Corrosion of polyaniline-coated steel in high pH electrolytes

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Abstract

Cyclic polarization measurements made on steel, iron oxalate-coated steel and polyaniline in a high pH solution and in the absence of chloride ions showed no tendency of the surface towards pitting corrosion. In all cases, the pitting potential was similar to the protection potential. Chlorides in the caustic solution caused significant pitting in the bare steel and slight pitting in the oxalate coated steel. The polyaniline coated-steel showed no pitting in the chloride-containing alkaline solution. Scratches through the polyaniline coating did not initiate pitting in the polyaniline coated steel surface when tested in the chloride-containing solutions.

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1. Introduction

Polyaniline, polypyrrole, polythiophene and polyfuran are organic polymers that exhibit conductivity in the semiconductor regime. Conductive polymers are often used as corrosion resistant coatings \cite{1-4} but have also found applications in light emitting diodes \cite{5} and sensor devices \cite{6}. The most widely studied polymer is polyaniline (PANI) because of its air and thermal stability, ease of processing and increased corrosion protection to coated steel. Although the mechanism of enhanced corrosion protection of steel by PANi is still unresolved, studies have pointed to a shift in the passivation potential of steel due to PANi. Wessling \cite{7} showed PANI-coated steel induced surface oxides. Further studies focused on the reversibility of PANi and its role on oxygen reduction in solution \cite{8}.

Most investigations into the corrosion protection of steel using PANi show the need to dissolve this polymer in an organic solvent such as N-methylpyrrolidinone (NMP) or m-cresol prior to coating steel. MacDiarmid and Ahmad \cite{9} were granted a patent claiming increased protection of steel using PANi. However, it was necessary to dissolve PANi in an organic solvent prior to coating the steel. Recently, Attar and Scantlebury \cite{10} found little corrosion protection of steel in near neutral salt solutions. The steel may not have been totally coated with PANi due to its limited solubility in water. To overcome the difficulties of coating steel with PANi, studies focused on composite organic coatings, occluded PANi an organic matrix. Talo et al. \cite{11} showed good corrosion protection of steel with mixed PANi–epoxy coatings. Schauer et al. \cite{12} studied the corrosion protection of iron coated with PANi followed by an epoxy top-coat. They also postulated an iron oxide intermediate layer and changes in the oxygen reduction reaction due to PANi.

One concern about dissolving PANi in a solvent such as NMP is the inherent de-doping process due to the relatively high pH of the solvent. Controversy revolves around the best form (conductive vs non-conductive) of PANi for corrosion protection. Several studies showed un-doped PANi performed better than doped PANi \cite{13-15}. Most corrosion studies focus on the protection of PANi-coated steel in either acidic or near-neutral solutions containing chloride ions. In acidic to near neutral pH solutions, the PANi coating is doped and the emeraldine green form of PANi exist on the steel. This emeraldine green form of PANi is the only conductive form. Much less is known about the corrosion protection of PANi on steel in alkaline media, particularly if chloride ions are present in solution. In an alkaline medium, PANi is in situ de-protonated to

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the emeraldine-base form. There have been limited studies of the corrosion protection of the EB form of PANi.

This study was done to determine the corrosion protection of PANi in a 0.1N NaOH solution with and without chloride ions. The PANi coating was deposited electrochemically thus eliminating the need for organic solvents. It is shown that PANi protects steel in the high pH electrolyte even with chloride ions in solutions. The effects of scratches through the PANi coating on the corrosion protection is also presented.

2. Experimental

PANi coatings were deposited on steel from an oxalic acid solution. The electrolyte contained 0.3 M oxalic acid and 0.1 M aniline. The polymerization solution was prepared by first diluting oxalic acid in doubly distilled water, then slowly adding the aniline. The aniline–oxalic acid solution formed white crystals, which re-dissolved after about 30 min of mixing. All studies were done at room temperature. The working electrode was a piece of 1018 steel. The steel was anodically cleaned at 4.0 V in a solution containing 50 g/l NaOH at 50°C. The steel was rinsed in distilled water and activated by immersion in 0.1N HCl for 3 s. The steel was doubly rinsed prior to electrochemical studies.

An EG&G PAR 273 potentiostat was used in all studies. Iron(II) oxalate coatings were prepared from the aniline–oxalic acid solution by polarizing the steel working electrode to −0.4 V vs Ag/AgCl for 60 s. PANi was deposited on steel galvanostatically at 3–4 mA/cm² vs a silver/silver chloride reference electrode. A platinum mesh served as the counter electrode. All corrosion studies were done using an EG&G flat corrosion cell. The working electrode had an exposed area of 1 cm². A Ag/AgCl reference electrode and a Pt mesh counter electrode were used in all studies. Two solutions were used for the CP corrosion studies, 0.1N NaOH and 0.1 NaOH containing 5 g/l NaCl. CP measurements were conducted from −0.25 V of the open-circuit potential, \( E_{oc} \), to +0.8 or +0.9 V at a scan rate of 1 mV/s. The scan reversed until it crossed the original trace.

The iron oxalate layer and PANi coatings were studied using X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and scanning electron microscopy (SEM). A Kratos Axis 115 XPS instrument was used to study the surface composition of the various coatings. Sample analysis was done within 2 h after preparing the films. An aluminum target with a monochromator was used in all studies. XPS spectra were recorded from 0 to 1400 eV. Detailed spectra of specific regions were recorded after ten sweeps. Deconvolution of overlapping peaks was done using a mixed Lorentzian (30%)–Gaussian (70%) fit. AFM analysis was performed using a Digital Nanoscope III instrument. Several scanning heads were employed, the largest capable of 100 µm. Imaging was done using a deflection mode. The PANi coatings were examined using SEM. Analysis was done on various samples using a Leo 1530 field-emission scanning electron microscope, FE-SEM. The accelerating voltage was 4–5 kV and images were taken from 100 × to 50,000 ×. Sample analysis was done within 2 h after preparing the films.

![Fig. 1. AFM top-view image of steel substrate.](image-url)
3. Results and discussion

AFM studies on the steel substrate, the intermediate iron oxalate layer and the PANi coating are shown in Figs. 1–3. The bare steel surface shows small crevices or polishing lines. Small cracks are also seen throughout the surface. Polarization of the steel in the aniline–oxalate solution prior to PANi deposition results in the formation of an intermediate Fe(II) oxalate layer [16]. The large polygonal crystals seen in Fig. 2 are about 0.5–3.0 μm in size. PANi deposited on the iron oxalate layer seen in Fig. 3 shows a rounded-mound structure even though aniline polymerized on the Fe(II) oxalate crystallites. The PANi layer is not compact. Small holes or trenches are seen in this layer but the defects in the PANi coating do not penetrate to the steel substrate. XPS measurements made on the PANi coating showed no Fe(2p) signal indicating the PANi coating completely covered the steel surface.

Cyclic polarization (CP) scans were made to determine propensity of the steel substrate, the Fe(II) oxalate layer and the PANi coating to pit (pitting corrosion) in the high pH environment. During a CP scan, the potential is initially scanned from about –250 mV of the open-circuit potential (E_{oc}) to E_{oc} then scanned in the positive direction from the E_{oc} until a large increase in current density is observed, at a corresponding potential (E_{pit}-pitting potential). When
the scan reaches a pre-determined potential, $E_{rev}$, it reverses and scans in the cathodic direction. The potential, where the loop closes on the reverse scan is the protection potential, $E_{pro}$. If pitting occurs during the test, a hysteresis loop is seen on the reverse trace. If the pitting and protection potentials are the same, there is little tendency for pitting in the sample. If $E_{pro}$ is more negative than $E_{pit}$, pitting could occur. Generally, the larger the hysteresis loop, the greater the propensity towards pitting.

CP scans made on the steel substrate, the Fe(II) oxalate layer and the PANi coating in the caustic solution without chloride ions showed no tendency towards pitting corrosion, Fig. 4(a)–(c) and Table 1. In all cases, $E_{pro}$ was similar to $E_{pit}$. There is a sharp

Table 1

| Sample          | Fe substrate | Fe oxalate layer | Fe-PANi layer |
|-----------------|--------------|------------------|--------------|
| No Cl$^-$       |              |                  |              |
| $E_{oc}$        | $-0.525$     | $-0.980$         | $-0.409$     |
| $E_{pit}$       | $0.520$      | $0.485$          | $0.446$      |
| $E_{rev}$       | $0.900$      | $0.800$          | $0.800$      |
| $I_{lim}$ (mA/cm$^2$) | 10    | 8                | 8            |
| Pitting?        | No           | No               | No           |
| With Cl$^-$     |              |                  |              |
| $E_{oc}$        | $-0.446$     | $-0.903$         | $-0.355$     |
| $E_{pit}$       | $0.464$      | $0.562$          | $0.560$      |
| $E_{rev}$       | $0.800$      | $0.900$          | $0.800$      |
| $I_{lim}$ (mA/cm$^2$) | 9     | 2                | 10           |
| Pitting?        | Yes          | Yes              | No           |

Fig. 4. CP trace of (a) bare steel in the caustic solution; (b) Fe(II) oxalate layer in the caustic solution; (c) PANi coating in the caustic solution.

Fig. 5. CP trace of (a) bare steel in the caustic-chloride solution; (b) Fe(II) oxalate layer in the caustic-chloride solution; (c) PANi coating in the caustic-chloride solution.
Fig. 6. SEM of (a) steel surface after CP scan in caustic medium; (b) pitting in the steel caused by Cl⁻ in the OH⁻ solution; (c) PANi coating on steel in the OH⁻ medium showing slight deterioration of PANi layer; (d) PANi surface from OH⁻ Cl⁻ solution showing slight cracking but no pitting.
Fig. 6. (Continued)
Fig. 7. CP scan of a scratched PANi coating in the caustic-chloride solution.

decrease in current density in the iron oxalate coating commencing at 1 mA/cm², –0.75 V. This decrease in corrosion current is due to the passive oxalate layer covering the surface. In the presence of chloride ions, both the bare steel and the iron oxalate coating showed considerable pitting as seen in Fig. 5(a) and (b). In both cases, \( E_{pcorr} \) was more negative than \( E_{pit} \) and hysteresis loops are seen in both cases. However, the PANi coating on steel polarized in the caustic solution containing chloride ions showed no tendency toward pitting Fig. 5(c). \( E_{pcorr} \) is about the same potential as \( E_{pit} \) and there no hysteresis loop in the scan. After removal of the PANi coated-steel sample from the corrosion cell, no visible signs of corrosion were seen on this PANi electrode. Therefore, the PANi coating appears to prevent a steel substrate from pitting corrosion in a high caustic medium. XPS measurements made on the PANi-coated steel after corrosion tests in the high pH electrolyte showed predominantly the benzenoid structure, where the nitrogen is bonded to carbon through a single bond (–NH–). It was shown previously that the reduction of the emeraldine base form of PANi to the reduced form, leucoemeraldine, is due to the redox capability of PANi inducing protective surface oxide formation on the steel surface [17].

SEM analysis of the steel and the PANi-coated steel in the caustic and chloride media are shown in Fig. 6(a)–(d). The surface of the steel exposed to the OH⁻ solution showed no gross surface features. Previously, it was shown that the steel acquires a stable potential in the Fe₂O₃ domain [18]. The steel surface is passivated and shows no tendencies towards corrosion in the alkaline medium, Fig. 4(a). However, in the presence of Cl⁻, pitting is seen throughout the surface (Fig. 6(b)) and agrees well with the CP scan of Fig. 5(a). The protective oxide formed in the OH⁻ solution was attacked by the Cl⁻ ions causing the pitting. The PANi-coated steel showed no significant changes in surface morphology after corrosion testing in the OH⁻ solution (Fig. 6(c)). Small cracks were observed on the surface of the PANi film, but no changes in the PANi clusters or general surface features were noted. The cracks increased slightly in size after corrosion testing in the OH⁻/Cl⁻ medium. However, unlike Fig. 6(b) which showed pitting on the surface of the steel, no signs of pitting were seen in Fig. 6(d). The PANi layer protected the underlying steel from further corrosion which was confirmed by Fig. 5(c). It is possible that the redox capability of PANi induced or maintained the Fe₂O₃ layer sufficient enough to prevent pitting corrosion [7,8,12,18].

The effects of scratching through the PANi coating down to the bare steel were investigated. Most organic coatings applied over steel offer sufficient corrosion protection only if the steel is completely encased by the coating. If the organic coating develops a crack, pit or pore corrosion of the underlying steel may occur and corrosion is often accelerated due to the high, localized corrosion current density at the crack or pit. As PANi coatings do not exhibit the typical values of \( R_{corr} \) for protective coatings (PANI— \( R_{corr} \) about 10⁴ ohm cm²). It is interesting to determine the effects of defects through the PANi coating and the resultant corrosion protection. The scratched PANi coating was tested only in the chloride-containing caustic medium since no pitting was observed in the chloride-free solution for bare steel. CP results shown in Fig. 7 reveal no tendency towards pitting in this scratched sample. This is surprising since bare steel is exposed through the PANi coating. Pitting was seen on the bare steel without any PANi layer. The PANi-coated steel may have induced an oxide layer on the steel similar to the finding of Wessling [7].

4. Conclusions

PANI-coated steel panels protect steel from corrosion in high pH solutions even in the presence of chloride ions. The presence of the oxalate underlayer does not appear to contribute to the overall corrosion protection of the PANi layer as evident from pitting seen in this sample in solutions containing chloride ions. However, the oxalate layer is necessary to achieve good adhesion of PANi to steel. PANi is sufficient to prevent pitting corrosion of steel in high pH media containing chloride ions. Scratched PANi samples also protected the steel from corrosion in this caustic-chloride medium. CP results showed no pitting corrosion in the scratched area.

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