J Solid State Electrochem (2002) 6: 73–84
DOI 10.1007/s100080100212

REVIEW

Dennis E. Tallman · Geoff Spinks · Anton Dominis
Gordon G. Wallace

Electroactive conducting polymers for corrosion control

Part 1. General introduction and a review of non-ferrous metals

Received: 29 January 2001 / Accepted: 6 March 2001 / Published online: 17 July 2001

Abstract There is an intensive effort underway to develop new corrosion control coatings for structural metals. In part, this effort has been motivated by the desire to replace chromium(VI)-containing coatings currently used for corrosion control of iron and aluminum alloys. Cr(VI) has been shown to be hazardous to the environmental and to human health, and its use in many countries will be sharply curtailed in the coming years. Electroactive conducting polymers (ECPs) represent a class of interesting materials currently being explored for use in corrosion control coating systems, possibly as a replacement for Cr(VI)-based coatings. The electroactivity and the electronic conductivity (or semiconductivity) of ECPs set them apart from traditional organic coatings. As with chromate, interesting and potentially beneficial interactions of ECPs with active metal alloys such as steel and aluminum are anticipated, with concomitant alteration of their corrosion behavior. A review of this active research area will be presented in two parts. Here in Part 1, a general introduction to the topic of corrosion control by ECPs will be presented, including an overview of corrosion and its control by traditional methods, an introduction to ECPs and their properties, and a discussion of the processing issues surrounding the use of ECPs as coatings. Part 1 also includes a review of the literature on the use of ECPs as coatings (or components of coatings) on non-ferrous active metals, principally aluminum and aluminum alloys, although some work on zinc, copper, silver, titanium and silicon will also be described. In Part 2 of this review (to be published in the next issue of this journal), the rather extensive literature on the use of ECPs for the corrosion control of ferrous alloys (steels) will be reviewed.

Keywords Electroactive conducting polymers · Corrosion control · Aluminum · Aluminum alloys · Non-ferrous metals

Abbreviations *CP*: cyclic polarization · *EB*: emeraldine base · *ECP*: electroactive conducting polymer · *EIS*: electrochemical impedance spectroscopy · *ENM*: electrochemical noise method · ES: emeraldine salt · *PET*: poly(ethylene terephthalate) · *PODP*: poly(3-octadecylpyrrole) · *POP*: poly(3-octylpyrrole) · *SEM*: scanning electron microscopy · *SPAN*: sulfonated polyaniline · · *SVET*: scanning vibrating electrode technique · *XPS*: X-ray photoelectron spectroscopy

Introduction

Corrosion and its control

The corrosion of structural metals, such as the alloys of iron and aluminum, has been described as extractive metallurgy in reverse [1], suggestive of the rather large free energy change which drives the conversion of the metal (in elemental form in the alloy) back to its native oxidized state. It is estimated that corrosion and its consequences cost developed nations between 3% and 5% of their gross domestic product [2, 3, 4], amounting to over 100 billion dollars a year in the United States alone. Since nothing can be done to alter the thermodynamics of the corrosion process, corrosion control strategies focus on controlling the dynamics (slowing the kinetics and/or altering the mechanism) of the process. It is also important to recognize that corrosion involves at least one oxidation reaction (usually the metal undergoing corrosion) and at least one reduction reaction (typically involving dioxygen, hydrogen ion and/or water, depending on conditions). These reactions occur at the metal surface, forming what is commonly referred to

---

D.E. Tallman (✉)
Department of Chemistry,
North Dakota State University, Fargo, ND 58105-5516, USA
E-mail: dennis_tallman@ndsu.nodak.edu

G. Spinks · A. Dominis · G.G. Wallace
Intelligent Polymers Research Institute,
University of Wollongong, Northfields Avenue,
NSW 2500, Australia

as a corrosion cell. Importantly, reducing the rate of either (or both) of these processes reduces the rate of corrosion.

A variety of strategies have been developed to control the dynamics of corrosion and are discussed in detail elsewhere [1]. For example, cathodic protection (employing either a sacrificial anode or an external power supply) may be used to decrease the potential of the metal, slowing its rate of oxidation. Conversely, anodic protection may be employed to maintain a protective passive (oxide) layer on the metal surface and/or reduce the rate of the reduction process. Anodic and/or cathodic inhibitors, usually small organic molecules, may be used and function by adsorbing on the metal surface so as to impede either oxidation of the metal (anodic inhibitor) or the reduction reaction (cathodic inhibitor).

At the present time, the most common corrosion control strategy involves application of one or more organic coatings to the metal. An active corrosion cell requires the presence of an oxidant at the metal surface as well as a mechanism for ion movement along the surface between the anodic and cathodic sites of the corrosion cell (to maintain charge balance). Such ion movement at the interface usually occurs within a thin layer of electrolyte that forms on the metal surface. Coatings reduce the rate of corrosion by reducing the rate of access of these essential ingredients (e.g., dioxygen, water and ions such as H^+) to the interface. The coating also serves to increase the resistance of ion movement at the interface (i.e., the ohmic polarization of the corrosion cell), which also contributes to a reduction in corrosion rate. Eventually, water, dioxygen and ions from the environment penetrate the coating and reach the metal interface. Defects in the coating (natural or accidentally introduced) expedite this process. Thus, a coating system approach is typically used whereby a primer coating is applied to the metal followed by a topcoat having the desirable barrier and perhaps appearance properties. The primer coating is chosen for good adhesion to the metal and often contains active ingredients to further reduce the corrosion rate once the barrier has been breached. It is this latter function for which electroactive conducting polymers (ECPs) may have an important role.

The active ingredients in primer coatings vary, but common ones include heavy metals such as the zinc-containing primers for corrosion control of steel and the chromate-containing primers for corrosion control of aluminum alloys and galvanized steel. Furthermore, the surface of aluminum alloys is often pretreated with a chromate-containing solution to develop a rather thick oxide layer (or conversion coating) prior to application of the primer. The desire to eliminate heavy metals in general, and chromium in particular, from coating systems arises from environmental and health concerns [5]. Some of the newer alternative coating systems being explored include low-temperature cationic plasma deposition, sol-gel and ceramer coatings, various new inorganic and organic inhibitors and ECPs [5, 6].

Electroactive conducting polymers

The ECPs to be considered in this review are conjugated polymers that exhibit electroactivity, display some level of conductivity or semiconductivity, and are partially oxidized (p-doped) and, thus, contain counter anions for overall charge neutrality. Such polymers can be classified into three general types, based on the nature of the p-doping (oxidation) process:

1. Type 1: protonic/electronic doping involving both proton and anion incorporation into the polymer (e.g., polyaniline, Fig. 1).
2. Type 2: electronic doping with anion incorporation (e.g., polypyrrole or polythiophene, Fig. 2).
3. Type 3: electronic doping with cation expulsion, either from a covalently attached acid group (also called self-doped, e.g., sulfonated polyaniline, Fig. 3) or from a sufficiently large, physically entrapped, immobile acid (or salt, e.g., a polyelectrolyte).

We emphasize that this classification is based on the nature of the principal doping process during polymer synthesis. Upon redox cycling, both cation and anion movement can be observed with all three types of ECPs. All three types of polymers have been and continue to be investigated for use in corrosion control coatings, either directly as a primer coating or surface treatment, or as a component blended with more conventional coatings. It should also be noted that the partially oxidized and conducting emeraldine salt of polyaniline (Type 1 polymer) can be dedoped using a base and without concomitant electron transfer to yield the non-conducting but still oxidized emeraldine base form (Fig. 1b). This form of polyaniline has also been investigated for its corrosion control properties.

As noted above, ECPs are redox-active materials, with equilibrium potentials that are positive relative to those of iron and aluminum, as is the potential of chromate (see Table 1). Thus, as with chromate, interesting and potentially beneficial interactions of ECPs with active metal alloys such as steel and aluminum are anticipated, with concomitant alteration of their corrosion behavior. The potentials of Table 1 suggest that the mechanism is likely to involve anodic protection. However, other factors may also be important such as metal complexation, perhaps with concomitant interface stabilization, and counterion release, where the counterion might be selected for its known corrosion inhibition.

ECP coating formation

Both chemical and electrochemical oxidation have been used to form ECPs [7]. One of the challenges in developing conducting polymer coatings has been to overcome the difficulty in processing these materials. The general lack of solubility and fusibility make the formation of coatings on active metals difficult.

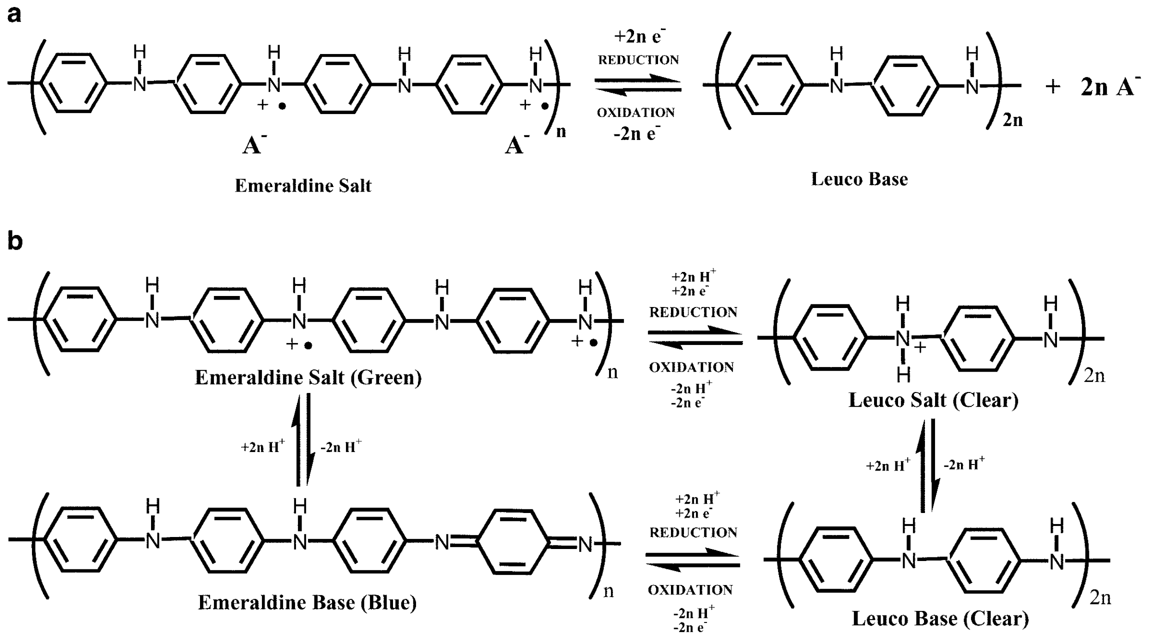


Fig. 1 **a** Type 1 ECP: polyaniline redox scheme showing anion (A^-) expulsion upon reduction. **b** Polyaniline square scheme showing the proton and electron transfers (the anions associated with the salt forms are omitted for clarity). The fully oxidized form (pernigraniline) is not shown

The most convenient way to produce ECP coatings on conductive metal substrates is via electrochemical polymerization according to Scheme 1 or Scheme 2. With such an approach the metal to be coated is used as the anode in an electrolytic bath containing monomer, supporting electrolyte (K^+A^-), solvent and a counter/reference electrode system. The reaction is initiated by application of a potential or constant current sufficient to induce polymerization, while being careful to avoid corrosion of the metal. However, oxide layer formation on the metal during electropolymerization and deposition may be useful in promoting adhesion. The electrochemical method provides accurate control over the rate of polymerization and localizes the reaction on the surface to be coated. However, it suffers from limited speed of processing, cost of production and the fact that the metal surface may be altered by exposure to the positive potentials required to induce the polymerization.

Alternative coating procedures involve the use of preformed polymers, but simple polypyrroles, polythiophenes and polyanilines are neither soluble in most common solvents nor are they fusible, making thermal processing impossible. Consequently, a number of approaches used to render ECPs more processable have been investigated.

To render polypyrroles more soluble, alkyl or alkylsulfonate groups have been attached to the pyrrole monomer prior to polymerization [8, 9]. This results in markedly enhanced solubility in organic or aqueous media, respectively. Electrochemical methods [10] can be used to produce alkylated polypyrroles with high solubility (400 g L^{-1}) in organic solvents and reasonable conductivity (1–30 S cm^{-1}).

Both electrochemical and chemical oxidation have been used to produce 3-substituted alkylsulfonated pyrroles [11]. Conductivities in the range

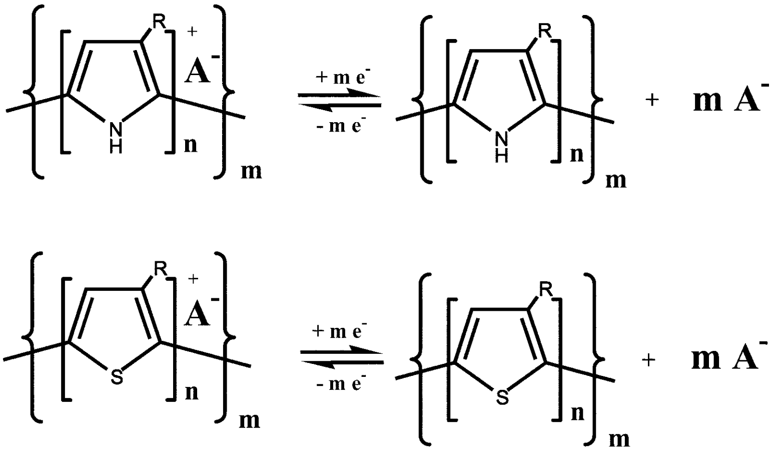


Fig. 2 Type 2 ECP: polypyrrole (*top*, R = H) and polythiophene (*bottom*, R = H) redox scheme showing anion (A^-) expulsion upon reduction. Typically, $n = 2$–4, symbolizing a positive charge for every 2–4 monomer units

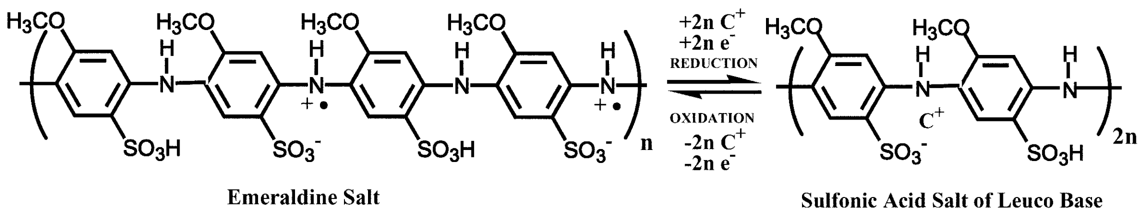
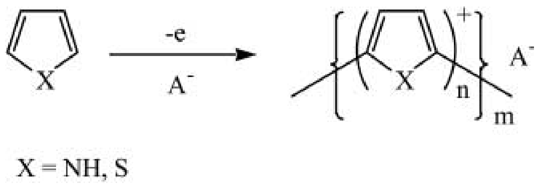


Fig. 3 Type 3 ECP: a sulfonated (or self-doped) polyaniline redox scheme showing cation (C^+) incorporation upon reduction

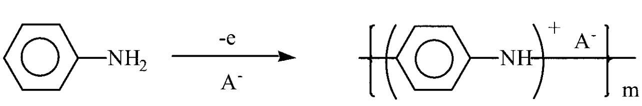
Table 1 Reduction potentials for a variety of redox couples important in corrosion, including active metals, chromate and electroactive conducting polymers

Redox couple	Reduction potential (vs. SHE at pH 7)
Mg/Mg^{2+}	–2.36
Al/Al_2O_3	–1.96
Zn/Zn^{2+}	–0.76
Fe/Fe^{2+}	–0.62
H_2/H_2O	–0.41
H_2O/O_2	+0.82
CrO_4^{2-}/Cr_2O_3	+0.42
Polypyrrole	–0.1 to +0.3[a]
Polyaniline	+0.4 to +1.0[a]
Polythiophene	+0.8 to +1.2[a]

[a] For the ECPs, an approximate range of electroactivity is provided, the actual reduction potentials depending on the dopant (counterion) and doping level, the electrolyte and other experimental variables. These potential ranges can be further modified (through electronic or steric effects) by placing appropriate substituents on the polymer ring system



Scheme 1



Scheme 2

0.001–0.500 S cm^{-1} were obtained, with lower conductivity products obtained from chemical polymerization. Others [12, 13] have prepared homopolymers and copolymers of polypyrroles with alkylsulfonate groups attached via the N-group. This N-group substitution decreases the polymers' inherent conductivity.

Polythiophenes can also be rendered either organic solvent soluble [14] or water soluble [15] using these derivatization approaches. The incorporation of ionizable sulfonic acid groups onto the aniline rings or the aniline nitrogen atom, either pre- or post-polymerization, has provided routes to self-doped, water-soluble polyanilines ([16, 17, 18] and references cited therein). Water-soluble sulfonated polyanilines have also been recently synthesized under high pressure to obtain products with higher molecular weight [19]. The polymerization of aniline monomers containing alkyl or alkoxy ring substituents also leads to polymers with improved solubility in organic solvents [20, 21].

Formation of colloidal dispersions is an attractive alternative route to solution processing in water, as this allows for post-synthesis handling while retaining reasonable conductivity. It has been shown that addition of ECP colloids to a water-based latex paint increased conductivity and electroactivity as expected, but also increased paint adhesion [22].

Conducting polymer colloids can be produced chemically [23] or electrochemically [15] by oxidation of monomer in the presence of a steric stabilizer. Colloids produced electrochemically are formed by impeding the polymer deposition on the electrode surface using a steric stabilizer in solution. This technique allows a wide range of dopants to be incorporated into the polymer to give different properties. A range of dopants have been incorporated into ECPs for corrosion inhibition studies [24].

Polypyrrole and polyaniline colloids can be successfully prepared via chemical oxidation using fine colloidal silica as a dispersant [25]. The colloids have a low percentage of conducting polymer but the composites still have reasonable conductivity, indicating interconnectivity. Silica-stabilized colloidal polyanilines have also been produced using the electrohydrodynamic route [26]. Such nanocomposites may have excellent properties when mixed with other polymers or paint formulations for corrosion protection. Core shell particles have been produced both chemically [27] and electrochemically [28]. Using polyurethane as the core enables dispersions with excellent film-forming capabilities to be produced. Most of these approaches are yet to be fully exploited in the area of corrosion protection.

For organic solvent solubility, an alternative approach to solubilizing polyanilines and polypyrroles is the use of surfactant-like dopant anions. With polypyrrole this has recently been achieved via oxidation of the pyrrole monomer with ammonium persulfate in the presence of dodecylbenzenesulfonate [29, 30]. Similarly, the conducting emeraldine salt form of polyaniline can be readily solubilized in a range of organic solvents via the use of camphorsulfonic acid or dodecylbenzenesulfonic acid as the dopant [31, 32].

An alternative approach that provides materials with film-forming/coating capabilities is the formation of polymer blends. This has been shown to be feasible for polyanilines [33] and polypyrroles [34].

Other relevant reviews

Finally, we mention here previous reviews and other relevant papers with extensive bibliographies. General reviews have recently appeared by Jeffcoate et al. [35] on advanced environmentally compliant coatings (43 references) and by Cohen [5] (82 references) and by Twite and Bierwagen [6] (71 references) on Cr replacements for protecting aluminum alloys. Beck et al. [36] has written a review on the electrodeposition of polypyrrole from aqueous and nonaqueous electrolytes on commodity metals (31 references, mainly on the author's work). McAndrew [37] reviewed the use of ECPs (especially polyaniline) in corrosion-resistant coatings (29 references). Sitaram et al. [38] reviewed the literature on the use of polyaniline and other conducting polymers as corrosion inhibitors (26 references). Yagova et al. [39] reviewed papers dealing with protective polyaniline coatings on steels (25 references) and Zarras et al. [40] reviewed research on conducting polymers as corrosion-protective coatings (62 references). Finally, Lu et al. [41] provided a tutorial and review on corrosion inhibition of metals by conductive polymers as well as original results from their laboratory (69 references).

In the sections that follow, the literature on the use of ECPs for corrosion control of non-ferrous metals will be reviewed. Part 2 (to appear in the next issue of this journal) will review the rather extensive literature on the corrosion control of ferrous metals by ECPs.

Aluminum and aluminum alloys

Aluminum alloys are important structural metals, particularly in the aerospace industry. Pure aluminum metal (without alloying elements) is rather corrosion resistant, a result of a passive film that forms on the metal surface. However, pure aluminum metal does not posses adequate strength for most aerospace applications and must be alloyed with other metals, notably copper, magnesium, manganese, silicon, iron, zinc and other minor constituents. These alloys are classified by a numbering system that reflects both the chemical composition and the heat treatment (tempering) of the alloy [42]. For example, Al 2024-T3 and Al 7075-T6 are important alloys used in the fabrication of aircraft and have been the most extensively studied Al alloys for research on corrosion control by ECPs. The high strength of these alloys is achieved in large part by the introduction of Cu, at levels up to 5% by weight in Al 2024-T3. However, the introduction of Cu and other alloying elements leads to the formation of Cu-rich intermetallic phases (particles) heterogeneously distributed throughout the alloy [42, 43]. For example, the S phase (Al_2CuMg) particle is the most abundant type of particle in Al 2024-T3, comprising approximately 61% by number of all second-phase particles and 2.7% of the alloy surface area [44]. It is such Cu-rich intermetallic phases that result in the establishment of local galvanic cells on the alloy surface, resulting in localized corrosion attack [43, 44, 45, 46]. The Al-Cu-Mg-X alloys (the Al 2XXX series) are among the most corrosion-prone of the aluminum alloys in common use. The microstructure of these alloys will undoubtedly play an important role in understanding corrosion control of these alloys by ECPs.

Compared to the number of studies on steel (covered in Part 2 of this review), there have been far fewer studies of the corrosion control of Al alloys by ECPs. Most of this work has involved either polyaniline or polypyrrole. Thus, the following discussion is subdivided into three subsections: polyaniline, polypyrrole and other ECPs.

Polyaniline

Several forms of polyaniline have been explored for the corrosion protection of aluminum alloys, including the emeraldine salt (ES) form on Al 2024-T3 [47, 48], the emeraldine base (EB) form on Al 3003 and on Al 2024-T3 [49], molecular complex forms (ES form with polyelectrolyte counterions, a Type 3 ECP) on Al 7075 [50, 51, 52, 53, 54] and a self-doped sulfonated form (also a Type 3 ECP; see Fig. 3) on Al 3003 and on Al 2024-T3 [49]. The coatings in these studies were all cast from a solution of the ECP. ECP coatings on Al 2024, 6061 and 7075 alloys have also been formed using polyaniline blended with other polymers chosen for their adhesion [55]. Finally, simultaneous aluminum anodization and polyaniline deposition on Al 5657 has been described, leading to a composite polyaniline-aluminum oxide film [56]. Each of these approaches will be considered in this section.

The earliest work involving polyaniline on aluminum alloy appears to be by Racicot and co-workers [50, 51, 52, 53, 54, 57]. A molecular complex of polyaniline with a polyanion was synthesized by a template-guided synthesis, yielding a "double-strand" polyaniline. The polyanion can be selected so as to impart desirable properties to the coating material, such as increased solubility (or dispersibility) in common solvents and improved adhesion to the substrate and/or topcoat. Electrostatics and molecular entanglement holds the complex together and, consequently, there is little tendency for the polyaniline to lose dopant and conductivity. The polyanion was typically a vinyl copolymer containing both carboxylic acid groups and alkyl side groups to facilitate processing and adhesion. In one report [50] the specific polyanion was not revealed, but simply referred to as PolyE. In a subsequent report [52] the polyanion was the copolymer poly(methyl acrylate-*co*-acrylic acid). In both reports the polyaniline material was dissolved in ethyl acetate and sprayed onto Al 7075 alloy panels that had been polished with 600 grit emery paper, degreased and rinsed with de-ionized water. Coating film thicknesses were not specified but were described as thin. No topcoats were employed in these studies.

Potentiodynamic scans of the polyaniline/PolyE-coated sample [50] revealed a corrosion current two orders of magnitude lower than that of an uncoated but anodized Al specimen. A scribe made in a polyaniline/PolyE coating remained corrosion free after 1-week immersion in 0.5 M NaCl solution. The polyaniline/poly(methyl acrylate-*co*-acrylic acid) coating was investigated by salt-spray and also by immersion in either 0.5 M NaCl or 0.5 M NaCl at pH 3.6, using electrochemical impedance spectroscopy (EIS) to assess the immersion performance [52]. Comparisons were made with Al alloy treated with Alodine-600 (a chromate conversion coating). In each case the polyaniline coating performed as well or better than the Alodine treatment. The authors suggested formation of an oxide or oxide-like interfacial layer between the conducting polymer and the alloy surface, a consequence of anticipated oxidative interactions between the ECP and the alloy (Table 1). Modeling of the EIS results reveals a third time constant consistent with a third interface between the polymer coating and the alloy's surface, and scanning electron microscopy (SEM) of the alloy surface after removal of the coating reveals a dense and smooth oxide-type surface morphology [53].

Epstein and co-workers [49] investigated the corrosion protection abilities of polyaniline in the EB form (Fig. 1b) and also of a self-doped sulfonated polyaniline (SPAN, Fig. 3) on aluminum and on the aluminum alloys 3003 and 2024-T3. The EB film (ca. 20 μm thick) was solvent cast on Al 3003 coupons which were then exposed to a 0.1 M HCl bath at 80 °C for 2 h. In a separate experiment, aluminum films (> 100 nm) were evaporated onto EB films (formed by solvent-casting onto glass) and then exposed to HCl vapors. In each of these experiments, X-ray photoelectron spectroscopy (XPS) was used to examine the backside of the metal (the side opposite to the coated side). A reduction in the oxidized Al 2p peak (relative to the metallic Al 2p peak) for both types of samples was interpreted as evidence of corrosion protection. These results suggest that the EB film, an oxidized though non-conductive form of polyaniline, exhibits a throwing power capable of modifying the corrosion behavior of the metal at uncoated surfaces somewhat distant from the polymer film.

Samples of either EB- or SPAN-coated Al 2024-T3 (a copper-rich alloy) were immersed in 0.1 M NaCl for either 10 or 66 hours [49]. Visual inspection, potentiodynamic scans and XPS studies all revealed less corrosion of the coated samples compared to the uncoated materials. Significantly, the XPS studies also showed a much-reduced copper concentration in the top several hundred angstroms of the alloy. The authors proposed a model whereby the EB or SPAN dissolved away the Cu-containing corrosion products, thereby eliminating the galvanic couple between copper and aluminum and reducing the corrosion rate.

The fundamental interactions of polyaniline with Al 2024-T3 and Al 7075-T6 alloys were investigated by Tallman and co-workers [47, 48]. EIS and the electrochemical noise method (ENM) were used to probe behavior of these coated alloys under immersion in dilute Harrison solution [0.35% $(NH_4)_2SO_4$, 0.05% NaCl]. The counterion was dinonylnaphthalenesulfonic acid. During the first few days of immersion of the coated alloys (without topcoat), both EIS and ENM indicated strong metal-polymer interactions, characterized by a continuous increase in a charge transfer resistance and a concomitant decrease in the immersion solution pH. An active metal was required for the interaction since no such changes were observed when the Al alloy was replaced by platinum. Without a topcoat, the polyaniline coating on each alloy failed after ca. 20–25 days immersion. Various polyaniline-coated metals (steel, Al 7075-T6 clad with an aluminum layer clad to the alloy surface, and platinum) all exhibited the same open-circuit potential of ca. 0.2 V vs. SCE, indicating that the ECP controlled the open-circuit potential and ennobled each of the active metals. A mechanism consistent with these observations was proposed involving oxidation of the alloy surface accompanied by reduction and dedoping of the ECP. Without a topcoat, this process continued to coating failure.

With an epoxy topcoat and under immersion in dilute Harrison solution, polyaniline-coated Al 2024-T3 exhibited improved corrosion protection compared to an epoxy topcoat alone, although the performance was not as good as with an Alodine 1200 (chromate conversion coating)-treated alloy with epoxy topcoat. Furthermore, the polyaniline-coated samples exhibited an interesting behavior in the low-frequency region of the impedance spectrum upon immersion. In the early stages of immersion, the ECP appeared to lower the impedance of the coating system by at least an order of magnitude compared to either the epoxy alone or the Alodine-epoxy samples, this in spite of the higher coating thickness of the ECP-coated sample. Since both ions and electrons can move through ECP coatings, it was suggested that the ECP lowers the interfacial impedance by providing a mechanism for facile charge transfer between the epoxy coating (where conductance is by ions) and the metal (where conductance is by electrons). Upon prolonged immersion, the ECP-coated samples showed an increase in the low-frequency impedance. Such behavior generally is not seen with inert barrier coatings and was attributed to the redox-active nature of the ECP coating and an interaction between the polyaniline and the Al alloy, resulting in a higher impedance at the alloy/ECP interface [48]. Similar immersion behavior with other ECPs on Al alloy has been observed [58].

Polyaniline-polymer blends were investigated by Lu and Elsenbaumer [55]. In particular, blends of polyaniline with poly(ethylene terephthalate) (PET) and an unspecified binder were formulated by the authors and coatings were applied to 2024, 6061 and 7075 aluminum alloys by hot dip or spray. They also investigated a commercially available polyaniline coating, Ormecon's Corrpassiv. Pitting corrosion was then investigated in 3.5% NaCl using ENM, EIS and cyclic polarization (CP) techniques. Although details are sketchy [55], it appears the polyaniline-based coatings were not as effective at reducing pitting corrosion on Al 2024 as a polypyrrole coating (see next section).

Finally, we note the direct electrochemical deposition of polyaniline onto 5657 aluminum alloy described by Runge-Marchese and McNallan [56]. The polyaniline deposited simultaneously with aluminum anodization, yielding films that exhibited uniform and continuous dual-phase structures, with concomitant sulfonation of the polyaniline during the process in the anodizing electrolyte of 2 M H_2SO_4. It was suggested that a non-protonated aluminum salt of polyaniline was formed, which resulted in bonding of the polymer to the pores of the oxide structure. This might explain the absence of the dark-green color of these films that is characteristic of protonated polyaniline. The adhesion of the film was comparable to and the corrosion resistance superior to the sealed oxide films obtained from conventional two- or three-step anodization processes. The corrosion resistance of the composite polyaniline-aluminum oxide film (500 h exposure to 5% salt spray at 35 °C) was attributed to the efficient sealing of the oxide pore structure by the polyaniline-aluminum reaction product. An active role of the polyaniline in maintaining the composite oxide layer through redox interaction was not considered. A similar approach to producing conducting polymer-aluminum oxide composite coatings on aluminum has been suggested by Kinlen and co-workers [59]. For completeness, we also mention the deposition of polybithiophene into porous silicon, forming similar composite oxide structures [60].

Polypyrrole

There have been far fewer reports on the use of polypyrrole-based coatings for the corrosion control of aluminum. The work of Lu and Elsenbaumer [55], mentioned in the previous section, examined the pitting behavior of metals protected by polyaniline- and polypyrrole-based polymer blends. The polypyrrole coating investigated was Conquest (DSM, The Netherlands), a polypyrrole dispersion in polyurethane. Primer coatings (no topcoat) were cast on Al 2024-T3 and a hole drilled through the coating to expose the metal. The samples were immersed in 3.5% NaCl and the current was monitored using electrochemical noise instrumentation. A bare alloy sample showed a significant current increase, indicating pitting corrosion after ca. 1.5 h immersion. The polypyrrole-coated alloy showed no signs of pitting corrosion (no current increase) throughout the duration of the experiment (5 h). As noted in the previous section, the polypyrrole coating appeared to be more effective at suppressing pitting corrosion within the defect than polyaniline-based coatings [55].

A recent report by He and co-workers [61] describes use of a scanning vibrating electrode technique (SVET) to probe the interactions between aluminum 2024-T3 alloy and poly(3-octylpyrrole) (POP). A 3 μm thick coating of POP was solvent-cast onto the metal substrate, a defect was introduced into the coating and the current density above the defect and above the coating was measured by the SVET as a function of immersion time in dilute Harrison solution. With an epoxy-coated control sample, current flow was observed immediately upon immersion, with both anodic and cathodic currents confined to the defect area. With the POP-coated sample, there was a significant delay of over 20 h before any current flow was detected. This delay was attributed to the formation and/or stabilization of a passive layer in the defect by the ECP. This result is in agreement with the observations of Lu and Elsenbaumer [55]. After the delay period, current flow was observed, but only reduction current was observed within the defect. The oxidation reaction was always localized on a coated region of the metal substrate. Further analysis attributed the oxidation current to metal oxidation (pitting) at Cu-rich regions of the alloy beneath the POP coating. Further experiments were reported to be in progress to identify the metal(s) being removed and the role of POP in their removal.

The above experiments involving POP were performed without a topcoat. In a separate study conducted by Gelling et al. [58], long-term immersion of samples to which a polyurethane topcoat was applied on top of the POP-coated alloy revealed excellent long-term protection (no defect introduced in these experiments). Six such samples under continuous immersion in dilute Harrison solution have maintained high impedance and have shown no signs of failure after approximately 2.5 years immersion. By comparison, six control samples in which a chromated-epoxy primer was substituted for the POP have all shown signs of failure. In similar experiments, a poly(3-octadecylpyrrole) (PODP) coating also exhibited good corrosion protection, although its performance was inferior to that of POP. Although both POP and PODP exhibited good adhesion to the alloy surface, the cohesion of the PODP coating was inferior to that of the POP (no attempt at cross-linking was employed in either case). It was suggested that the difference in corrosion protection was due in part to this difference in cohesion.

Beck and co-workers [36, 62, 63, 64] have studied the electrochemical deposition of polypyrrole directly onto various commodity metals including aluminum. Nearly pure aluminum metal (99.5%) was used in these experiments and well-adhering homogeneous films could be obtained in non-aqueous solvents (acetonitrile and methanol) containing small amounts of water and with certain organic electrolytes, e.g. NBu_4BF_4 [62].

Perhaps of more practical interest was the demonstration that such films could also be obtained in aqueous electrolytes containing 0.1–0.8 M oxalic acid (known for producing a porous oxide layer on aluminum). In this case, pre-treatment of the metal by either diamond paste polishing or by anodic activation into the pitting region was an essential step prior to electrodeposition. It was suggested that overoxidized polypyrrole filled the Al_2O_3 pore structure (a composite dielectric) that was sandwiched between the aluminum substrate and a conducting polypyrrole overlayer. Corrosion protection of the polypyrrole coating was not assessed in these studies.

In a more recent report, Naoi and co-workers [65] suggest that surfactant sulfonates such as sodium *n*-dodecylbenzenesulfonate lead to a bilayered Al_2O_3/polypyrrole formation with high current efficiency and suppression of the usual concomitant dissolution of the aluminum. The surfactant appears to promote an electronically conducting path of polypyrrole within the Al_2O_3 layer that, in turn, leads to simultaneous growth of the Al_2O_3 and polypyrrole films. Here again corrosion protection was not evaluated.

These approaches to the direct electrochemical deposition of ECPs on active metals show promise for developing strongly adherent composite Al_2O_3/ECP films. Furthers studies are needed to determine the corrosion protective properties of such films.

Other ECPs on aluminum alloy

There have been only a few reports of the use of other conducting polymers for corrosion control of aluminum. Zarras and co-workers [40, 66, 67, 68, 69] have explored the corrosion inhibition of aluminum alloy by coatings of poly[2,5-bis(*N*-methyl-*N*-alkylamino)phenylenevinylenes]. The butylamino derivative was found to be very effective at reducing pitting corrosion of Type II anodized aluminum T3 plates exposed for 1 month alternately to seawater immersion and air [66]. The pitting potential shifted from ca. – 0.3 V (vs. Ag/AgCl) for an uncoated anodized plate to ca. + 0.5 V for a polymer-coated anodized plate and the maximum corrosion current was ca. 100-fold smaller. The mechanism of corrosion protection was not specifically addressed.

The redox reaction between aluminum and poly(3-methylthiophene) was investigated by Uehara et al. [70] in an effort to improve photovoltaic devices based on these materials. The ECP was grown electrochemically onto a gold electrode and Al was then vacuum-deposited onto the ECP. The corrosion of the aluminum layer was then investigated using a variety of techniques, including visible absorption spectroscopy, ESR spectroscopy, XPS and SEM. When doped with perchlorate ion, the ECP underwent a redox reaction with the Al, resulting in the dedoping of the polymer and corrosion of the Al, leading to the formation of $Al(ClO_4)_3$ salt. Not surprisingly, electrochemically dedoping (i.e., reducing, see Fig. 2) the polymer before vacuum-deposition of the Al was effective in blocking this redox reaction. Since these studies apparently were carried out in the solid state (i.e., immersion was not employed), the results suggest that active metal-ECP interactions may occur prior to significant solvent and ion ingress through the coating. However, humidity and oxygen levels during these experiments were not reported.

Sakmeche and co-workers [71] describe conditions under which homogeneous and adherent coatings of poly(3,4-ethylenedioxythiophene) can be obtained on aluminum metal (as well as on iron and mild steel) by direct electropolymerization. The approach makes use of an aqueous anionic micellar medium of sodium dodecylsulfate in the presence of perchlorate or phthalate ions. For aluminum, 98% faradaic yield was obtained at a current density of 2 mA cm^{-2} and film thicknesses of 0.5–3 μm were obtained. These films exhibited good redox stability (over 50 redox cycles with small losses of electroactivity), but unfortunately had poor adherence to the aluminum surface (in contrast to iron, where excellent adherence was achieved after surface pre-treatment using 10% nitric acid). Attempts to improve adhesion to Al using the procedure described by Huesler and Beck [63, 64] for electropolymerization of polypyrrole on Al were unsuccessful. Hence, corrosion protection on Al was not reported, although significant protection of coated steel surfaces was noted.

Finally, we note that Aeiyach and co-workers [72] report excellent adhesion of polythiophene films that were electrodeposited galvanostatically onto Al metal from dichloromethane containing 0.1 M NBu_4PF_6. XPS measurements at the metal/polymer interface indicated strong bonding interactions between the metal and the carbon and sulfur atoms of thiophene. The conductivity of these films (10^{-4} S cm^{-1}) was lower than typically observed for films deposited onto Pt (10 S cm^{-1}), attributed to a smaller doping level of the films deposited onto Al. Corrosion protection was not reported.

Polythiophenes may be particularly interesting polymers for application to corrosion control coatings. Derivatization of the thiophene monomer is considerably less complicated than derivatization of other ECP monomers (e.g., pyrrole), making a range of substituted polymers readily available [73]. The solubility, conductivity and redox potential of these polymers can be varied over a wide range by appropriate substitution. For example, the redox potential of polythiophenes can be varied by more that a volt, which suggests optimization of the redox potential for the particular active metal of interest. We have begun to investigate these aspects of polythiophenes in our laboratory.

Other non-ferrous metals

Aside from aluminum, there have been only a few reports of ECPs applied to other nonferrous active metals for the purpose of corrosion control. These metals include copper, silver, zinc, titanium and magnesium. In this section we briefly review these studies.

Brusic and co-workers [74, 75] have investigated the use of polyaniline and its derivatives for the corrosion protection of copper and silver, with possible application in the microelectronics industry. Unsubstituted polyanilines in base (undoped) and salt (doped with either HCl or dodecylbenzenesulfonic acid) forms were investigated. Additionally, substituted polyanilines with either ethoxy or propyl groups in the *ortho* position were evaluated, each in either the base or salt forms (with HCl or toluenesulfonic acid dopants). The polymers were spin coated (95–510 nm thickness) onto Cu or Ag foils or onto Cu- or Ag-coated silicon wafers. The substituted polyanilines in the base form showed the best corrosion protection, even superior to the commonly used corrosion inhibitor benzotriazole. The protection was attributed to the complete inhibition of the oxygen reduction reaction. Although metal oxides are present on the surfaces of copper and silver, these oxides do not provide a significant passivation of the metal. Thus, ECPs on these metals are not likely to function by an anodic protection mechanism (as suggested for Fe and Al alloys). Rather, these polymers may function primarily as barrier coatings, in which case the base form of each coating would be the more effective form, as observed. The superior performance of the ethoxy derivative was attributed to the better coverage and better adhesion of this polymer to the metal surface.

Attempts to grow polyaniline films directly on zinc or zinc-nickel alloy from an oxalic acid medium were unsuccessful owing to formation of an insulating passive layer that prevented electropolymerization [76]. More recently, a two-step process has been used to successfully electropolymerize aniline on zinc (and also on mild steel) [77]. First, a 1-µm layer of polypyrrole was deposited galvanostatically at a rather high current density of 10 mA cm^{-2} in the presence of sodium salicylate. Very little dissolution of the substrate occurred during this pre-treatment. In the second step, aniline was polymerized in the presence of tosic acid, the best adhesion with minimum dissolution of the zinc occurring with galvanostatic deposition at current densities of 2 mA cm^{-2} or lower. The polyaniline apparently deposits on top of the polypyrrole, forming a bilayer structure. The adhesion between the polyaniline and polypyrrole was rather poor, as revealed by a tape pull-off test. Nevertheless, the stability of the zinc/polypyrrole/polyaniline samples to continuous potential cycling in 2 M tosic acid was respectable, with only a small loss in electrochemical response after 2 h of cycling (almost no loss of response for mild steel samples). This stability to potential cycling was taken as a measure of the ability of the ECP coatings to protect the underlying substrate from oxidation. It was suggested that part of the anticorrosion properties of ECP coatings is a result of displacing the electroactive interface from the metal/solution to the polymer/solution interface [77].

In one of the earliest reports on the use of ECPs for corrosion control, Deng and co-workers [78] described the use of poly(3-methylthiophene) to poise the potential of titanium at an intermediate value between the active and transpassive potential regions. These authors suggested that through galvanic coupling the potential of a passive metal was maintained at the potential adopted by the polymer film. They demonstrated that oxygen reduction on the surface of the ECP film was necessary to maintain the charge in the film (i.e., its oxidation state) and poise the potential in the passive region for an indefinite period of time. The kinetics of oxygen reduction was improved dramatically by incorporating Pt particles (50–200 nm diameter) on the surface of the poly(3-methylthiophene). For these films with deposited Pt, the steady-state open-circuit potential (ca. 0.55 vs. SCE when not galvanically coupled to titanium) was relatively independent of the ECP film thickness, the Pt loading or the oxygen concentration. When galvanically coupled to titanium, the steady-state open-circuit potential decreased as the area ratio of Ti to ECP increased, dropping to ca. 0.45 V for an area ratio (Ti/ECP) of 11. Even at this ratio the potential of the titanium was poised in the passive region. All measurements in this work were made with physically separated ECP films and titanium electrodes. Attempts to grow the ECP directly on passivated titanium substrates led to discrete patches of deposited polymer. On the other hand, the authors point out that uniform coverage of the substrate surface is unnecessary. In related work, Deng and Smyrl [79] reported the application of electroactive metal hexacyanometalate films on TiO_2/Ti surfaces for corrosion protection where again the galvanic interaction between the film (notably Prussian blue) and the Ti poised the potential of the system in the passive region. Again, catalytic oxygen reduction appeared to be essential to stabilize the potential in the passive region.

Extremely durable and adhesive polypyrrole films have been produced electrochemically on thin chemically pre-oxidized Ti layers [80]. Although this work was directed toward improving ECP adhesion for microactuator development, the approach may be relevant for developing adherent coatings for corrosion control. The films survived over 6000 reduction oxidation cycles without delamination. Several explanations were offered to explain the adhesion, the most likely one being the formation of a composite Ti-oxide/polypyrrole structure analogous to that described earlier for polyaniline deposition on aluminum alloy [56].

Eisazadeh and co-workers [22] described a conductive electroactive paint prepared by mixing polypyrrole colloids (75–200 nm) and an acrylic latex formulation in water. The polypyrrole content ranged from 20 to 80% (w/w) and films were formed on lead, stainless steel, and a steel sheet coated with a zinc-aluminum alloy (Zincalume) by dipping the substrates into a solution of the paint. The films were found to be strongly adherent to all substrates, with maximum adhesion at ca. 50% polypyrrole. All ECP-containing films exhibited greater adhesion than the unmodified acrylic paint, although the mechanism of the enhanced adhesion is unclear. The conductivities of the various paint compositions were similar to those reported for conventional metal or carbon-filled paints and the coatings exhibited electroactivity typical of polypyrrole. A proposed application of these paints was for EMI protection coatings. Corrosion control by these paints was not investigated.

Truong and co-workers [81] reported effective corrosion protection of magnesium by an acrylic paint containing polypyrrole. Polypyrrole powder doped with 5-sulfosalicylic acid was mixed with the acrylic paint, 10 wt% providing optimum performance. Magnesium alloy specimens (98.14% Mg, 1.64% Mn) were coated (120 μm average coating thickness), in some cases a defect was introduced, and the samples were subjected to a variety of measurements including salt spray tests, immersion tests, open-circuit potential measurements, potentiodynamic scans and EIS. Compared to control specimens of the alloy coated with acrylic paint without polypyrrole, the ECP-based paint exhibited significant corrosion protection in salt spray and immersion tests. The control samples completely failed after 200 h in the salt spray chamber, whereas the ECP-containing samples exhibited only minimal corrosion after 1000 h. Under immersion conditions (6 h in 3.5 wt% NaCl), the control samples exhibited thick white deposits of corrosion products and continuous gas evolution at the defect, whereas the ECP-containing sample exhibited a smooth grey deposit in the defect with minimal gas evolution. Anodic potentiodynamic scans indicated a much larger passive region for the ECP-containing samples (ca. 223 mV for the 20 wt% coating, decreasing as the polypyrrole content of the coating decreased) than for the control (ca. 57 mV).

Interestingly, in the work cited immediately above, the EIS of the polypyrrole-containing samples (20 wt%) exhibited significantly lower impedance in the low-frequency region (below 0.1 Hz) than a control sample without polypyrrole but containing 20 wt% TiO_2 to introduce similar porosity in the coating [81]. The presence of the ECP lowered the low-frequency impedance of the coating by approximately two orders of magnitude. As noted earlier in this review, we also have reported two cases where a similar phenomenon has been observed: one in which a polyaniline coating on aluminum alloy with an epoxy topcoat exhibited lower impedance in the low-frequency region than a control sample without the polyaniline layer [48]; and one in which similar behavior was observed with a polypyrrole primer coating and a polyurethane topcoat [58]. With barrier coatings, higher impedance is usually associated with improved corrosion resistance, yet in the three studies referenced above the best corrosion performance was with ECP-containing coatings that exhibited lower impedance than the respective controls. The lower impedance observed by Truong et al. may be explained by the ability of the ECP to provide a more facile mechanism of charge transfer between the electrolyte (an ionic conductor), the binder (an ionic conductor once water and ions have permeated the coating) and the metal (an electronic conductor) [48]. Since the ECP is both an electronic and ionic conductor, ions are readily exchanged at the ECP/binder interface whereas electrons are readily exchanged at the ECP/metal interface, thus facilitating overall charge transfer between electrolyte and metal and lowering the impedance in the low-frequency region.

Summary

ECPs continue to be explored as components of corrosion control coating systems for non-ferrous metals, particularly aluminum and its alloys and other active metals that exhibit passive behavior. The mechanisms by which ECPs function as corrosion control agents are still under investigation, but a few general concepts are beginning to emerge.

First, the oxidized form of an ECP does not make a good barrier coating since the rather high ionic content of the polymer permits easy ingress of water and other ions. Such coatings without a topcoat do not last very long when subjected to immersion or salt spray, but then neither do more traditional (yet highly effective) primer coatings such as chromated-epoxy primer. A possible exception is the EB form of polyaniline (Fig. 1b), which is an oxidized (but nonconducting) form of the polymer (and thus is an oxidant), devoid of ions. As noted in this review, some workers have found the EB form of polyaniline to be an effective corrosion inhibitor. It is not altogether clear whether these observations are a result of the better barrier properties of this form or are due to other properties of the polymer such as its oxidation state, ability to form complexes with metal ions, etc.

Second, the redox state of the ECP is certainly an important factor. In most cases the corrosion control is attributed to the ability of the ECP to maintain the metal in a passive potential regime, a result of the oxidative power of the ECP and also of the galvanic coupling between the metal and the polymer, which in turn is possible because both the metal and the ECP are electronic conductors. This phenomenon would explain the ability of the ECP to protect exposed metal in a defect. The extent to which this might occur in an oxidized but nonconducting polymer such as the EB of polyaniline is not clear. One would not expect significant galvanic coupling in this case, but on the other hand, partial doping of the polymer through interactions with the metal and/or the electrolyte may lead to sufficient conductivity.

Third, the electronic conductivity of these polymer films probably plays an important role, not only in the galvanic coupling mentioned above, but also for providing an interface at which the cathodic reaction can take place, thus maintaining the polymer in an oxidized state. Additionally, the cathodic reaction such as oxygen reduction would be removed from the metal interface, occurring instead at the (outermost) ECP interface. It has been suggested that this latter feature may ameliorate the problem of cathodic disbondment of the coating, associated with the increase in pH that accompanies oxygen reduction [82]. At this stage it is not clear how conducting the ECP need be. High conductivity may not be essential. Semiconductivity may be sufficient.

Finally, there is the issue of adhesion of the ECP to the active metal surface. An advantage of incorporating ECPs into a binder such as epoxy or polyurethane is the good adhesion that such binders provide. On the other hand, such strategies typically lead to less ECP in contact with the metal surface with perhaps a reduction in corrosion protection. Solvent-cast coatings of pure ECP (i.e., no binder) often suffer from low to moderate adhesion and/or cohesion, since cross-linking of these typically low molecular weight polymer molecules does not occur to an appreciable extent. Cross-linking of derivatized ECPs (e.g., the sulfonated polyaniline of Fig. 3) may lead to more robust ECP films. On the other hand, solvent-cast ECP films with only modest adhesion can yield impressive corrosion protection [58]. A promising approach being developed in our laboratory is the direct electrodeposition of ECPs on active metals using an electron transfer catalyst. A polypyrrole film so deposited on Al 2024-T3 exhibits adhesion of ca. 6.2 MPa (900 lb/sq. in.).

Much of the research on corrosion control by ECPs has been conducted on iron and steel, and a rather large body of literature now exists. In Part 2 of this review the use of ECPs for corrosion control of ferrous metals will be examined.

Acknowledgements D.E.T. acknowledges support by the United States Air Force Office of Scientific Research through grant no. F49620-99-1-0283, North Dakota State University. G.G.W. acknowledges the continued support of the Australian Research Council in the form of a Senior Research Fellowship.

References

1. Jones DA (1996) Principles and prevention of corrosion. Prentice Hall, New York
2. Cherry BW (1995) Mater Forum 19:1–7
3. Bennett LH, et al. (1978) Economic effects of metallic corrosion in the United States. National Institutes of Science and Technology, Washington
4. Cederquist SC (1999) Mater Performance 38:26–28
5. Cohen SM (1995) Corrosion 51:71–78
6. Twite RL, Bierwagen GP (1998) Prog Org Coat 33:91–100
7. Wallace GG, Spinks GM, Teasdale PR (1997) Conductive electroactive polymers. Technomic, Lancaster, Pa., USA
8. Ruehe J, Ezquerra T, Wegner G (1989) Makromol Chem Rapid Commun 10:103–8
9. Patil AO, Ikenoue Y, Wudl F, Heeger AJ (1987) J Am Chem Soc 109:1858–1859
10. Ashraf SA, Chen F, Too CO, Wallace GG (1996) Polymer 37:2811–2819
11. Havinga EE, Ten Hoeve W, Meijer EW, Wynberg H (1989) Chem Mater 1:650–659
12. Reynolds JR, Sundaresan NS, Pomerantz M, Basak S, Baker CK (1988) J Electroanal Chem Interfacial Electrochem 250:355–371
13. Sundaresan NS, Basak S, Pomerantz M, Reynolds JR (1987) J Chem Soc Chem Commun 621–622
14. Bryce MR, Chissel A, Kathirgamanathan P, Parker D, Smith NRM (1987) J Chem Soc Chem Commun 466–467
15. Barisci JN, Mansouri J, Spinks GM, Wallace GG, Kim CY, Kim DY, Kim JY (1997) Colloids Surf A 126:129–135
16. Chen S-A, Hua M-Y (1996) Macromolecules 29:4919–4925
17. Nguyen MT, Kasai P, Miller JL, Diaz AF (1994) Macromolecules 27:3625–3631
18. Wei XL, Wang YZ, Long SM, Bobeczko C, Epstein AJ (1996) J Am Chem Soc 118:2545–2555
19. Chan HSO, Ng S-C, Wong PML, Neuendorf AJ, Young DJ (1998) Chem Commun 1327–1328
20. Wei Y, Hariharan R, Patel SA (1990) Macromolecules 23:758–764
21. Gazotti WA Jr, De Paoli M-A (1996) Synth Met 80:263–269
22. Eisazadeh H, Spinks G, Wallace GG (1993) Mater Forum 17:241–245
23. Aldissi M, Armes SP (1991) Prog Org Coat 19:21–58
24. Innis PC, Spinks G, Wallace GG (1998) 56th Annu Tech Conf Soc Plast Eng 1224–1228; (1998) Chem Abstr 130:44593
25. McCarthy GP, Armes SP, Greaves SJ, Watts JF (1997) Langmuir 13:3686–3692
26. Aboutanos V, Barisci JN, Kane-Maguire LAP, Wallace GG (1999) Synth Met 106:89–95
27. Wiersma AE, van der Steeg LMA, Jongeling TJM (1995) Synth Met 71:2269–2270
28. Aboutanos V, Kane-Maguire LAP, Wallace GG (2001) Synth Met (in press)
29. Lee JY, Song KT, Kim SY, Kim YC, Kim DY, Kim CY (1997) Synth Met 84:137–140
30. Lee JY, Kim DY, Kim CY (1995) Synth Met 74:103–106
31. Cao Y, Qiu J, Smith P (1995) Synth Met 69:187–190
32. Neoh KG, Pun MY, Kang ET, Tan KL (1995) Synth Met 73:209–215
33. Heeger AJ (1995) Trends Polym Sci 3:39–47
34. Ruckenstein E, Yang S (1993) Polymer 34:4655–4660
35. Jeffcoate CS, Voevodin NN, Khobaib M, Reynolds LB, Kuhn WK, Donley MS (1998) Int SAMPE Symp Exhib 43:2113–2122
36. Beck F, Huelser P, Michaelis R (1992) Bull Electrochem 8:35–44
37. McAndrew TP (1997) Trends Polym Sci 5:7–11
38. Sitaram SP, Stoffer JO, Okeefe TJ (1997) J Coat Technol 69:65–69
39. Yagova IV, Ivanov SS, Bykov IV, Yagov VV (1998) Protection Met 34:132–136
40. Zarras P, Stenger-Smith JD, Ostrom GS, Miles MH (1999) ACS Symp Ser 735:280–292
41. Lu W-K, Basak S, Elsenbaumer RL (1998) Corrosion inhibition of metals by conductive polymers. In: Skotheim TA, Elsenbaumer RL, Reynolds JR (eds) Handbook of conducting polymers. Dekker, New York, pp 881–920
42. Hatch JE (ed) (1984) Aluminium: properties and physical metallurgy. American Society for Metals, Metals Park, Ohio, p 424
43. Chen GS, Gao M, Wei RP (1996) Corrosion 52:8–15
44. Buchheit RG, Grant RP, Hlava PF, McKenzie B, Zender GL (1997) J Electrochem Soc 144:2621–2628
45. Barbucci A, Bruzzone G, Delucchi M, Panizza M, Cerisola G (2000) Intermetallics 8:305–312
46. Garner A, Tromans D (1979) Corrosion 35:55–60
47. Tallman DE, Pae Y, Chen G, Bierwagen GP (1998) 56th Annu Tech Conf Soc Plast Eng 1234–1237; (1998) Chem Abstr 130:44595
48. Tallman DE, Pae Y, Bierwagen GP (2000) Corrosion 56:401–410
49. Epstein AJ, Smallfield JAO, Guan H, Fahlman M (1999) Synth Met 102:1374–1376
50. Racicot R, Clark RL, Liu HB, Yang SC, Alias MN, Brown R (1995) Proc SPIE Int Soc Opt Eng 2528:251–258

51. Racicot RJ, Clark RL, Liu HB, Yang SC, Alias MN, Brown R (1996) Mater Res Soc Symp Proc 413:529–534
52. Racicot R, Brown R, Yang SC (1997) Synth Met 85:1263–1264
53. Racicot RJ, Yang SC, Brown R (1997) Mater Res Soc Symp Proc 458:415–420
54. Yang SC, Racicot RJ, Clark RL, Liu H, Brown R, Alias MN (The Board of Governors for Higher Education, State of Rhode Island and Providence Plantations, USA) (1997) Electroactive polymer coatings for corrosion control on metal. PCT Int Appl WO 9703127, CAN 126:200741
55. Lu W-K, Elsenbaumer RL (1998) 56th Annu Tech Conf Soc Plast Eng 1276–1279; (1999) Chem Abstr 130:344261
56. Runge-Marchese JM, McNallan MJ (1998) 56th Annu Tech Conf Soc Plast Eng 1392–1396; (1999) Chem Abstr 130:44522
57. Brown R, Yang S, Racicot R, Clark R (1998) Corros Adv Mater Syst Proc Corros/98 Res Top Symp 71–80; (1999) Chem Abstr 129:101209
58. Gelling VJ, Wiest MM, Tallman DE, Bierwagen GP, Wallace GG (2001) Prog Org Coat (in press)
59. Kinlen PJ, Lawless LM, Menon VP (Zipperling Kessler, Germany) (1999) Anodically formed intrinsically conductive polymer-aluminum oxide composite as a coating on aluminum. PCT Int Appl WO 9925778, CAN 131:6652
60. Schultze JW, Jung KG (1995) Electrochim Acta 40:1369–1383
61. He J, Johnston-Gelling V, Tallman DE, Bierwagen GP, Wallace GG (2000) J Electrochem Soc 147:3667–3672
62. Beck F, Huelser P (1990) J Electroanal Chem Interfacial Electrochem 280:159–166
63. Huelser P, Beck F (1990) J Appl Electrochem 20:596–605
64. Huelser P, Beck F (1990) J Electrochem Soc 137:2067–2069
65. Naoi K, Takeda M, Kanno H, Sakakura M, Shimada A (2000) Electrochim Acta 45:3413–3421
66. Zarras P, Stenger-Smith JD, Miles MH (1997) Polym Mater Sci Eng 76:589–590
67. Zarras P, Stenger-Smith JD, Miles MH (1997) Abstracts, 213th ACS National Meeting, San Francisco, April 13–17, MSE-354
68. Zarras P, Stenger-Smith JD, Ostrom GS, Merwin LH, Cameron DA, Reynolds JR (1998) Polym Prepr Am Chem Soc Div Polym Chem 39:67–68
69. Stenger-Smith JD, Miles MH, Norris WP, Nelson J, Zarras P, Fischer JW, Chafin AP (United States Dept. of the Navy, USA) (1999) Amino functional poly(*para*-phenylenevinylene)s as protective coatings. USP 863884 (abandoned)
70. Uehara K, Ichikawa T, Serikawa T, Yoshikawa S, Ehara S, Tsunooka M (1998) Thin Solid Films 322:198–205
71. Sakmeche N, Aaron J-J, Aeiyach S, Lacaze P-C (2000) Electrochim Acta 45:1921–1931
72. Aeiyach S, Bazzaoui EA, Lacaze PC (1997) J Electroanal Chem 434:153–162
73. Roncali J (1992) Chem Rev 92:711–738
74. Brusic V, Angelopoulos M, Graham T (1995) 53rd Annu Tech Conf Soc Plast Eng 1397–1405; (1995) Chem Abstr 124:148755
75. Brusic V, Angelopoulos M, Graham T (1997) J Electrochem Soc 144:436–442
76. Camalet JL, Lacroix JC, Aeiyach S, Chaneching K, Lacaze PC (1998) Synth Met 93:133–142
77. Lacroix JC, Camalet JL, Aeiyach S, Chane-Ching KI, Petitjean J, Chauveau E, Lacaze PC (2000) J Electroanal Chem 481:76–81
78. Deng Z, Smyrl WH, White HS (1989) J Electrochem Soc 136:2152–2158
79. Deng Z, Smyrl WH (1991) J Electrochem Soc 138:1911–1918
80. Idla K, Inganas O, Strandberg M (2000) Electrochim Acta 45:2121–2130
81. Truong VT, Lai PK, Moore BT, Muscat RF, Russo MS (2000) Synth Met 110:7–15
82. Kinlen PF, Silverman DC, Jeffreys CR (1997) Synth Met 85:1327–1332