

## Corrosion inhibition of polyaniline and poly(*o*-methoxyaniline) on stainless steels

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### Abstract

Polyaniline films were grown by electrochemical deposition on 316 and 304 stainless steels and their corrosion performance monitored by following the open circuit potentials in acidic solutions. Poly(*o*-methoxyaniline) was successfully polymerised on stainless steel electrodes, as shown by cyclic voltammetry and impedance spectroscopy, and provided corrosion inhibition in a similar manner to polyaniline. In 0.5 M H<sub>2</sub>SO<sub>4</sub> the potential climbed to over 0.4 V (SHE), to values typical of the partially oxidised form of the polymer and of the metal substrate in a passive state with low rates of corrosion. In 0.5 M HCl, the steels were maintained in a passive state for some hours to days (lasting longer with a thicker polymer film), prior to a drop in potential to −0.15 V after the onset of pitting corrosion. The fluctuations of potential seen in 0.5 M HCl are explained by regions of the oxidised polyaniline, produced by dissolved O<sub>2</sub>, reaching the metal and causing an increase in the potential, and by pits formed at higher potentials rapidly reducing an already oxidised film leading to a drop in the potential.

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### 1. Introduction

Organic polymers have established roles in corrosion prevention. These include organic inhibitors, generally rich in  $\pi$  bonds, which adsorb onto a metal surface to reduce the number of active sites, and barrier coatings which slow the transport of corrosive agents to the metal and the removal of corrosion products. Recent developments in the area of conducting polymers such as polyaniline are pointing to a new way in which organic polymers may assist in corrosion protection, providing a potential cheap alternative to chromium and phosphate treatments and their associated pollution. In this technology, the electroactive polymer is itself capable of maintaining, and even repairing, the native passive film on the metal, with a subsequent lowering of the rate of corrosion.

Conducting polymers are unusual in that they can be doped to highly conductive states approaching the conductivities of metals. Their ability to store and transport charge is seen as a key feature in their reported ability to anodically protect metals against rapid rates of corrosion. Conducting polymers such as polypyrrole and polythiophene have

already been found to be very effective at stabilising photo-active materials such as cadmium sulfide and gallium arsenide, by providing a corrosion-resistant coating which improves the life-time of these materials [1].

One problem with the use of conducting polymers on active metals is the high positive potentials required to form the polymers by electrochemical means (potentials of the order of 1 V are needed to oxidise aniline to polyaniline), at which point many metals are corroding too rapidly to allow a conducting polymer to form on their surface. For many years, the conventional wisdom was that conducting polymers could only be formed on inert metal electrodes (including stainless steels), a position that is no longer held. Polypyrrole and polyaniline are now readily grown on copper and iron electrodes with a suitable choice of electrolyte such as oxalic acid [2,3].

In 1985, DeBerry showed how polyaniline could be grown on 410 and 430 stainless steels [4]. In acidic solutions the polyaniline film was held in the partially oxidised conductive state by dissolved oxygen, which enabled it to maintain the stainless steels in a passive state for several hours to several days, with greatly reduced rates of corrosion, even when the sample was scratched with a sharp knife. In acidic chloride solutions oscillations in the corrosion potential were seen as partial breakdown of the passive metal oxide

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film occurred, before being reformed through the action of polyaniline. The ultimate failure of each sample was matched by a large decrease in the corrosion potential, from values of +0.4 to 0.6 V (SHE) down to  $-0.23$  V.

A number of studies on corrosion inhibition involving conducting polymers followed in the mid-1990s, with an upsurge in interest over the past 3–4 years. Many of these reports have concentrated on polyaniline applied as a solution or a dispersion to iron or steels, often followed by an epoxy top-coat to protect the polyaniline-containing phase and provide an additional barrier against corrosive agents. The polyaniline is usually formed by chemical oxidation, since the electrochemical preparation is rightly seen as impractical for many applications. Approaches have included polyaniline dissolved in *N*-methylpyrrolidinone [5–9], DMSO [10], blended with an epoxy resin using an alkyl phenol as a co-solvent [11], and commercial formulations such as VERSICON [12–14], PANDA [13,15,16], and CORREPAIR [17] or CORRPASSIV [18], which have led to reduced rates of corrosion at the various steels employed. XPS studies have identified the iron oxides  $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$  underneath the polyaniline-containing phase [6,12]. In other reports, soluble polyanilines such as poly(*o*-methoxyaniline) [19] and poly(*o*-ethoxyaniline) [20] have been considered for use as organic inhibitors, and reduced rates of corrosion at iron in HCl have been observed. The use of substituted polyanilines prepared by chemical oxidation has also been considered. Poly(methoxyaniline), also known as poly(anisidine), has proven to be an efficient corrosion inhibitor when incorporated into paint formulations, with the corrosion protection ascribed to the formation of complexes with the metal surface [21].

Studies involving the electrochemical formation of polyaniline have also continued, with the substrates including mild steel in nitric acid [22], oxalic acid [23] or *p*-toluene sulfonic acid [24], stainless steels and directly on iron in oxalic acid [3,25]. In the main, polyaniline has proven effective in providing protection against corrosion. A particular improvement was found with the addition of dispersed platinum to increase the rate of oxygen reduction and subsequent maintenance of the passive film mediated by the conducting polyaniline [26].

In this study, films of polyanilines were grown by electrochemical means on 304 and 316 stainless steels to further study the key interactions between the conducting polymer, the underlying metal and the passive film formed on the metal surface under anodic conditions. The possibility of using a substituted derivative, poly(*o*-methoxyaniline), for corrosion protection is a major focus. The presence of the methoxy substituent on the polymer backbone produces a form which is soluble in a wider range of solvents than the parent polyaniline, which creates more options for polymer processing. The relationship between the thickness of the polymer film (ca. 20–200 nm) and the extent of corrosion inhibition has been examined by monitoring the corrosion potential and by other electrochemical techniques.

## 2. Experimental

Aniline and *o*-methoxyaniline were freshly distilled and stored in the dark under  $\text{N}_2$ . Solutions were made up using Milli-Q grade water, and all chemicals were of analytical reagent grade.

The iron, stainless steel 316L and 304 electrodes were formed from 0.6 cm diameter rods of 25 cm length which were constructed in Teflon holders to leave an area of  $0.28 \text{ cm}^2$  exposed to the solution. For other experiments, the rods were not encased in Teflon but were dipped directly into each solution with  $6 \text{ cm}^2$  in contact with the electrolyte; once the polyaniline was formed on the steel, and the electrode placed in a test solution, none of the bare metal was left exposed to the solution by inserting the electrode only so far as to leave some polyaniline out of the solution. The electrodes were freshly abraded with 600 and 1200 grade emery papers prior to each experiment (which will remove any existing passive film). The electrochemical cell also included a platinum coil counter electrode and a saturated calomel electrode (242 mV); all potentials are reported here on the hydrogen scale.

The conducting polymers were formed by cycling the potential between 0.2 and 1.0 to 1.1 V (SHE) at 50 mV/s in deaerated 0.5 M  $\text{H}_2\text{SO}_4$  solutions containing 0.1 mol/l aniline or *o*-methoxyaniline monomer. A PAR 283 potentiostat was used to control the potential scans and to measure the open circuit potentials, which were recorded using a PICO ADC-16 analog to digital converter with PicoLog software. Electrochemical impedance measurements were made using a PAR 1025 frequency response detector, using five points per decade over a frequency range of 0.01 Hz to 100 kHz, a 5 mV voltage perturbation, and a 5 min hold at the test potential prior to taking the impedance measurements. The electrodes were rinsed briefly with Milli-Q water before being transferred to a test solution. All experiments were conducted at room temperature.

## 3. Results

### 3.1. Polyaniline on stainless steel discs

Corrosion potentials for the bare stainless steels were first obtained in the acidic sulfate and chloride media chosen for this study. For the 316 stainless steel electrode, values of  $-0.08$  and  $-0.11$  V (SHE) were obtained in deaerated 0.5 M  $\text{H}_2\text{SO}_4$  and 0.5 M HCl, respectively, while for the 304 electrode, lower  $E_{\text{corr}}$  values of  $-0.10$  and  $-0.18$  V were obtained, corresponding to more active rates of corrosion. The 400 series stainless steels are known to display  $E_{\text{corr}}$  at around  $-0.20$  V in 0.5 M  $\text{H}_2\text{SO}_4$ , and bare Fe a value close to  $-0.30$  V. When the solutions were not deaerated, the  $E_{\text{corr}}$  values were 25–50 mV more positive in each case (see Table 1). In 0.5 M HCl slow cyclic voltammograms revealed a pitting potential around 0.36 V on 316 and 0.24 V on 304

Table 1

Open circuit potentials of stainless steel electrodes, with and without a polyaniline coating, tested in (non-deaerated) H<sub>2</sub>SO<sub>4</sub> and HCl solutions

Electrode	Preparation in 0.5 M H <sub>2</sub> SO <sub>4</sub> (at 50 mV/s)	Test solution	Initial <i>E</i> /V vs. SHE	Final <i>E</i> /V vs. SHE	Time to failure
<b>With no conducting polymer</b>					
316 disc	Freshly abraded	0.5 M H <sub>2</sub> SO <sub>4</sub>	−0.06		–
		0.5 M HCl	−0.08		–
304 disc	Freshly abraded	0.5 M H <sub>2</sub> SO <sub>4</sub>	−0.07		–
		0.5 M HCl	−0.13		–
316 rod	Five scans to 1.0 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	0.25	0.67 (20 days)	–
	One scan to 1.0 V	0.5 M HCl	0.12	−0.09	2 h
	5–50 scans to 1.0 V	0.5 M HCl	0.14	−0.03	3–8 h
<b>With polyaniline</b>					
Fe disc	50 scans to 1.1 V in 0.3 M oxalic acid	0.5 M H <sub>2</sub> SO <sub>4</sub>	−0.3		<10 s
316 disc	80 scans to 1.1 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	0.40		–
	55 scans to 1.1 V	0.5 M HCl	0.1–0.3	0.1 (70 h)	–
316 rod	Five scans to 1.0 V	0.5 M HCl	0.23	−0.08	25 min
	15 scans to 1.0 V	0.5 M HCl	0.1–0.2	−0.07	79 h
	40 scans to 1.0 V	0.5 M HCl	0.2–0.5	0.3 (11 days)	–
304 disc	75 scans to 1.1 V	0.5 M HCl	0.3–0.4	−0.15	50 h
<b>With poly(methoxyaniline)</b>					
316 disc	75 scans to 1.1 V	0.5 M H <sub>2</sub> SO <sub>4</sub>	0.3–0.5	0.6 (21 days)	–
	30 scans to 1.1 V	0.5 M HCl	0.1–0.5	−0.1	95 h
	75 scans to 1.1 V	0.5 M HCl	0.1–0.4	−0.08	17 days

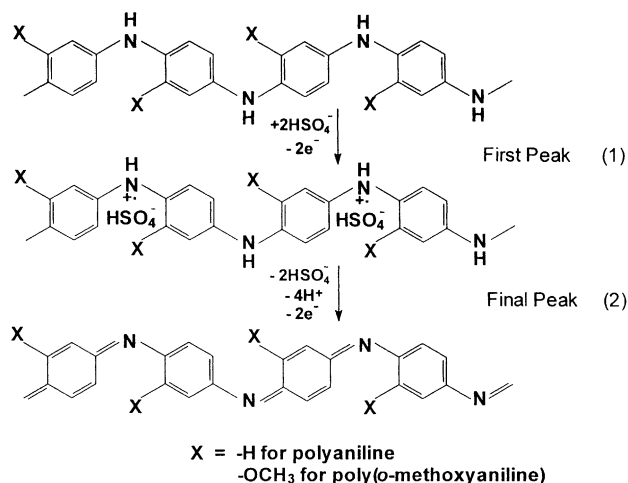
Where polyaniline or poly(methoxyaniline) has been coated on the steels, 0.1 M of the respective monomers were present in the preparation solution.

stainless steels, and protection potentials on the reverse scan of 0.25 V on 316 and 0.15 V on 304; as expected the passivation current was 10-fold greater in HCl compared to the H<sub>2</sub>SO<sub>4</sub> solution.

Control experiments were also preformed in which a 316 stainless steel electrode was cycled repeatedly from 0.2 to 1.0 V in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 50 mV/s, replicating the conditions under which the conducting polymers were grown by electrochemical polymerisation below, but in the absence of an oxidisable monomer. Following five scans to 1.0 V, the 316 electrode displayed an initial open circuit potential of 0.25 V, in the passive range, which drifted up to 0.67 V over the course of 20 days of testing (Table 1). When 316 electrodes were prepared using between 1 and 50 scans in 0.5 M H<sub>2</sub>SO<sub>4</sub> and tested in 0.5 M HCl, the potential commenced at 0.12–0.14 V and then dropped to values less than −0.03 V, typical of a freshly abraded electrode, after a few hours. At this point the passive film had been disrupted and higher rates of corrosion set in. While the time to failure was shorter for electrodes prepared by a single scan to 1.0 V in 0.5 M H<sub>2</sub>SO<sub>4</sub>, the time to failure was more variable with electrodes subject to a greater number of preparative scans; that is, while a thicker passive film might be expected with more preparative scans, this did not necessarily increase the time to failure under the experimental conditions used.

When a 316 stainless steel electrode was cycled in 0.5 M H<sub>2</sub>SO<sub>4</sub> with 0.1 M aniline, behaviour consistent with the

formation of a conducting polymer was seen in cyclic voltammograms. On the first scan a large anodic peak was seen at 0.1 V (SHE), corresponding to the formation of a passive oxide film on the steel surface, a peak which was absent in subsequent scans. As the scanning was continued as far as 1.0–1.1 V (but not higher, to avoid the degradation of the polymer which occurs at more positive potentials), there was little sign of film growth for the next 10–20 scans, then anodic peaks at 0.45 and 0.95 V typical of polyaniline were seen to develop (Fig. 1a), which correspond to the following (reversible) processes:



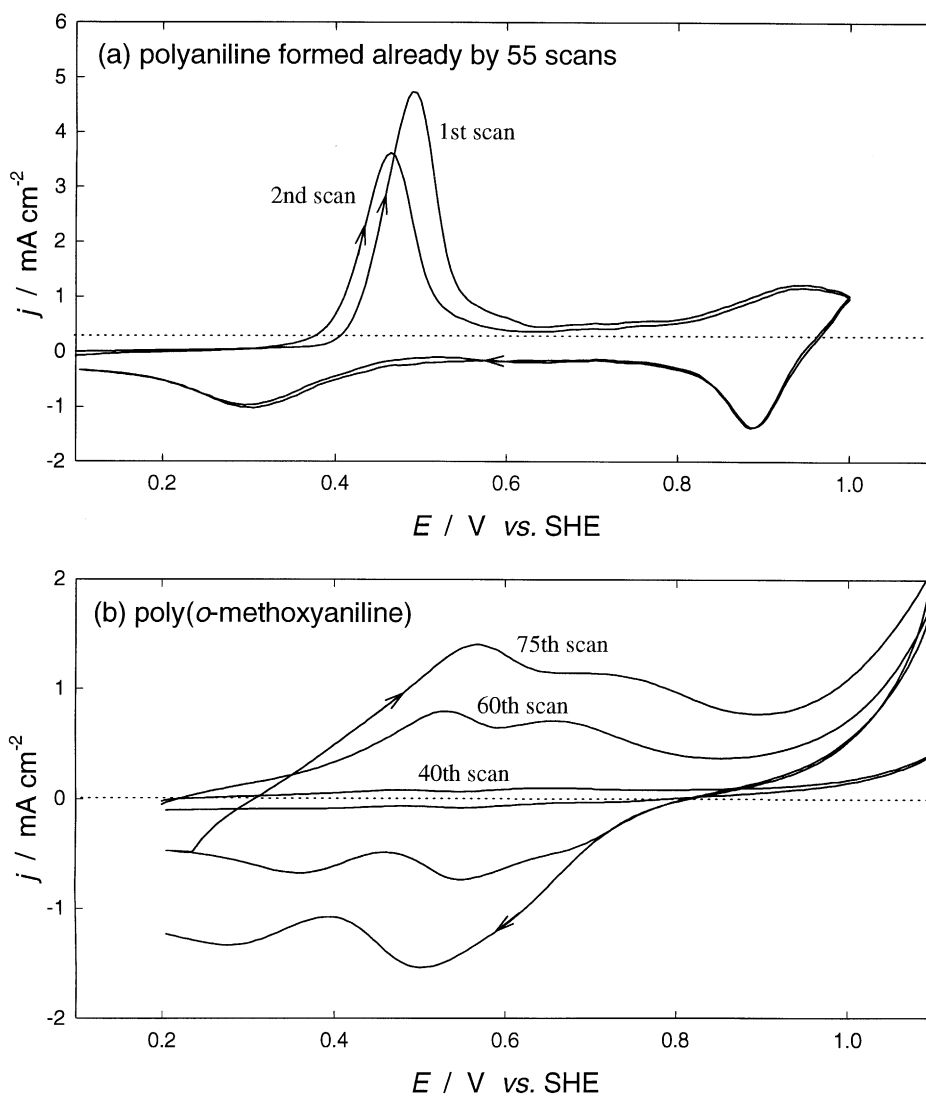


Fig. 1. Cyclic voltammograms of: (a) polyaniline film already formed by 55 scans to 1.1 V (SHE) in 0.1 M aniline and 0.5 M  $\text{H}_2\text{SO}_4$  on a 316 stainless steel disc, now in 0.5 M  $\text{HCl}$  with the first scan after 5 min reduction at 0.1 V; (b) poly(*o*-methoxyaniline) during its formation from 0.1 M *o*-methoxyaniline and 0.5 M  $\text{H}_2\text{SO}_4$  on a 316 SS disc.

Between 0.4 and 0.9 V, the polyaniline film is partially oxidised (also called emeraldine at this point), and is known to be highly conducting [27].

The height of the first anodic peak was used to provide an indication of the thickness of the polymer film. The film formed by 55 scans to 1.1 V showed an anodic peak current, starting from a fully reduced film, of 4.7  $\text{mA/cm}^2$ , which corresponds to a film about 160 nm thick (see [28] for details on how this notional thickness is obtained). Upon continuous cycling the anodic peak on the second and subsequent scans is lower due to incomplete reduction of the polymer during the course of the reverse scan. When the anodic peak current was examined as a function of scan rate ( $v$ ), the peak current was found to be proportional to  $v^{0.65}$ , which is closer to the value of  $v^{0.5}$  expected for a process under diffusion control than to the value of  $v^{1.0}$  usually seen for a surface process; a value of  $v^{0.75}$  was obtained for polyaniline on a platinum

substrate. This result indicates that the movement of counter anions into the film is a limiting factor in the first oxidation process for polyaniline on stainless steels.

When the polyaniline-covered 316 electrode, originally formed with the polymer in the fully reduced state, was placed in 0.5 M  $\text{H}_2\text{SO}_4$ , a potential close to 0.4 V was immediately established and remained steady for some hours. This result is similar to that obtained in the control experiment on 316 in the absence of a polymer coating, and corresponds to the stainless steel being maintained in a passive state with an associated low rate of corrosion. At the same time this potential is not sufficiently negative to completely reduce a partially oxidised polyaniline film, which is expected to develop by chemical oxidation due to dissolved  $\text{O}_2$ .

This is in contrast to films of polyaniline grown on bare Fe from a 0.3 M oxalic acid solution. In this case the open

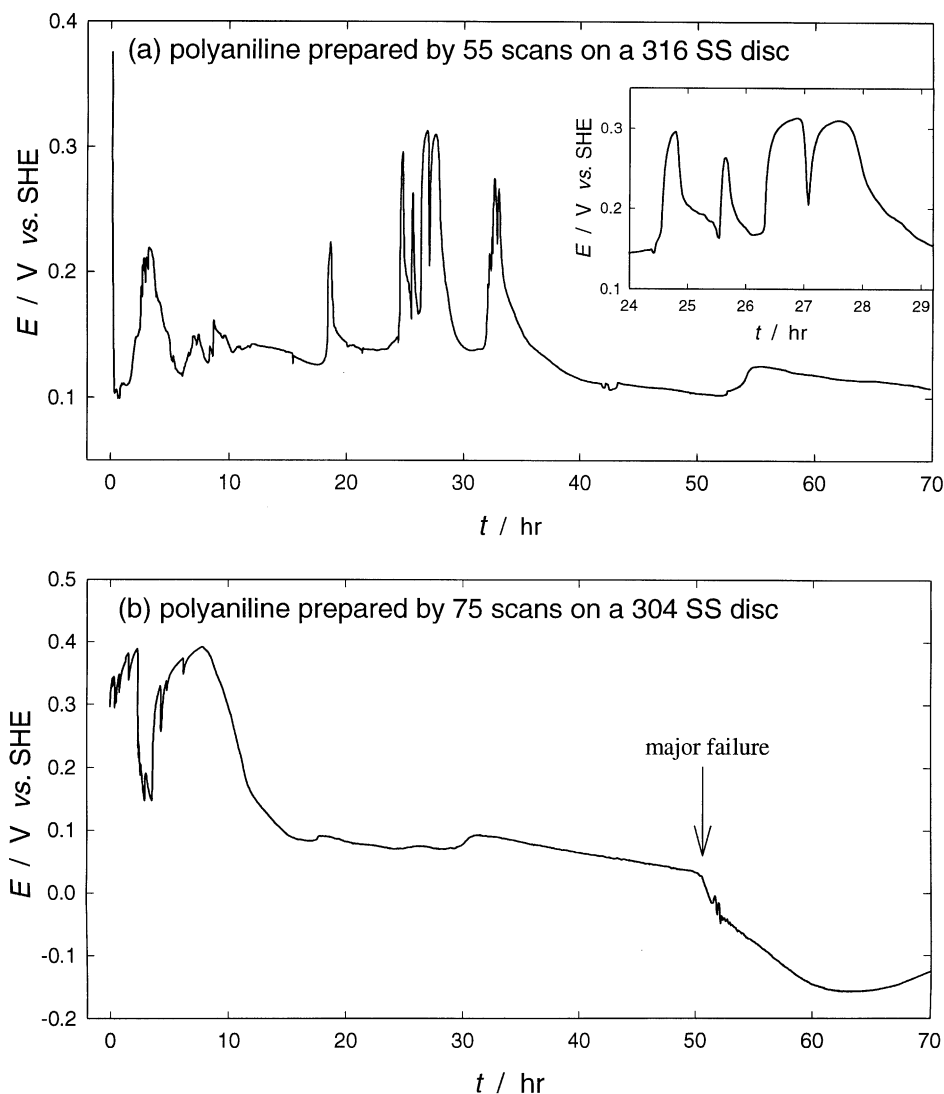


Fig. 2. Open circuit potentials of polyaniline films formed by scanning to 1.1 V in 0.1 M aniline and 0.5 M  $\text{H}_2\text{SO}_4$  and tested in 0.5 M HCl: (a) film formed by 55 scans on a 316 SS disc, and (b) by 75 scans on a 304 SS disc.

circuit potential decreased rapidly to  $-0.3$  V in oxalic or sulfuric acids, which matches the value of  $E_{\text{corr}}$  on bare Fe in these acids. However, polyaniline remained in electrical contact with the Fe substrate, as seen by the typical polyaniline oxidation and reduction currents which persisted in later cyclic voltammograms, with little lowering of the current response.

When a more corrosive acidic chloride medium was used, the potential at a polyaniline-coated 316 stainless steel electrode declined to a value of 0.1–0.15 V, sometimes within a few minutes, and on other occasions over the course of some hours (Fig. 2a). At this potential the stainless steel would still be in a passive state, while the polyaniline film would be fully reduced. At times the potential was seen to rise to around 0.3 V, close to the first oxidation peak for polyaniline, and approaching the pitting potential of 0.36 V for the bare 316 stainless steel. This behaviour was not seen in the control experiments in the absence of a polymer

coating, where the potential never increased beyond 0.15 V. As the insert shows, the rise from 0.15 to 0.25 V was quite rapid, while the further increase to 0.3 V was a slower process; conversely the drop in potential from 0.3 to 0.2 V was rapid and the return to 0.3 V or continued fall to 0.15 V was more gradual. Two models will be given in Section 4 to explain these events.

For the film formed by 55 scans to 1.1 V, the potential of 0.1 V was still stable after 70 h exposure to 0.5 M HCl (Fig. 2a and Table 1). This is in contrast to several control experiments with a passive anodic film initially present but without polyaniline, in which case the time to failure was always less than 8 h. On the other hand, a thicker film of polyaniline formed by 75 cycles to 1.1 V on a more active 304 stainless steel electrode showed a major failure after 50 h (Fig. 2b), at which point the potential fell to  $-0.15$  V, a typical value for the  $E_{\text{corr}}$  of 304 in HCl. Once this point had been reached the conducting polymer was no longer capable

of providing significant corrosion protection for the underlying metal. Only after the potential fell to values in this range was pitting seen to have occurred.

### 3.2. Polyaniline on stainless steel rods

A further study was made of the time to electrode failure in 0.5 M HCl for polyaniline films of various thicknesses on 316, in this case using stainless steel rods with 6 cm<sup>2</sup> of metal exposed to the electrolyte. Films were prepared by 5, 15 and 40 scans to 1.0 V in 0.1 M aniline with 0.5 M H<sub>2</sub>SO<sub>4</sub>. However, the polyaniline coverage was somewhat uneven, with darker patches corresponding to a thicker deposition of polyaniline seen over some areas of the rods, in contrast to the more even coverage seen at the disc electrodes.

The currents in cyclic voltammograms were very small for the five scan preparation, indicating only a minimal

deposit of polyaniline, while for the 15 scan preparation the currents were five times greater, and a further 10 times larger for the 40 scan preparation. While the potential at a freshly abraded 316 electrode falls immediately to a value close to  $-0.1$  V in 0.5 M HCl, the five scan polyaniline film held the potential at 0.2 V for some 25 min before the potential rapidly declined and evidence of pitting was seen (Fig. 3a and Table 1). On the other hand, the 15 scan film maintained the potential at values between 0.1 and 0.2 V for 79 h—in the time preceding the failure the polyaniline was observed to dissolve away from the electrode, producing a green solution. The 40 scan film produced potentials in the range of 0.2–0.5 V for over 11 days, with no sign of imminent failure. The potential for the 40 scan film was seen to oscillate markedly during this time, with each oscillation lasting up to an hour or more. At the end of the run there was some sign of pitting in the polyaniline layer

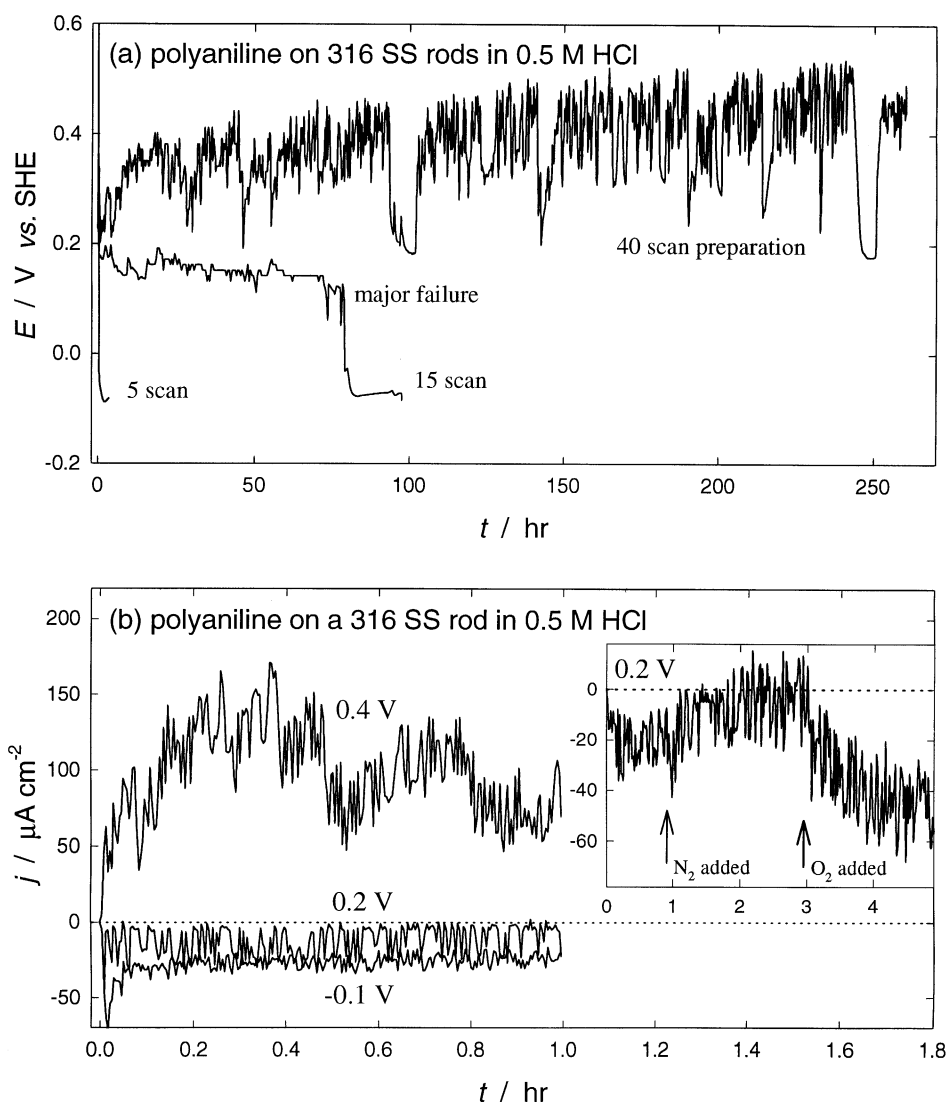


Fig. 3. (a) open circuit potentials of polyaniline films formed in 0.1 M aniline and 0.5 M H<sub>2</sub>SO<sub>4</sub> on 316 SS rods by 5, 15 and 40 scans to 1.1 V, and tested in 0.5 M HCl; (b) current vs. time for the 40 scan film held at constant potentials of  $-0.1$ ,  $0.2$  and  $0.4$  V the insert shows the effect of deaerating with N<sub>2</sub> or introducing O<sub>2</sub> on the current at  $0.2$  V.



adjacent to the point where the solution had covered the electrode, but not in the polyaniline layer which was fully immersed in the acidic electrolyte. At a potential of 0.5 V in 0.5 M HCl, the pitting potential of 0.36 V has been exceeded and the initiation of pitting is expected so long as the chloride ions still have effective access to the metal substrate, which is likely given that polyaniline films are known to be porous in character [29]. At a potential of 0.5 V, polyaniline is clearly in a partially oxidised and conducting state and was dark green in colour.

More information can be obtained about the significance of these potential values by holding the electrode at a constant potential and monitoring the resulting current. A polyaniline-coated 316 stainless steel electrode was held at a range of potentials from  $-0.1$  to  $0.5$  V in  $0.5$  M HCl. For potentials from  $-0.1$  to  $0.2$  V, an unsteady cathodic current was seen (Fig. 3b), which was likely due to reduction of traces of  $O_2$  in the solution. The current values declined closer to zero once the solution was deaerated with  $N_2$ , although a similar level of noise in the signal continued, and the cathodic current increased again upon introducing  $O_2$  into the solution (see the insert on Fig. 3b). The fact that dissolved  $O_2$  could still access the metal substrate is a further indicator of the porous character of the polyaniline films. It also suggests that polyaniline units in close proximity to the steel could be readily oxidised by  $O_2$ , and then pass their charge on to sustain the passive oxide film, rather than relying entirely on distant partially oxidised polyaniline units migrating through an otherwise reduced film. At  $0.4$  V, a little more positive than the pitting potential on the bare steel of  $0.36$  V, a fluctuating anodic current in the range of  $60$ – $160$   $\mu\text{A}/\text{cm}^2$  was obtained, while at  $0.5$  V the current was seen to rise steadily to over  $800$   $\mu\text{A}/\text{cm}^2$  in the course of an hour, due to the establishment of pitting corrosion visible at the end of the rod and the associated increase of current with time.

Electrochemical noise and current oscillations are well known in ferrous alloy electrodes in the presence of chloride under acidic conditions [30]. The interplay of pit growth, and of repeated passive film formation and breakdown, can produce current oscillations of several seconds in duration. In the present experiments on stainless steels, the additional factors of a polyaniline layer being charged and discharged, and of  $O_2$  diffusing through the porous polymer layer, creates a different set of conditions in which some fluctuation is seen in the current at constant potential, and longer oscillations in the open circuit potential.

### 3.3. Poly(*o*-methoxyaniline) on stainless steel discs

A conducting polymer was readily formed from an acidic solution of *o*-methoxyaniline at the 316 stainless steel electrode in a similar manner to the formation of polyaniline. Low currents were seen in cyclic voltammograms taken to  $1.1$  V until after the 40th scan (Fig. 1b). From this point two anodic peaks were seen at  $0.55$  and  $0.75$  V due to the two

step oxidation of the substituted polyaniline (reactions 1 and 2 with  $x = -\text{OCH}_3$ ), with two cathodic peaks seen on the back scans due to the reverse reduction processes. This cyclic voltammogram is comparable to that obtained for the formation of poly(*o*-methoxyaniline) on a platinum electrode [31], with a  $0.3$  V potential range ( $0.4$ – $0.7$  V), in which poly(*o*-methoxyaniline) exists in a partially oxidised and highly conducting state, but more limited than the  $0.5$  V range seen for the parent polyaniline. One difference displayed by films of poly(*o*-methoxyaniline) formed on platinum is that the peaks are sharper, and a third set of peaks are also seen due to branched forms [31]. The films formed on the stainless steels appear to be less uniform, producing broader peaks which overlap considerably (the first anodic peak occurs at  $0.45$  V on platinum, but was delayed until  $0.55$  V on the 316 stainless steel).

For a film of poly(*o*-methoxyaniline) formed by a total of 75 scans to  $1.1$  V, the height of the first anodic peak at  $1.5$   $\text{mA}/\text{cm}^2$  was consistent with a film thickness of about  $50$  nm [28]. The anodic current at the first peak was proportional to  $v^{0.88}$ , as opposed to the  $v^{0.65}$  dependence observed with polyaniline, pointing to a process under diffusion control to a lesser extent.

Electrochemical impedance spectroscopy (EIS) is often used in corrosion studies to characterise the complex reaction systems involved. It is possible to use the polarisation resistance,  $R_p$ , taken from the diameter of the partially-formed semicircle in Nyquist plots, as an indicator of the corrosion rate. Generally, larger  $R_p$  values point to slower rates of corrosion. For steels covered with polyaniline-containing coatings, the value of  $R_p$  at the open circuit potential has been used to study corrosion mechanisms and rates [12,15,17–19]. The presence of a polyaniline coating on mild steel in  $1$  M HCl has been shown to lead to increased  $R_p$  values, particularly following an acidic treatment to render the polymer conductive and electroactive [17]. In another study  $R_p$  values were seen to increase with time for polyaniline-coated steel in  $3\%$  NaCl, which was attributed to an increasingly thick oxide layer and partial reduction of polyaniline; a linear region at low frequencies was ascribed to the movement of counter ions through the solution [15]. The larger resistance values obtained in EIS for undoped, as opposed to doped polyaniline on carbon steel panels, has led to the suggestion that the undoped form provides superior corrosion protection by providing more limited access of the components responsible for corrosion to the underlying steel [9], but this is based on the assumption that polyaniline forms a dense, non-porous film, which is often not the case [29].

When the impedance was recorded for electrochemically produced films in  $0.5$  M HCl at potentials in which polyaniline is partially oxidised, the response was dominated by the conducting polymer. For example, a similar picture was obtained in the impedance response of poly(*o*-methoxyaniline) on 316 stainless steel (Fig. 4), as for polyanilines on inert metals such as platinum [32]. When the polymer was

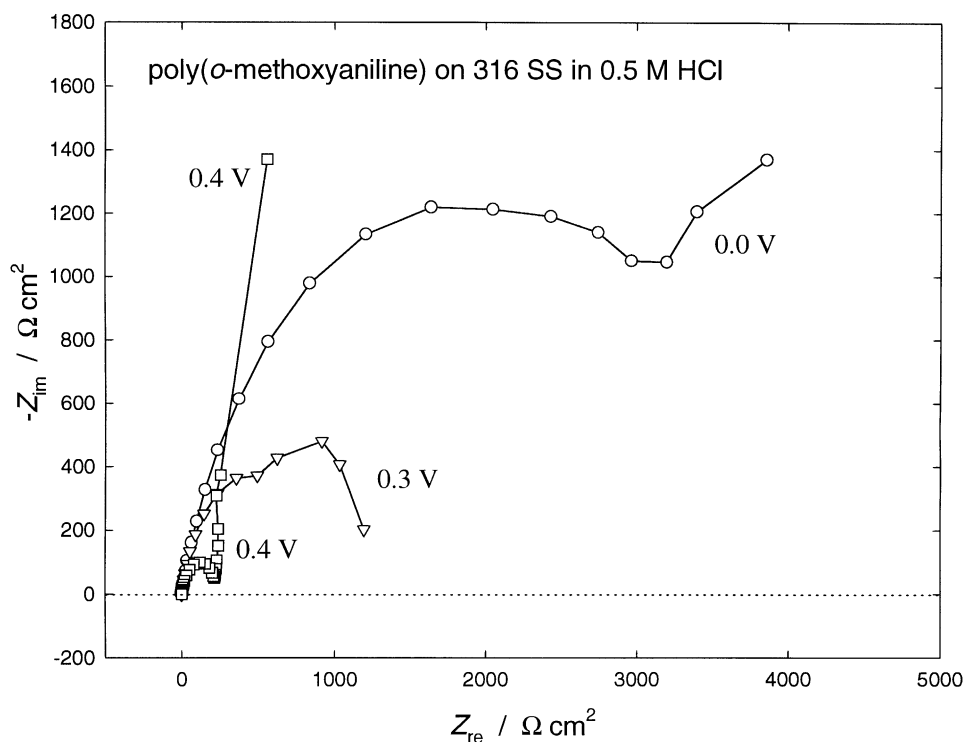


Fig. 4. Nyquist plot from 0.01 Hz to 100 kHz of a poly(*o*-methoxyaniline) film formed by 100 scans to 1.05 V in 0.1 M *o*-methoxyaniline and 0.5 M H<sub>2</sub>SO<sub>4</sub> on a 316 SS disc and tested in 0.5 M HCl at 0.0, 0.3 and 0.4 V.

fully reduced and insulating at 0 V, a relatively large value of  $R_p$  of 4000  $\Omega \text{ cm}^2$  was seen. At lower frequencies a Warburg component was observed, typical of a background process under diffusion control, probably the reduction of traces of dissolved O<sub>2</sub>. As the potential was increased, and the polymer was oxidised to a conductive state, the semicircle tightened up and much lower values of  $R_p$  were obtained from 0.3 V, and by 0.6 V a minimum value of 70  $\Omega \text{ cm}^2$  was produced. This lowering of  $R_p$  would suggest that the electrode is more susceptible to corrosion, and by 0.36 V the pitting potential for the bare metal has been passed. However, the response is dominated by the diminished resistance of the conducting polymer itself, and information about the resistance to corrosion of the underlying stainless steel is largely lost. The large capacitive-type component at 0.4 V, with a vertical rise at lower frequencies, is again very typical of the polyanilines [33].

When the 316 electrode covered with the poly(*o*-methoxyaniline) film, initially in the fully reduced state, was left in monomer-free 0.5 M H<sub>2</sub>SO<sub>4</sub>, the potential varied between 0.3 and 0.5 V (as occurred with and without polyaniline), just short of first oxidation peak, for some 15 h (Fig. 5a). The potential then increased to a steady value of 0.65 V, well into the partially oxidised range for the polymer. Traces of O<sub>2</sub> in the test solution continued to oxidise the polymer which could then maintain the stainless steel in a passive state with low rates of corrosion.

In 0.5 M HCl the poly(*o*-methoxyaniline) served to keep the corrosion rate low for several days, prior to the rapid drop

in potential and onset of pitting seen with polyaniline itself. As for polyaniline, the time to failure was increased by using a thicker polymer film (Table 1). One film formed by 75 scans to 1.1 V lasted for 11 days (first 6 days shown in Fig. 5a), while another formed by 30 preparative scans lasted only 4 days (Fig. 5b). In each case the potential remained close to 0.15 V, with oscillations to values as high as 0.5 V, before the final drop to  $-0.1$  V and electrode failure. The inserts in Fig. 5 illustrate how the fluctuations in potential sometimes involve a more rapid increase in potential from 0.15 to 0.25 V (Fig. 5a), approaching the partially oxidised state of the polymer, and a more gradual return to a value close to 0.15 V. On other occasions, when the potential had reached values between 0.4 and 0.5 V, in which case poly(*o*-methoxyaniline) is in a partially oxidised state throughout, the decline in potential was the more rapid (Fig. 5b), with the return climb lasting up to 1 h.

#### 4. Discussion

The schemes often proposed for the corrosion inhibition of polyaniline on active metals rely on traces of O<sub>2</sub> oxidising polyaniline to a partially oxidised and conducting form (as in reaction 1). The oxidised polymer, acting as a catalyst between O<sub>2</sub> and the metal substrate, then removes electrons from the metal or alloy, to form and maintain a passive oxide layer, with subsequent low rates of corrosion [4,6,10,12].



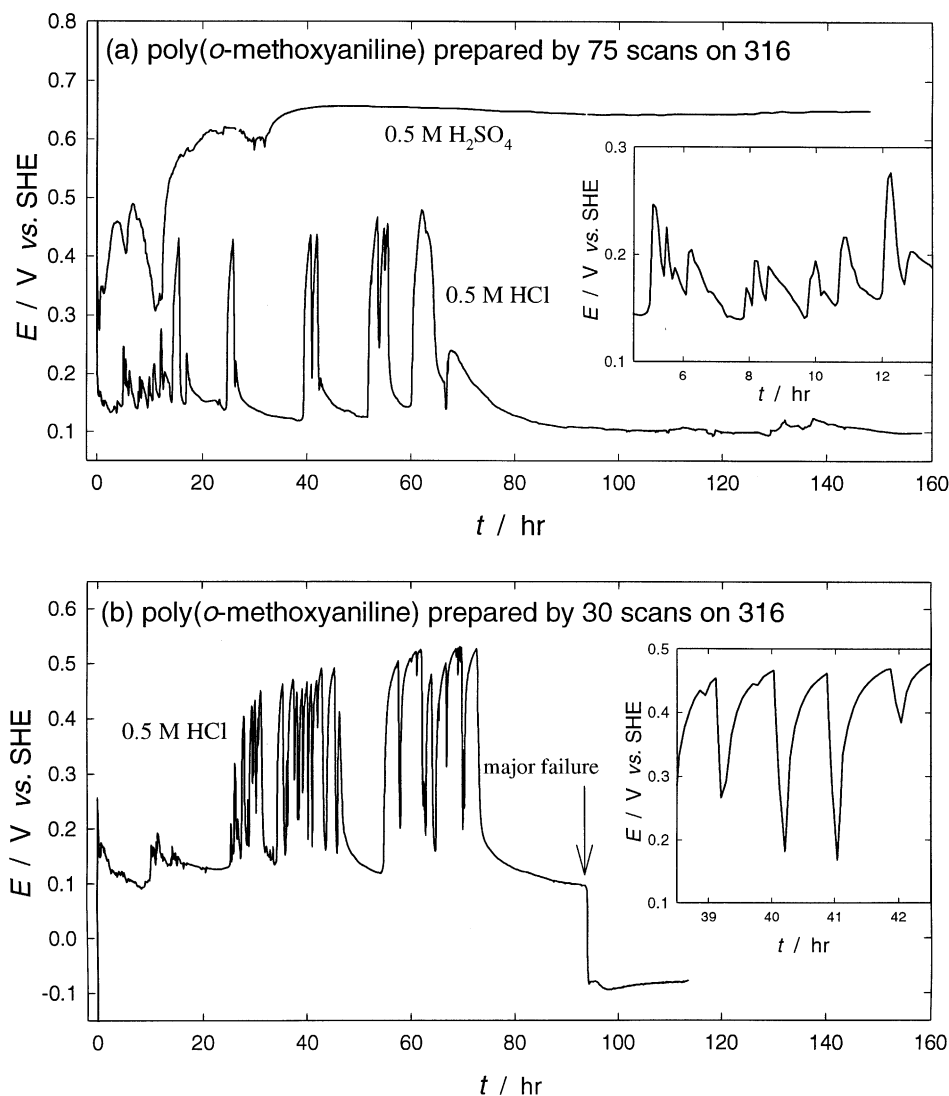


Fig. 5. Open circuit potentials of poly(*o*-methoxyaniline) films in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HCl, formed by: (a) 75 scans, and (b) 30 scans to 1.1 V in 0.1 M *o*-methoxyaniline and 0.5 M H<sub>2</sub>SO<sub>4</sub> on a 316 SS disc.

Our results indicate that polyaniline cannot remain in a partially oxidised state on pure iron in acid solutions, since the rate at which electrons are passed to polyaniline due to metal corrosion is greater than the rate at which the conducting polymer can be oxidised by O<sub>2</sub>. However, even in a predominantly reduced state, any positively charged polyaniline units can eventually pass their charge on to the metal substrate, assisting in the formation of a passivating iron oxide layer which serves to lower the rate of corrosion. With stainless steels in sulfuric acid, passivation of the metal can be achieved with polyaniline in a partially oxidised state, principally by the formation of chromium and nickel oxides to protect the underlying metal. In this case polyaniline or poly(*o*-methoxyaniline) can reach a steady state in which it is highly conducting and active as a catalyst between O<sub>2</sub> and the metal oxide, in that it can continue to promote the passivation reaction by the alternative pathway it provides, while itself being regenerated rather than consumed.

Under the higher rates of corrosion that arise in the presence of chloride, the charge generated within the polymer film by the action of O<sub>2</sub> is not always produced rapidly enough to repair the passive film at the rate at which it is being broken down under the influence of the chloride ion (which has the effect of raising the passive current 10-fold). A more active metal will demand a greater oxidising power from the polyaniline with an earlier onset of pitting corrosion once the polyaniline is exhausted. This will occur both by a lack of partially oxidised units (as the corrosion current exceeds the current supplied by the reduction of O<sub>2</sub>), and through a loss of film conductivity due to the degradation of the polymer which is expected under these active conditions. In each case the thicker the polyaniline film, the more catalytic material is available to passivate the metal, and the longer the system remains protected prior to the onset of pitting corrosion. This implies that polyaniline-containing formulations will

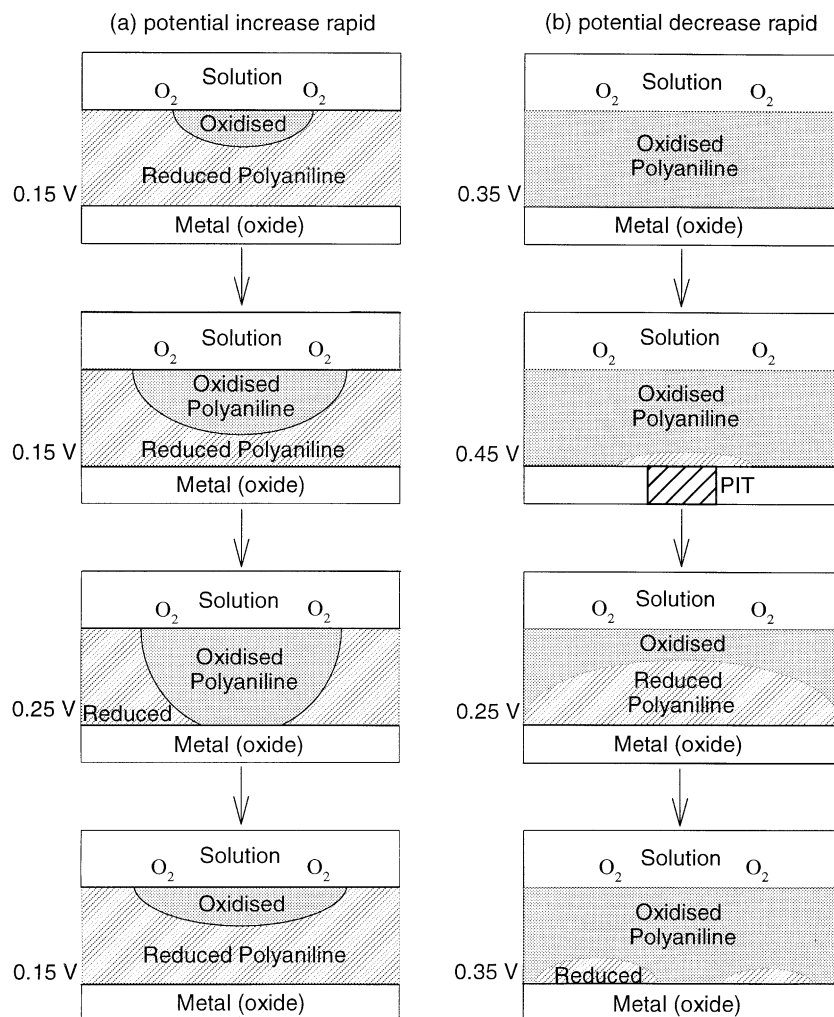


Fig. 6. Two models for the variations in potential seen for polyaniline films on stainless steels in HCl solutions: (a) oxidised units of polyaniline reaching the metal substrate to produce a rapid rise in potential; (b) pit formation exhausting areas of oxidised film to give a rapid drop in potential.

be more effective when they contain a higher concentration of the conducting polymer.

Two types of oscillation were seen in 0.5 M HCl: sometimes the potential rose quickly from a value of about 0.15–0.25 V, and then declined more slowly; while on other occasions the increase in potential was more gradual up to 0.4–0.5 V, and the decline to 0.25 V was more rapid. The following two scenarios are possible explanations of these two events.

It must first be emphasised that the reduction of conducting polymers starts at the interface with the metal substrate and moves out to more distant regions. The complete reduction of polyaniline is a slow process because of the insulating layer of fully reduced polyaniline which first develops at the metal surface; the outer regions of the polymer may take several hours to be fully reduced, with a logarithmic dependence upon time [34]. This is the origin of the so-called “first cycle effect” seen in Fig. 1a, where the charge passed on the first anodic scan is always larger following reduction for

several minutes than on subsequent scans, due to the greater amount of reduced material available for oxidation. Conversely, any positive charge produced in outer regions of the film must transverse the inner insulating layer to reach the metal and help maintain the passive oxide film.

In the first case in which the rise in potential was fairly rapid, we begin with polyaniline in a fully reduced and insulating state at 0.15 V (Fig. 6a). When partially oxidised regions of polyaniline diffuse through, or grow to such an extent, that a large amount of positive charge is released into the metal at one time, the potential moves to more positive values and the passive oxide film is strengthened in the process. As this new charge is gradually used up by the metal, the inner surface of the polymer is again reduced and the potential gradually declines.

On the other hand, when the potential carries on to more positive values in the 0.4–0.5 V range, and then undergoes a rapid decline to the insulating state at 0.25 V, a second event may be involved (Fig. 6b). In this case local breakdown, or

pitting, in the passive film can occur, since the pitting potential of 0.36 V for the bare stainless steel has been exceeded. A rapidly corroding pit area will quickly use up the available oxidised polymer as an electron sink, having the effect of repairing the passive film, and driving the potential below both the pitting and the protection potential (at 0.25 V for 316 stainless steel). The polyaniline can then be reoxidised by O<sub>2</sub> allowing the potential to again climb to more positive values.

## 5. Conclusions

Poly(*o*-methoxyaniline), formed by electrochemical polymerisation, behaved in a similar manner to polyaniline with regard to the corrosion protection of stainless steels. The metal oxide passive layer on the 316 stainless steel persisted for several weeks or more in sulfuric acid with or without a polyaniline film present, while the ultimate failure of each sample in hydrochloric acid occurred later with a thicker polymer film present. These results were due to the competition between polyaniline being oxidised by dissolved O<sub>2</sub> and the underlying metal using up the polyaniline charge to maintain a passive oxide film. The interplay of events in HCl led to oscillations in the open circuit potential, with increases in potential occurring when oxidised polyaniline units reached the underlying steel, and decreases in potential following the formation of pits.

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