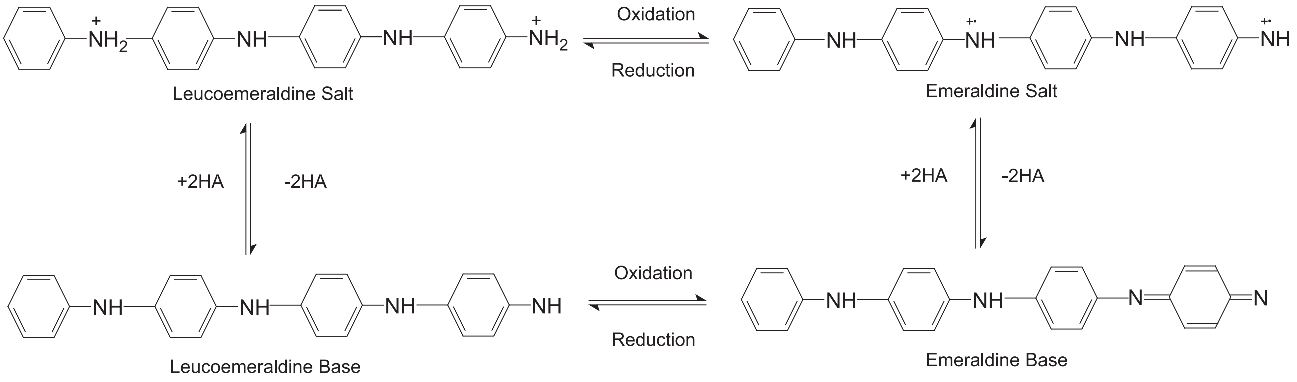


Fig. 2. Scheme showing the leucoemeraldine and emeraldine redox states of polyaniline and the level of doping.

solution phase. These data also show that the presence of acetate or borate have little influence on the rate of iron dissolution at the uncoated or coated electrodes. During these measurements, the polymer maintained a green colouration being consistent with the emeraldine salt form of the polymer. The fact that the polymer remained in this partially reduced state with dissolved oxygen in the electrolyte, which induces oxidation of the polymer, points to a galvanic interaction between the polymer and the iron substrate, where oxidation of the iron substrate maintains the polymer in the partially reduced state.

This oxidation of the iron substrate can be seen also from the impedance data presented in Fig. 4, in which the Nyquist plots measured under open-circuit conditions for polyaniline-coated iron, polyaniline-coated platinum and pure iron in the acidified chloride-containing acetate solutions are presented. These data were recorded following a 15-h immersion period. The experimental data are represented by the symbols while the solid traces refer to the simulated data. The simulated data were generated using a one-time constant equivalent circuit for pure iron, a two-time constant model for the polyaniline-coated iron electrode and a resistor in series with a charging capacitance for the polyaniline-coated platinum electrode. In all cases, a constant phase element was used as opposed to a pure capacitor. The values

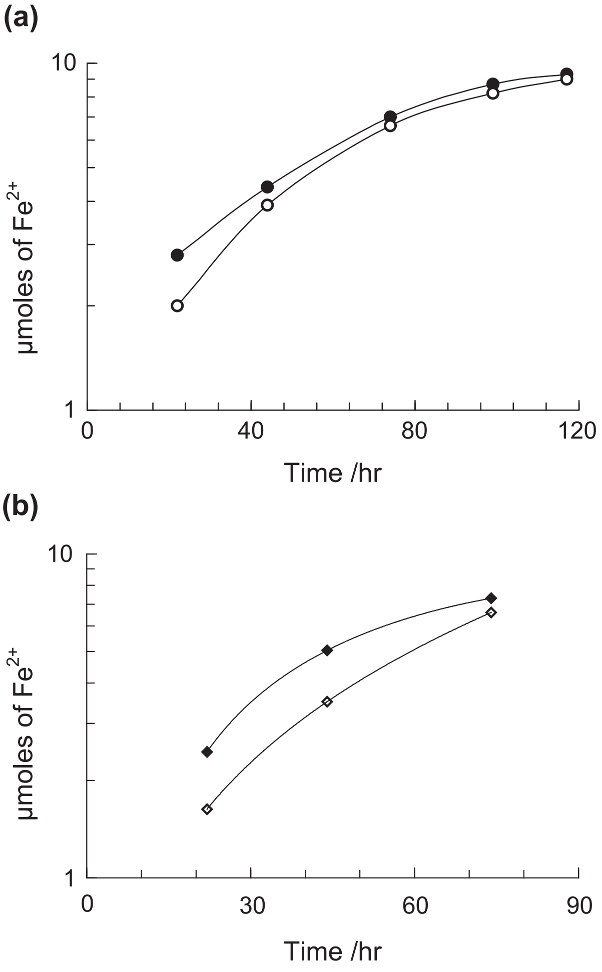


Fig. 3. Moles of iron released plotted as a function of immersion time for polyaniline-coated iron (open symbols) and uncoated iron (closed symbols) immersed in (a) acetate solution containing 0.015 mol dm^{-3} NaCl, pH 3.5 and (b) borate solution, containing 0.015 mol dm^{-3} NaCl, pH 3.5.

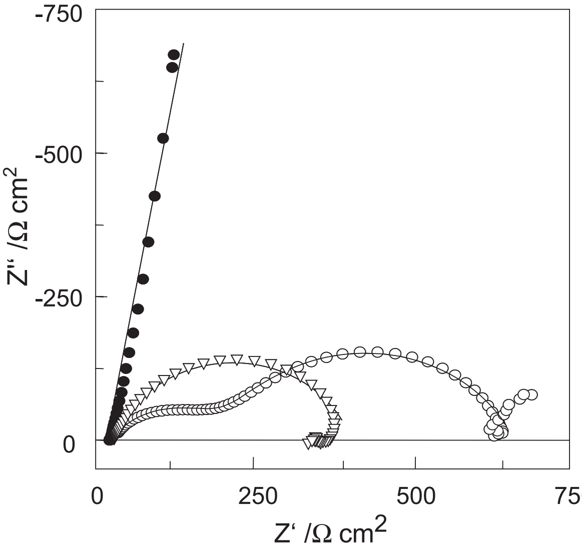


Fig. 4. Impedance data recorded following a 15-h immersion period in the acetate solution containing 0.015 mol dm^{-3} NaCl, pH 3.5 for (●) polyaniline-coated platinum; (▽) uncoated iron and (○) polyaniline-coated iron.

associated with the various impedance parameters and the equivalent circuits used are presented in Table 1. There is a considerable difference between the polyaniline-coated iron and polyaniline-coated platinum electrodes. In the case of the platinum system, the impedance data are dominated by the conducting properties of the doped polyaniline, with a low resistance, 17.0 Ω cm^2, and a high charging capacitance. Also, the active dissolution of iron in the acidic acetate solution can be seen clearly; the charge-transfer resistance was calculated as 380 Ω cm^2, while the capacitance was 160 μF cm^{-2}; but, dissolution of the iron substrate contributes to the impedance response of the polyaniline-coated iron electrode. It appears that the first time constant corresponds to the polymer, while the second time constant, corresponding to the semicircle at lower frequencies, stems from the activity of the iron substrate. In this case, the resistance of the polymer is of the order of 200 Ω cm^2, considerably higher than the value observed with the platinum system. This may be connected with the fact that the polyaniline is maintained in the reduced state by the oxidizing iron. The reduced state has a lower conductivity. Alternatively, doping of the polymer with iron corrosion products may reduce the inherent conductivity of the polymer, giving rise to a similar increase in the resistance. However, it can be seen from a comparison of the data recorded for the coated and uncoated iron substrates that the polymer provides very little corrosion protection.

The behaviour of the polyaniline-coated and uncoated iron electrodes in the acidified borate solution under anodic polarization conditions is shown in Fig. 5. In these experiments, the electrodes were polarized from the open-circuit potential, at a rate of 0.5 mV s^{-1}, and following a 3-h immersion period in the electrolyte solution. Following the 3-h immersion, the polymer-coated electrode adopts an open-circuit potential of -0.55 V (SCE) compared to -0.60 V (SCE) for the uncoated electrode; an ennoblement of approximately 50 mV compared to the 200 mV ennoblement observed on initial immersion. Intense dissolution of the iron electrode is seen at potentials anodic to the open-circuit potential and a limiting current of approximately 3.5 mA cm^{-2} is seen at potentials more anodic than -0.33 V (SCE). Although it is clear from these data that the polyaniline coating provides little protection to the substrate in terms of the initiation of the corrosion events, there is a significant difference between the limiting currents observed for the uncoated and coated electrodes. Indeed, the limiting currents differ by an order of magnitude. This seems to be connected with the barrier properties of the polyaniline, which limit the diffusion of the soluble corrosion species from the metal interface.

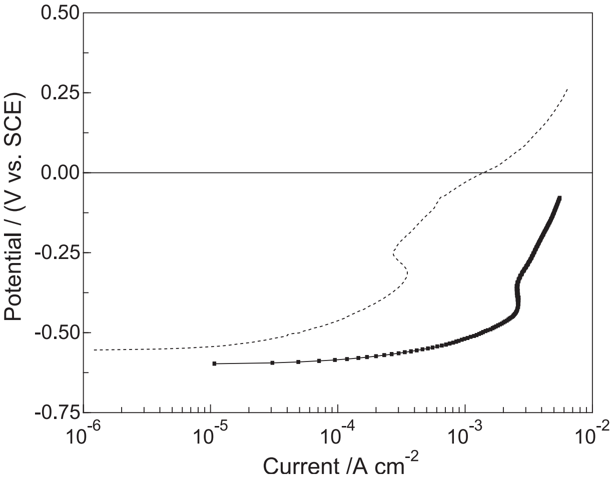


Fig. 5. Anodic polarization plots for (– – –) polyaniline-coated iron and (—) uncoated iron in acidified borate solution containing 0.015 mol dm^{-3} NaCl.

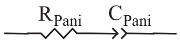
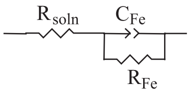
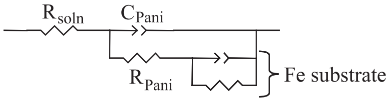
These data show clearly that the polyaniline coatings (emeraldine salt), although providing some level of corrosion inhibition, fail to adequately protect the iron substrate under these acidic conditions.

3.3. Electrochemical behaviour of polyaniline-coated iron in alkaline media

In Fig. 6, cyclic voltammograms recorded in alkaline nitrate, acetate and borate solutions containing chloride anions are shown for the polyaniline-coated iron electrode. Although not shown here, these data are similar to the

Table 1

Equivalent circuits and impedance parameters determined from the impedance response of polyaniline-coated iron, platinum and uncoated iron in the acetate solution

Model		R_{soln} Ω cm^2	R_{Pani} Ω cm^2	R_{Fe} Ω cm^2	C_{Pani} mF cm^{-2}	C_{Fe} mF cm^{-2}
Pt_{Pani}		——	17.0	——	30.0	——
Fe		29.0	——	380	——	0.16
Fe_{Pani}		24.0	200	——	0.02	——

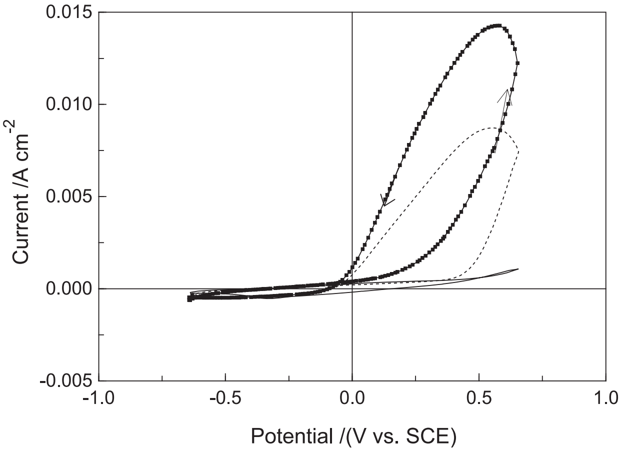


Fig. 6. Cyclic voltammograms recorded at 50 mV s^{-1} for polyaniline-coated iron in the alkaline 0.015 mol dm^{-3} NaCl, pH 10.5 (—) borate solution; (**—**) nitrate solution and (– – –) acetate solution.

electrochemical behaviour of uncoated iron in these solutions. Large oxidation waves, arising from the dissolution of the iron substrate, are seen in the potential interval 0.25 to 0.50 V (SCE) in the acetate and nitrate solutions. However, in the presence of borate, which is conducive to the formation of passive films on iron [21], oxidation of the substrate is not observed. It appears from these studies that transport of the chloride, acetate, nitrate and borate species occurs readily across the polymer interface to react with the iron substrate.

However, on immersion in the alkaline solutions the polymer coatings appeared to modify the local dissolution behaviour of the underlying metal. This can be seen from the data presented in Table 2 and Fig. 7. In Table 2, the breakdown potentials are shown for the coated and uncoated electrodes as a function of the immersion time in the alkaline borate solution. The breakdown potentials and standard deviations were calculated from four separate measurements. On initial immersion, the breakdown potentials are some 100 mV lower for the polymer-coated electrodes; but following an additional 2-h immersion period, the coated electrodes breakdown at potentials approximately 400 mV higher than those measured for the uncoated electrodes. The polarization behaviour of the polymer-coated and uncoated electrodes at this point is seen in Fig. 7. The passive current densities are of the order of 1.0 μA cm^{-2}. These low currents measured for the polymer-coated electrode are consistent with the fact that the polymer is de-doped and nonconducting, Fig. 2. On further immersion, an additional increase in the breakdown potentials is seen, Table 2, with the breakdown potentials measured for the polymer-coated electrodes being only slightly higher than those seen with the uncoated electrodes.

Table 2
Breakdown potentials shown as a function of immersion time for polyaniline-coated iron and uncoated iron in a pH 10.3 borate solution containing 0.015 mol dm^3 NaCl

Immersion time (h)	Breakdown potentials (mV vs. SCE)	
	Coated electrode	Uncoated electrode
0	162 ± 13	288 ± 12
2	813 ± 119	472 ± 109
16	897 ± 73	820 ± 181

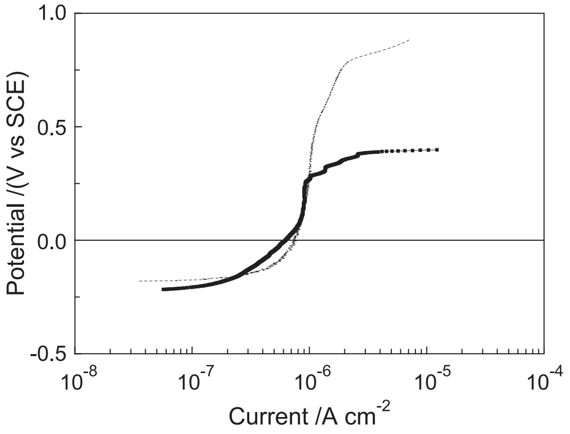


Fig. 7. Anodic polarization plots, recorded at a scan rate of 0.5 mV s^{-1} in the alkaline, pH 10.5 borate solution containing 0.015 mol dm^{-3} NaCl for (– – –) polyaniline-coated iron and (**—**) uncoated iron.

These variations in the breakdown potentials with increasing immersion time in the alkaline solution are consistent with oxide growth at the iron interface. In the case of the uncoated electrode, there is a clear ennoblement in the breakdown potentials with further growth of the oxide/hydroxide films, which is promoted by increasing the immersion time. However, the significantly higher values recorded for the polymer system following a 2-h immersion time suggest a clear interaction between the polyaniline and the iron substrate, which promotes the development of a highly protective oxide layer.

Although, the electrosynthesized polyaniline layer is doped initially, the film is de-doped and transformed to the emeraldine base on immersion in the alkaline solution,

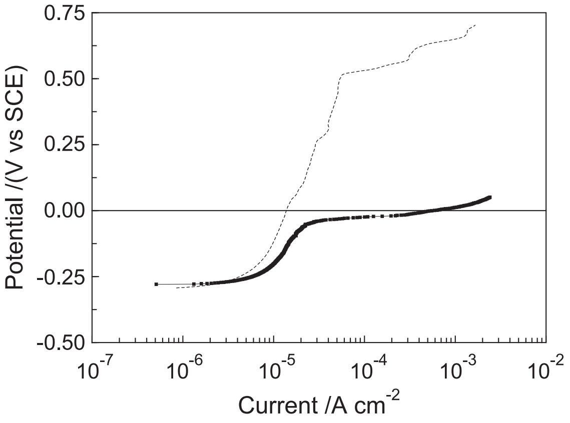


Fig. 8. Anodic polarization plots recorded at a scan rate of 0.5 mV s^{-1} in the alkaline (pH 10.5) 0.05 mol dm^{-3} EDTA and 0.015 mol dm^{-3} NaCl solution for (– – –) polyaniline-coated iron and (**—**) uncoated iron.

Fig. 2. Consequently, it is the interactions between the emeraldine base and the iron substrate that result in the ennoblement of the pitting potentials. These findings are consistent with previous studies [3,22,23]. For example, Fahlman et al. [23] found that a chemically synthesized emeraldine coating applied to iron decreased the corrosion rate, as measured in a humidity chamber. This was explained in terms of the withdrawal of charge from the iron by the emeraldine base, which in turn enabled the passivation of the surface. The fact that lower breakdown potentials are observed initially with the polymer-coated substrate, Table 2, may be connected with a slow transformation of the emeraldine salt to the emeraldine base; but also, the polymer coating will inhibit the transport of oxygen and hydroxyl anions to the iron interface. This, in turn, inhibits the rate of oxide/hydroxide growth.

In order to study these transport properties further, the complexing agent ethylenediamine tetraacetate (EDTA) was added to the alkaline chloride-containing solution and the anodic polarization behaviours of the coated and uncoated electrodes were recorded. In order to facilitate interaction of the EDTA species with the iron substrate, the electrodes were immersed in the solution for 2 h and then polarized from the open-circuit potential at a relatively slow scan rate of 0.5 mV s^{-1}. These data are shown in Fig. 8. Breakdown of the passive film formed on the uncoated iron electrode is seen at approximately -40 mV (SCE). However, a considerable shift in this breakdown potential is seen for the polyaniline-coated electrode, reaching values of 525 mV (SCE). The low breakdown potential recorded for the uncoated electrode is consistent with the chelating properties of EDTA [24–26], which limit the formation of the passive layer. However, the polyaniline coating hinders the transport of the bulky EDTA species, thus enabling formation of the passive layer.

4. Conclusions

Polyaniline coatings electrodeposited from an oxalic acid solution onto iron had a limited effect on the corrosion protection of iron in acidic solutions, containing acetates and borate anions. However, in an alkaline borate solution, where the conducting polyaniline was converted to the emeraldine base, the coating had a clear beneficial effect on the local breakdown of the iron by chloride anions. Relatively small anions, such as acetates, nitrates and borates, were transported readily across the emeraldine base. However, the emeraldine base inhibited the transport of the much larger EDTA species to the iron interface.

Acknowledgements

The authors gratefully acknowledge the support of this work by Enterprise Ireland, under the Research Innovation Fund.

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