REVIEW

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Electroactive conducting polymers for corrosion control

Part 2. Ferrous metals

Abstract This paper reviews the literature describing the effects of conducting polymer coatings on the corrosion rate of ferrous alloys (iron, steel and stainless steel). The literature is interpreted in terms of the proposed mechanisms of corrosion protection: barrier, inhibitor, anodic protection and the mediation of oxygen reduction. The most intriguing aspect of the reported literature are the studies demonstrating corrosion protection when deliberate defects were introduced into the coating to expose the bare metal. These studies show that protection afforded by conducting polymer coatings is not due to simple barrier protection or inhibition alone. Many studies illustrate that the polymer/metal interface is modified to produce passivating oxide layers and that charge transfer reactions occur between the metal and polymer. These studies support the proposed anodic protection mechanism, as do the reports of significant ennoblism. On the other hand, there is considerable variation in the reported shift in corrosion potential and these highlight the influence of substrate preparation, coating composition and mode of application and the nature of the electrolyte on the corrosion protection provided by the conducting polymer. For example, the evidence suggests that the emeraldine base form of polyaniline is superior to the emeraldine salt in terms of corrosion protection for steel. However, the number of direct comparisons is small and the reasons for the differences are not well understood. Also not well understood are the role of the counterion release and local pH changes on pinhole protection. It is also argued that the conducting polymer reduces the likelihood of large increases in pH at the polymer/metal interface and so stabilizes the coating against cathodic disbondment. Further work is clearly needed to increase the protection period by further studies on the corrosion protection mechanism so that the polymer composition and processing methods may be optimized.

Keywords Polyaniline · Polypyrrole · Steel · Iron · Corrosion

Abbreviations *AFM*: atomic force microscopy · *ATMP*: aminotris(methylenephosphoric acid · *BSA*: benzenesulfonic acid · *CSA*: camphorsulfonic acid · *DBSA*: dodecylbenzenesulfonic acid · *DNNSA*: dinonylnaphthalenesulfonic acid · *DSA*: dodecylsulfonic acid · *EB*: emeraldine base · *EC*: equivalent circuit · *ECN*: electrochemical noise · *ECP*: electroactive conducting polymer · *EDX*: energy dispersive X-ray · *EIS*: electrochemical impedance spectroscopy · *ES*: emeraldine salt · *LP*: linear polarization · *NMP*: N-methyl-2-pyrrolidone · *OCP*: open circuit potential · *PANi*: polyaniline · *PANi-LE*: leucoemeraldine · *PCS*: plain carbon steel · *POP*: poly(3-octylpyrrole) · *PPy*: polypyrrole · *PR*: pore resistance · *PTh*: polythiophene · *pTS*: p-toluenesulfonate · *SEM*: scanning electron microscopy · *SRET*: scanning reference electrode technique · *SS*: stainless steel · *SVET*: scanning vibrating electrode technique · *VOC*: volatile organic compounds · *XPS*: X-ray photoelectron spectroscopy

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Introduction

There is considerable experimental evidence that suggests that conducting polymer coatings are effective in lowering the corrosion rate of met0als when exposed to aqueous environments. In our earlier review (Part 1, previous issue of this journal) we described the general properties and processing of conducting polymers and reviewed the

literature relating to conducting polymer coatings on non-ferrous alloys. In this paper, we review the literature describing the effect of conducting polymer coatings on the corrosion resistance of iron, steel and stainless steel.

Table 1 summarizes the information available from the published literature for polyaniline coatings on ferrous alloys. It is obvious from Table 1 that a comprehensive study of the mechanisms of corrosion protection is difficult owing to the wide variations in experimental procedures used (coating type, substrate preparation, corrosive environment, test method). Consequently, there is still some conjecture as to the exact mechanism(s) operating. This article reviews the evidence supporting and, in some cases, opposing the various mechanisms that have been proposed. For simplicity, the review concentrates firstly on polyaniline (PANi) coatings, then considers polypyrrole (PPy) coatings on steel.

Table 1 Evidence from exposure testing of corrosion suppression by PANi coatings on iron, steel and stainless steel

Substrate	Method of pre-treatment	Type of polymer coating(s)	Test method	Observations	Ref
Iron	Degreased and ultra-sonically cleaned	Electrochemically deposited PANi-ES (oxalate) with a scratch	0.4 M NaCl or 0.1 M HCl. Amount of soluble iron analysed for immersions up to 1 week	PANi-ES coating reduced the amount of iron in solution compared with bare steel and PPy-coated steel	[18]
Mild steel	NA	PANi-ES formed by re-doping the EB cast from NMP. Dopants were pTS, TCE and Zn(NO$_3$)$_2$. Top-coated with epoxy or polyurethane (PU) and scratched to metal	3.5% NaCl, 0.1 M HCl. Outdoor exposure at beach/acidic site. Visual observations	Samples with PANi primers showed very little corrosion, while PU-coated samples were heavily corroded at scratch. pTS counterion found to be the best	[16, 17]
Mild steel	Solvent clean, acid etch, alkaline clean	PANi-ES (DNNSA) directly deposited from toluene. De-doping/re-doping used to exchange counterions. No topcoat; no scratch	Immersion in 3.5% NaCl. Outdoor exposure at marine/industrial site. Visual observations	PANi coatings showed less corrosion that bare metal. Best counterion was benzenesulfonate	[52]
Mild steel	NA	PANi-ES (Versicon) mixed with phenoxy or acrylic binder. Topcoated with epoxy or PU and scribed to metal	Salt fog exposure. Visual observations. Comparison of PANi primers with conventional zinc-containing primers	Samples with PANi primer were superior to zinc-containing primers in terms of blister size, blister density and scribe activity	[57]
Mild steel	NA	PANi-EB deposited from NMP solution and converted to PANi-ES (pTS). Topcoated with epoxy and hole drilled to metal	Immersion in 3.5% NaCl or 0.1 M HCl. Visual observations for immersion up to 8 weeks	Extent of rusting at the hole was found to increase in the order: PANi-ES < PANi-EB < epoxy. Better protection occurred in the acid	[10]
Mild steel	Abrasion and degreasing	Commercial CorrRepair system (without pre-treatment). No scratch	Immersion in 1 M NaCl or 1 M HCl. Visual observation of blistering	Blisters appeared after 2, 5 and 20 days for the topcoat, PANi primer and the PANi primer/topcoated samples, respectively	[39]
Mild steel	Solvent degrease	PANi-ES and PANi-EB coatings and PANi-EB mixed with other binders. Coatings were scratched to the metal	Immersion in 1 M NaCl or 3% NaCl. Salt spray. Visual observations	PANi-EB superior to PANi-ES; PANi-EB blended with polyimide (PI) superior to PI alone; no difference between PANi-EB blended with epoxy and epoxy alone	[6]
Mild steel	Polished and degreased	PANi-ES (CorrPassiv) with various epoxy topcoats and either with or without scratches	Outdoor exposure for 8 months	Less intercoat delamination and under-rusting occurred with topcoats of lower water permeability	[1]
Mild steel	NA	Epoxy-polyester powder coatings with various amounts of PANi-ES (Versicon or PANDA). Coatings scribed	Salt spray exposure. Visual observations of corrosion at scribe	Improved scribe corrosion resistance when >5% PANi added	[14]
Mild steel	NA	PANi-ES primer with clear top coat	Salt fog exposure	NA	[77]
Mild steel	NA	PANi-ES primer with various topcoats. Scribed to metal	Salt fog exposure to 1000 h. Visual observations	Underfilm corrosion suppressed and no evidence of rust in scratch. Blister density depends on topcoat used, with epoxy superior to acrylics	[12, 13]

Polyaniline coatings

Barrier protection

Two classical corrosion protection methods commonly associated with organic materials are barrier protection and inhibition. Isolating the metal surface from the corrosive environment (e.g. by painting) is effective as long as the barrier remains intact. Scratches or exposed edges can allow access of the corrosive environment to the metal so that corrosion initiates and commonly accelerates through mechanisms such as cathodic disbondment.

Schauer and co-workers [1] have reviewed the mechanism of protection offered by PANi on iron and considered the electrochemical and barrier effects, including the role of a topcoat. The water vapour permeability of a commercial polyaniline primer (Omercon Chemie) was found to be similar to that of commercially available epoxy coatings. However, the PANi primer in this case consists of a blend of PANi dispersed in an insulating polymer matrix with the concentration of PANi less than 5% (w/w). The water permeability of neat PANi coatings has not been reported in the corrosion literature. Transport of volatiles (including oxygen) through PANi films has been the subject of interest in another field of research, namely novel membranes. In these studies it has been shown that the oxygen permeability is dependent upon the oxidation state of the polyaniline, with the permeability decreasing with increasing doping [2]. Yang et al. [3] also observed that the permeability of gases depended on the degree of protonation of the polyaniline.

Clearly the coating of a metal with conducting polymer will produce some sort of barrier effect. Beck et al. [4] used electrochemical impedance spectroscopy (EIS) to investigate the effect on corrosion rate of electrochemically formed PANi, PPy and polythiophene (PTh) layers on iron. An inhibition of corrosion was only observed for coatings greater than 1 μm thick and this effect was attributed to a barrier effect (electrochemical interactions were considered insignificant). Wessling [5] noted that the corrosion current of PANi-coated steel was lower than bare steel and that the reduction in current was greater when thicker PANi coatings were applied to the metal. This result is similar to the findings of Beck et al. [4] and may imply a barrier effect of the PANi. Of course, the thickness of the polymer coating also determines its redox capacity and may influence the ability of the coating to anodically protect the metal, as discussed below.

A number of workers have suggested that the emeraldine base (EB) form of PANi is an effective corrosion barrier. McAndrew and co-workers [6], for example, coated mild steel with EB, ES (emeraldine salt) or with EB blended with other polymer binders and used EIS to study the corrosion processes of unscribed samples in 1 M NaCl. The pore resistance (PR) of the various coatings was determined from EIS data. The PR of PANi-EB was two orders of magnitude higher than that of mild steel coated with the ES form of polyaniline (in this case containing the counterion p-toluenesulfonate, pTS). The low pore resistance of the doped polymer was attributed to its polyelectrolyte nature that allows easy ingress of electrolyte into and through the coating. Blending of PANi-EB with polymer binders increased the PR compared with the binder alone, which correlated with a better salt fog resistance of the former. The high diffusion resistance of EB to corrosive ions has also been considered responsible for barrier protection by a number of other workers [6, 7, 8].

Many other studies, however, have shown that PANi coatings (ES and EB) appear to offer more than simple barrier protection. Wei and co-workers [9], for example, compared Tafel plots of mild steel coated with PANi-EB with barrier coatings (polystyrene and epoxy). Their results were taken as evidence that the PANi-EB offered more than simple barrier protection, since they performed better than other barrier coatings.

The most compelling evidence that PANi coatings are not simple barriers, however, comes from those studies where corrosion protection was observed when deliberate defects were introduced into the coatings. Lu and co-workers [10] and Pud et al. [11] have studied the effect of neat PANi-ES and PANi-EB primers with epoxy topcoats on the corrosion of mild steel in chloride solutions. A hole was drilled through the epoxy/PANi coatings to the steel surface in both studies. When PANi primers were present the corrosion rate was found to be lower compared with epoxy-only coated samples (also with a hole drilled to the metal). Scribed samples with PANi coatings have been shown to be superior to samples with a topcoat only by many other workers [6, 12, 13, 14, 15, 16, 17, 18]. These findings suggest that mechanisms other than simple barrier protection are operating.

Corrosion inhibitors

Inhibition usually involves the adsorption of organic species onto the metal surface to form a monomolecular barrier. As with barrier coatings, the adsorbed molecules can restrict the anodic and/or cathodic corrosion reactions (e.g. electron transfer) and slow the corrosion rate. Santos et al. [19] describe the inhibitor action as involving the displacement of adsorbed water from the metal surface by soluble organic species (Org):

$$Org_{sol} + nH_2O_{ads} \rightarrow Org_{ads} + nH_2O_{sol} \qquad (1)$$
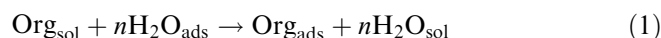
It is interesting to note that a number of studies have indicated that monomeric aniline and functionalized aniline derivatives are effective corrosion inhibitors for iron and steel. Bouayed et al. [20] investigated theoretically and experimentally the inhibitor effects of monomeric aniline on iron. Klavetter et al. [21] have
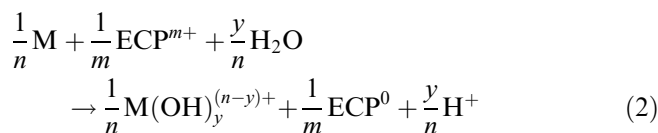
used model compounds of phenylenediimine moieties to study the interaction of PANi with stainless steel. They found spectroscopic evidence that the protonated diimine model compound forms a ligand with the electron-rich surface metal orbitals. This "pi-acid" interaction promotes adhesion and is the reason why the model compounds are effective corrosion inhibitors for stainless steel (SS). The authors suggest that the same inhibition mechanism may be responsible for the corrosion protection afforded by PANi coatings. Luo et al. [22] studied the inhibition of corrosion of mild steel in acid solutions of various alkylamines and monomeric aniline. Previous work [23, 24, 25] had reported that aniline is an effective inhibitor for steel corrosion in acidic solutions. Studies on the effect of chloride ions on the inhibitor efficiency found that chloride ions adsorb on the positively charged metal. The protonated aniline is then attracted to the negatively charged chloride ion layer, so that a hydrophobic adsorbed layer is formed on the surface of the metal. This layer reduced the corrosion rate significantly. Vishwanatham and Emranuzzaman [26] observed that monomeric aniline absorbs onto the steel surface and acts as an inhibitor for corrosion in hydrofluoric acid.

Interestingly, there is also evidence that water-soluble polyaniline acts as a corrosion inhibitor. *Ortho*-substituted poly(ethoxyaniline) was found to be an effective inhibitor for iron in acid chloride solutions [27]. Adsorption of the polymer to the iron surface was studied.

In summary, a number of studies clearly show that there is a strong tendency for aniline and polyaniline to adsorb onto metal surfaces. This adsorption is likely to promote strong adhesion and this, in turn, will assist in the corrosion protection of metals by polyaniline coatings.

Anodic protection

Kinlen and co-workers [15] have proposed that the electrochemistry of electroactive conducting polymers (ECPs) is responsible for anodic protection of substrate metals and also in the stabilizing of polymer coatings from cathodic disbondment (see later). The anodic protection occurs by moving the corrosion potential to the passive region for the metal of interest in the electrolyte of interest. The proposed reaction between the oxidized form of the polymer (ECP^{m+}) and the metal (M) is:

$$\frac{1}{n}M + \frac{1}{m}ECP^{m+} + \frac{y}{n}H_2O$$
$$\rightarrow \frac{1}{n}M(OH)_y^{(n-y)+} + \frac{1}{m}ECP^0 + \frac{y}{n}H^+ \quad (2)$$

The ECP can be re-oxidized by atmospheric or dissolved oxygen:

$$\frac{m}{4}O_2 + \frac{m}{2}H_2O + ECP^0 \rightarrow ECP^{m+} + mOH^- \quad (3)$$
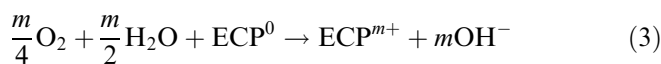
The following sections review the experimental evidence supporting the mechanism of anodic protection of iron, steel and stainless steel. There are two types of studies that are commonly performed: electrochemical tests to determine a shift in the corrosion potential of the metal in the more noble direction (so-called "ennobling"); and surface analysis of the reaction layer formed beneath PANi coatings and at pinholes in PANi-coated steels.

Ennobling

To achieve passivation, the corrosion potential must be shifted anodically (ennobling) to the passive region for the metal of interest in the environment to be encountered in service. The passivation potentials for various steels are given in Table 2 [28] for immersion in 1 M H_2SO_4 and the values agree with other literature values [29]. The passivation potentials given in Table 2 can be used as a guide in selecting polymers for the anodic protection of steels. However, the actual passivation potential depends upon the nature of the corrosive environment (pH, O_2 concentration, etc.), which may be unknown at localized corrosion sites (pits, blisters, etc.).

Shift in corrosion potential

Many studies have shown that the corrosion potential (E_{corr}) of PANi-coated metals is higher than the bare metal in the same electrolyte. Table 3 summarizes these findings. There are considerable differences in the E_{corr} value reported and the shift in corrosion potential (ΔE_{corr}) is dependent on the form of PANi and the corrosive environment. The E_{corr} for PANi-ES coated steel in 3% NaCl has been reported to increase by as much as $+800$ mV [5], reflecting the high oxidation potential of the polymer compared to uncoated steel. Talo et al. [30] also reported a large ($+500$ mV)

Table 2 Passivation potentials and passive state currents for iron and steel in 1 M H_2SO_4 (after Ahmed and MacDiarmid [28])

Type of iron/steel	Passivation region (V, vs. SCE)	Passive state current (mA/cm^2)
Pure iron wire (99.99%)	$+0.55$ to $+1.15$	0.5
Pure iron strip (99.87%)	$+0.50$ to $+0.95$	2.03
Mild steel (1018)	$+0.50$ to $+0.95$	30
Stainless steel (304)	-0.10 to $+0.85$	1.4×10^{-3}
Stainless steel (410)	$+0.10$ to $+1.00$	4.7×10^{-3}
Stainless steel (430)	-0.20 to $+1.00$	95×10^{-3}

Table 3 Summary of electrochemical corrosion test data for open circuit or corrosion potentials measured for PANi-coated steels

Metal	Method of pretreatment	Type of polymer coating(s)	Test method	E_{corr}	ΔE_{corr}	Ref
Mild steel	Solvent degrease.	PANi-EB incorporated as pigment in epoxy binder	Open circuit potential (OCP) in 3.5% NaCl	–0.3 V	+0.15 V	[34]
Mild steel	Abrade and degrease	PANi-EB deposited from NMP solution and converted to PANi-ES (pTS). Topcoated with epoxy and hole drilled to metal	OCP and linear polarization in 3.5% NaCl and 1 M HCl	–0.7 V (ES and EB in acid); –0.85 V (ES and EB in NaCl)	0 V (ES and EB in acid); –0.3 V (ES and EB in NaCl)	[10, 31, 32]
Mild steel	Abrade and degrease	PANi-EB or PANi-ES (pTS, CSA, DSA or DBSA) primer with epoxy topcoat and hole drilled to metal	Linear polarization in 3.5% NaCl and 0.1 M HCl	–0.63 V	0–60 mV decrease	[11]
Mild steel	Grit blast and degrease	PANi-EB	Linear polarization in 3% NaCl	–0.8 V	+0.1 V	[19]
Mild steel	Polished and ultrasonically cleaned	PANi-ES (CSA) blended into epoxy binder	OCP and linear polarization in 0.6 M NaCl or 0.1 M HCl	–0.1 V	+0.5 V	[30]
Mild steel	Degreased	PANi-EB cast from NMP and then doped with HCl to ES (Cl⁻)	OCP in 3.5% NaCl and 0.1 M HCl	–0.52 V (ES in acid); –0.7 V (ES in NaCl); –0.66 V (EB in NaCl)	+0.02 V (in acid); +0.025 V (ES in NaCl); +0.08 V (EB in NaCl)	[9]
Mild steel	Abraded	EB oligomers and PANi-EB	OCP in 5% NaCl	–0.63 V (EB); –0.11 V (oligomer)	+0.1 V (EB); +0.51 V (oligomer)	[35]
Mild steel	Abraded and solvent degrease	PANi-EB	Potentiodynamic polarization in 0.1 M NaCl (deaerated)	–0.37 V	+0.35 V	[33]
Mild steel	Polished and degreased	PANi-ES (CorrPassiv) with various epoxy topcoats and either with scratches	EIS in 0.5 M NaCl at OCP	–0.1 V for PANi primer; –0.1 to +0.1 V for PANi primer/ epoxy topcoat	–	[1]
Mild steel and stainless steel	Abrade and solvent degrease	PANi-ES (Versicon)	Linear polarization in 3% NaCl (steel) or 0.1 M H₂SO₄ (SS)	–0.20 V (steel); +0.30 V (SS)	+0.25 V (steel); +0.30 V (SS)	[5]
Stainless steel	Abraded.	PANi-EB	OCP in 0.1 M H₂SO₄ and 0.1 M HCl	+0 V (HCl)	+0.55 V (HCl)	[28]
Stainless steel	NA	EC-deposited PANi-ES (ClO₄⁻)	OCP in 1.0 M H₂SO₄	0 V	+0.5 V	[46]
Stainless steel	NA	EC-deposited PANi-ES	OCP in 1.0 M H₂SO₄ or in 3.5% NaCl	NA	Increase	[78]
Stainless steel	Polished	EC-deposited PANi-ES (ClO₄⁻)	Potentiodynamic studies in 1.0 M H₂SO₄	–0.70 V	+0.06 V	[51]
Stainless steel	Grit blast and solvent degrease	PANi-EB	Potentiodynamic polarization in 3% NaCl	–0.70 V	+0.11 V	[19]
Iron	Polished and solvent degrease	PANi-EB	VOC in 3.5% NaCl	–0.55 V	+0.35 V	[79]

increase in E_{corr} over uncoated steel; however, in this case the PANi-ES was blended with epoxy. The high electrical resistance of the epoxy would cause an apparent increase in E_{corr}, so the effects of PANi-ES additions are unclear in this case. Pud et al. [11] have reported a smaller increase of +60 mV in E_{corr} when PANi-ES coated steel was drilled to reveal the metal. In this case the E_{corr} represents the equilibrium value of the galvanically coupled PANi-ES and steel. Interest-ingly, Lu et al. [10, 31, 32] in identical studies reported a decrease in E_{corr} of the PANi-ES coated steel (with drilled hole) of –300 mV.

Many studies have shown a shift in E_{corr} for PANi-EB coated steels. Fahlman et al. [33] reported an increase of +350 mV for PANi-EB on steel; Santos et al. [19] observed an increase of +100 mV; Attar et al. [34] reported an increase of +150 mV for an EB/epoxy blend on steel; Ahmed and Macdiarmid [28] noted a very large

shift of $+550$ mV for EB coated on stainless steel and tested in 0.1 M HCl. Interestingly, Wei et al. [35] observed a much higher increase in E_{corr} for EB oligomers ($+510$ mV) coated on to mild steel and tested in 5% NaCl compared with EB polymer coatings ($+100$ mV).

Generally, the shift in E_{corr} has been observed to be less pronounced in acid chloride solution than in saline. Lu et al. [10, 31, 32] observed no change in E_{corr} in 1 M HCl acid, but a -300 mV shift in NaCl solution.

In summary, it is apparent that many observations of ennobling have been reported for PANi coatings on steel and stainless steel. The exact magnitude of the potential shift, however, is difficult to ascertain because of the differences in metal preparation, polymer type and corrosive environment used.

Scanning reference electrode studies of pinholes

Kinlen et al. [36] have also investigated the mechanism of corrosion protection by PANi coatings using a scanning reference electrode technique (SRET). For PANi-ES coated steel it was observed that exposed metal at pinholes in the coating were anodic regions, while the cathodic regions occurred on the PANi surface and extended some distance from the pinhole. The galvanic activity ceased after several days immersion, possibly owing to the passivation of the pinhole. When PANi-ES [counterion: aminotris(methylenephosphoric acid), ATMP] was mixed with poly(vinylbutyral) and cast on mild steel, the same galvanic reactions are believed to occur and again galvanic activity ceases after several days immersion. With PANi-EB coatings there was no evidence of galvanic activity using the SRET. With epoxy topcoats containing multiple pinholes it was observed that some pinholes were anodic and others were cathodic. The galvanic activity at the pinholes decreased with time when PANi-containing primers were used beneath the epoxy topcoat. When epoxy was used alone, there was no such decrease in activity over time. PANi-containing topcoats were formulated with different dopants and it was found that the rate of decay in galvanic activity depended upon the type of dopant used. Kinlen found that the effectiveness of PANi-ES doped various acids decreased in the following order: aminotris(methylenephosphoric acid) (**I**) > methylphosphoric acid (**II**) > sulfonic acids (e.g. *p*-toluenesulfonic acid, **III**).

Other workers have also noted galvanic effects when polyaniline was coupled to ferrous alloys. Mukherjee [37], for example, observed that PANi-ES was responsible for reducing charge transfer reactions when combined with iron-based metallic glasses. However, Ono et al. [38] report that electrodeposited PANi-ES on iron accelerates the cathodic reaction during corrosion testing. The galvanic activity is very much dependent upon the nature of the environment (pH, etc.) and the ratio of the anode to cathode area. It is not surprising, therefore, that conflicting observations have emerged.
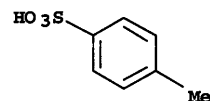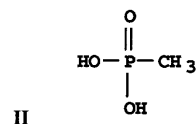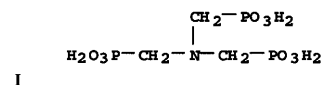
Formation of a reaction layer

Evidence that PANi in contact with steel produces a modified interface comes from many studies. The beneficial effects of the modified interface for corrosion protection were demonstrated by Li et al. [39]. In their studies, a PANi-containing primer was applied to the metal surface and the coated metal was immersed in either 1 M NaCl or 1 M HCl for 24 h. The coating was then removed from the metal by dissolution in NMP and the corrosion rate of the uncoated, modified metal was determined by EIS in 1 M HCl. A clear difference in corrosion rate was observed between the unmodified and modified samples. The charge transfer resistance decreased in the order: PANi-coated steel immersed in 1 M HCl before PANi removal > PANi-coated steel immersed in 1 M NaCl before PANi removal > unmodified steel. The results were described in terms of a passive layer forming on the metal surface due to contact with the polyaniline.

Oxide layer formation

A number of visual observations of the metal surface have indicated that contact with PANi induces the formation of a protective oxide layer. Wessling [5], for example, observed a striking colour change when PANi (Versicon) coatings were removed from a steel surface. The original surface was shiny, but after coating removal the surface was described as "light to dark grey, matt and spotted". When PANi was coated onto polished iron and then removed, examination of the surface by scanning electron microscopy (SEM) revealed several steps in the "passivation" process: (1) etching to reveal grain boundaries and crystal orientation; (2) deposition of an iron oxide layer. Electrochemical studies on the "passivated" surface (i.e. after coating removal) showed the same E_{corr}, but significantly lower current at potentials anodic to E_{corr}. Talo et al. [30] observed a light grey oxide layer on mild steel after coating with a PANi/

epoxy blend and immersion in salt water or hydrochloric acid. The oxide was studied using X-ray photoelectron spectroscopy (XPS), which revealed the surface was coated with iron oxide, fluoride and possibly iron hydroxide or organo-iron compounds.

Lu and co-workers [10] investigated the oxide layer formed on the bare steel surface on samples made by first coating the steel with PANi (ES or EB), followed by epoxy and then with a hole drilled to the metal surface. Visual observations indicated that the metal became covered with a greyish oxide and microscopic studies showed that the oxide first formed around the periphery of the hole and then grew toward the center upon further immersion in either HCl or NaCl. The distance of oxide growth from the edge of the PANi coating was limited to about 2 mm, although in one instance (PANi-ES/epoxy coated steel in HCl) this distance was found to be as high as 6 mm.

Epstein et al. [33, 40, 41, 42] have studied the interaction between polyaniline and steel using XPS and electrochemical corrosion techniques. The substrate used was cold rolled steel that was solvent degreased and, in some cases, abraded before casting EB from NMP to form coatings. The samples were tested either by immersion in 0.1 M NaCl or by exposure to high humidity in an environmental chamber.

XPS revealed that all samples had a two-layer oxide consisting of a Fe_2O_3 layer (1.5 nm) over a thicker Fe_3O_4 layer (3.5 nm) [10, 41]. Fahlman et al. [41] found that the thickness of the top layer did not change greatly with exposure to a corrosive environment, whereas the bottom Fe_3O_4 layer thickness depended on the type of coating. With EB there was no change in oxide layer thickness, while PANi-ES (Cl^-) and uncoated Fe showed a substantial thickening of the Fe_3O_4 layer (to > 15 nm). Even when the EB coating was applied to the underside of a steel sheet and the topside was examined using XPS [42], no change in oxide thickness was observed for up to 7 days exposure (at 80 °C). In contrast, the uncoated steel showed significant oxide thickening even after 1 day exposure.

In another study [33], iron was sputter coated onto EB and exposed to ambient air for 1 week. Iron species were present throughout the entire 1 μm thickness of the EB film and evidence of charge transfer from iron to the imine nitrogen of EB was noted. These results were interpreted as the iron forming metal-polymer complexes with the EB.

Kinlen and co-workers [15] have studied the oxide layer chemistry on mild steel using XPS. PANi-ES was applied to the surface of the degreased steel and then dissolved with xylene. The surface composition of the steel was measured before and after the coating was applied, with the major changes being a reduction of iron oxides to hydroxides, loss of Mn alloying element and residual PANi with sulfonic acid dopant.

Pud and co-workers [11] investigated the nature of the oxide layer formed between PANi and steel when the PANi was applied in different ways. These workers found that the passive layer forms when the PANi-EB (neutralized Versicon in NMP) is cast onto the steel and is further modified when the PANi-EB is converted to PANi-ES by immersing in acid (pTS in water). In contrast, less effective oxide layer formation occurs when the PANi-ES is cast directly on the steel. The latter coatings were formed by doping the PANi-EB with various sulfonic acids [camphorsulfonic acid (CSA), dodecylsulfonic acid (DSA) and dodecylbenzenesulfonic acid (DBSA)] and dissolving in chloroform or xylene. No oxide layer was visually noted for coatings formed from the doped PANi-ES, whereas a grey oxide could be seen on the metal surface when the PANi-EB was cast on the surface and this polymer was subsequently doped to the PANi-ES. All coatings were prepared to 10–15 μm and covered with an epoxy topcoat, following which a 1.5 mm diameter hole was drilled through the coatings to reveal the metal. Some delamination was observed after drilling and an attempt was made to account for the larger hole size by depositing copper on the metal and measuring the exposed metal area (after electrochemical corrosion testing).

Mass spectrometry (MS) studies by Sauerland and Schindler [43] also provide evidence for complexation between Fe and PANi. PANi (Versicon, Zipperling) coated stainless steel probes were ionized by UV light and the fragments examined by MS. Intense iron signals were observed for the PANi coated on stainless steel.

Schauer et al. [1] used reflectance IR spectroscopy to study the oxide layer on steel when coated with PANi-ES (dispersed in a polymer binder) and at various stages during immersion in salt water. These workers observed two phases of corrosion behaviour. In the passive stage the oxides were predominately stable γ-Fe_2O_3 and α-Fe_2O_3, while in the active stage of corrosion the oxides were found to be unstable γ-FeOOH.

Polyaniline reactivity

Beard and Spellane [44] observed the reduction of PANi-EB to PANi-LE (leucoemeraldine) after the former was coated onto mild steel and exposed to atmospheric conditions. XPS studies clearly indicated a transfer of charge from the metal to the polymer and heating the PANi-EB-coated steel in vacuum enhanced this process. Heating in air caused a re-oxidation of the PANi-LE to PANi-EB. Similar studies with the PANi-EB on glass produced no changes in the oxidation state of the polymer. The findings are, therefore, consistent with the mechanism of passivation of steel through electrochemical interaction of the EB with the steel surface.

Bernard et al. [45] observed the opposite effect for PANi-EB-coated iron in a neutral chloride solution. Raman spectroscopy showed the formation of polarons (emeraldine salt) after exposure of the PANi-EB-coated iron to the solution.

In DeBerry's original work [46], the PANi-ES was found to be reduced to a less-doped form during the re-

passivation of pits that form when PANi-ES-coated stainless steel is immersed in a chloride-containing electrolyte. Once the substrate was re-passivated the PANi became a dark green colour again owing to re-oxidation by oxygen. Schauer et al. [1] also noted colour changes when PANi-coated steels were immersed in salt water. In this case the colour change was from green to blue (EB) and was often accompanied by blister formation. The pH of the blisters was found to be 12–13, presumably due to oxygen reduction reactions.

Other mechanisms

Inhibition of ion diffusion rates

Fahlman et al. [41] have proposed a mechanism for corrosion protection for EB-coated steel (or iron). The mechanism is a variation on the "grain-boundaries-pores" model [47] for corrosion of steel in the presence of a Fe_2O_3/Fe_3O_4 oxide layer. Steel corrosion occurs at the Fe/Fe_3O_4 oxide interface by diffusion of water through the porous oxide (nm size pores). Fe^{2+} ions diffuse up through the oxide along grain boundaries or through vacancy hopping. At the Fe_2O_3/Fe_3O_4 oxide interface the Fe^{2+} ions react with O^{2-} or water that has diffused down through the Fe_2O_3 oxide to produce mainly Fe_3O_4.

When PANi-EB is coated onto the steel or iron surface, electrons are donated from the metal to the LUMO level (lowest occupied molecular orbital) of the polymer, thus producing a positively charged metal surface (0.5–1.0 Å thick [48]). Since the Fe_3O_4 is a semi-metal of conductivity 10^2 S/cm and Fe_2O_3 is a semiconductor [49], the charge is built up at the Fe_3O_4/Fe_2O_3 interface rather than at the Fe/Fe_3O_4 interface. The electron deficiency of the Fe_3O_4 layer will change its chemical potential, "making it harder to (further) oxidize the iron ions and hence the steel samples become more resistant to corrosion". The charged layer also inhibits diffusion of Fe^{2+} and O^{2-} ions, which slows corrosion.

Shift of electrochemical interface

One mechanism for corrosion protection by PANi suggests the displacement of the electroactive interface from the metal/solution interface to the polymer/solution interface alters the passive state of the metal [1, 50]. Schauer et al. [1] describe a mechanism similar to that shown in Fig. 1. These workers argue that a concentration gradient of O_2 across the PANi layer and the electronic conductivity of the PANi layer promotes the cathodic reaction at interface II rather than interface I. This separation of the anodic and cathodic reactions prevents the increase in pH at the metal surface, thereby maintaining stable oxides such as Fe_3O_4, γ-Fe_2O_3 and α-Fe_2O_3.

The increased resistance to cathodic disbondment for PANi-coated steels has also been attributed to a similar
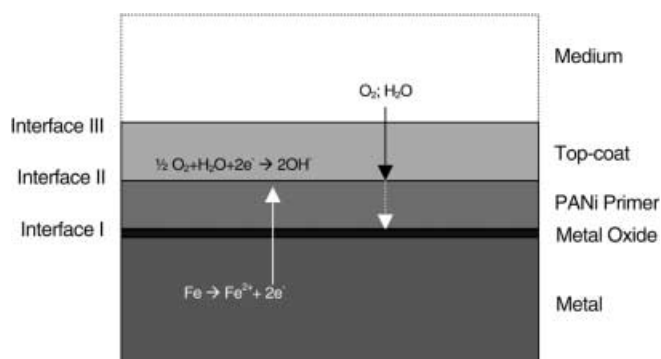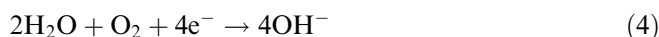

Fig. 1 Proposed reaction mechanism showing the separation of anodic and cathodic reaction sites (after [1])

process [1, 15]. Cathodic disbondment of coatings occurs when cathodic reduction of O_2 occurs at the polymer/metal interface, causing an increase in local pH:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \qquad (4)$$

When this reaction occurs at the periphery of a scratch or pinhole, the increase in pH decreases the polymer-metal adhesion and disbondment occurs. The ECP may alleviate this process by promoting the cathodic reaction on its surface, rather than at the metal/polymer interface. The conducting polymer acts as an electrocatalyst, first being reduced:

$$ECP^{m+} + me^- \rightarrow ECP^0 \qquad (5)$$

and then re-oxidized as shown in Eq. 3, so that the overall cathodic reaction is given by Eq. 4, where $m = 4$. Kinlen [15] also found that a complex of iron-PANi more readily reduces oxygen (Eq. 3) than PANi-LE alone. Thus, the complex formed by reaction of iron with PANi produces a more efficient electrocatalyst. Malik et al. [51] incorporated Pt microparticles in PANi-ES and found that the oxygen reduction was further catalysed by the Pt particles.

The net result of the electrocatalytic reduction of O_2 by PANi is the increase in electrolyte pH at the polymer/electrolyte surface, rather than at the polymer/metal interface as occurs in conventional coatings. PANi-ES also reacts with OH^- to form PANi-EB, which has a further buffering effect on the electrolyte pH:

$$PANi - ES + OH^- \rightarrow PANi - EB + H_2O + A^- \qquad (6)$$

Through these mechanisms the emeraldine salt limits the increase in pH at the polymer/metal interface. The lower interface pH increases the stability to cathodic disbondment and slows the spread of corrosion compared to conventional coatings.

Interestingly, McAndrew et al. [6] describe the effect of PANi-EB on mild steel in terms of creating a basic surface that is more resistant to corrosion. According to the iron/steel Pourbaix diagram (Fig. 2), a higher pH promotes the passivation of the steel surface. However, as described above, a high pH at the polymer/metal in-
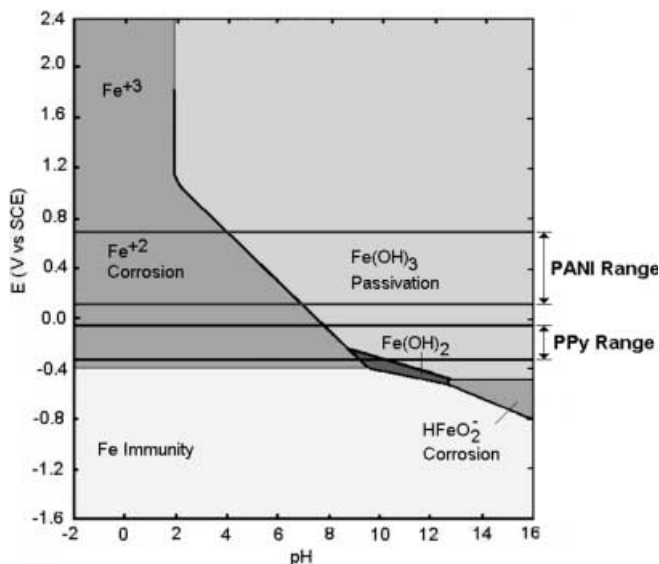
Fig. 2 Pourbaix diagram for steel in water. *Horizontal bands* show the reported range of reduction potentials for PANi and PPy. Note that PPy is not stable at high pH and that PANi is converted from the emeraldine salt (ES) to the emeraldine base (EB) above pH≈4

terface promotes failure through cathodic disbondment. The actual overall mechanism remains unclear and probably involves a number of processes with one possibly dominating over others, depending on the period in the "corrosion cycle".

Emeraldine salt versus emeraldine base

There is considerable debate as to which form of PANi offers the greatest corrosion protection: ES or EB. Direct comparisons have been made between the two forms of polyaniline and in both studies it was found that the EB was superior to ES [6, 10]. The reasons for the differences in performance are not understood at this stage, although the different forms of the polymer differ substantially in properties (conductivity, permeability, reduction potential) and composition (counterion).

Ennobling

Lu et al. [10, 31, 32] observed no differences in E_{corr} for ES and EB primed steel (with epoxy topcoats and hole drilled to metal) when tested in salt and acid-chloride electrolytes. In contrast, Wei et al. [9] observed a much higher ennobling effect for EB primed steel compared to ES primed steel, again with epoxy topcoats and a hole drilled to the metal, when tested in 3.5% NaCl. The opposite effect was noted by Schauer et al. [1], who reported a transition from passive to active corrosion behaviour, and an associated decrease in E_{corr}, when PANi-ES was converted to PANi-EB during immersion in salt solution.

The exact effect of the form of PANi on the ennobling phenomenon remains unclear. Both forms of the polymer are electroactive and can be reversibly reduced to the leucoemeraldine base. Accurate values of the reduction potentials for ES and EB are not available, but it is likely that both forms are more noble than iron. Thus, it is to be expected that the galvanic couple between ES or EB and iron/steel would produce an ennobling effect. The efficiency of the galvanic coupling is influenced by any iR drop (and so the conductivity of the polymer, which itself depends on the initial structure and degree of doping) and the relative size of the anode (steel) and cathode (PANi). It is not surprising, therefore, that contradictory results have been reported for the ennobling effect of ES and EB coupled to steel.

Barrier protection

Some reports suggest that the EB form of PANi is a more effective barrier than ES. The high diffusion resistance of EB to corrosive irons is considered responsible for barrier protection [6]. Measured values of the diffusion rates of ionic species in ES and EB are not available, however. In one report, the permeability of gases through free-standing PANi films was examined as a function of the degree of protonation of the polymer [3]. It was found that the O_2 permeability increased by an order of magnitude as the polymer was de-protonated from the emeraldine salt to the emeraldine base.

Dominis et al. [52] reported polarization resistance values for ES- and EB-coated steel tested in 500 ppm NaCl solution. The polarization resistance of ES was more than an order of magnitude lower than that obtained for EB-coated steel. The lower polarization resistance obtained for the ES-coated steels was considered to be due to the poorer barrier properties of ES compared to EB. The poor barrier properties were ascribed to the higher ionic and electronic conductivity of ES compared to EB.

Anodic protection

Studies of the passivation mechanism using XPS have shown differences in oxide layer formation between EB- and ES-coated steels. Fahlman et al. [41] found that the thickness of the bottom Fe_3O_4 oxide layer did not change with EB, while ES (Cl⁻) (and uncoated Fe) showed a substantial thickening. Their results are explained by the inhibition of ion diffusion through the semi-passive oxide layer when in contact with EB.

Summary

The discussion of the relative effects of EB versus ES is complicated by many factors. Commonly, the comparison between the two forms of PANi have been made by

first casting the EB onto the steel surface and then conversion of the EB to ES by immersion in acid. Pud and co-workers [11] found, however, that this process produced a different oxide layer at the metal/polymer interface than occurs when ES is directly cast on to the metal. Another complication arises from the fact that ES and EB are interconvertible and, indeed, Bernard et al. [45] have shown that the conversion of EB to ES occurs upon immersion of EB-coated iron in salt water. As mentioned above, Schauer et al. [1] reported the exact opposite: the conversion of ES to EB when coated onto steel and immersed in salt water (in this study the ES was dispersed as a powder throughout a polymer binder).

Role of the counterion

Dominis et al. [52] have investigated the effects of PANi-ES coatings on steel with different counterions by ambient exposure testing. Organic acid-doped ES [pTS, benzenesulfonic acid (BSA), dinonylnaphthalenesulfonic acid (DNNSA)] showed little visible corrosion after 2 months, whereas inorganic acid-doped ES (especially Cl^- doped) corroded rapidly (1–2 weeks).

Kinlen et al. [36] have also suggested that different counterions will affect the performance of PANi coatings for corrosion protection. Whereas sulfonic acid is corrosive to carbon steel [53], phosphonates are effective corrosion inhibitors for steel in aqueous solutions [54]. As described above, Kinlen and co-workers found more effective corrosion resistance for PANi-ES doped with ATMP compared with more conventional pTS-doped PANi-ES. The reason for the differences in performance was ascribed to complex formation between dissolved iron and the dopant that has been released from the PANi. The insoluble iron-dopant complex passivates the metal and slows down corrosion at pinholes. The mechanism is shown in Fig. 3, as described initially by Barisci et al. [55].

Role of the topcoat

Several studies have indicated that the degree of corrosion protection is dependent upon the properties of the topcoat when the polyaniline is applied as a primer layer [1, 56, 57]. Sitaram et al. [56] did not detect any differences in performance of polyaniline-coated steel with different types of topcoats. However, inferior performance was observed when the polyaniline was blended in with the topcoat polymer (e.g. epoxy) compared to when the polyaniline was applied as a base coat.

Schauer et al. [1] studied the performance of systems with polyaniline primer and epoxy topcoats, where the epoxies were chosen to have varying barrier properties. Polarization resistance values during immersion were obtained from EIS and clearly distinguished between the epoxy topcoats (no PANi layer): the higher the water vapour permeability of the epoxy, the lower the R_p value and the more rapidly the R_p value decreased during immersion. For PANi/epoxy systems the same trend was apparent for the different epoxy topcoats; however, the R_p values were considerably higher than for the epoxy-only coated steels and the rate of decay of the R_p values with time was much lower. PANi-only coated steel showed intermediate levels of R_p and rate of decay with time. Blisters and delamination occurred for the systems with high water permeability.

As described above, Schauer et al. [1] attribute the corrosion protection mechanism of PANi to a separation of the cathodic and anodic reaction sites. The barrier properties of the topcoat are clearly important, since typical blistering and delamination of the PANi primer occurred when no topcoat was used and when an epoxy topcoat of high water permeability was used. According to Shauer et al., a good barrier is important in limiting the O_2 supply at the metal interface (interface I in Fig. 1): if oxygen is available at the metal interface, then the cathodic reactions will occur at that interface, leading to alkalization, blistering and delamination. On the other hand, if oxygen supply is restricted by an effective barrier, then the cathodic reaction is more likely to occur at the primer/topcoat interface (interface II), according to Schauer et al. As described above, the shift of the cathodic reaction away from the metal surface is likely to reduce the rate of cathodic disbondment and, hence, the rate of underfilm corrosion. Although water permeation rates were reported for the different epoxy

Fig. 3 Possible mechanism of passivation of exposed metal surfaces at pinholes. Galvanic coupling of the exposed iron to the ES causes reduction of the ES to the leucoemeraldine base (LB) of polyaniline. The release of the counterion (A^-) from the PANi may form an insoluble iron complex that passivates the metal surface. Subsequent reduction of dissolved oxygen causes an increase in local pH and oxidation of LB to the emeraldine base (EB) of PANi
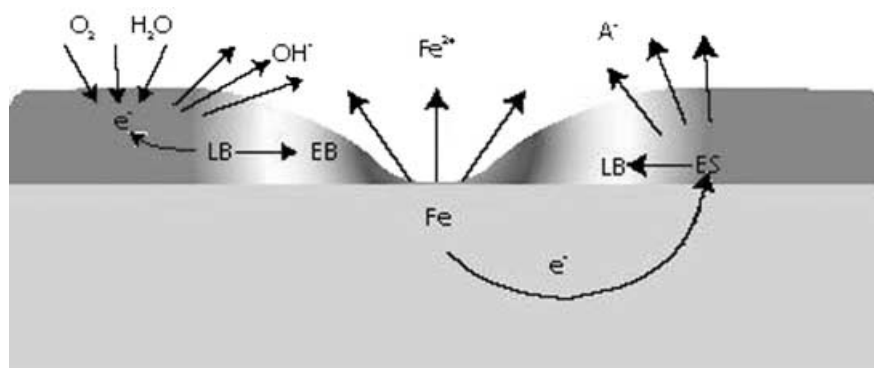
topcoats used by Schauer et al., there was no information provided on the relative rates of oxygen permeability. It is, therefore, difficult to assess the validity of the proposed mechanism.

Modeling of the corrosion processes

Some attempts have been made to model the corrosion processes when polyaniline coatings are present by using EIS data and fitting to various equivalent circuits.

Schauer et al. [1] proposed the equivalent circuit (EC) model shown in Fig. 4. No discussion of the appropriateness of the model was provided.

Kinlen and co-workers [57] proposed a similar EC for their system, which again involved PANi-ES powder dispersed in a polymer binder as the primer layer and a barrier topcoat (Fig. 5). The EC proposed by Kinlen was modeled on samples having a scribe mark made to the metal surface. The elements of the EC are similar to that proposed by Schauer et al., with the exception that the Warburg element is replaced by a resistance/capacitance in parallel.

Li and co-workers [39] reviewed the EIS data obtained for PANi-primed and topcoated steel (same system as investigated by Schauer et al.) with the EIS expected for conventional coatings. The ECs are shown in Fig. 6. Insulating coatings provided short-term protection by a barrier mechanism. Blisters eventually develop beneath the coating and lead to accelerated corrosion and cathodic disbondment. Similarly, PANi-only coatings (PANi dispersed throughout a polymer binder) also failed by blistering within a short time. In contrast, a PANi primer coupled with an insulating topcoat gave substantially improved corrosion protec-

tion. The EIS studies showed that the PANi primer was a poor barrier such that rapid proton diffusion through the coating meant that the passive layer dissolved faster than the PANi could repassivate the surface. An insulating topcoat reduced the corrosion rate by limiting the diffusion of corrosive species to the PANi/metal interface. This extra barrier limits the dissolution rate of the passive layer, so that the PANi can maintain the passive state. The EC for the case of PANi primer with insulating topcoat is given in Fig. 7. Although the Warburg impedance is shown as diffusion throughout the polymer coating, no finite length effect was observed in the EIS spectrum at low frequency. This anomaly remains to be resolved. Interestingly, Wessling and Posdorfer [13] investigated similar systems (PANi containing primer with topcoats) over the same frequency range (to 50 mHz) but did not observe the Warburg diffusion tail.

Tallman et al. [58] also reported a Warburg diffusion tail in their studies of PANi coatings on steel. In this study, the PANi was applied as a neat coating and no topcoat was used. Tallman et al. also reported that the diffusion tail extended to very low frequencies and was, therefore, probably associated with diffusion of species through the electrolyte, rather than through the polymer coating. Tallman et al. argued that the diffusion was probably due to cation (M^+) diffusion to the polymer to neutralize the PANi counterion made redundant in the polymer coating by the reduction of the PANi ES to LE:

$$ES^+A^- + M^+ + e^- \rightarrow LE^0A^-M^+ \tag{7}$$
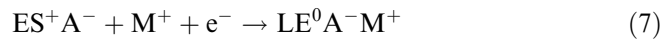
The EIS data of Tallman et al. also showed a semi-circle at high frequencies. The semi-circle was attributed to a

Fig. 4 Equivalent circuit used to fit EIS data for PANi-ES primed steel with epoxy topcoats and tested in 0.5 M NaCl (after [1]). The PANi primer consisted of PANi-ES powder dispersed throughout a polymer binder
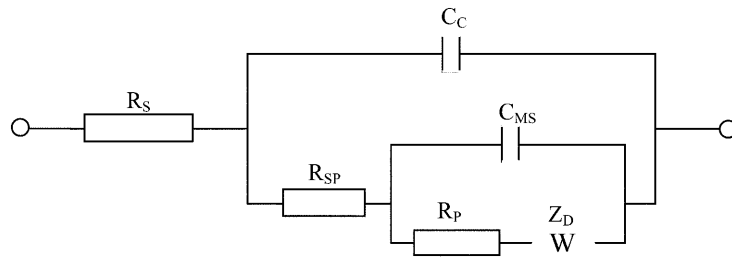
R_S electrolyte resistance
R_{SP} electrolyte resistance in pores of coating
R_P polarisation resistance
C_C coating capacitance
C_{MS} metal – solution interface capacitance
Z_D Warburg impedance

Fig. 5 Equivalent circuit for scribed samples coated with PANi-ES primer (PANi powder dispersed in polymer binder) with a barrier topcoat (after [57])
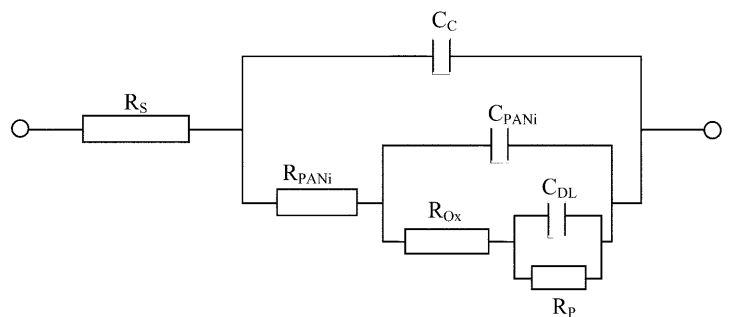
R_s electrolyte resistance
C_C coating capacitance
R_{PANi} polyaniline resistance
C_{PANi} polyaniline capacitance
R_{Ox} oxide resistance
C_{DL} double-layer capacitance
R_P polarisation (corrosion) resistance

Fig. 6 Equivalent circuits proposed for **a** impervious insulating coating, **b** insulating coating with blisters and **c** electroactive coating (without blisters) (after [39])
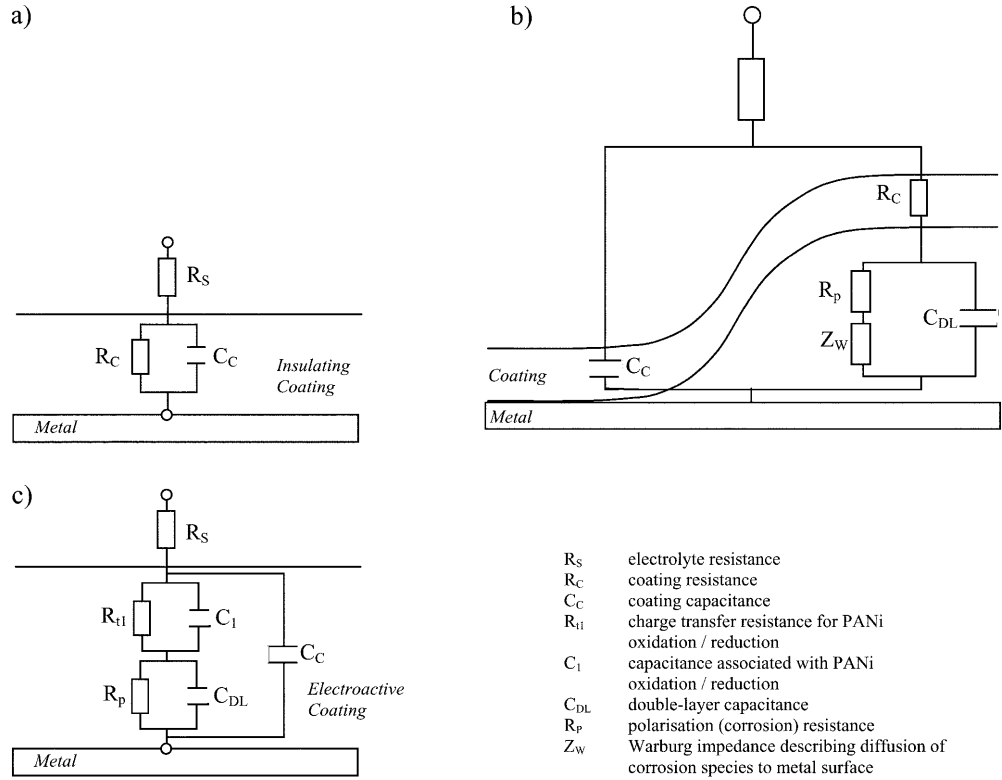
a)

b)

c)

R_S	electrolyte resistance
R_C	coating resistance
C_C	coating capacitance
R_{t1}	charge transfer resistance for PANi oxidation / reduction
C_1	capacitance associated with PANi oxidation / reduction
C_{DL}	double-layer capacitance
R_P	polarisation (corrosion) resistance
Z_W	Warburg impedance describing diffusion of corrosion species to metal surface

Fig. 7 Equivalent circuit representing a PANi primer with an insulating topcoat (after [39])

R_S	electrolyte resistance
R_C	coating resistance
C_C	coating capacitance
C_{DL}	double-layer capacitance
R_P	polarisation (corrosion) resistance
Z_W	Warburg impedance describing diffusion of corrosion species to metal surface
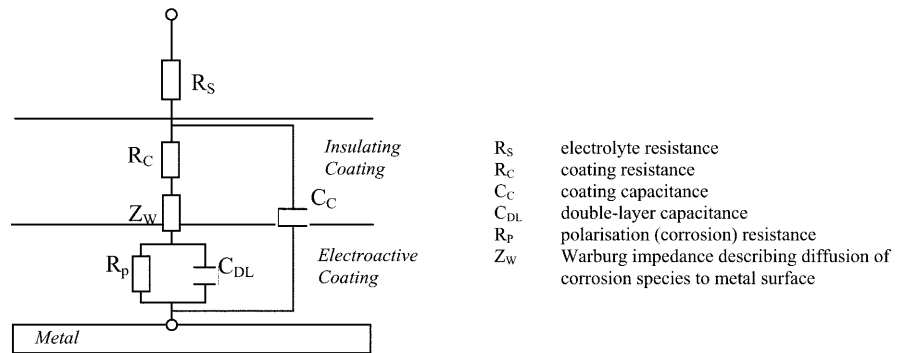
charge transfer reaction (charge transfer resistance and double layer capacitance in parallel) and this reaction was considered to involve the oxidation of the steel by the PANi. The charge transfer resistance was observed to increase with immersion time, which is consistent with a thickening of the oxide layer and a reduction in conductivity of the PANi (ES→LE) due to the redox couple.

In summary, it is clear that the EC modeling of the corrosion processes provides valuable insight into the probable mechanisms of corrosion protection that occur. However, the variability in the reported models reflects the need for further work in this area. The validity of any model is underpinned by the EIS data used to test the models, and there are clearly considerable variations in the EIS data reported for seemingly similar systems. Further work is needed to clarify this situation.

Polypyrrole coatings

After PANi, polypyrrole is the most studied conducting polymer with respect to corrosion resistance on functional metals, including plain carbon steel (PCS). Unlike PANi, polypyrrole is not readily available in soluble form and most studies on corrosion protection have used electrodeposition techniques to form PPy coatings. The pyrrole monomer is (unlike aniline) a non-carcinogenic compound and the polymer is generally higher in conductivity and has a lower reduction potential than

polyaniline. The different properties and application method of PPy are likely to lead to differences in corrosion protection in comparison to PANi coatings.

Preparation of PPy coatings on steel

Electropolymerization of PPy on steel

PPy can be applied to substrates by the electropolymerization process, either potentiostatically or galvanostatically. The electrodeposition conditions can be optimized to give smooth, adherent coatings on steel and iron. The parameters that have been shown to play a part in PPy film quantity and quality include: electrolyte composition and agitation, monomer concentration, current density, time, temperature, type of solvent, water quantity in the reaction cell, and the type and size of the counterion used.

Schirmeisen and Beck [59] studied galvanostatically coated PPy deposited on iron and other functional metals. The electropolymerization was investigated from various non-aqueous and aqueous electrolytes and they found that iron dissolution occurs under all test conditions, with one exception. It was found that smooth and adherent PPy coatings are produced on iron only from the aqueous nitrate solution. Ferreira et al. [60] overcame the dissolution problem by substrate pretreatment in aqueous 10% HNO_3 prior to electrodeposition. Many other studies, reviewed in the next section, used the partial passivation of the steel surface by nitrate and other species as a means to successfully electrodeposit PPy coatings on steel.

In 1994, Haase and Beck [61] described a method of galvanostatic polymerization of strong adherent N-substituted pyrrole films on iron (and on platinum for comparison). In this study, iron passivation was attained in aqueous oxalic acid or potassium nitrate solutions, and in an organic propylene carbonate matrix. Chronopotentiometry, XPS and SEM techniques were used to identify the formation of an iron(II) oxalate interlayer between the steel and PPy coating.

Recently, De Bruyne et al. [62, 63] electrodeposited PPy of about 800 nm thickness on 6 μm polished steel from aqueous 0.5 M Na_2SO_4 and 0.1 M oxalate $(H_2C_2O_4)$ solutions, and confirmed the advantages of oxalic acid in the electrolyte. Similar results have been obtained by Krstajić et al. [64]. De Bruyne concluded that the iron oxalate intermediate layer developed prior to the electropolymerization step and was primarily responsible for the adherence of the conducting polymer layer. Iroh and Su [65, 66] have also recently shown that the iron oxalate interlayer forms during an "induction period" before polymer deposition occurs. They [66] found that the induction period was evident when electropolymerization was conducted from acidic media; however, no induction period was observed in alkaline electrolytes. Coherent, smooth and adherent films were made from low pH electrolytes using a low applied current density. On the other hand, high current density values in alkaline solution lead to brittle and poorly adherent PPy coatings. These results were further confirmed in a recent paper by Su and Iroh [67].

Casting of soluble PPy

Tallman et al. [68] investigated the corrosion properties of soluble poly(3-octylpyrrole) (POP) coatings (scribed) on cold-rolled steel (Q-panel) in 3% NaCl. This monomer (**IV**) has an octyl chain attached to the 3-position to impart solubility [68, 69].

IV
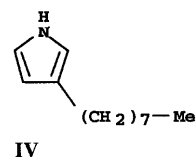
The polymer is galvanostatically synthesized on a Pt working electrode at a current density of 1 mA/cm^2 from a solvent mixture of CCl_4 (80%) containing 0.1 M 3-octylpyrrole monomer, 0.1 M tetrabutylammonium perchlorate and 0.025 M tetrabutylammonium p-toluenesulfonate. The soluble fraction of the polymer is then recovered from the mother liquor and re-dissolved into CCl_4/acetonitrile solvent (50/50) [70]. The final cast polymer coatings were electroactive and conductive (ca. 5×10^{-3} S cm^{-1}) [70]. Tallman et al. [68] then used the scanning vibrating electrode technique (SVET), SEM and energy dispersive X-ray (EDX) analysis to investigate the specimens under consideration.

Mechanisms of corrosion protection

Anodic protection

Galvanic coupling
Beck et al. [71] reported the so-called "auto-undoping" of PPy when coupled to iron in the presence of aqueous electrolytes as the corrosion process occurs through polymeric pores. Krstajić et al. [64] also reported the auto-undoping phenomenon of PPy when coupled to steel in sulfuric acid. The evidence for PPy reduction came from the increase in overall impedance of the system during immersion. The impedance data was modeled by an equivalent circuit that described the corrosion process as occurring through pores in the PPy coating. As described in more detail below, the corrosion rate was found to be determined by the rate of reduction of the PPy coating.

Ennobling effect

Large shifts in E_{corr} of PPy-coated steel compared with the bare steel have been reported [67, 72]. Su and Iroh [67], for example, report very large increases in E_{corr} for electrodeposited PPy on steel. In this case the PPy was deposited from oxalate electrolyte and a shift of nearly $+600$ mV in E_{corr} was observed for the coated steel compared with the bare steel in 1 M NaCl. In contrast, an iron(II) oxalate coating on the steel produced a slight decrease in E_{corr} of ~90 mV. Idla and co-workers [72] reported a shift in E_{corr} of 300–400 mV for PPy-coated steel compared with bare steel.

Reut et al. [73] investigated the effect of surface treatment (acid pickling and polishing) techniques on the corrosion potential. Distinctive differences in E_{corr} values were observed for non-treated and mechanically or chemically treated PCS:

1. Untreated PCS: $E_{corr} = -730$ mV (vs. SCE).
2. Polished PCS: $E_{corr} = -525$ mV.
3. Chemically (HNO$_3$) treated PCS: $E_{corr} = -200$ mV.
4. PPy/pTS on untreated PCS: $E_{corr} = -332$ mV.
5. PPy/pTS on polished PCS: $E_{corr} = -214$ mV.
6. PPy/pTS on chemically treated PCS: $E_{corr} = +120$ mV.

The results show that surface treatments can lead to a significant ennobling of the steel surface. For each pre-treatment, however, it was observed that a further shift of $+200$–400 mV in E_{corr} was produced by electrodeposting a PPy/pTS coating on to the pretreated steel. These workers also reported that a more adherent and less porous PPy/pTS layer was deposited onto the chemically pretreated steel compared to the untreated PCS.

In contrast, Krstajić et al. [64] reported that PPy coatings cannot provide anodic protection of mild steel in sulfuric acid. These workers report only a short-term enobling effect upon initial immersion. The steady-state E_{corr} value was found to be very similar to the bare steel in the same electrolyte. From this observation it was concluded that the corrosion of PPy-coated steel was dominated by the dissolution of iron at the steel/electrolyte interface at the bottom of pores in the PPy coating.

Passivation

As reported above, there is considerable evidence for the formation of passive layers at the steel/PPy interface during electrochemical polymerization of PPy onto steel surfaces. It is likely that the passive layers also affect the corrosion resistance of the steel.

Studies by Tallman et al. [74] also indicate that passive layers form during initial immersion of PPy-coated steel when the coating was applied from solution. EIS and electrochemical noise (ECN) techniques indicated that the polymer/steel couple undergoes an electron transfer immediately on immersion, as evident from current flow and potential oscillations observed in the ECN experiments. In addition, during the first 5 days of full immersion the electrolyte pH decreased and the charge transfer resistance increased. These observations were interpreted as being consistent with the steel surface being oxidized and the polymer becoming partly reduced.

SVET studied by He et al. [68] show passivation occurring at scratches in the POP-coated steels. It was reported that the defective area always produces an anodic current and that the cathodic current is always distributed uniformly across the conducting polymer surface. Thus, the authors postulate that oxygen reduction (cathodic site) occurs at the POP/electrolyte interface "with electron transfer from the steel to oxygen being mediated by POP". The process drives the corrosion process in the scribed area, which ultimately leads to localized passivation. In addition, the current flow was initially almost zero during an "induction time" before increasing progressively with time to peak at about 5 h (100 mA/cm^2) of full immersion. Afterwards, the current density gradually decreased as the scribe mark became covered with corrosion products. The onset time was longer for POP-coated steel relative to chromated-epoxy specimens, i.e. 3 h versus 40 min.

Idla et al. [75] pursued the study of adhesive PPy films, of about 200 nm thickness, on mild steel using atomic force microscopy (AFM) and XPS. The AFM study of the metal/polymer interface showed areas of different morphology, where polymeric adhesion and disbondment occurs. It was also shown by XPS that large chemical variations occur at the interlayer, i.e. a sulfur-rich layer forms at the interface which is indicative of specific counterion accumulation.

Inhibition

It is also possible that PPy films may act as inhibitors for steel in corrosive environments. Stupnisek-Lisac and Metikos-Hukovic [76] investigated substituted pyrroles for PCS protection during HCl pickling at between 20 and 60 °C. Non-toxic *N*-arylpyrroles having carbaldehyde (-CHO) or amine groups were studied, which can either form condensates (large molecular deposits) or polymerize, in situ, on the PCS surface. The inhibition effect was studied by linear polarization (LP) techniques. Stupnisek-Lisac et al. [76] reported that *N*-arylpyrroles having carbaldehyde groups show the highest inhibition efficiency at 40 °C, while *N*-arylpyrroles having amine groups improve the inhibition effectiveness with increasing temperature between 20 and 60 °C. Furthermore, the *N*-arylpyrrole monomer having one carbaldehyde group is catalyzed by metal ions in situ, and forms large molecules that eventually absorb on the substrate surface. *N*-Aryl-pyrrole monomers having two carbaldehyde groups are said to be more efficient, but only up to 40 °C. At

higher temperatures these large molecules become destabilized with a consequential decrease in inhibition. On the other hand, *N*-arylpyrrole monomers having amine groups substituted in the phenyl ring are better inhibitors because of the compound's polymerization ability [76]. Generally, *N*-arylpyrrole derivatives modified the PCS surface by either molecular condensation or polymerization that subsequently inhibits the metallic dissolution rate.

Other mechanisms

As mentioned above, Krstajić et al. [64] described the corrosion rate of PPy-coated steel as determined by the rate of reduction of the polymer. PPy-oxalate films of 2.5 µm thickness were observed to reduce the corrosion rate by a factor of 20 compared to bare steel in 0.1 M H_2SO_4. EIS and EC modeling indicated that the corrosion occurred in pores in the PPy coating, with the main cathodic reaction being the reduction of PPy (replacing the reduction of H^+ as the main cathodic reaction on bare steel). The total impedance of the system increased during immersion for the first few days and this was interpreted as being caused by the slow reduction of the PPy film around the pores. With the polymer reduction, the diffusion of ions through the polymer becomes more difficult, so the rate of further polymer reduction decreases. As a consequence, according to the model of Krstajić et al., the corrosion rate also decreases.

Conclusions

Experimental evidence clearly demonstrates the ability of either PANi or PPy coatings to provide corrosion protection to steel. In both cases the mechanism of corrosion protection is yet to be fully elucidated. This task is complicated by the fact that the mechanism most likely varies as a function of corrosion conditions. Clearly, the polymer coating offers some degree of barrier protection, although conventional barrier polymers (e.g. epoxy, polyester, polyurethane) are commonly used as topcoats with conducting polymer primers. It is the action of the conducting polymer when the barrier is breached that is the most intriguing and potentially useful aspect of their ability to slow metal corrosion. The experimental evidence shows that the conducting polymer galvanically coupled to the metal causes an anodic shift in the corrosion potential and some argue that this shift causes passivation and anodic protection. This mechanism is supported by studies of stable oxide formation on the metal surface after contact with the conducting polymer. Less certain, however, is the role of the counterion release and local pH changes on pinhole protection. Indeed, it is also argued that the conducting polymer reduces the likelihood of large increases in pH

at the polymer/metal interface and so stabilizes the coating against cathodic disbondment.

There is need for further studies to clarify these mechanisms of corrosion protection by conducting polymers. Some reports have indicated that the protection offered by conducting polymers is only relatively short term. Tallman [58], for example, has found that PANi coatings on steel (without topcoats) break down after ~50 days immersion, after which rapid substrate corrosion occurs. Understanding the changes occurring in the polymer and at the polymer/metal interface may allow greater control over the corrosion processes and increase the stability of the polymer to more practically acceptable terms (5+ years).

Furthermore, the properties and characteristics of the polymer coating are determined by processing and coating technologies that are yet to be optimized. It is in this area that there is significant room for improvement. Production of polymers with a well-defined molecular weight or dispersions with a well-defined particle size remains a challenge. Production of such solutions or dispersions in a form compatible with conventional spraying or casting techniques and providing a coating compatible with subsequent layers is also an issue.

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