

# Development of an Intrinsically Conducting Polymer-Based Low-Cost, Heavy-Duty, and Environmentally-Friendly Coating System for Corrosion Protection of Structural Steels

Final Report for NCHRP IDEA Project 157(A)

Prepared by: Tongyan Pan Illinois Institute of Technology

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by

Tongyan Pan, Ph.D., P.E. Assistant Professor

Department of Civil, Architectural, and Environmental Engineering Illinois Institute of Technology

March 31, 2016

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## **EXECUTIVE SUMMARY**

This NCHRP–IDEA project explores the use of  $\pi$ -conjugated polymers, a type of Intrinsically Conducting Polymer (ICP), for developing a more cost-effective, heavy-duty, and environmentally friendly two-layer coating system to replace the conventional zinc-rich threecoat system for corrosion protection of structural steels. A waterborne  $\pi$ -conjugated polymer, two-strand polyaniline: poly (acrylic acid) complex (PANi Complex), was synthesized with three corrosion-potential potentials: (1) ennobling steel surfaces, (2) smearing-out oxygen to reduce coating delamination, and (3) smart self-healing initiated corrosion. The PANi Complex was then mixed in an epoxy matrix to make the primer layer of the two-layer coating system. The primer was then topcoated to ensure the durability, aesthetics, and compliance with air quality regulations. The PANi-based two-coat system avoids the expensive removal of mill scale of steel as required in applying the conventional zinc-rich system, leading to an over 50% cost reduction. Made of 100% organic materials, the two-coat system has low material and production costs and nearly zero environmental impacts.

In laboratory conditions, the techniques of Scanning Kelvin Probe Force Microscopy (SKPFM) and Electrochemical Impedance Spectroscopy (EIS) were first used to evaluate the corrosionprotection capability of the PANi-based primer layer. The evaluation results show that the primer has measurable anti-corrosion capability that depends on the usage of PANi and the type of matrix material used. A prototype two-layer coating system including the PANi-based primer and a polyurethane topcoat was further manufactured. The ASTM Salt-Spray Test and EIS were used to prove the corrosion-protection performance of the prototype two-layer system. After the proof of concept, a non-waterborne epoxy was used to fabricate a different PANi-based primer. These two PANi-based primers and two commercial primers (a zinc-rich primer and an epoxyonly primer) were used to make eight two-layer coating systems using two widely used topcoats. The ASTM Salt-Spray Test, Cyclic Salt Fog/UV Exposure Test, Pull-Off Adhesion Test, and the techniques of EIS, SKPFM, and Scanning Electron Microscope (SEM) were used to evaluate the long-term performance of the eight systems. Based on the laboratory-based evaluation, six groups of two-layer coating systems were then subjected to an outdoor-exposure test to evaluate their field durability in terms of their surface gloss reduction, color change, adhesion change, and surface deteriorations.

Based on the comprehensive laboratory and field tests, the matrix material of primer in which the PANi is mixed was found to play an important role in the long-term performance of a coating. The waterborne epoxy is effective in dispersing PANi nano-particles and has zero volatile organic content; however, it does not bond to the steel surface as strongly as the regular non-waterborne epoxy. The topcoat material also plays an important role in the long-term anti-corrosion performance of coatings; polyurethane has higher durability than epoxy as a topcoat material. The PANi-based systems possess long-term corrosion protection comparable to the performance of the conventional zinc-rich three-layer system based on the one-year field evaluation. To make more definitive conclusions and reliable recommendations, the research team suggests continuing testing and observing the samples under field conditions until most samples have deteriorated.

## CHAPTER 1 INTRODUCTION

## **1.1. Background and Significance**

Steels play an important role in the development of modern technological societies, owing to their superior properties in strength, hardness, workability, and the relatively low cost of production [1-4]. Being a thermodynamically spontaneous process under the general service conditions of civil infrastructure, corrosion has been a tenacious and therefore costly phenomenon on structural steels since the building of the world's first steel bridge using massively produced steel in 1874 [3]. Corrosion of steels, in the form of multiple corrosion cells on the steel surface, is an electrochemical process including four key elements; that is, an anode that donates electrons, an cathode where electrons are accepted, an electrolyte that supports the electrochemical reactions to close the circuit of a corrosion cell [5]. The occurrence of steel corrosion exposing a steel surface to an electrolyte that sustains oxygen or other reducing agents can be easily met in the service conditions of steels.

Corrosion deteriorates steels by consuming the iron element and producing porous iron oxides of low mechanical capacity and environmental resistance [6]. For structural steels, corrosion can also induce accelerated fracture or fatigue, known as stress corrosion cracking and corrosion fatigue [7]. Being thermodynamically spontaneous, corrosion and corrosion-related facture or fatigue problems are pervasive threats to steels, which cost the U.S. economy about \$300 billion per year [8]. The corrosion and corrosion prevention-related annual costs have been estimated to constitute a significant part of the gross national products around the world, and corrosion issues are obviously of great importance in modern societies [8, 9]. In principle, the protection of steels from corrosion can be accomplished by disfunctionizing any or a combination of the four elements of corrosion cells. Two different modes of strategies have evolved in the history of fighting corrosion; that is, the passive vs. active strategies [10-13]. Passive strategies of corrosion protection use a barrier layer to mechanically isolate the electrodes from contacting corrosive agents [10]. Coating, for example, is the most widely used passive strategy for corrosion protection of steels [11]. Active strategies for steels directly participate in the electrochemical reactions of corrosion to prevent or mitigate the oxidation of anode material, such as by supplying electrons needed for redox reactions from an external source or by adding inhibitors to the electrolyte to reduce its corrosiveness [12]. Active strategies are more costly than passive strategies due to higher installation and maintenance costs.

The current state of practice in corrosion protection of steels relies on the three-coat system consisting of a zinc-rich sacrificial primer, a mid-layer of mechanically robust epoxy, and a UV-resistant top-layer. The three-coat systems each need an inspection for potential major repair or replacement every <10 years [14]. The zinc-rich, three-coat system however has a high life-cycle cost, which is \$3 to \$4 per square foot or about six times higher than its predecessor—the lead/chromium-based paint that has since been banned as a result of human health and environmental concerns [3, 15]. In addition, the shop making of the three-coat system requires labor-intensive blast cleaning and long dry-to-handle time between the coatings of different layers [14]. Today, the trade-off between the productivity and cost is a major challenge for the steel and coating makers.

Intrinsically conducting polymers (ICPs) are a specific type of organic polymer; that is, the  $\pi$ conjugated polymer that possesses electrical conductivity together with the advantageous properties of general polymeric materials in strength, flexibility, stability, and ease of handling [16, 17]. ICPs have been recognized as a class of interesting materials currently being explored for use in corrosion control coating systems [16-19]. The potential anti-corrosion properties of ICPs were originally suggested by MacDiarmid [18] and subsequently verified in experiments in a layered coating system [20–24]. In addition to the barrier function of general polymer coatings, three fundamental anti-corrosion mechanisms were proposed for ICPs based on laboratory experimental data; that is, (1) ennobling of metallic surfaces to achieve anodic protection [18-20]; (2) smearing-out oxygen off the ICP-metal interface to reduce coating delamination [21, 24], and (3) smartly self-healing of corrosion [22-26], each based on a unique property of ICP. The mechanism of metallic-surface ennobling stems from the electric charge storage capability of ICPs that plays a major role in passivating metallic surfaces [18–21]. The mechanism of oxygen smearing-out depends on an ICP's electronic conductivity by which the electrons can shift from the ICP-metal interface to the ICP surface or inside the ICP where the oxygen will be reduced [21]. The self-healing mechanism of ICPs relies on its ionic conductivity, which determines the release rate of inhibitors to mitigate active corrosion [22–24].

In utilizing ICP's anti-corrosion properties, particularly in fabricating corrosion protection coatings, there have been contradicting observations made regarding its anti-corrosion capabilities [18-21]. The inconsistent performance of ICP coatings has been ascribed mostly to the quick reduction and limited ennobling performance of ICPs [18-21]. From the engineering perspective, the anti-corrosion capabilities of ICPs have not been reliably engineered into an applicable coating product. To produce an ICP-based coating system with adequate corrosion protection capacity, research work is needed in optimizing the formulation and coating techniques of ICPs to synergistically launch their beneficial anti-corrosion mechanisms.

Optimization of an ICP-based coating system however is subject to various constraints considering the different electrochemical natures of the anti-corrosion mechanism of an ICP. The doping and polymerization approaches directed to fostering one property may contradict the others [27]. For example, to foster the steel-surface ennobling capability an ICP needs to be doped to a level at which its charge storage capability assures that the substrate steel is well positioned in the passivated zone per the Pourbaix diagram. This doping level however may limit the ICP's electrical and/or ionic conductivities, leading to a depressed oxygen smearing-out and/or smart inhibition capabilities [23, 24]. Another challenge in optimizing ICPs is the selection of proper dopants that are capable of inhibiting corrosion and controlling the doping process. A dopant capable of inhibiting corrosion must also be managed to favor release of counter-ions.

To make practical applications, the ICPs must also provide satisfactory binding to the steel surface and good durability in the typical in-service conditions. To meet these two goals, ICPs have been used to fabricate the primer layer; that is, mixed in a low-VOC binder, such as the waterborne polyvinyl-butyral that has good binding with the steel surface, which is then coated with one or two layers of epoxy or other polymers to ensure the durability, aesthetics, and compliance with air quality regulations [28]. Within this context, this IEDA research project aims to develop a new ICP-based coating system with a lower cost, but longer anti-corrosion life than the existing three-coat systems.

#### **1.2. Research Objective**

This research was designed to develop a low-cost, heavy-duty, and environmentally friendly two-layer coating system to replace the more expensive conventional zinc-rich three-coat system for corrosion protection of steel structures such as highway steel bridges. A promising ICP; that is, a  $\pi$ -conjugated polymer that has shown the promising anti-corrosion capabilities mentioned above including (1) ennobling steel surfaces, (2) smearing-out oxygen to reduce coating delamination, and (3) smart self-healing initiated corrosion will be included in a primer layer with such anti-corrosion capabilities synergistically launched. A topcoat of epoxy or polyurethane will be employed to ensure the durability, aesthetics, and compliance with air quality regulations. With combined capabilities of steel-surface ennobling, oxygen smearing-out, and corrosion self-healing the multi-layer ICP-based coating system can be reasonably expected to offer comparable or better anti-corrosion performance than the conventional zinc-rich coating systems, but at significantly reduced costs in production, coating applying, and maintenance. To achieve the objective, research work is needed in the following aspects:

- Synthesizing a promising  $\pi$ -conjugated polymer and fabricating an ICP-based coating system.
- Scanning Kelvin Probe Force Microscopy (SKPFM)-based evaluation of surface passivity of steel substrate and interfacial charge transport behavior of the ICP-based coating system.
- Electrochemical Impedance Spectroscopy (EIS)-based evaluation of the electronic and ionic conductivities of the ICP-based coating system.
- Laboratory evaluation of the ICP-based system using ASTM accelerated corrosion tests.
- Field evaluation of the ICP-based coating system.
- Optimization of the ICP-based coating system.

## **1.3. Literature Review**

## 1.3.1. ICP-Based Coatings

Since the pioneering work on polyacetylene by Shirakawa et al. [29], ICPs have been extensively studied for various possible applications in different areas, such as in energy storage systems, electrocatalysis, electrodialysis membranes, sensors and anti-corrosion coatings [21, 30-38]. Since it was reported to have potential anti-corrosion properties by MacDiarmid [18], ICPs have become a class of novel materials explored for corrosion control in coatings of metals owing to their electrical conductivity and ease of synthesis by means of general chemical and electrochemical methods [37–42]. Baldissera and Ferreira investigated the corrosion protection performance of an epoxy resin-based coating system containing polyaniline (PANi) in 3.5% NaCl solution using the technique of EIS and found that the addition of PANi to the resin increased its corrosion protection efficacy [40]. Olad et al. prepared the coatings of PANi/Zn composites and nano-composites using the solution casting method and evaluated the electrical conductivity and anti-corrosion performances of the two types of coatings. They found that the PANi/Zn nano-composite coatings exhibited improved electrical conductivity and a corrosion protection effect on a mild steel [41]. Armelin et al. compared the protection performance of

epoxy paint containing different conducting polymers including polyaniline emeraldine salt, polyaniline emeraldine base, polyaniline emeraldine salt composite with carbon black, polypyrrole composite with carbon black, and poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulphonate). Based on the comparison of testing results, they anticipated that conducting polymer could be a promising anti-corrosion alternative for inorganic anticorrosive additives used in paint formulations [42].

Due to the different categories of corrosion phenomena, various protection mechanisms using ICPs have been proposed, such as barrier protection, corrosion inhibitors, anodic protection, and cathodic protection [43-46]. The barrier mechanism entails disconnecting the metal surface from the corrosion environment [21], while corrosion inhibitors can slow down the rate of corrosion resulting from the formation of a monomolecular, protection layer on the substrate surface [43, 44]. Anodic protection shields metals from corrosion by passivating the metallic materials through the formation of oxide layers that change the electrode potential in the passive region [45]. For the mechanism of cathodic protection, ICPs may provide an interface that maintains the polymer in an oxidized state so that the cathodic reaction would shift from the ICP-metal interface instead of occurring at the interface [21, 38]. It is noteworthy that anodic and cathodic protection can occur simultaneously on the surface of metals [38, 46].

ICP coatings can be applied to a metal surface by various techniques, including primarily the electropolymerized coatings, paint-blended coatings, and casting-based coatings, which are effective in accomplishing the expected anti-corrosion performance and obtaining the required properties [38]. Electropolymerization of ICPs is used to overcome the insoluble issue of ICPs in common solvents for anti-corrosion protection and can be carried out using the cyclic voltammetry technique, potentiostatic technique, or galvanostatic technique [47-49]. Cyclic voltammetry electropolymerization of ICPs utilizes the limit potentials of monomer oxidation and reduction [50]. Potentiostatic electropolymerization of ICPs takes place under a constant voltage [51], whereas galvanostatic electropolymerization of ICPs is based on a constant current [52]. Blending is another commonly used technique for ICP-based coatings, because such coatings possess both the mechanical properties of conventional polymers and the electrical properties of conductive polymers. The process of applying an ICP coating includes two steps: that is, dissolution of a polymer in a proper solvent and diffusion of the mixture on a substrate surface [53]. Electropolymerization is a superior technique for applying ICP coatings; however, it is expensive when compared with the method of blending and casting ICP coatings and electropolymerization is limited to small structures. For the casting of ICPs, the most significant problem is to select a proper solvent to dissolve ICP. However, the method of blending and casting ICPs is cheaper, easier, and applicable to large structures [38].

The use of ICPs for anti-corrosion protection has attracted much attention and industrial-level development has begun. The three most commonly available ICPs for corrosion protection are polyaniline (PANi), polypyrrole (PPy), and polythiophene (PTh) [17, 54–57]. Among these ICPs, PANi has received more attention and intensive research has been performed because PANi and its derivatives are easy to synthesize through general chemical or electrochemical methods [58–60]. PANi, under the normal ambient conditions, is a mixed-state polymer due to the compositions of benzoid and oxidized quinoid units [63] that exist in three different insulating forms; that is, the leucoemeraldine base (LB), emeraldine base (EB), and pernigraniline base (PB) [17, 55]. EB includes two benzoid units of which the quinoid unit is nonconductive but a useful

form owing to its high stability at room temperature [62]. Emeraldine salt (ES), which can be formed by oxidation of LB or protonation of EB, is electronically conductive and commonly used in corrosion control of metals [63].

The electrodeposition of PANi on metals can be achieved in various acids such as sulfuric, phosphoric, phosphonic, hydrochloric, and oxalic acid [64–72]. Bernard et al. conducted research to investigate the best conditions for PANi electrodeposition and found that PANi formed in phosphoric acid solutions at pH of 4.5 gave higher corrosion protective performance in a PANi-based mixture than that formed in oxalic or sulfuric acids [68, 69]. Nguyen conducted the PANi electrodeposition in the neutral aqueous media on mild steels and the results show that the electrolytic medium allows the deposition of PANi films with properties similar to those obtained in acidic aqueous media [70]. Yağan et al. conducted electrodeposition of PANi coatings on the 304 stainless steel in an oxalic acid solution using the potentiodynamic synthesis technique [71]. Kraljić and Mandić electrosynthesized PANi coatings on steel samples in sulphuric and phosphoric acids solution, respectively [72].

In the current state of practice, PANi has been studied for corrosion protection on various metallic substrates and is used in anti-corrosion coatings owing to their ease of synthesis chemically or electrochemically, as well as the increased environmental stability and different redox states that allow for easy regulation of the desired properties [73-78]. Gašparac and Martin conducted a variety of experimental tests to investigate the mechanism of corrosion protection of PANi in high corrosive H<sub>2</sub>SO<sub>4</sub> solutions. They elucidated that the corrosion protection of PANi is ascribed to the passivation of steel surface owing to the oxidized and doped emeraldine–salt form of PANi that maintained the potential of steel electrodes in the passive region [73]. Ozyılmaz et al. conducted research to determine the corrosion performances of PANi-coated steels in sulphuric and in hydrochloric acid solutions using EIS and anodic polarization curves. The results show that the PANi coating is stable and protective for steels immersed in 0.05 M sulphuric acid solution [74].

Based on electrochemically and chemically formed PANi powder, Grgur et al. investigated the protective abilities of PANi-based composite coatings against the corrosion of mild steels. The results show that the commercial coating containing 5 wt% PANi has superior anti-corrosion characteristics in a 3% NaCl solution [75]. Kohl et al. assessed the effect of PANi salts with various dopant types on the mechanical and corrosion properties of organic protective coatings. The PANi-based organic coatings exhibited comparable results for all types of PANi dopants and improved particularly the corrosion resistance of the coatings with low pigment volume concentrations [76]. Gonçalves et al. investigated the anti-corrosion performance of alkyd paints containing PANi and PANi derivatives applied on carbon steel surfaces. Both the cyclic voltammetry analysis and accelerated corrosion experiments showed a significant improvement in the anti-corrosion performance of the coatings containing PANi or PANi derivatives compared with conventional coatings [77]. Sathiyanarayanan et al. conducted a study to investigate the corrosion protection performance of a vinyl coating containing sulphonate doped PANi, using the open circuit potential method and the techniques of EIS and FTIR. The results show that the PANi-based coatings are able to maintain the potential in the noble range and protect steel in acid and in neutral media due to the formulation of iron-PANi complexes beneath the coating along with a passive oxide layer on steel surfaces [78].

#### 1.3.2. Evaluation Methods for ICP-Based Coatings

### 1.3.2.1. Electrochemical Impedance Spectroscopy (EIS)

Research electrochemists and material scientists have been using EIS for studying the electrochemical behavior of composite and layered systems since the 1970s [79–81]. EIS involves relatively simple operations, but gives highly accurate measurements that can be correlated to multiple complex material variables from mass transport, rates of chemical reactions, and dielectric properties to the levels of defects, microstructure, and compositional influences on the conductivities of solid phases. Because EIS can provide a large amount of information of a system, it has numerous research and engineering applications such as studying redox reaction at electrodes, batteries, fuel cells, membranes, corrosion coatings and paints, and conductive polymers [81-83]. In particular, EIS has been used extensively in investigating the fundamental electrochemical and electronic processes in multi-layer systems of membranes and films [81, 84].

Jüttner used EIS to investigate the effect of surface inhomogeneities on corrosion processes [85]. Kashyap et al. discussed the application of EIS in biofuel-cell characterization and pointed out that EIS is a well-established, non-intrusive, non-destructive, semi-quantitative, and efficient technique for identification of circuit elements [86]. Mu et al. investigated the corrosion behaviors of isolated short-scale and long-scale Q235B steels in a simulated tidal zone using EIS and found that the corrosion rate of the isolated short-scale Q235B steel in the tidal zone acquired by EIS well agrees with the corrosion weight loss results [87]. Amirudin and Thieny reviewed the application of EIS on the degradation of polymer-coated metals and noted that EIS was suitable for the studying of polymer-coated metals; for example, monitoring the in situ degradation of polymer-coated metals in atmospheric exposure [88]. Zheludkevich et al. conducted research to demonstrate the possibility of the investigation of the self-healing properties of protective coatings applied on a metal surface by EIS. They found that EIS can be effectively employed as a routine method to study the self-repair properties of different protective systems [89].

## 1.3.2.2. Scanning Kelvin Probe Force Microscopy (SKPFM)

Since its first introduction by Nonnenmacher et al. in 1991 [89], the technique of Kelvin Probe Force Microscopy (KPFM) has become a unique method for characterizing the electrical properties of metallic and semiconductor surfaces [90]. Based on the working principle of KPFM, the more advanced technique of SKPFM was developed later for studying the nano-scale electrochemical processes on/at various surfaces and interfaces, such as the evolution of corrosion on a steel surface and the corrosion-driven delamination at the interface between an organic coating and a metal surface [26, 91-96].

Leng et al. and Rohwerder and Stratmann [97–100] were among the early groups that studied the fundamental mechanisms of cathodic delamination using the technique of Scanning Kelvin Probe (SKP). The SKP technique allows for the in situ investigation of the fundamental electrochemical reactions by measuring potential profiles along the delaminating interface. These studies were conducted at the above-100  $\mu$ m resolution and reported the micron-level corrosion

phenomena. The more advanced technique of SKPFM is capable of acquiring the information on corrosion mechanism and coating delamination at the submicroscopic scales [96]. The SKPFM has the similar physical principles of deriving surface potential as the SKP and is more sensitive to the convolution between the probe tip and surface features. Many researchers reported that the VPD measured by SKPFM correlated well with the localized corrosion behavior of metals [101, 102]. SKPFM has been successfully used in ex situ corrosion studies on uncoated metal and alloy surfaces [98–101]. The topography and potential results scanned by SKPFM in these studies showed that the high resolution by SKPFM satisfied the needs for corrosion studies. SKPFM has also been used in both open-air and immersed conditions to characterize alloy surfaces and predict their localized corrosion prediction of the aluminum brazing sheet material in a sea-water acidified environment. Senöz et al. recently used SKPFM as a high resolution imaging tool for in situ corrosion and the intermetallic particles within an aluminum alloy [92, 93].

#### 1.3.2.3. Laboratory-Based Accelerated Corrosion Test

An American Iron and Steel Institute (AISI) Task Force evaluated all existing laboratory-based accelerated corrosion tests in 1980 [112]. Such tests provided a controllable corrosive environment for simulating the field corrosion conditions for specimens of uncoated and coated metals exposed in a test chamber. The salt spray (fog) test is a standardized and popular accelerated laboratory test for evaluating the corrosion protection capability of coatings, owing to the test's inexpensive, quick, well-standardized, and reasonably repeatable properties [113]. As one of the most widespread and long established corrosion tests, the salt spray test has been used not only in the predication of the corrosion resistance of a coating, but also in placing the coating process of different systems on a comparative basis. Important test standards using the salt spray test include the ISO9227, JIS Z 2371, ASTM G85, and ASTM B117 as the first internationally standard salt spray test [113]. The testing equipment of the salt spray test basically consists of a closed chamber in which a salt water (5% NaCl) solution is atomized into uniform droplets on specimens from a spray nozzle using pressurized air at temperature between 15°-30°. Thus, a corrosive environment of dense salt water in the chamber was produced and the test samples will be exposed to severely corrosive conditions. The salt spray test solutions can be changed depending on the tested materials and the testing solutions for steel-based materials, and normally are prepared at a neutral pH of 6.5 to 7.2 [114]. The salt spray test has gained worldwide popularity, although it is insufficient in simulating the realistic field corrosive conditions.

In realistic field corrosive conditions, all metals need to be protected against corrosion in the cyclic wet-and-dry atmospheric environment. Thus, cyclic weathering corrosion testing has become a popular corrosion test method in recent years because it can provide a more realistic corrosion condition than the traditional salt spray tests. In the cyclic weathering corrosion testing, the corrosion rates, structural and morphological changes of samples are more similar to those seen outdoors [115]. Thus, cyclic weathering tests are more effective for evaluating corrosion protective coatings and can give better correlation to outdoors testing than the salt spray tests. Nevertheless, the salt spray test, with low cost and easy operation, is still popular for the quick

evaluation of anti-corrosion performance of coatings. Today, much research on evaluating the anti-corrosion performance of coatings is being conducted using both the cyclic weathering corrosion test and the salt spray test [116–120]. Thee et al. conducted a wet-dry cyclic corrosion test for simulating a coastal atmosphere to investigate the corrosion monitoring of steel under an electrolyte film [116]. Yadav et al. conducted research by using the EIS technique and cyclic corrosion test to study the corrosion behavior of galvanized steel under wet-dry cyclic conditions including various drying periods [117]. Qian et al. conducted cyclic corrosion tests simulating wet/dry seawater to investigate the inhibition effect of tannic acid on mild steel corrosion [118]. Manivannan et al. conducted the salt spray test per ASTM B117 to investigate the corrosion behavior of cast Mg-6Al-1Zn+XCa magnesium alloy, aged at different temperatures. Sathiyanarayanan et al. synthesized a polyaniline-TiO<sub>2</sub> composites (PTC) and investigated the corrosion protection behavior of PTC containing coating on steel using EIS and the salt spray test [119].

ASTM D5894 standard practice for cyclic salt fog/UV exposure of painted metal, (alternating exposures in a fog/dry cabinet and a UV/condensation cabinet) has been practiced as a common standard for cyclic corrosion test [120]. Both the salt spray test per ASTM B117 and the cyclic salt fog/UV exposure of painted metal test per ASTM D5894 have been widely used to provide standardized evaluation for the corrosion resistance of coating systems, by producing corrosive attack to the coated panels to predict their suitability as a protective coating [121].

#### 1.3.2.4. Pull-Off Adhesion Test

One of the most desirable properties of a coating system is the strong adhesion it has relative to the substrate surface, which in practices is known to greatly influence the long term performance of the coating system [122-124]. The adhesion test was commonly used to determine how strongly a coating is bonded to the substrate. The knife test and pull-off adhesion test are two commonly used adhesion tests. The knife test has been used for many years to evaluate the adhesion of coating due to its simplicity. For the knife test, successive X or V cuts through the interface between coating and substrate with a utility knife are made to define the test section and eliminate the effect of cohesive forces by coating. When making the cut using a utility knife, the coating will lift from the substrate unless the adhesion strength is larger than the shear stress caused by the applied cutting [125]. Because of its portability, the knife test can be conducted at any location. However, it is relatively susceptible resulting in error and subjectivity for adhesion ratings [126].

Another popular method for evaluating adhesion of coating is the pull-off test during which a loading fixture (dolly or stud) is adhered on the surface of the dried coating by a thermally curable adhesive. After then a portable adhesion tester is used to apply an increasing force until the coating disbands or the adhesive fails. It is noteworthy that roughening the surface of the loading fixture with sandpaper or light abrasive blasting is helpful for obtaining accurate results before bonding it to the surface of coating. Two commonly used adhesion testers are the fixed-alignment mechanical adhesion tester and the fixed-alignment pneumatic adhesion tester. The two methods have different pull force ranges [124]. Currently, the commonly used standard procedure for the pull-off adhesion test is ASTM D4541: the standard test method for pull-off strength of coatings using portable adhesion testers [127].

### 1.3.2.5. Scanning Electron Microscope (SEM)

The technique of scanning electron microscope (SEM) is commonly used to produce images of a solid-state sample by scanning the sample along parallel lines using a fine probe of electrons of high energy [128]. The electrons can interact with atoms in the sample and generate various signals carrying information of surface topography and composition of the sample. Since developed in the early 1950s, SEM has evolved to be one of the most powerful instruments in many research areas such as archaeology, geology, engineering, and medical and physical science thanks to its large depth of field and high-resolution images [129–131]. The application of SEM in corrosion protection coatings have been reported in many studies [132–134].

Capelossi et al. applied a hybrid sol-gel coating on the 2024-T3 Clad aluminum sheet and evaluated the morphology of the sealed anodic films and their thicknesses using SEM and field emission scanning electron microscopy (FE-SEM). The results showed that the hybrid sol-gel can increase the resistive properties of the pores by deterring aggressive species from penetrating into the barrier layer [132]. Bellotti et al. assessed antifouling coatings performance at early stages of immersion in natural and artificial sea waters by scanning the surface condition of samples using SEM. It was helpful for adjusting formulations, and reducing testing time and economics cost by predicting possible results in short time impression tests using EIS [133]. Sugiarti et al. deposited coatings on a carbon steel substrate and studied the effect of Co concentration and temperature on the oxidation and hardness properties of the carbon steel by observing microstructure and morphology of the coatings using SEM and transmission electron microscopy (TEM) [134].

## 1.3.2.6. Outdoor Exposure Test

The weathering resistance to undesirable changes in the natural outdoor environment has been commonly used to evaluate the durability of organic coating [135]. The major determinant factor of the outdoor environment is the geographic location of the exposure with considerations of the differences in solar radiation, temperature, moisture, and pollutants in different geographic locations. Solar radiation, temperature, and moisture are among the most damaging weathering factors [136, 137]. Sunlight, particularly the shorter UV-A and UV-B wavelengths of the solar spectrum, is the primary cause for weathering degradation of organic-based coatings [136, 137]. Temperature can cause degradation in coatings by thermal expansion and relative thermal-mechanical movement. Moisture, by means of hydrolysis reactions, is a key factor for both organic and inorganic coatings [136–138]. Hot/wet (subtropical/tropical), hot/arid (desert), and temperate (higher latitude freeze/thaw) are commonly used as the testing climates that could give the greatest degradation effects on coatings [136].

Selection of the exposure angle of test samples is a critical step in designing an outdoor weathering test scheme [137, 138]. Architectural and other coatings on non-wood substrates are often exposed at either a 45° inclination angle, or "station latitude," which is 26° for South Florida and 34° for Arizona [137]. The 45° exposure is the most common because it provides a good compromise for "direct normal incidence" through the year as the sun elevation varies seasonally with a reasonable wet time. In addition, test fixtures, specimen mounting, and time of

exposure or length of the test are also important variables for the outdoor weathering test [137]. The most popular exposure options for the outdoor exposure test include fixed-angle exposures and accelerated exposures. Fixed-stand exposure normally has a constant orientation related to the test method or specification and can be open-backed or mounted on a backing substrate, or under glass such as with some textiles and furnishings [137–140]. Accelerated exposures allow fast track exposure testing owing to adjusted inclination. For example, the TracRac units can rotate during the day to follow the sun so that exposed samples maintain a normal solar incidence position [137, 139].

Many practices that illustrate the procedure of an outdoor weathering test can be found in the literature [137-143]. ASTM G07 introduced the standard procedure for atmospheric environmental exposure testing of nonmetallic materials [141]. ASTM D-4141 specifies the procedures regarding how to conduct accelerated outdoor exposure tests of coating [142]. Kodumuri and Lee conducted the FHWA 100-year coating study in which the outdoor weathering test was developed with wooden racks inclined at 30 degrees facing south [143]. In order to evaluate the performance of one-coat systems for new steel bridges, Yao et al. conducted outdoor exposure tests with a 45° wooden rack facing south in Sea Isle City, New Jersey [14].

### **CHAPTER 2 SYNTHESIS AND CHARACTERIZATION OF A WATERBORNE ICP**

#### 2.1. Introduction

For coating applications on steel structures such as highway bridges, it is desirable to have a conductive polymer that is dispersible in general solvents or water in order to facilitate painting by brushing or spraying. Water is a particularly desirable solvent for its merit of zero volatile organic content (VOC). VOC today has caused increasing environmental concerns for conventional coating materials. The commonly used ICPs, such as single-strand polyanilines, in their electrically conductive form, however have very low solubility in water. Their rigid polymer backbone and high cohesive energy make them difficult to get dissolved, dispersed, or melted. Although high mechanical shear/disturbance can help disperse PANi in paints, an enhanced capability of dispersion in water by molecular modification is more desirable.

To increase the dispersion of PANi in water, this study takes the approach of building adducts of aniline monomers with a proper chemical species that has high solubility in water and is capable of forming a strong non-covalent bind with the aniline monomers as well. Under appropriate reaction conditions, the aniline monomer(s) within the individual adducts will then be polymerized into a type of polyaniline with desired dispersion capability in water. The poly (acrylic acid) was selected as the chemical species to build adducts with aniline monomers, forming multiple poly(acrylic acid):(aniline)n ( $n \ge 1$ ) adducts in an aqueous solution.

After polymerization, the polyaniline: poly(acrylic acid) complex possesses a two-strand structure, including one strand of PANi as an intrinsically conducting polymer and one strand of PAA that provides polar and ionic functional groups dispersible in water (or other polar organic solvents). This two-strand conducting polymer is an inter-polymer complex between an ICP and a polymeric dopant, which was synthesized using a template-guided polymerization method that facilitated the formation of a side-by-side and non-covalently bonded molecular complex. In the template-guided synthesis, the poly(acrylic acid) functions as a template that adsorbs the aniline monomer to form an adduct. The adsorbed aniline monomers are then polymerized to form polyaniline that is non-covalently bonded to the poly(acrylic acid). This strategy of molecular modification aims to produce a two-strand complex that can be stably dispersible in water at the ambient conditions. Figure 1 illustrates the two-strand polyaniline: poly(acrylic acid) structure.



Figure 1. Two-strand polyaniline: Poly(acrylic acid) as a polymeric complex.

Different from conventional single-strand conducting polymers, this new two-strand conducting polymer is dispersible in water and has high stability in the conductive state. The dispersibility of polyaniline: poly(acrylic acid) structure in water is owing to the polar and ionic functional groups provided by the second strand: poly(acrylic acid); while the stable conductive state of the

two-strand structure results from the strong bond between the polymeric dopant and the conducting polymer chain.

According to Wrobleski et al. [144] and Yang et al. [145], the water-dispersibility, electroconductivity, and the stability of electro-conductivity of two-strand polymeric complexes depends on the amount of aniline monomer units relative to that of carboxylic functional groups in the polymeric complex, which can be quantified in terms of the mole ratio value of the two species. Notably, the carboxylic functional groups come from the poly(acrylic acid). In this study, we started at a mole ratio value of 1:1 for these two species to synthesize the conducting  $\pi$ conjugated polymer.

This chapter first synthesized a waterborne two-strand polyaniline: poly(acrylic acid) complex. Then, Transmission Electron Microscopy (TEM) was used to characterize the synthesized PANi particles in the purified aqueous dispersion. Third, the conductivity of the synthesized two-strand polyaniline: poly(acrylic acid) complex was characterized using two simple methods: (1) measurement of resistance by a Multimeter and (2) conductivity demonstration in an electrical circuit and accurate determination of the conductivity of the synthesized waterborne ICP.

# 2.2. Materials and Procedures for PANi Synthesis

To synthesize the two-strand conducting polymer; that is, the polyaniline: poly(acrylic acid), the following ingredients, solvent, or catalytic materials were purchased from Sigma-Aldrich Co., including aniline monomer, poly(acrylic acid), methanol, hydrochloric acid, hydrogen peroxide solution, and Iron(III) chloride. Laboratory devices, utensils and supplies necessary to the manufacturing of the targeted  $\pi$ -conjugated polymer were purchased from Sigma-Aldrich Co. and other stores.

# 2.2.1. Experimental Procedures

The process of synthesizing polyaniline: poly(acrylic acid) includes four major steps.

Step 1: Making adduct poly(acrylic acid):(aniline)<sub>n</sub>

Step 2: Emulsifying poly(acrylic acid):(aniline)<sub>n</sub>

Step 3: Polymerizing the emulsified poly(acrylic acid):(aniline)<sub>n</sub> adduct

Step 4: Purifying the mixture to obtain aqueous solution of synthesized conducting polymer.

It is noteworthy that the polymeric complex from Step 3 may contain free polyelectrolyte, uncomplexed PANi, unreacted aniline, low-molecular weight oligomers, and inorganic ions. These impurities were removed using filtration and dialysis.

# 2.2.2. Observations and Analyses

Step 1: Making adduct poly(acrylic acid): $(aniline)_n$ , when poly(acrylic acid), methanol, and distilled water were mixed under rigorous stirring, flocculent poly(acrylic acid) was seen (in Figure 2). After stirring for 15 minutes, the flocculent solution changed to be transparent. In this

process, the viscosity of the mixture increased as the aniline monomers were absorbed onto the poly(acrylic acid), forming extended chains. The pH value of the mixture was about 5.



Figure 2. Solution turning to a white emulsion after adding of aniline.

Step 2: Emulsifying poly(acrylic acid):(aniline)<sub>n</sub>, at the moment when the 2 M lignosulfonate was added to the solution obtained from Step 1, the mixture turned milky-white immediately (see Figure 3b). This is caused by the decreased degree of ionization of the poly(acrylic acid):(aniline)<sub>n</sub> adduct as the hydrochloric acid is added. After around 1 minute, the mixture changed to be nearly transparent (see Figure 3c). This phenomenon reflects that when the solution was continuously stirred, the macro adduct emulsion transformed into micro adduct emulsion with smaller particle size that scattered only the shorter wavelength region of the visible light.



Figure 3. Observations in Step 2 of the synthesis of polyaniline:poly(acrylic acid): (a) before adding Lignosulfonate, (b) during the addition of Lignosulfonate, and (c) shortly after adding Lignosulfonate

Step 3: Polymerizing the emulsified poly(acrylic acid):(aniline)<sub>n</sub> adduct, one minute after three drops of 1 M aqueous ferric chloride and 3 ml 30% of hydrogen peroxide were added to the emulsified poly(acrylic acid):(aniline)<sub>n</sub> adduct obtained from step 2 (under vigorous stirring), the solution turned to be light yellow-green (see Figure 4a). After 15 more minutes, the solution gradually turned to light green (see Figure 4b). For the following 30 minutes, the solution continuously changed its color from cyan blue (Figure 4c), through semi-translucent dark blue (see Figure 4d), to opaque dark green (see Figure 4e). The polymerization of the emulsified poly(acrylic acid):(aniline)<sub>n</sub> adduct was nearly completed in Step 3, and the mixture was stirred for 2 more hours to complete the reaction.



Figure 4. Color changes in Step 3 of the synthesis of polyaniline:poly(acrylic acid).

Step 4: Purifying the mixture to obtain the aqueous solution of synthesized conducting polymer, the dark green polymeric complex is obtained in a mixture form after two-day further reaction under stirring. Purification was conducted to remove impurities by first filtering off large particle impurities such as uncomplexed PANi and then dialyzing off unwanted small molecular weight impurities. Figure 5 shows the filtered and dialyzed aqueous dispersion of the synthesized conducting polymer.



Figure 5. Purification of synthesized PANi complex after two-day's polymerization reaction: (a) dispersion being filtered, (b) dialysis of filtered dispersion, and (c) dialyzed dispersion.

## 2.3. TEM Characterization of Synthesized PANi Dispersion

TEM was used to characterize the synthesized PANi particles in the purified aqueous dispersion. Figure 6 shows the TEM equipment used in this study and the dispersed  $\pi$ -conjugated PANi particles that on average are 50–100 nanometers in size. Such size distribution indicates good stability of the water dispersion system of the PANi and will greatly facilitate the mixing of PANi into epoxy to make a sound primer layer.



Figure 6. TEM setup used and images of PANi particles at different levels of magnification.

# 2.4. Conductivity Characterization of Synthesized PANi

The conductivity of the synthesized two-strand polyaniline:poly(acrylic acid) complex was characterized first using two simple methods: (1) measurement of resistance by a Multimeter; (2) conductivity demonstration in an electrical circuit. An accurate determination of the conductivity of PANi was performed thereafter using a Multimeter. Before it is subjected to conductivity characterization and measurement, the two-strand polyaniline:poly(acrylic acid) complex was dried on a piece of filter paper using the dialyzed aqueous solution of PANi.

## 2.4.1. Resistance Measurement by Multimeter

The purified polyaniline:poly(acrylic acid) complex solution was painted on a piece of filter paper, which is known to be a good insulator when dry. The painted filter paper first was dried at 50°C for 48 hours and then subjected to resistance measurement at two different locations: the unpainted vs. PANi-painted as shown in Figure 7. It is clearly shown that the unpainted part of the filter paper gave an infinite value of resistance (indicating that it is not conductive) vs. a resistance value of 69.8 k $\Omega$  between two points on a PANi-painted part of the filter paper at about the same distance. This measurement indicates quite good conductivity of the developed PANi, with consideration of the thin PANi layer on the paper (~5 µm).



Figure 7. Resistance of PANi coat on filter paper: Unpainted (left) vs. PANi painted (right).

#### 2.4.2. Conductivity Characterization by a Circuit

A simple circuit was formed to show the conductivity of the PANi. The same PANi-painted filter paper used for the resistance measurement by Multimeter (as shown in Figure 7) was used to build the circuit (see Figure 8). A 9 V battery, a breadboard, and a 3.2 V LED light were used to form this circuit. The LED light is off when the circuit is open as shown in Figure 8a, and the LED light is on as the circuit is closed by the filter paper as shown in Figure 8b. This simple circuit clearly demonstrated the conductivity of the PANi polymer synthesized in this study.



Figure 8. Circuit-based conductivity characterization of the synthesized PANi: (a) open circuit (green LED on breadboard is off), and (b) closed circuit (green LED is on).

## 2.4.3. Direct Measurement of the Resistivity/Conductivity of PANi

The two-strand PANi complex synthesized in the first quarter was painted and dried on a paper filter for direct measurement of its resistivity or conductivity. Figure 9 shows this operation. The sample was first fixed at two ends by two metallic clips that are good conductors (with trivial

electro-resistance as measured by the Multimeter). The PANi sample has the dimensions of 0.6 in. (15.24 mm) in length (i.e., the distance between the two clips), 0.75 in. (19.05 mm) in width, and 50  $\mu$ m in thickness. The clips were used to ensure a uniform electrical field existing between the two clips. The resistance of the PANi sample across the distance between the two clips (along the length direction) was measured to be 18.5 k $\Omega$ . According to Eq. (1), the resistivity  $\rho$  of the PANi material was calculated to be 1.3  $\Omega \cdot m$ , which is equivalent to a conductivity of 0.77 S/m (the reciprocal of the resistivity). This measured conductivity of PANi is comparable to the conductivity values of general PANi materials synthesized by other researchers reported in literature, which essentially bolsters the validity of the experimental work performed in the study.

$$\rho = RA/L \tag{1}$$

where,  $\rho$  = resistivity; *R* = measured resistance; *A* = cross-sectional area of the sample; and *L* = length of the sample.



Figure 9. Direct measurement of electrical resistivity of synthesized PANi.

#### 2.5. Summary

In the task of synthesizing a waterborne ICP, a two-strand PANi complex was fabricated that is intrinsically conducting and can be stably dispersed in water at the ambient conditions. The dispersible PANi was mixed into a water-borne epoxy to make the primer layer of the proposed two-layer coating system. The TEM-based particle size analysis shows that the PANi exists in the form of nano-scale particles that are stably dispersed in an aqueous solution. Moreover, the demonstrated electro-conductivity of the synthesized PANi, by the directly measured resistance (using a Multimeter), the circuit-based conductivity characterization, and the direct measurement of resistivity, builds a solid starting point for the subsequent tasks of the project.

With the waterborne PANi confirmed to be a satisfactory intrinsically conducting polymer, in the next step the primer layer of the proposed two-layer coating system will be made by mixing the PANi (at different percentages) with a waterborne epoxy and regular epoxy as a control sample.

Characterization of the anti-corrosion behavior of the primer and the two-layer coating system will be the focus of research effort in the next step.

### CHAPTER 3 MANUFACTURING AND EVALUATION OF ICP-BASED PRIMER

### LAYER

The two-layer coating system targeted in this project will consist of a primer layer made of the mixture of intrinsically conducting PANi with a waterborne epoxy and a topcoat layer of robust epoxy or another polymer to provide mechanical toughness, further corrosion protection, aesthetics, and compliance with air quality regulations. The primer is expected to possess the anti-corrosion capabilities of PANi so as to achieve a longer corrosion protection of the substrate steel materials than conventional coatings. This task focused on making the primer mixture, coating it to the substrate surface, quantifying the anti-corrosion behavior of the primer layer using the technique of Electrochemical Impedance Spectroscopy (EIS), and verifying the three major anti-corrosion mechanisms of the PANi-based primer on the basis of the technique of Scanning Kelvin Probe Force Microscopy (SKPFM).

#### 3.1. Manufacturing and Evaluation of ICP-based Primer Layer

To make the primer mixture and coated samples, the following ingredients materials were purchased including (1) waterborne epoxy resin: EPI-REZ<sup>TM</sup> Resin 6520-WH-53 (Figure 10 left) and waterborne epoxy cuing agent: EPIKURE Curing Agent 6870-W-53 (Figure 10 right), both from MOMENIVE; and (2) Type S-35 ground (polished) finish steel panels made of a low carbon and cold rolled steel (SAE Designation: 1008/1010) as shown in Figure 11(a).



Figure 10. EPI-REZ<sup>™</sup> Resin and EPIKURE curing agent for making the pimer layer.

The intrinsically conducting PANi synthesized in Chapter 2 was used in this chapter to fabricate the primer layer of the proposed two-layer coating system. The water-dispersed PANi was mixed with a waterborne epoxy to make the primer layer, which was then spin-coated to the substrate (steel) surface at the thickness of 20  $\mu$ m. The usage of PANi nano-particles in the PANi-epoxy mixture is 5% by the dry mass of PANi with respect to the total mass of the PANi-epoxy mixture

excluding water. Two other groups of control samples were also prepared using the same substrate steel, with one group of uncoated samples (each having a bare steel surface) and the other group each coated with a 20-µm-thick epoxy layer (without PANi). These control samples and the PANi-epoxy-coated samples (see Figure 11) were then analyzed side by side using the techniques of EIS and SKPFM. The detailed process of fabricating the coated samples consists of four major steps.

**Step 1: Fabricating Epoxy-only Coating Material.** The resin component and curingagent component were mixed at a ratio of 1:1 to make the epoxy. Distilled water was then added to the mixture to achieve better mixing and easier coating on the steel panel. Based on many rounds of trials and errors, an appropriate amount of distilled water to add was found to be equal to the amount of epoxy by weight. More water will contribute to easy mixing, but slow down epoxy curing. Prior to the EIS analysis, the samples coated with epoxy were each slightly scribed to initiate corrosion.

**Step 2: Fabricating PANi-Epoxy Mixture.** The procedures and amounts of material ingredients used in Step 1 were adopted in Step 2 to make the epoxy matrix to which the PANi was to be added. The content of PANi in the PANi-epoxy blend is 5% by the dry mass of PANi with respect to the total mass of the PANi-epoxy blend excluding water. Since all the ingredient materials are waterborne, the PANi-epoxy mixture can be easily made at a high uniformity. Prior to the EIS analysis, the PANi-epoxy-coated samples were each scribed to initiate corrosion using the same scribing technique as was used to scribe the epoxy-coated samples.

**Step 3: Preparing Substrate Surface for Coating.** Prior to coating, proper surface preparation of the substrate surface is essential to ensure adequate adhesion and durability of the coating. As new ground-finish steel panels were used for coating, the substrate surfaces were rinsed first by acetone and then by distilled water.

**Step 4: Coating Substrate.** The epoxy material made in Step 1 and the PANi-epoxy mixture made in Step 2 were coated on steel panels by the method of spin-coating, which can precisely control the thickness of coating materials on the substrate. A 20-µm-thick layer was eventually deposited on each sample surface.



Figure 11. Test specimens: (a) uncoated, (b) epoxy-coated, and (c) PANi-primer-coated.

#### **3.2. Electrochemical Impedance Spectroscopy (EIS) Analysis**

In early 1970s, research electrochemists and materials scientists started to use the technique of EIS as a tool for studying difficult and complicated systems [79–84]. EIS is a popular analytical tool in materials research and development because it involves a relatively simple electrical measurement that can readily be automated. EIS results can be correlated to many complex materials variables from mass transport, rates of chemical reactions and corrosion and dielectric properties to defects, microstructure, and compositional influences on the conductance of solids. EIS is able to evaluate the performance of chemical sensors and fuel cells, and it has been used extensively to investigate membrane behavior in living cells. EIS is useful as an empirical quality control procedure; in addition, it can contribute to the interpretation of fundamental electrochemical and electronic processes [80–84].

## 3.2.1. EIS Technique

#### 3.2.1.1. Basics of EIS

The EIS technique when used for studying the corrosion behavior of metallic materials usually involves the use of three electrodes; that is, the working, counter, and reference electrodes, integrated in an electrochemical cell assembly. A small-magnitude alternating current (AC) signal, usually by an alternating potential, is applied between the working electrode (test sample) and the counter electrodes over a wide range of AC frequencies, and the response of the sample is measured in terms of its impedance (slope of the potential vs. current curve) and phase shift. The impedance and phase shift data are then interpreted to obtain the electrochemical properties of the sample. The method of equivalent electrical circuit is commonly used for interpreting the impedance and phase shift data [82-84].

To obtain a pseudo-linear response, electrochemical impedance is normally measured using a small excitation signal, which results in a sinusoidal response of the current to a sinusoidal potential at the same frequency, but shifted in phase [see Figure 12(a)] [82–84, 146]. The input alternating potential, responding alternating current, and the determined impedance are given in Eqs. 2, 3, and 4, respectively.

$$E_t = E_0 \sin(\omega t) \tag{2}$$

$$I_t = I_0 \sin(\omega t + \emptyset) \tag{3}$$

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$
(4)

where  $E_t$  is the potential at time t;  $E_0$  is the amplitude of the potential signal;  $\omega$  is the radial frequency;  $I_t$  is the response current signal at time t and is shifted in phase ( $\phi$ ) and has a different amplitude than  $I_0$ , the impedance; Z is expressed in terms of a magnitude;  $Z_0$  and a phase shift,  $\phi$ .

It is noteworthy that when the applied sinusoidal signal  $E_t$  is plotted on the X axis of a graph and the sinusoidal response signal  $I_t$  is plotted on the Y axis, Lissajous figure, an oval curve, will be plotted [see Figure 12(b)] and EIS spectrum data will be collected during the EIS measurement [146].



Figure 12. Sinusoidal response current (a) and Lissajous Curve (b) in a linear system.

The applied sinusoidal potential and the response sinusoidal current can also be expressed as Eqs. 5 and 6, respectively, using Euler transform Eq. 7.

$$E_t = E_0 \exp(j\omega t) \tag{5}$$

$$I_t = I_0 \exp(j\omega t - \emptyset) \tag{6}$$

$$\exp(j\emptyset) = \cos(\emptyset) + j\sin(\emptyset) \tag{7}$$

Finally the impedance can be represented as the complex form shown in Eq. 8.

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0(\cos(\phi) + j\sin(\phi))$$
(8)

Obviously, the impedance is composed of a real and an imaginary part, which will be collected and generate a very important EIS data, called Nyquist plot.

#### 3.2.1.2. Presentation of EIS Data

Nyquist and Bode plots are typical EIS measurement data. The Nyquist plot is the impedance plotted by the real part on the X axis and the imaginary part on the Y axis. In Nyquist plot, the Y axis is negative and each point represents the impedance at one frequency. From Figure 13 we know that the low frequency data are on the right side of the plot and higher frequency data are near to the original point. The impedance can be represented as a vector of length |Z|. The angle between this vector and the X axis is commonly called the "phase angle,"  $\phi$ . The Bode plot represents the relationship between impedance and frequency, also phase-shift with frequency. The frequency information corresponding to each point can be obtained in Bode plot. Figure 13 shows the Nyquist plot (left) and Bode plot (right) for a typical deteriorated coating [146].



Figure 13. Typical Bode plot (left) and Nyquist plot (right) for deteriorated coating in electrolyte.

EIS data are generally analyzed in terms of an equivalent circuit model that is composed of common electrical elements such as resistors, capacitors, and inductors. To be useful, the elements in the model should be on the basis of the physical electrochemistry of the system. Figure 14 shows a typical equivalent circuit model for coated metal exposed in electrolyte.  $R_s$  is the electrolyte solution resistance,  $R_{po}$  is the pore resistance,  $R_p$  represents the polarization resistance.



Figure 14. Simple EC model for deteriorated coating in electrolyte.

#### 3.2.1.3. Basic Equivalent Circuit Elements

#### • Electrolyte Resistance

The electrolyte solution resistance depends on the ionic concentration, temperature, type of ions, and the geometry of the area in which current is carried. The resistance is defined as [147]:

$$R = \rho \frac{l}{A} \tag{9}$$

where A is the area in which current is carried, l is length carrying a uniform current, and  $\rho$  is the solution resistivity. The reciprocal of  $\rho(\kappa)$  is conductivity of the solution,  $\kappa$  defined as:

$$\kappa = \frac{l}{RA} \tag{10}$$

Although most electrochemical cells do not have uniform current distribution through a definite electrolyte area, we usually do not need to calculate solution resistance from ionic conductance. Instead, we can calculate it by fitting experimental EIS data to an equivalent circuit model [146].

#### Polarization Resistance

Under the open circuit potential or corrosion potential, the potential of an electrode will be forced away from its value and polarization of the electrode occurred [84]. The polarization process causes current to flow through electrochemical reaction occurred at the surface of electrode. In the electrochemical cell, two different electrochemical reactions occurred, reduction and oxidation, both generate cathodic current and anionic current, respectively. The corrosion potential equilibrates at the potential where the cathodic and anodic currents are equal and the value of the current for either of the reactions is known as the corrosion current [146]. Eq. 11 shows the relationship between the potential of the current.

$$I = I_{corr} \left( \exp\left(\frac{2.303(E - E_{oc})}{\beta_a}\right) - \exp\left(\frac{-2.303(E - E_{oc})}{\beta_c}\right) \right)$$
(11)

where *I* is the measured cell current in amps,  $I_{corr}$  is the corrosion current in amps,  $E_{oc}$  is the open circuit potential in volts,  $\beta_a$  is the anodic beta coefficient in volts/decade (anodic Tafel constant),  $\beta_c$  is the cathodic beta coefficient in volts/decade (cathodic Tafel constant).

When applying a small signal, the corrosion current can be calculated based on the polarization resistance (Eq. 12) and according to research work [121], corrosion rate can be estimated according to Eq. 13.
$$I_{corr} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \cdot \frac{1}{R_p}$$
(12)

$$CR = K \frac{I_{corr}}{\rho} (EW) \tag{13}$$

where *CR* is corrosion rate, *K* is constant for converting units,  $\rho$  is alloy density (g/cm<sup>3</sup>), and *EW* is alloy equivalent weight (gram/equivalent).

It is noteworthy that both corrosion current ( $I_{corr}$ ) and corrosion rate (CR) are inversely proportional to the polarization resistance ( $R_p$ ). The larger the value of polarization resistance, the smaller are the values of corrosion rate and corrosion current.

### • Charge-Transfer Resistance

Metal substrate contacting to electrolyte can electrolytically dissolve into the electrolyte due to redox reaction, during which electrons enter the metal and metal ions diffuse into the electrolyte and results in charge transferring. The reaction type, concentration of the reaction products, potential, and temperature are main factors influencing the charge-transfer reaction. The Butler–Volmer equation (Eq. 14) is the most fundamental equation describing the relationship between the electrical current and potential on an electrode with the consideration of cathodic and anodic reaction.

$$I = I_0 \left( \exp\left(\frac{\alpha n F \eta}{RT}\right) - \exp\left(\frac{-(1-\alpha)n F \eta}{RT}\right) \right)$$
(14)

where  $I_0$  is exchange current density,  $\eta$  is overpotential, F is Faradays constant, T is temperature, R is gas constant,  $\alpha$  is reaction order, and n is number of electrons involved.

The Butler–Volmer equation is applicable when the polarization depends only on the chargetransfer kinetics. When the electrochemical system reaches to equilibrium with tiny overpotential, the charge-transfer resistance can be calculated briefly using the Eq. 15.

$$R_{ct} = \frac{RT}{nFI_0} \tag{15}$$

#### • Pore Resistance

The pore resistance is the resistance of charge-transfer paths in the coating and represents all possible resistances caused by defects such as weak areas of the coating, cracks, holidays, or holes extended throughout the coating. The pore resistance of the coating has been used to estimate delamination area after being exposed to corrosion environment. Eq. 16 shows the relationship between pore resistance and delaminated area.

$$A_d = \frac{R_{po}^o}{R_{po}} \tag{16}$$

where  $R_{po}^0 = \rho d$  is the specific pore resistance, assumed to be constant during the delamination process and the delaminated area decreases as the pore resistance increases [148, 149]; *d* is the

thickness of coating; and  $\rho$  is the specific coating resistivity that represents the resistivity of a completely delaminated coating. Delaminated area can be estimated from the pore resistance according to Eq. 17.

$$A_d = \frac{\rho d}{R_{po}} \tag{17}$$

Thus the delamination ratio D could be estimated using Eq. 18.

$$D = \frac{A_d}{A} \tag{18}$$

where *A* is the total exposed area of the coated metal.

### • Coating Capacitance

Two conducting plates can form a capacitor when separating by a dielectric and the value of the capacitance is related to the size of the plates, the distance between the plates and the properties of the dielectric (see Eq. 19).

$$C = \frac{\varepsilon_o \varepsilon_r A}{d} \tag{19}$$

where  $\varepsilon_0$  is permittivity of free space,  $\varepsilon_r$  is dielectric constant, A is surface of plate, and d is distances between two plates.

The capacitance of the intact coating normally is much smaller than a typical double layer capacitance, with the units of pF or nF.

### • Double Layer Capacitance

When a charged electrode is immersed into electrolyte, the ions will tend to stick on the electrode surface and separate the electrode from the ions with opposite charge and then a double layer formed on the interface between the electrode and surrounding electrolyte. It is noteworthy that the separation is normally very small, often with the order of angstroms. Accordingly, a bare metal immersed in an electrolyte will form a simple double layer that normally has an estimation value of capacitance of 20–60  $\mu$ F/cm<sup>2</sup>. Many factors can affect the value of double layer capacitance such as electrode potential, temperature, ionic concentrations, types of ions, oxide layers, and electrode roughness, impurity adsorption [82]. Similar to the pore resistance, the delaminated area can also be estimated from an experimental value of the double layer capacitance using Eq. 20.

$$A_d = \frac{C_{dl}}{C_{dl}^0} \tag{20}$$

where  $C_{dl}^{0}$  is the specific double layer capacitance that is assumed to be constant throughout that exposure time [148].

## • Constant Phase Element

Constant phase element (CPE) is commonly used to represent the behavior of a capacitor due to its non-ideal behave of acapacitor in EIS experiments [82, 83]. Eq. 21 shows the calculation of the impedance of a CPE:

$$Z_{CPE} = \frac{1}{(j\omega)^{\alpha} Y_{o}}$$
(21)

where  $Y_o$  is the capacitance and  $\alpha$  is an empirical constant,  $0 \le \alpha \le 1$ . When  $\alpha = 1$ , CPE acts as an ideal capacitor. Double layer capacitance and coating capacitance are usually modeled with a CPE.

# 3.2.2. Equivalent-Circuit Modeling of EIS Data

A Gamry EIS-300 potentiostat was used to perform the EIS analysis. The three-electrode test cell assembly used for EIS analysis is shown in the left part of Figure 15. EIS-300's accompanying software package for EIS analysis also includes a component for fitting the EIS measured Nyquist and Bode plots to an equivalent circuit model. The EIS software is capable of measuring the impedance values of a sample over the frequency range from 10  $\mu$ Hz to 1 MHz (see right part of Figure 15) [*147*].

After complete curing of the coating materials on the substrate surface (168 hours), each specimen was installed in the test cell with an area of 14.6 cm<sup>2</sup> exposed to the 5% NaCl electrolyte contained in the cell. For all the uncoated and coating-scribed samples, 3 hours of soaking time was specified before EIS analysis to initiate corrosion and allow the corrosion rate to reach an equilibrium state, which is important to the validity of the EIS analysis. The following parameters: 10 mV in AC voltage, a 100 kHz to 10 mHz frequency range, a decade of 10 points, and a 2,000-second delay time were set for the EIS analysis.

	Potentiostatic EIS							
	Default Save Re	store OK Cancel						
	Pstat	F IFC1000-03112						
	Test Identifier	Potentiostatic EIS						
	Output File	Epo0.5MNaCl20131022.DTA						
	Notes	0.5MNaCl+Epo						
	Initial Freq. (Hz)	100000						
	Final Freq. (Hz)	0.01						
	Points/decade	10						
	AC Voltage (mV rms)	10						
	DC Voltage (V)	0 C vs Eref 🕫 vs Eoc						
	Area (cm^2)	14.6						
	Conditioning	□ Off Time(s) 15 E(V) 0						
	Init. Delay	✓ On Time(s) 2000 Stab. (mV/s) 0						
	Estimated Z (ohms)	100						
<u></u>	Optimize for:	C Fast © Normal C Low Noise						

Figure 15. The three-electrode test cell used for EIS analysis and the GUI of EIS program.

Figure 16 shows the entire EIS system as it was used in an EIS analysis. During an EIS analysis, the open circuit potential w.r.t. time, Bode curve, and Nyquist curve are all automatically recorded by the EIS software. Based on the Bode plot and Nyquist plot, the corrosion characteristic of a coated sample can be further analyzed using a fitted equivalent circuit.



Figure 16. EIS system in the process of EIS analysis.



Figure 17. Equivalent circuit re-produced vs. EIS results of an uncoated sample.



Figure 18. Equivalent circuit reproduced vs. EIS results of an uncoated sample.



Figure 19. Equivalent circuit reproduced vs. EIS results of an uncoated sample.

The Bode plot and Nyquist plot for an uncoated sample, an epoxy-coated sample, and a PANi-epoxy-coated sample, shown in Figures 17, 18, and 19, respectively, were then analyzed using the equivalent circuit method. The equivalent circuit method entails fitting these curves to an equivalent circuit that would give the same or very close Bode plot and Nyquist plot. The best fitted equivalent circuits for the uncoated sample, epoxy-coated sample, and PANi-epoxy-coated sample are shown in Figure 20, and the equivalent-circuit re-produced Bode plot and Nyquist plot are shown togethre with the EIS-generated Bode plot and Nyquist plot in Figures 17, 18, and 19, respectively. Table 1 presents the modeled parameters by the equivalent circuit.



(b) Equivalent Circuit for Epoxy Coated Sample; (c) Equivalent Circuit for ICP Coated Sample

Figure 20. Equivalent circuit for uncoated, epoxy-coated, and PANi-epoxy-coated samples.

Elements	Uncoated	Epoxy-Coated	PANi-Epoxy-Coated	Units
$R_{po}$		65.12	2.158e3	ohm
$R_p$	150.0	8.451e4	6.950e6	ohm
$R_s$	9.500	23.82	6.112e-3	ohm
$Y_{o1}$	4.220e-3	34.32e-9	9.12e-8	$S \cdot s^a$
$\alpha_l$	0.752	0.932	0.721	
$Y_{o2}$	—	4.650e-4	4.800e-4	$S \cdot s^a$
$\alpha_2$		0.923	0.835	
Goodness of Fit	1.202e-3	5.110e-4	1.303e-3	—

Table 1. Summary of Modeled Parameters by the Best-Fit Equivalent Circuit

# 3.2.3. EIS Tested Data Analysis

Based on the equivalent-circuit modeled parameters, a series of indices were determined to characterize the anti-corrosion effects of the PANi-epoxy primer through comparing the level of coating delamination and corrosion rate/current at the steel-coating interface among the three groups of samples; that is, the uncoated, epoxy-coated, and PANi-epoxy-coated. Specifically, the delamination ratio at the primer/substrate interface, the breakpoint frequency, and estimated corrosion rate were used in this study for such comparison purpose.

# 3.2.3.1. Delamination Ratio Method

Delaminated area and delamination ratio are the two parameters commonly used for characterizing the corrosion intensity of coated metals and alloys. According to Eq. 20, we calculated the delaminated area for the uncoated, epoxy-coated, and PANi-epoxy-coated samples. The specific double layer capacitance  $C_{dl}^0$  was set to 25  $\mu$ F/cm<sup>2</sup> based on the research of Mansfeld et al. [80] and McCluney et al. [151]. Table 2 lists the delaminated area ( $A_d$ ) and delamination ratio (D) of the uncoated, epoxy-coated, and PANi-epoxy-coated samples. By comparing these delaminated areas and delamination ratios at the primer/substrate interface, it could be found the PANi-epoxy-coated samples gave the smaller delaminated area and smaller delaminated area and delamination ratio of the three groups. These delaminated area and delamination ratio ratio results suggest a superior anti-delamination property of the PANi-epoxy mixture.

Sample Designation	$A (\mathrm{cm}^2)$	$A_d$ (cm <sup>2</sup> )	D
Uncoated Sample	14.6	5.12	35.1%
Epoxy-Only Primer	14.6	0.242	1.7%
PANi-Epoxy Primer	14.6	0.107	0.7%

 Table 2. Delaminated Area and Delamination Ratio of the Three Groups of Samples

# 3.2.3.2. Breakpoint Frequency Method

The breakpoint frequency,  $f_b$ , as first used by Deflorian et al. [150], is another commonly used parameter for characterizing a coating system. The breakpoint frequency is the frequency at which a coating system undergoes an insulator to conductor transition, which happens when the phase angle between the input voltage and the response current is 45° [150]. According to Kouloumbi and Kyvelidis, the breakpoint frequency of a system is proportional to corrosion intensity and for different systems a higher breakpoint frequency suggests higher corrosion intensity [79]. The breakpoint frequencies of the epoxy-coated and PANi-epoxy-coated samples in exposure to the 0.5 M NaCl solution are shown in Figure 21.

It is noteworthy that the breakpoint frequency of the PANi-epoxy-coated sample is obviously lower than that of the epoxy-coated sample, which is located beyond the scanning frequency range. The breakpoint frequency results further confirm the superior anti-delamination property of the PANi-epoxy layer (relative to the epoxy-only layer of the same thickness).



Figure 21. Breakpoint frequencies of PANi-epoxy-coated vs. epoxy-coated samples.

### 3.2.3.3. Polarization Resistance Method

The polarization resistance method is one electrochemical way used to calculate the corrosion rate as is described in ASTM G 59 and G102 [151, 152]. According to the Eq. 12, the corrosion current is inversely proportional to polarization resistance. To compare the anti-corrosion performance of the three types of testing samples (uncoated, epoxy-coated, and PANi-epoxy-coated samples), corrosion current and corrosion rate were estimated using the Eqs. 12 and 13. As was mentioned previously, the SAE 1008/1010 steel panels (composition: 99.31%–99.7% Fe, 0.3%–0.5% Mn, 0.1% C, 0.05% S, 0.04% P) were used to make the test samples and the equivalent weight for SAE 1008/1010 steel (*EW*) is 18.50 calculated according to ASTM G102. The density of SAE 1008/1010 steel (*d*) is 7.872 g·cm<sup>-3</sup>. Conversion factor (*K*) is 3.27·10<sup>3</sup> mm·g·A<sup>-1</sup>·cm<sup>-1</sup>·yr<sup>-1</sup>. Anodic Tafel constant ( $\beta_a$ ) and cathodic Tafel constant ( $\beta_c$ ) is 80 mV·dec<sup>-1</sup> and 100 mV·dec<sup>-1</sup>, respectively, for the steel immersed in a 0.5 M NaCl solution for 40 minutes [153, 154]. Table 3 lists the corrosion current and corrosion rate for different types of coating.

Sample Designation	$R_p(\Omega \cdot \mathrm{cm}^2)$	$I_{corr} (\mathrm{A} \cdot \mathrm{cm}^{-2})$	$CR \ (\mu m \cdot yr^{-1})$
Uncoated	$2.190 \cdot 10^3$	$8.812 \cdot 10^{-3}$	6.772
Epoxy-Only Primer	$1.233 \cdot 10^{6}$	$1.564 \cdot 10^{-5}$	0.012
PANi-Epoxy Primer	$1.015 \cdot 10^8$	$1.902 \cdot 10^{-7}$	0.00015

Table 3. Corrosion Current and Corrosion Rate for Epoxy-Only and PANi-Epoxy Primer

The PANi-epoxy-coated sample exhibited obvious lower corrosion current and corrosion rate than that of the epoxy-only-coated sample. As expected, uncoated samples exhibit the largest corrosion current and corrosion rate, which are significantly higher than that of the epoxy-only and PANi-epoxy-coated samples. This observation also confirms the superior anti-corrosion property of the PANi-epoxy primer relative to the epoxy-only primer with the same thickness.

## 3.3. Scanning Kelvin Probe Force Microscopy (SKPFM) Analysis

The technique of SKPFM was developed primarily for studying the nano-scale electrochemical processes at various surfaces and interfaces, such as the evolution of corrosion on a steel surface and the corrosion-driven delamination at the interface between an organic coating and a metal surface [26, 91–96]. The Volta potential difference (VPD) is the driving force for the localized corrosion on steel surface and the technique of SKPFM is capable of analyzing the surface VPD at a high resolution [101–107]. Based on the VPD results, the primer's capabilities in ennobling steel surface and smartly healing initiated corrosion were evaluated. SKPFM is also capable of mapping high-resolution topography of the sample surface, which in this study was relied on to investigate the primer's capability for reducing coating delamination on steel surfaces. Therefore, the technique of SKPFM was used to investigate and verify the reported three major anticorrosion mechanisms of the PANi-based primer; that is, (1) ennobling substrate (steel) surface, (2) reducing coating delamination, and (3) smartly healing initiated corrosion.

## 3.3.1. Basics of SKPFM

Atomic force microscopy (AFM)-based SKPFM was normally used to measure the contact potential difference between conducting AFM tip and sample. Surface potential detection microscopy can be modeled as a parallel plate capacitor with variable distance. When the AFM tip and sample with different work function are brought together, electrical force will be generated between the tip and sample surface and electrons in plate with the lower work function will flow to another plate with the higher work function [see Figure 22(b)]. In Figure 22,  $W_t$  and  $W_s$  are the work function of the tip and sample;  $E_{F,t}$  and  $E_{F,s}$  are the Fermi energy of the tip and sample;  $E_v$  is the energy of an electron at rest in the vacuum nearby the surface; and d is the distance between the tip and sample. The relationship between work function, Fermi energy, and total energy in the vacuum can be defined in Eq. 22 as follows:

$$E_{\nu} = -W - E_F \tag{22}$$

The relationship of Volta or contact potential difference (CPD) between the tip and sample and work function can be defined as Eq. 23 [90], where, e is the electronic charge and  $V_{CPD}$  is the CPD between the tip and sample.

$$-eV_{CPD} = W_t - W_s \tag{23}$$

Figure 22(b) shows that the vacuum energy levels are aligned, but that the Fermi energy levels are different when the tip and sample surface were separated by a distance d and not electrically connected. To get to an equilibrium steady state, the Fermi energy levels will align through electron current flow when the tip and sample surface are close enough for electron tunneling [see Figure 22(c)]. At this time, the tip and sample surface will be charged and a  $V_{CPD}$  will form,

which can result in an electrical force on the contact area. This electrical force can be vanished by applying an external bias  $(V_{DC})$  with the same magnitude but opposite direction as the  $V_{CPD}$ . In other words, this applied voltage nullifies the surface charge in the contact area and is equal to the work function difference between the tip and sample. Consequently, if the tip work function is known, the work function of the sample can be calculated. To measure the work function of the sample, an AC voltage  $(V_{AC})$  and a DC voltage  $(V_{DC})$  are applied to the tip and the  $V_{AC}$  is used to generate oscillating electrical forces between the tip and sample surface, whereas,  $V_{DC}$  is used to eliminate the oscillating electrical forces results from  $V_{CPD}$ .



Figure 22. SKPFM working principle diagram (a); electric energy levels for tip and sample under: separation distance d without electrical connection (b), electrical contact (c), external bias ( $V_{DC}$ ) applied (d).

The total electrostatic force (*P*) in a capacitor can be determined by differentiating the energy function with respect to the separation of the tip and sample per Eq. 24 [92], where, *C* is the capacitance related to separation distance, *x* is the separation,  $\Delta V$  is the potential difference between the  $V_{CPD}$  and the voltage applied to the tip; i.e.,  $\Delta V = (V_{DC} - V_{CPD}) + V_{AC} \sin \omega t$ .

$$P = \frac{1}{2} \frac{dC}{dx} (\Delta V)^2 \tag{24}$$

Substituting the formula for voltage difference  $\Delta V$  into the previous equation (Eq. 22) and using the relation  $2 \sin 2x = 1 - \cos 2x$ , the total electrostatic force *P* between the tip and sample can be rewriten and split up into three components per Eq. 25, where the term  $P_{DC}$  contributes to the topographical signal; the term  $P_{\omega}$  at the frequency  $\omega$  can be used to measure the contact potential; and the term  $P_{2\omega}$  is used for capacitance microscopy.

$$P = P_{DC} + P_{\omega} + P_{2\omega} \tag{25}$$

$$P_{DC} = \frac{dC}{dx} \left[ \frac{1}{2} (V_{DC} - V_{CPD})^2 + \frac{1}{4} (V_{AC})^2 \right]$$
(26)

$$P_{\omega} = \frac{dc}{dx} [V_{DC} - V_{CPD}] \cdot V_{AC} \sin \omega t$$
(27)

$$P_{2\omega} = -\frac{1}{4}\frac{dC}{dx} \cdot (V_{AC})^2 \cdot \cos(2\omega t)$$
(28)

During measurement, a lock-in amplifier is used to detect the cantilever oscillation at frequency  $\omega$  and  $V_{DC}$  is adjusted to zero the electrostatic forces between the tip and the sample; thus, the

response at the frequency  $\omega$  becomes zero. The absolute values of the work function for sample can be obtained when the work function for the tip is first calibrated and known. In addition, the normal topographic scan methods at the resonance frequency  $\omega$  can be used independently. Thus, the topography and the contact potential of the sample can be determined simultaneously.

The Bruker MultiMode 8, an atomic force microscopy-based digital instrument, was used to investigate the corrosion protection performance of PANi-primer coating. The AM-SKPFM mode (a.k.a., the LiftMode) was used to scan the surface topography and CPD of samples, which is a two-pass procedure where the surface topography is obtained in the first pass and the surface potential is measured on the second pass. During the scanning, both surface topography and potential image are displayed on the screen simultaneously, which is known as the interleaved procedure. On the first pass, the tapping mode was used to determine and record the topography of the sample and no external voltage is applied to the probe tip. The cantilever vibrates mechanically near its resonant frequency by a small piezoelectric element. On the second pass, the tapping drive piezo is turned off and an oscillating voltage is applied directly to the probe tip.

If the DC voltage of the probe tip is different from that of the substrate, an oscillating electric force will be produced on the cantilever at the corresponding frequency. Thus, the cantilever vibrates and amplitude can be detected. The details of LiftMode surface potential imaging process were illustrated in Figure 23, where Label 1 means that the cantilever measures surface topography on first (main) scan (trace and retrace), and Label 2 means that the cantilever follows stored surface topography at the lift height above the sample while responding to electric effect on second (interleave) scan (trace and retrace). When the probe tip and sample have the same DC voltage, no force exists on the cantilever at the corresponding frequency and the cantilever oscillation amplitude will be zero. Therefore, by adjusting the DC voltage on the tip to have a zero oscillation amplitude, meaning that the tip voltage is the same as the surface potential, the local surface potential can be determined. The voltage applied to the probe tip is recorded by the NanoScope Controller to construct a voltage map of the surface.



Figure 23. Schematic illustration of LiftMode surface scanning by SKPFM.

# 3.3.2. SKPFM Measurement

Verification of the three anti-corrosion mechanisms proposed for the PANi-based primer entails comparing the SKPFM-scanned surface topography and the VPD of three groups of samples: (1) uncoated steel panels, (2) epoxy-only-coated steel panels, and (3) PANi-primer-coated steel panels. The PANi primer was made by mixing PANi nano-particles in the same type of epoxy as was used for the epoxy-only-coated steel panels. To effectively detect the targeted anti-corrosion mechanisms, the PANi-primer-coated steel panels were prepared using a high-weight percentage of PANi; that is, 20% of the dry weight of epoxy. The three groups of samples were all prepared

using the SAE 1008/1010 steel panel with the following dimensions: width 2.0 in. (51 mm), length 3.5 in. (89 mm), and thickness 0.032 in. (0.81 mm). The steel surfaces were cleaned using acetone followed by a 3-minute ultrasound bathing, and then were dried at the room temperature. The epoxy-only-coated panels and PANi-primer-coated panels were prepared using a spin coater to have a 20- $\mu$ m-thick coating layer, and were cured in the ambient condition for 5 days before being subjected to SKPFM analysis. Figure 24 shows the three groups of steel-panel samples. For SKPFM analysis, small-sized samples of 1 cm × 1 cm in length and width were prepared by cutting these steel-panel samples (for an early viewing, such small samples are shown in Figure 25).



Figure 24. Steel-panel samples: a) Uncoated, b) Epoxy-only-coated, and c) PANi-primer-coated.

The 1 cm  $\times$  1 cm samples prepared for studying the mechanisms of reducing coating delamination and smartly healing initiated corrosion were scribed with a 5-mm-long, substrate-exposed scratch on the coated surface in order to initiate corrosion. The 1 cm  $\times$  1 cm samples prepared for studying the mechanism of ennobling substrate surface were not scratched since the substrate steel was already exposed to the open-air ambient condition. Prior to the SKPFM analysis, for each 1 cm  $\times$  1 cm sample, the surfaces to be analyzed were first dampened with a 1 M aqueous solution of NaCl, rinsed with deionized water, and then set in the ambient condition for corrosion development. At the specified time for SKPFM scanning, the samples were positioned in the sample holder of SKPFM and scanned in the open-air ambient condition.

Figures 25 and 26 show photographs of the uncoated, epoxy-only-coated, and PANi-primercoated samples taken at two different corrosion stages, respectively; that is, 18 hours of corrosion development in the ambient condition after corrosion initiation and 96 hours of corrosion development in the ambient condition after corrosion initiation. Immediately after the removal of the surface rust materials, these samples were scanned to obtain the surface topography and VPD.



Figure 25. SKPFM samples after 18 hours of corrosion development in ambient condition: a) Uncoated, b) Epoxy-only-coated, and c) PANi-primer-coated.



Figure 26. SKPFM samples after 96 hours of corrosion development in ambient condition: a) Uncoated, b) Epoxy-only-coated, and c) PANi-primer-coated.



Figure 27. SKPFM setup at IIT used for surface topography and VPD measurements.

The Bruker MultiMode 8 SKPFM was used in this study and the AM-SKPFM mode (a.k.a. the LiftMode) was selected to scan the surface topography and VPD of samples. The conductive MESP probe was used to scan the VPD of the sample surfaces. Under the LiftMode, all the measurements were carried out in air at ambient condition. The scanning rate varied with the scan size and a lift scan height of 100 nm was applied according to Afshar et al. [91]. Figure 27 shows the SKPFM setup that was used for surface topography and VPD measurements. For comparison purpose, a group of uncoated samples that were not exposed to the NaCl solution for corrosion development were also scanned in the ambient conditions using the same imaging mode and parameters as were used for scanning the samples with corrosion developed. The

SKPFM measurements were then analyzed to evaluate the three anti-corrosion mechanisms of the PANi-based primer.

# 3.3.3. Analysis of SKPFM Data

# 3.3.1.1. Mechanism of Ennobling Steel Surface

The SKPFM scanned VPD was used to investigate the mechanism of steel-surface ennobling as was expected from the PANi primer. This mechanism was studied by comparing the VPD of the three uncorroded steel surfaces (denoted 0-hour in the left column of Figure 28) to the VPD of the three 18-hour corroded samples (denoted 18-hour in the right column of Figure 28). Notably, the VPD was not scanned over the coating but directly over the substrate surface for the coated samples. An effective solvent for dissolving cured epoxy; that is, the methylene chloride (dichloromethane, CH<sub>2</sub>Cl<sub>2</sub>) was used to remove the epoxy-only coating and the epoxy-based PANi primer to expose the substrate steel surface for SKPFM scanning. The SKPFM scanned VPD for the uncoated, epoxy-only-coated- then-removed, and PANi-primer-coated- then-removed samples were shown in row 1, row 2, and row 3 of Figure 28, respectively.

The surface VPD of the uncoated, 0-hour-corroded sample was obtained by scanning a new steel sample upon immediate exposure to the ambient condition; that is, with no corrosion developed on the scanned surface, whereas the surface VPD of the uncoated, 18-hour-corroded sample was scanned on the same sample, but after 18 hours of corrosion in the ambient condition. The surface VPD of the epoxy-only-coated, 0-hour-corroded sample was scanned in the ambient condition over an epoxy-removed steel sample with no corrosion developed on the epoxyremoved surface. The surface VPD of the epoxy-only-coated, 18-hour-corroded sample was scanned over the substrate surface of the same sample that had been re-coated with a 20-umthick epoxy layer, set in the ambient condition for 18 hours of corrosion development, and then coating-removed for SKPFM scanning. Similarly, the surface VPD of the PANi-primer-coated, 0-hour-corroded sample was scanned in the ambient condition over a PANi-removed sample with no corrosion developed on the primer-removed surface; while the surface VPD of the PANi-primer-coated, 18-hour-corroded sample was scanned over the substrate surface of the same sample that had been re-coated with a 20-µm-thick PANi-primer, set in the ambient condition for 18 hours after the corrosion-initiation by the NaCl solution, and then coatingremoved for SKPFM scanning.

The most phenomenal observation from Figure 28 is the VPD changes between the two scans over the same sample (but at different corrosion stages) in each row of Figure 28. The range of VPD increased dramatically after 18-hour corrosion development for the uncoated steel sample in row 1. For the epoxy-only-coated and removed scans in row 2, the 18-hour scan showed apparent increases in VPD relative to the 0-hour scan, meaning likely occurrence of corrosion on the epoxy-only-coated steel. However, for the PANi-primer-coated and removed scans in row 3, the 18-hour scan showed a slightly reduced range of VPD than the 0-hour scan, meaning suppressed corrosion potential on the PANi-primer-coated steel. Since the epoxy- and PANi-coated samples were prepared using the same steel and corroded in the same condition, the reduced VPD by the PANi primer verifies the surface-ennobling mechanism of the PANi primer.



Figure 28. SKPFM scanned VPD of uncoated (row 1), epoxy-only-coated (row 2), and PANiprimer-coated (row 3) samples after 0-hour and 18-hour corrosion development.

# 3.3.1.2. Mechanism of Reducing Coating-Delamination

The SKPFM scanned surface topography of the epoxy-only-coated and the PANi-primer-coated samples was analyzed to evaluate the mechanism of coating-delamination reduction expected from the PANi primer. This mechanism was studied by comparing the levels of delamination heights on the two groups of coated samples after 18 hours and 96 hours of corrosion development. The SKPFM scanning was conducted over a coated area close to the edge of the 5-mm scratch, where corrosion-induced delamination could most probably occur. Figure 29 shows the surface topography images of the epoxy-only-coated sample scanned at three different moments during corrosion development; that is, 0 hours, 18 hours, and 96 hours after corrosion initiation.

The range of surface height increases with the corrosion time comparing the three scanned corrosion moments, indicating exacerbated delamination of the epoxy coating as time went on. Figure 29 also shows the area of delamination for the epoxy-only coating at the three different corrosion times. To that end, the height of 200 nm (measured from the lowest point of the surface of the 20- $\mu$ m-thick epoxy coating) was set as the reference level, above which all locations are shown in the color blue. The above 200 nm areas for the epoxy coating are 5.21  $\mu$ m<sup>2</sup>, 24.76  $\mu$ m<sup>2</sup>, and 44.06  $\mu$ m<sup>2</sup> for the three scanning moments, respectively, which indicates the increased delamination and reduced longevity of the epoxy coating.



- a. Epoxy-Only-coated, 0-Hour Corrosion Development
- b. Epoxy-Only-coated, 18-Hour Corrosion Development
- c. Epoxy-only-coated, 96-Hour Corrosion Development

Figure 29. SKPFM scanned surface topography of the epoxy-only-coated sample: a) 0-hour corroded, b) 18-hour corroded, and c) 96-hour corroded

Figure 30 shows the surface topography images of the PANi-primer-coated sample scanned at 0 hours, 18 hours, and 96 hours after corrosion initiation. Again, the height of 200 nm above the lowest point of PANi primer was set as the reference level, and all locations exceeding this level are shown in blue. The above 200 nm areas for the PANi primer are 1.01  $\mu$ m<sup>2</sup>, 0.65  $\mu$ m<sup>2</sup>, and 9.46  $\mu$ m<sup>2</sup> for the three scanning moments, respectively. In comparison with the three above 200 nm areas of the epoxy coating, the probability of delamination is significantly reduced. According to existing research, a high level of hydroxide anions (OH<sup>-</sup>) is a major reason for the delamination of organic coatings off steel surfaces [96]. The electronically conductive PANi

primer enables transference of electrons from the steel  $\parallel$  primer interface (when corrosion is initiated) to within and/or on top of the primer layer, which will shift the oxygen reduction sites and lower the pH level at the steel  $\parallel$  primer interface to reduce coating delamination.



- a. PANi-Primer-coated, 0-Hour Corrosion Development
- b. PANi-Primer-coated, 18-Hour Corrosion Development
- c. PANi-Primer-coated, 96-Hour Corrosion Development

Figure 30. SKPFM scanned surface topography of the PANi-primer-coated sample: a) 0-hour corroded, b) 18-hour corroded, and c) 96-hour corroded.

# 3.3.1.3. Mechanism of Smartly Healing Initiated Corrosion

In comparison to the mechanism of surface-ennobling, the mechanism of smartly healing corrosion takes a longer time to show effect. As such, in this study the 96-hour VPD was scanned by SKPFM to evaluate the mechanism of smartly healing initiated corrosion by the PANi primer, over a region close to the scratch edge. Figure 31 shows the scanned regions in two snapshot images taken as the epoxy-only-coated sample and the PANi-primer-coated sample were scanned at the time of 96-hour corrosion development. Figure 31(a) shows an obvious delamination area (surrounded by the green-colored curve) on the epoxy-only-coated sample, in which the blue line indicates the left boundary of the scratch and the red-colored rectangle defines the scanned region. The left boundary of the scratch and the scanned region for the PANi-primer-coated sample were shown in Figure 31(b) in the same manner as for the epoxy-only-coated sample. The PANi-primer-coated sample however does not demonstrate an obvious delamination area along the scratch boundary.

Figure 32 shows the VPD map of the epoxy-only-coated steel substrate versus the VPD map of the PANi-primer-coated steel substrate, both scanned after 96 hours of corrosion development. The epoxy-only-coating and the PANi primer demonstrated rather different effects on the VPD of the substrate steel. Although the epoxy-only coating and the PANi primer both enabled low potential for the part beyond the intact steel-primer interface, the VPD ranges of these two samples were very different; that is, 9.8 V on the epoxy-only-coated surface vs. 5.1 V on the PANi-primer-coated surface. For the epoxy-only-coated sample, the enabled low potential appeared in the region to the right-hand side of the red-colored curve in Figure 32(a), which is

coating-delaminated according to Figure 31(a). For the PANi-primer-coated sample, the enabled low potential appeared in the region to the right-hand side of the red-colored curve in Figure 32(b), which crosses the boundary of the scratch according to Figure 31(b).



Figure 31. SKPFM scanned regions for epoxy-only (a) and PANi-primer (b) coated samples.

The low-potential effect by the epoxy-only coating is in agreement with reported research findings that there exists an obvious potential decrease from the intact metal-polymer interface to the scratched defect, and that the potential decreases with the distance away from the metal-polymer interface [26, 97–100]. According to Fürbeth and Stratmann, the delamination formation under an organic coating is related to the galvanic coupling formed between the oxidation and reduction sites located in the defect and the metal-polymer interface [99]. The PANi primer however appears to mitigate the formation of such galvanic coupling and primer delamination by reducing the VPD difference between the scratched defect and the steel-primer interface as demonstrated in Figure 32.



Figure 32. VPD of epoxy-coated (a) and PANi-primer-coated (b) steel after 96-hour corrosion.

This long-term anti-corrosion effect of the PANi primer (in contrast to the short-term surfaceennobling effect by the PANi primer) can be ascribed to the self-healing mechanism enabled on a steel surface. According to Dominis [155], a PANi coating can intelligently release dopant anions as corrosion inhibitors. Kinlen et al. further found that the anion dopants released by PANi can form a stable adduct with iron ions, which could mitigate the corrosion of steels [156]. When corrosion gets initiated at the steel-primer interface, the reduction of polyaniline-Emeraldine salt (PANi-ES) to polyaniline-Leucosalt (PANi-LS) is driven by the electrons released in corrosion. This reduction can release dopants that react with iron ions to form a passive film on the corroding sites, depending on the type of dopant used in PANi. Along with the formation of the passive film, the released dopants can also form iron sulphonate complex compounds underneath the coating [156–161]. In the field conditions, PANi-LS can be reoxidized to be PANi-ES through capturing ions from the surrounding environment [161, 162]. This cycling process between PANi-ES and PANi-LS makes PANi a viable coating material that can smartly heal launched corrosion [73, 163, 164]. The reactions and processes involved in this smart healing mechanism are illustrated in Figure 33.



Figure 33. Possible reactions and processes for smart healing mechanism.

## 3.4. Summary

A primer layer was fabricated in this task using the synthesized intrinsically conducting PANi. The water-dispersed PANi was mixed with a waterborne epoxy to make the primer layer, which was then spin-coated to the substrate (steel) surface at the thickness of 20  $\mu$ m. The usage of PANi nano-particles in the PANi-epoxy mixture is 5% by the dry mass of PANi relative to the total mass of the PANi-epoxy mixture excluding water. Two other groups of control samples are also prepared using the same substrate steel, with one group of uncoated samples (each having a bare steel surface) and the other group each coated with a 20- $\mu$ m-thick epoxy layer (without PANi). These control samples and the PANi-epoxy-coated samples were then analyzed side by side using the techniques of EIS and SKPFM.

A standard analytical procedure by EIS is applied to characterize the corrosion behavior of three groups of samples when exposed to a 0.5 M NaCl solution, from which the Nyquist presentation and Bode presentation of the EIS results were analyzed using the method of Equivalent Circuit. Prior to the EIS analyses, the samples coated with epoxy or PANi-epoxy mixture each are slightly scribed to initiate corrosion using the same scribing technique. Based on the fitted equivalent circuit, three characterization methods; that is, the delamination ratio method,

breakpoint frequency method, and polarization resistance method, are used to extract the anticorrosion effect of the PANi inclusions in the primer layer. All three characterization methods confirmed the superior anti-delamination property of the PANi-epoxy layer (relative to the epoxy-only layer of the same thickness).

The technique of SKPFM was utilized for verifying the three major anti-corrosion mechanisms proposed for the PANi-based primer. The surface-ennobling mechanism of the PANi-based primer was supported by the significantly suppressed short-term (18-hour) VPD enabled by the PANi primer, in comparison with the short-term VPD enabled by the epoxy-only coating. The PANi primer's delamination-reduction mechanism was verified by the much greater surface height measured on the epoxy-only coating relative to the surface height measured on the PANi primer. The mechanism of smartly healing initiated corrosion, as was expected from the PANi-based primer, was evaluated by comparing the long-term (96-hour) VPDs of the uncoated, epoxy-only-coated, and PANi-primer-coated surfaces. The significantly lowered range of VPD measured on the PANi-primer-coated steel surface, relative to the VPD range measured on the epoxy-only-coated steel surface, supported this mechanism for the PANi primer. The work conducted in this task builds a firm base for fabricating the proposed two-layer coating system and evaluating the system's overall anti-corrosion capacity using laboratory and field experiments, which will be the research focuses of the following tasks.

# CHAPTER 4 MANUFACTURING AND LABORATORY EVALUATION OF

# PROTOTYPE TWO-LAYER COATING SYSTEM

Electroactive PANi has been studied to develop new organic coating systems with high corrosion resistance [165–172] since its first observed enhancement of corrosion protection on a metallic material in 1985 [18]. The waterborne electroactive PANi synthesized in this NCHRP-IDEA project was used to fabricate a PANi-based primer (by mixing with a waterborne epoxy), which exhibited excellent corrosion resistance on steel panels. In this task, the fabricated PANi-based primer was topcoated with a polyurethane layer to develop a prototype two-layer coating system. The two-layer system is expected to possess high anti-corrosion capabilities so as to achieve a longer corrosion protection of the substrate steel materials than the conventional three-layer coatings. This chapter focused on making the two-layer coating system, coating it to the substrate surface, and quantifying its anti-corrosion performance using the standard Salt-Spray Test per ASTM B117 and the technique of Electrochemical Impedance Spectroscopy (EIS).

# 4.1. Preparation of Two-Layer Coating System

SAE 1008/1010 steel panels (composition: 0.06% max manganese, 0.15% max carbon, 0.03% max phosphorus, and 0.035% max sulfur) was acquired at the dimensions of  $51 \times 89 \times 0.81$ mm from the company Q-Lab and used as the substrate for the corrosion study in this task. Prior to coating and the corrosion study, the panels were ground using the standard 1200 grid paper, cleaned first in acetone and then ultrasound bathed in ethanol for 3 minutes. Before coating and corrosion study, the samples were dried at the ambient room temperature (25°C).

An amount of 2.5 g of PANi was mixed in 25 of g waterborne epoxy and 10 g of water to make a 5 dry-wt.% of PANi containing epoxy primer. After stirring for 15 minutes, 25 g of curing agent was added and stirred for 15 more minutes. A control group of panels coated with an epoxy-only primer was made in the same way but without adding PANi. Both the PANi-based primer and epoxy-only primer were spin-coated on the cleaned steel panels to achieve a dried thickness of 100  $\mu$ m. The coated steel panels were first cured at the ambient room temperature (25°C) for 24 hours; then a commercial polyurethane topcoat (Minwax) with clear color was applied on the primer-coated steel panels to achieve an additional died thickness of 100  $\mu$ m. The top-coated samples were dried at the ambient room temperature (25°C) for 7 days before the salt-spray test and EIS analysis.

# 4.2. Salt Spray Test

# 4.2.1. Testing Procedures

To compare the anti-corrosion performance of the PANi-based, two-layer coating system (PANi/polyurethane) to the epoxy-based, two-layer coating system (epoxy/polyurethane), four samples were made for each coating system. These coated steel samples were subjected to the Salt-Spray test following the standard procedures of ASTM B117. To initiate substrate corrosion, a scribe mark of 15 mm long and 0.5 mm wide was made to penetrate through the two-layer

coating using a sharp instrument according to the test method ASTM D1654 [173]. The scribe mark was made on each sample to expose the underlying steel substrate before Salt-Spray testing.

The prepared samples were placed in the spray chamber (Inland Testing Equipment, Model SS60) and continuously sprayed with 5% NaCl solution with a pH value at 7. Before running the test, the temperature inside the testing chamber and saturated-air pail were adjusted to 35°C and 47°C, respectively. During the Salt-Spray Test, the back and edges of the panel samples were sealed using JVCC PWT-20C heavy-duty corrosion control tape. Throughout the testing process, the samples were subjected to assessment for the degree of blistering (ASTM D714) [*174*], degree of rusting (ASTM D610) [*175*], and degree of delamination at certain times. Figure 34 shows the arrangement of samples in the spray chamber: (a) before a test and (b) during an on-going test in accordance with ASTM B117. Weight gains owing to the corrosion product deposited on all scribed panels were measured to indicate the extent of corrosion of the two groups of samples during the Salt-Spray Test. This was done by weighing the test samples and comparing with their original weights.



Figure 34. Salt-Spray Test according to ASTM B117: (a) before testing, (b) during testing.

# 4.2.2. Data Analysis

The degree of blistering, degree of rusting, and degree of delamination were examined for the PANi/polyurethane system and the epoxy/polyurethane system subjected to the Salt-Spray Test. Figure 35 shows the samples of Salt-Spray Test at 240 hours, 480 hours, and 720 hours for the two systems.

The PANi/polyurethane-coated panels showed slight amounts of rust at the three observation moments, which was located mainly within the scribe line. More meaningfully, there was no delamination shown between the coating layer and the substrate surface across the entire surface of the panels. In contrast, the epoxy/polyurethane-coated panels showed significantly more rust along the scribe line. Moreover, the epoxy/polyurethane coat showed clear, large delamination along the scratched line. The amounts of corrosion rust and the severity of delamination on the epoxy/polyurethane-coated panels apparently increased with time of salt-spray testing.



Figure 35. Salt-Spray Test of PANi/polyurethane vs. epoxy/polyurethane samples at different times.

Table 4. Summary of Corroded Area and Delamination Area after Salt-Spray T	a and Delamination Area after Salt-Spray Test
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	Sample	Corroded Area (%)			Delamination Area (%)			
Coated System	No.	240 h	480 h	720 h	240 h	480 h	720 h	
	1	0.00	0.00	0.07	0.00	0.00	0.00	
DAN: un den	2	0.94	1.69	2.73	0.00	0.00	0.00	
PANi under Polyurethane	3	1.28	1.81	1.88	0.00	0.00	0.00	
	4	0.00	0.00	0.00	0.00	0.00	0.00	
	Average	0.55	0.87	1.17	0.00	0.00	0.00	
	1	1.58	2.02	2.25	44.74	50.02	57.42	
Epoxy under Polyurethane	2	0.95	1.46	1.63	37.84	45.63	52.02	
	3	1.37	2.55	2.73	52.42	57.72	87.67	
	4	0.90	1.70	1.97	46.07	57.41	82.76	
	Average	1.2	1.93	2.14	45.27	52.7	69.97	

To quantitatively assess the degree of rusting and delamination the total exposed area, corroded area, and delamination area of the panels were measured. The percentage of corroded area and delamination were calculated and shown in Table 4. The average corroded area and delamination area at different immersion times were compared between the PANi/polyurethane system and the epoxy/polyurethane system. The results showed that the averaged corroded area on the epoxy/polyurethane-coated panels is significantly larger than that on the PANi/polyurethane-

coated panels. Also, the delamination of the epoxy/polyurethane system increased with time. The PANi/polyurethane-coated panels, in contrast, did not show detectable delamination. Obviously, the PANi/polyurethane-coating system is able to mitigate delamination and has superior anticorrosion capability to the epoxy/polyurethane system.

The ASTM D714 specifies a series of value to indicate the severity of blistering: blistering standards No. 10 represents no blistering, standard No. 8 represents the smallest size blister easily seen by unaided eye, and standards No. 6, 4, and 2 represent progressively larger size. None of the PANi/polyurethane-coated panels and epoxy/polyurethane-coated panels show signs of blistering. Figure 36 presents the average corroded area and average delamination area for the PANi/polyurethane and epoxy/polyurethane systems.



Figure 36. Average corroded and delamination areas of PANi/polyurethane and epoxy/polyurethane systems.

Similarly, the ASTM D610 specifies a series of values to indicate the severity of rusting: rusting Grade 10 means that the percent of surface rusted is less than or equal to 0.01 percent, Grade 6 means that the percent of surface rusted is greater than 0.3 percent and up to 1.0 percent, Grade 5 means that the percent of surface rusted is greater than 1.0 percent and up to 3.0 percent. By analogy, the degree of delamination can be assessed, with Grade 10 representing a surface delamination ratio less than or equal to 0.01 percent, Grade 1 representing a surface delamination ratio greater than 33.0 percent and up to 50.0 percent, and Grade 0 representing a surface delamination ratio greater than 50 percent. Table 5 summarized the results of the degree of blistering, degree of rusting, and degree of delamination at the different observation times. It is noteworthy that the more severe delamination between the coating material with the substrate. As such, the PANi/Polyurethane system demonstrated more improved overall performance than the Epoxy/Polyurethane system.

Times	PA	Ni/Polyuretha	ine	Epoxy/Polyurethane		
(h)	B <sup>a</sup>	R <sup>b</sup>	D <sup>c</sup>	B <sup>a</sup>	R <sup>b</sup>	D <sup>c</sup>
0	No.10	10	10	No.10	10	10
240	No.10	6	10	No.10	5	1
480	No.10	6	10	No.10	5	0
720	No.10	5	10	No.10	5	0

Table 5. Surface Deteriorations of Samples Subjected to Salt-Spray Test

B<sup>a</sup>, degree of blistering (ASTM D714); R<sup>b</sup>, degree of rusting (ASTM D610); D<sup>c</sup>, degree of delamination.

The weight gains of the test samples under the PANi/polyurethane system and the epoxy/polyurethane system were recorded at 0 h, 240 h, 480 h, and 720 h of Salt-Spray Test. As presented in Table 6 and Figure 37, it is clear that the weight of all epoxy/polyurethane-coated panels increased with exposure time in salt fog; especially, they had an obvious increase at the first 240 hours of exposure time in salt fog. Although the weight of all PANi/polyurethane-coated panels also increased with exposure time, the weight gains were not as obvious as the epoxy/polyurethane-coated panels. Therefore, the PANi/polyurethane-coated panels had less corrosion product formed in comparison with the epoxy/polyurethane-coated panels, and the PANi/polyurethane system showed higher corrosive protection performance than the epoxy/polyurethane system.

	Times (h)	Sample 1	Sample 2	Sample 3	Sample 4
	0	40.38	40.43	39.78	40.68
PANi under	240	40.45	40.51	39.84	40.7
Polyurethane	480	40.5	40.74	39.93	40.69
	720	40.63	40.79	39.98	40.72
	0	40.49	40.17	39.45	40.5
Epoxy under	240 40.91		40.52	39.72	41.2
Polyurethane	480	40.96	40.66	39.91	41.36
	720	41.03	40.73	40.15	41.53

Table 6. Summary of Weight Gains of Four Test Panels with Time



Figure 37. Weight gains of test samples at different Salt-Spray testing time.

### 4.3. Electrochemical Impedance Spectroscopy (EIS) Analysis

### 4.3.1. Testing Procedure

The Gamry EIS-300 Potentiostat again was used to control the electrochemical cell that was subjected to a frequency-rich perturbation signal of a small amplitude. Table 7 gives the parameters and conditions of the EIS analysis. All EIS analyses were performed using the three-electrode compartments. At different times of the Salt-Spray Test, the coated samples were analyzed by EIS, using the substrates as the working electrode. The EIS analysis was performed under potentiostatic control at the open circuit potential.

Counter electrode	Graphite
Reference electrode	Saturated calomel electrode (Ag/AgCl)
Electrolyte	5% NaCl solution
Tested area	$14.6 \text{ cm}^2$
Tested temperature	Ambient temperature
Frequency range	0.01–100,000 Hz
AC potential	10 mV
DC potential	0 mV
Delay time	200 seconds

Table 7. EIS Test Parameters and Conditions Adopted for Studying

The EIS data were acquired at hour-intervals of 0, 24, 48, 72, 96, and 120 after the beginning of the Salt-Spray Test for each group of two-layer coating systems. In the EIS test, the open circuit potential with respect to time, Bode curve, and Nyquist curve were recorded, and the method of

equivalent circuit model was used to analyze the Bode and Nyquist spectra. The equivalent circuit model typically consists of a reference electrode (SCE), a working electrode (test panels), an electrolyte resistance  $R_s$ , a pore resistance  $R_{po}$ , a polarization resistance  $R_p$ , a coating capacitance  $C_c$ , and a double layer capacitance  $C_{dl}$ . After rounds of trial and optimization, the best-fit equivalent circuit models were developed for the Bode and Nyquist spectra. The values of the elements in the best-fit equivalent circuit were used for evaluating the corrosion protection capability of the PANi/polyurethane system and the epoxy/polyurethane system.

## 4.3.2. Data Analysis

The anti-corrosion performance of the two two-layer coating systems was further characterized by EIS analysis. During the test, the EIS data (Bode and Nyquist plots) were recorded across the frequency from  $10^5$  Hz to  $10^{-2}$  Hz. When the coat-scratched panels were exposed in the corrosive electrolyte; that is, 5% NaCl solution, an oxide layer formed and covered the substrate. For the epoxy/polyurethane coating system, the corrosion will continue developing and more rust will be formed, whereas for the PANi/polyurethane system, PANi can passivate the exposed substrate surface. Figure 38 shows the impedance of the epoxy/polyurethane system vs. frequency at different time of immersion in 5% NaCl solution, and Figure 39 shows the impedance of the PANi/polyurethane-coated system versus frequency at different times of immersion in 5% NaCl solution.



Figure 38. Bode plots of epoxy/polyurethane-coated steel panel immersed in 5% NaCl cSolution.

According to Figure 38, the epoxy/polyurethane system has the highest impedance at the beginning of the immersion in the 5% NaCl solution. After 24 hours of immersion, the impedance decreased about 90%, which can be explained by the initiation of corrosion. From 24 hours to 120 hours of immersion, the impedance of the coating system decreased slowly as the corrosion products deposited on the scraped substrates to reduce the rate of corrosion. However,

for the PANi/polyurethane system (see Figure 39), the impedance value stayed in a small range during the 120-hour immersion time (the impedance even slightly increased), which can be explained by the formation of complex adducts between the PANi ingredients and iron ions.



Figure 39. Bode plots of PANi/polyurethane-coated steel panel immersed in 5% NaCl solution.

Two equivalent circuit models were constructed to interpret the EIS spectrum based on methods developed in existing research works [18, 176–178]. Figure 40 (a) and (b) show the equivalent circuits for the PANi/polyurethane system and epoxy/polyurethane-coated system, respectively. Capacitors in EIS experiments act like a constant phase element [176–179], a constant phase element was used to construct the equivalent circuit model in this study. In the equivalent circuit models, R.E. denotes reference electrode, W.E. represents working electrode,  $R_s$  is resistance of electrotype solution,  $Y_c$  is coating capacitance,  $R_{pore}$  is pore resistance of coating,  $Y_h$  is healing layer capacitance,  $R_h$  represents resistance of healing layer,  $Y_{dl}$  is double layer capacitance,  $R_p$  represents polarization resistance,  $Y_o$  represents capacitance of oxide layer,  $R_o$  represents resistance of oxide layer, and  $a_c$ ,  $a_h$ ,  $a_o$ , and  $a_{dl}$  are regressed constants. Base on rounds of trials and optimizations, these two equivalent circuit models best fit the EIS measurement data of the PANi/polyurethane and epoxy/polyurethane systems, respectively.

According to Mansfield [180], the pore resistance  $R_{pore}$  measures the porosity and degradation of the coating; the increase of coating capacitance  $Y_c$  with time is related to the water uptake of the coating; the polarization resistance  $R_p$  and double layer capacitance  $Y_{dl}$  can specify the delamination of the top coat and the onset of corrosion at the interface. In addition, the accumulation of corrosion products also can increase the coating capacitance. Therefore, in general, our coated metal system that performs well in corrosion can be characterized by high resistances of  $R_{pore}$ ,  $R_h$ , and  $R_p$ , also stable capacitances of  $Y_c$ ,  $Y_h$ , and  $Y_{dl}$ . The parameters in the equivalent circuit models were extracted for the EIS measured data and the results are shown in the Table 8.





Figure 40. Equivalent circuit for (a) PANi/polyurethane and (b) epoxy/polyurethane systems.

Coating	Time (h)	$R_s$ ( $\Omega$ )	$egin{array}{c} R_{pore} \ (\Omega) \end{array}$	<i>Y<sub>c</sub></i> (S*s^n)	$egin{array}{c} R_h \ (\Omega) \end{array}$	$\frac{Y_h}{(\mathbf{S}^*\mathbf{s}^n)}$	$R_o$ ( $\Omega$ )	Y <sub>o</sub> (S*s^n)	$R_p$ ( $\Omega$ )	<i>Y<sub>dl</sub></i> (S*s^n)
ł	0	4.14E-02	1.02E+04	4.41E-09	_		2.16E+04	1.57E-07	9.06E+05	1.19E-06
than	24	82.97	1.06E+03	1.71E-08	_	_	70.21	6.17E-12	1.38E+05	3.07E-05
/uret Syste	48	3.08E-02	1.12E+03	3.98E-08			763.8	1.56E-06	6.11E+04	3.11E-05
/Poly ated	72	1.91E+02	1.19E+03	1.21E-08			708.1	3.40E-06	3.48E+04	3.87E-05
poxy Co:	96	7.35E+01	6.34E+02	1.23E-08			196.1	8.33E-06	2.53E+04	2.55E-05
E	120	2.65E-07	6.33E+02	4.87E-07			1.98E+04	3.21E-05	2.50E+04	7.47E-03
	0	3.91E-01	6.18E+04	1.41E-09	2.34E+04	5.91E-08	1.15E+06	1.12E-06	6.64E+06	1.56E-07
hane em	24	3.04E+03	2.88E+05	1.94E-09	3.13E+05	3.63E-08	5.04E+05	3.97E-07	4.43E+06	8.68E-07
uretl Syste	48	9.52E-02	3.32E+05	2.32E-09	1.97E+06	1.57E-07	1.38E+06	1.17E-07	1.77E+06	6.20E-06
Poly ated	72	3.89E+00	3.18E+05	2.73E-09	2.74E+06	2.20E-07	3.65E+05	3.42E-07	1.29E+06	1.65E-05
ANi/ Coi	96	1.40E+00	6.36E+05	3.45E-09	4.66E+05	3.59E-09	1.46E+06	6.52E-07	1.80E+06	2.45E-05
Р	120	2.23E+02	5.21E+05	3.12E-09	7.98E+05	5.54E-09	1.17E+06	5.47E-07	2.13E+06	7.59E-06

Table 8. EIS Results for the Epoxy/Polyurethane and PANi/Polyurethane Coating Systems

Figure 41 shows that the pore resistance  $R_{pore}$  of the PANi/polyurethane system is much larger than that of the epoxy/polyurethane system. Also, the  $R_{pore}$  of the PANi/polyurethane increased with immersion time. However, the pore resistance of the epoxy/polyurethane system decreased with immersion time. The capacitance  $Y_c$  of the PANi/polyurethane system stayed about the same value; however, the capacitance of the epoxy/polyurethane-coated system varied with time, especially after 120 h of immersion time in 5% NaCl solution. The phenomenon could be ascribed to the accumulation of corrosion products on the surface of the exposed substrate.



Figure 41.  $R_{pore}$  and  $Y_c$  of PANi/polyurethane and epoxy/polyurethane systems.

Figure 42 shows that the polarization resistance  $R_p$  of the PANi/polyurethane system is also obviously larger than that of the epoxy/polyurethane system; the  $R_p$  decreased first and then increased with immersion time. However, the polarization resistance of the epoxy/polyurethane system consistently decreased with immersion time. In addition, the double layer capacitance  $Y_{dl}$ of the PANi/polyurethane system had no change with the immersion time; however, the double layer capacitance of the epoxy/polyurethane system changed with immersion time, especially after 100 h of immersion time. This can be explained by the delamination of the topcoat or the initiation of corrosion at the interface. This result is consistent with the observations in the Salt-Spray Test.



Figure 42.  $R_p$  and  $Y_{dl}$  of PANi/polyurethane and epoxy/polyurethane systems.



Figure 43. *R*<sub>o</sub> and *Y*<sub>o</sub> of PANi/polyurethane and epoxy/polyurethane systems.

Figure 43 shows that the oxide layer resistance  $R_o$  of the PANi/polyurethane system is much larger than that of the epoxy/polyurethane system. The fluctuation of the oxide layer resistance of the PANi/polyurethane system is mainly due to the reaction between the polyaniline ingredients and iron ions. The onset of the corrosion at interface could cause the release of polyaniline dopant, which can react with the iron ions of rust or other iron-oxide products. After the reaction, a complex adducts layer could be formed to cover the oxide layer to increase the resistance to corrosion. The resistance of oxide layer at the interface of the epoxy/polyurethane system however is low compared with the PANi/polyurethane-coated system. The results also shows that the oxide layer capacitance  $Y_o$  of the PANi/polyurethane system remained the same throughout the immersion time; the oxide layer capacitance of the epoxy/polyurethane system however shows a clear increase after 24 hours in 5% NaCl solution. This could be explained by the accumulation of corrosion products at the interface.

Overall, in comparison to the epoxy/polyurethane system, the PANi/polyurethane system produces less rust and showed higher delamination resistance. The anti-corrosion benefit of the PANi/polyurethane system was further demonstrated in the EIS analysis. The PANi/polyurethane system exhibited high delamination resistance and corrosion resistance based on the parameters obtained using the best-fit equivalent circuits including the resistance of porosity, the coating capacitance, the polarization resistance, and the double layer capacitance. The demonstrated overall anti-corrosion capacity of the proposed two-layer coating system laid a solid foundation for future field evaluations of the final product.



Figure 44. Time dependence of corrosion current for epoxy/polyurethane and PANi/polyurethane testing samples.

The polarization resistance method described in ASTM G59 and G102 was used again to estimate the corrosion current and corrosion rate. According to Eqs. 12 and 13, a series of parameters were chosen and estimated following some research work [153, 154] before calculating the corrosion current and corrosion rate, such as 18.50 for equivalent weight of SAE 1008/1010 steel (*EW*), 7.872 g·cm<sup>-3</sup> for density of SAE 1008/1010 steel (*d*), conversion factor (*K*) using  $3.27 \cdot 10^3$  mm·g·A<sup>-1</sup>·cm<sup>-1</sup>·yr<sup>-1</sup>, anodic Tafel constant ( $\beta_a$ ) and cathodic Tafel constant ( $\beta_c$ ) are 80 mV·dec<sup>-1</sup> and 100 mV·dec<sup>-1</sup>, respectively for the iron immersed in 0.5 M NaCl solution [153, 154]. Figures 44 and 45 show the time dependence of corrosion current and corrosion rate for different types of coatings.



Figure 45. Time dependence of corrosion rate for epoxy/polyurethane and pANi/polyurethane testing samples.

For the PANi/polyurethane system, both corrosion current and corrosion rate increased slightly during the first 60 hours and later became stable especially the values that had a slight decrease. However, the corrosion current and corrosion rate of the epoxy/polyurethane system exhibited obviously increase with increasing time. During EIS testing, corrosion initiated at the scribed line of the substrates and propagated from the defect part to intact-coated part. Epoxy-only coating systems could deter the propagation and thus the corroding area increased, which results in the increasing of corrosion current and rate. However, the PANi-based coating system can release dopant, which will form a complex compound and then inhibit corrosion propagation once the corrosion occurred. On the basis of the comparison of the epoxy-only and PANi-based coating systems, one can conclude that PANi-based coating system exhibited high anti-corrosion performance, especially it can effectively deter the corrosion propagation once the corrosion occurred.

# 4.4. Summary

A prototype two-layer coating system was manufactured in this task, which includes a PANibased primer and a polyurethane topcoat. To verify whether the fabricated two-layer coating system possess high anti-corrosion capabilities, an epoxy-over-polyurethane coating system was made as the control system. The standard Salt-Spray Test per ASTM B117 and the technique of EIS was used to quantify their anti-corrosion performance.

To compare the anti-corrosion performance of the PANi/polyurethane coating system with the epoxy/polyurethane coating system, four samples were made for each coating system and were subjected to the Salt-Spray Test. Throughout the testing process, the samples were subjected to assessment for the degree of blistering, degree of rusting, and degree of delamination at certain times. The testing results show that none of the PANi/polyurethane-coated panels and

epoxy/polyurethane-coated panels had signs of blistering; the epoxy/polyurethane-coated panels showed significantly more rust along the scribe line comparing to the PANi/polyurethane-coated panels; the severity of delamination on the epoxy/polyurethane-coated panels apparently increase with time of Salt-Spray testing. In addition, by checking the weight gains during the testing, the PANi/polyurethane-coated panels had less corrosion product formed in comparison to the epoxy/polyurethane-coated panels. As such, PANi/polyurethane system demonstrated improved overall performance than the epoxy/polyurethane system.

EIS analyses were conducted after the start of the Salt-Spray Test for each group of the two-layer coating system. Bode and Nyquist data were recorded and analyzed by equivalent circuit method. The values of the elements in the best-fit equivalent circuit was extracted for evaluating the anticorrosion capability of the PANi/polyurethane system w.r.t. the epoxy/polyurethane system. On the basis of the polarization resistance extracted from the equivalent circuit, the corrosion current and corrosion rate were also estimated to evaluate the anti-corrosion performance of the PANi/polyurethane system and the epoxy/polyurethane system. According to the parameters obtained from the best-fit equivalent circuits, the PANi/polyurethane system exhibited high delamination resistance method indicates that the epoxy/polyurethane system exhibited obviously increased corrosion current and corrosion rate when time increased; however, the PANi/polyurethane system exhibited a negligible and stable corrosion current and corrosion rate, which demonstrate that the PANi/polyurethane system.

### **CHAPTER 5 LABORATORY EVALUATION OF LONG-TERM PERFORMANCE OF**

### **DEVELOPED TWO-LAYER COATING SYSTEM**

A prototype two-layer coating system was fabricated in the prior task by coating a regular commercial polyurethane on the top of the waterborne electroactive PANi-based primer. A series of tests and analysis demonstrated that the synthesized waterborne electroactive PANi could effectively improve the anti-corrosion performance of a regular epoxy coating. To evaluate the long-term anti-corrosion performance and the durability of PANi-based two-layer coating systems, an organic solvent-based epoxy is added to the evaluation scheme in this task to fabricate a second PANi-based primer (in addition to the existing PANi-based primer made of waterborne epoxy). For these two primers and two other commercial ones (a zinc-rich primer and an epoxy-only primer), two widely used topcoat materials were obtained to make a total of eight two-layer coating systems. These two-layer systems are expected to possess comparable or higher anti-corrosion capabilities and longer durability than the conventional three-layer coatings. The ASTM B117 Salt-Spray Test and the ASTM D5894 Cyclic Salt Fog/UV Exposure Test were performed to simulate the accelerated corrosion environment. At different stages of the tests, the Standard Pull-Off Adhesion Test per ASTM D4541 is used to evaluate the adhesion capacity of the coating and the technique of Electrochemical Impedance Spectroscopy (EIS), Scanning Kelvin Probe Force Microscope (SKPFM), and Scanning Electron Microscope (SEM) are used to evaluate the anti-corrosion capacity.

#### 5.1. Preparation of Two-layer Coating Systems

To fabricate the coating samples for the accelerated corrosion tests, steel panels per the SAE Designation of 1008/1010 were acquired from Q-Lab at the dimensions of  $51 \times 89 \times 0.81$  mm. Prior to coating and being subjected to corrosion, the panels were ground using the standard 1200-grid paper, cleaned in acetone and ultrasound-bathed in ethanol for 3 minutes, and then D.I. water rinsed and dried at the ambient room temperature ( $25^{\circ}$ C). The evaluation scheme includes two types of ICP-based primer, one made of a waterborne epoxy as the binder matrix for primer and the other made of a regular non-waterborne epoxy as the binder matrix for primer. These two ICP-based primers form a 2 × 2 testing matrix with two widely used topcoat materials; that is, a topcoat epoxy and a topcoat polyurethane. These ICP-based two-layer systems are expected to possess longer and/or higher anti-corrosion capacity than the conventional three-layer coatings. In addition to the four coating systems, two commercial primers, a zinc-rich, epoxy-based primer and an epoxy-only primer, were included in the testing scheme as control systems. These two commercial primers were topcoated with a topcoat epoxy and a topcoat polyurethane, respectively, making a total of eight two-layer coating systems to test in this study as listed in Table 9. Three replicate samples of each system were made for testing.

An organic solvent-based epoxy and a waterborne epoxy were used to make the two ICP-based primers. A high-performance acrylic polyurethane and a fast-cure epoxy were used as the topcoat material. Zinc pigment was obtained to make the epoxy-based zinc-rich primer. These primer and topcoat materials are commonly used in the applications of steel bridge repairs and maintenance. According to the manufacturer's recommendation, different combinations of
primers and topcoats were used to make the eight two-layer coating systems. For these coating systems, the primer was coated on the cleaned steel panels to achieve a dry film thickness of 100  $\mu$ m. After 24-hour of drying at the ambient room condition (25°C), the topcoat was applied onto top of the primer film to achieve an additional dry thickness of 125  $\mu$ m.

System Number	Coating Description	Nominal Dry-Film Thickness (µm)	Max VOC Content (g/L)
1	Zinc-rich Epoxy (P1)/Polyurethane (T1)	100/125	340/300
2	Zinc-rich Epoxy (P1)/Epoxy (T2)	100/125	340/250
3	PANi Epoxy (P2)/Polyurethane (T1)	100/125	340/300
4	PANi Epoxy (P2)/Epoxy (T2)	100/125	340/250
5	Epoxy (P3)/Polyurethane (T1)	100/125	250/300
6	Epoxy (P3)/Epoxy (T2)	100/125	250/250
7	PANi Waterborne Epoxy (P4)/Polyurethane (T1)	100/125	340/300
8	PANi Waterborne Epoxy (P4)/Epoxy (T2)	100/125	340/250

Table 9. Two-Layer Organic Coating Systems Tested in This Study

P = Primer, T = Topcoat.

Systems 1, 2, 5, and 6 were fabricated according to the manufacturer's recommendations and used as the control systems. Systems 3, 4, 7, and 8 each consist of a primer made by mixing the conductive ICP into an organic solvent-based or waterborne epoxy and a commonly used topcoat. Systems 1 and 2 have a zinc-rich primer using the organic solvent-based epoxy in which zinc-dust pigment accounts for 90 wt.% (dry weight) as was made according to the manufacturer's recommendation. Systems 3, 4, 7, and 8 each have an ICP-based primer in which the ICP accounts for 5 wt.% (dry weight). It is noteworthy that Systems 1–6 used the same organic solvent-based epoxy to make the primer. Systems 7 and 8 used the same waterborne epoxy to make the primer. All two-layer samples were dried at the ambient temperature (25°C) for 7 days before conducting the Salt-Spray Test (ASTM B117) and the subsequent pull-off adhesion test (ASTM D4541) and EIS analysis, SKPFM analysis, and SEM analysis.

# **5.2. Accelerated Laboratory Tests**

### 5.2.1. Testing Procedure

Two laboratory-based accelerated corrosion tests, ASTM B117 and ASTM D5894, were conducted to evaluate the performance of the eight coating systems. The standard Salt-Spray Test per ASTM B117 uses a 5% sodium chloride solution to simulate the sea water corrosive environment and was conducted for a total of 4,032 hours in this study. The Cyclic Salt Fog/UV Exposure Laboratory Test per ASTM D5894 uses a dilute solution of 0.35% ammonium sulfate  $[(NH_4)_2SO_4]$  and 0.05% sodium chloride in which the test specimens were exposed to alternating periods of a 168-hour fluorescent UV/condensation condition and a 168-hour cyclic salt fog/dry condition. The fluorescent UV/condensation cycle was 4-hour UV at 60°C and 4-hour condensation at 50°C using UVA-340 nm fluorescent lamps. Figure 46 shows the fluorescent UV/condensation test apparatus and UV detector.



Figure 46. Fluorescent UV/condensation test apparatus.

Table 10. Testing Conditions of Each 336-Hour Test Cycle per ASTM B117 and ASTM D5894

Testing Condition	ASTM B117	ASTM D5894
Salt fog spray: 336 hours	al	
Wet condition: 5 wt.% sodium chloride at 35°C	v	
UV-condensation: 168 hours		
Test cycle: 4-h UV/4-h condensation		
UV lamp: UVA-340 fluorescent lamps		al
UV temperature: 60°C		N
Condensation temperature: 50°C		
Condensation humidity: 100% RH		
Salt fog-dry air: 168 hours		
Test cycle: 1-h wet/1-h dry air		
Fog cycle: $0.35$ wt.% (NH4) <sub>2</sub> SO <sub>4</sub> + $0.05$ wt.% NaCl at		
room temperature		
Dry air cycle: at 35°C		

Figure 47 shows the fluorescent UV/condensation test apparatus and detected UVA intensity during the Cyclic Salt Fog/UV Exposure Test per ASTM D5894. The standard procedure requires a UV level of 0.89 W/( $m^2 \cdot nm$ ) at 340 nm, which is equivalent to 30.2 mW/cm<sup>2</sup> exposure in a cyclic UV exposure test. The salt fog/dry condition consists of a cycle of one-hour fogging at ambient temperature and one-hour drying at 35°C. Table 10 gives the detailed condition of ASTM B117 and ASTM D5894. To evaluate the anti-corrosion durability of the eight two-layer coating systems, three replicate samples of each system were subjected to each test, respectively.



Figure 47. UVA intensity detected by Sper Scientific UV light meter.

To initiate substrate corrosion, a diagonal scribe mark of 1 in. (25.4 mm in length and 0.5 mm in width) was made to penetrate the two-layer coating materials using a sharp scriber according to the method ASTM D1654 [*176*]. The scribe was made on each sample to expose the underlying substrate material before the accelerated corrosion tests. The rear side of the panel was coated by a tolerant epoxy using a HVLP spray gun and dried at the ambient temperature. Edge sides of the sample were sealed carefully using a heavy-duty corrosion control tape (JVCC PWT-20C). Throughout the corrosion tests, all panels were examined for surface blistering and rusting in accordance to the standard method of ASTM D610 [*178*] and ASTM D714 [*177*], respectively.

# 5.2.2. Data Analysis

The surfaces of all tested samples were examined visually after 4,032 hours for each accelerated corrosion test. ASTM B117 (Salt-Spray Test) provides quick and simple evaluation for natural outdoor exposure conditions, which gives good predictions for waterborne coatings that develop early blistering [*184*]. ASTM D5894, on the other hand, gives more realistic field-condition prediction by simulating the cycles of UV exposure and fogging. The coating performance based on surface failures after the two accelerated laboratory tests were analyzed and compared below. A photograph of one tested panel is shown in Figure 48 for each system, exhibiting different levels of corrosion at the scribe location.



Figure 48. Coated steels samples after 4,032-hour Salt Spray Test and Cyclic-Weathering Test.

## 5.2.1.1. Surface Deterioration

None of the coating systems showed visible surface failures at locations away from the scribe mark after each test. This demonstrates good barrier functions of both coating systems. Comparing the test results of tests ASTM B117 and ASTM D5894, the coating systems under ASTM D5894 condition exhibited poorer performance than under the ASTM B117 condition, especially for the coating systems with an epoxy topcoat (Systems 2, 4, 6, and 8). This indicates that the ASTM D5894 gave a more corrosive condition than ASTM B117. By visual inspection, zinc-rich, primer-based coating systems showed superior anti-corrosion performance. For System 1, slight brown-colored rust material can be seen accumulated at the scribe mark after 4,032 hours in ASTM B117. In addition, visible gray-colored corrosion products of zinc can be viewed along the scribe marks. The samples after 4,032 hours in ASTM D5894 also showed slight brown-colored rust with visible corrosion products of zinc along the scribe mark. The accumulated corrosion products of zinc in the coated samples did not cause delamination around the scribe mark. System 1 showed satisfactory anti-corrosion performance.

After the 4,032-hour accelerated corrosion tests, both samples of System 2 showed gray-colored corrosion products of zinc along the scribe mark. All samples from ASTM D5894 exhibited visible brown-colored rust and obvious delamination around the scribe mark as shown in the magnified window. This indicates that more corrosion products formed and propagated from the scribe mark to the intact surface of substrate under UV exposure.

Regarding System 3, the samples showed visible brown-colored rust along the scribe mark and at the bottom left corner after 4,032-hour exposure in tests ASTM B117 and ASTM D5894. No visible delamination was observed along the scribe marks. The samples coated by System 3 in general showed comparable anti-corrosion performance under tests ASTM B117 and ASTM D5894.

As for System 4, the samples also showed visible brown-colored rust along the scribe mark after 4,032-hour exposure in tests ASTM B117 and D5894. Apparently, there is more brown-colored rust along the scribe mark of the samples in ASTM D5894 than in ASTM B117, which further suggests the better protection by the polyurethane topcoat than by the epoxy topcoat. No visible delamination was observed along the scribe marks.

System 5 exhibited a heavy corrosion situation around the scribe mark. Visible delamination can be observed along the scribe mark and even along the edges of the samples. Samples in ASTM D5894 showed roughly the same extent of corrosion as the samples in ASTM B117.

Samples of System 6 exhibited the worst corrosion situation along the scribe mark among all the tested coating systems after 4,032-hour exposure in tests ASTM B117 and ASTM D5894. Obvious delamination areas were observed around the scribe, especially for samples from ASTM D5894, the maximum size of delamination area is about 9 mm. Samples in ASTM D5894 showed even worse corrosion results than samples in ASTM B117 due to the UV exposure.

For System 7, there is visible brown-colored rust along the scribe mark after 4,032-hour exposure in tests ASTM B117 and ASTM D5894, with visible delamination. The samples in ASTM D5894 also showed brown-colored rust along the edges of the heavy-duty corrosion control tape. Sample exposure in ASTM D5894 exhibited a little heavier corrosion than samples in ASTM B117.

With an epoxy topcoat, System 8 showed obvious brown-colored rust along the scribe mark after tests ASTM B117 and ASTM D5894. Samples in ASTM D5894 showed higher creepage development and higher delamination than those in ASTM B117. The maximum delamination is 4 mm wide around the scribe mark in samples of ASTM D5894. Samples in ASTM D5894 showed more severe corrosion than samples in ASTM B117 due to the poorer UV resistance of the epoxy topcoat. Thus, the epoxy topcoat used exhibited lower durability than the polyurethane topcoat.

Based on the visual examinations of the surface deterioration of the eight two-layer coating systems, the following conclusions can be drawn.

- 1. The zinc-rich systems (Systems 1 and 2) have good anti-corrosion durability and the systems with a primer layer made of epoxy only (Systems 5 and 6) give the poorest anticorrosion durability. The zinc-rich systems however may have accumulated corrosion products of zinc along the scribe mark to cause delamination around the scribe area (as observed in System 2).
- 2. The coating systems with a PANi-based primer (Systems 3, 4, 7, and 8) demonstrated long-term anti-corrosion durability through the 4,032-hour corrosion test with and without UV exposure.
- 3. The UV-exposure test; that is, Test B, poses a more severe corrosion environment than the standard Salt-Spray Test: Test A per ASTM B117. The more severe surface deterioration and delamination shown on Systems 2, 4, 6, and 8 when exposed to Test B condition indicates that UV has significant effect on epoxy topcoat. This effect needs to be further evaluated in the future field test.
- 4. The PANi-based primer made of waterborne epoxy as in System 7 has poorer anticorrosion performance than the PANi-based primer made of a non-waterborne epoxy as in System 3. This could be caused by the lower cohesion strength of the waterborne epoxy primer than the non-waterborne epoxy primer.

ASTM D714 specifies a numerical scale from 10 to 0 to indicate the severity of surface blistering [177]. No. 10 represents no blistering, No. 8 represents the smallest-size blister that can be easily seen by unaided eyes. In addition, Dense (D), Medium dense (MD), Medium (M), and Few (F) were selected to indicate frequency per this reference standard. By visually checking the tested samples, Systems 2, 4, 6, and 8 showed some blistering around the scribe mark. ASTM D610 specifies a series of values to rank the severity of surface rusting [178]. Rust Grade 10 represents a rusted surface of less than or equal to 0.01%. Rust Grade 9 represents a rusted surface of greater than 0.01% and up to 0.03%. Table 11 showed the blistering and rusting results for the eight coating systems tested in this study.

Test Type			Coating System								
		1	2	3	4	5	6	7	8		
Degree of	ASTM B117	10	4-F	10	4-F	10	4-F	6-F	4-F		
Blistering	ASTM D5894	10	2-F	10	2-F	10	2-M	4-F	2-F		
Degree of	ASTM B117	9-S	9-S	8-S	8-S	6-S	6-S	8-S	8-S		
Rusting	ASTM D5894	9-S	8-S	8-S	7-S	6-S	5-S	8-S	8-S		

Table 1. Average Deterioration after 4,032-hour Exposure in Accelerated Corrosion Tests

F = Few (frequency); M = Medium (frequency); S = Spot Rusting, small localized rusting at a few places.

### 5.2.1.2. Scribe Rust Creepage

Many research studies have demonstrated that rust creepage at a scribe mark is a sensitive and useful parameter in determining coating durability and that the plot of rust creepage against exposure time was fairly linear [182]. Some researchers pointed out that coating corrosion rate is proportional to the slope of the plotted line, but inversely proportional to incubation time after the creepage becomes visible [181].

This evaluation technique described in standard test method ASTM D7087-05a [183] was used in this study to compare coating performance at the scribe mark. According to this method, the test specimen was marked using a tracing pen and some key points were marked on the test panel following the scribe line. For example, the line between points g and h (in Figure 49) is the center line, which represents 80% of the scribe line, and contours formed by points i, j, k, and lrepresent the borderline of the creepage area (see Figure 49). The entire corroded side of the scribed panel was traced on a transparent plastic sheet and later the transparent plastic sheet, including all scribe creepage trace, was scanned with a ruler and saved to an image file. Image software capable of capturing and opening the image file of trace was used to obtain the creepage area, which is the area inside the traced line. Next, net mean creepage was calculated using the following equation [183]:

$$C_{net} = (A_{iilk} - A_0) / (2L)$$
<sup>(29)</sup>

where  $C_{net}$  represents mean creepage in mm,  $A_{ijlk}$  is the area inside the boundary of *ijkl* by tracing and imaging,  $A_0$  is area inside the boundary of *ijkl* before exposure, ( $A_0 = 10 \text{ mm}^2$ ), and L is the length between points g and h along the scribe (20 mm).



Figure 49. Photography of trace and markings for area integration of creepage area around the scribe line.

The creepage results of all coating systems are presented in Table 12. Zinc-rich coating systems (Systems 1 and 2) performed the best (with smaller creepage), followed by the PANi-based coating systems.

Test Type	System No.	1	2	3	4	5	6	7	8
1022 h Tost A	$A_{ijkl} (\mathrm{mm}^2)$	12	12	13	18	36	37	15	16
4,052-11 Test A	$C_{net}$ (mm)	0.05	0.05	0.075	0.2	0.15	0.175	0.125	0.15
4 022 h Teat D	$A_{ijkl}$ (mm <sup>2</sup> )	12	13	14	24	40	49	15.6	16.4
4,052-11 Test B	$C_{net}$ (mm)	0.05	0.075	0.1	0.35	0.75	0.975	0.14	0.16

Table 12. Creepage Developed in All Coating Systems

Figure 50 shows the creepage at the scribe mark for all the coated panels during Test A and Figure 51 shows the creepage at the scribe mark for all the coated panels during Test B. From Figures 50 and 51, it is clear that the rust creepage linearly increases with testing time. System 6 showed the largest slope for both Tests A and B, which indicated that System 6 had the highest corrosion rate and the poorest anti-corrosion durability. System 1 showed the smallest slopes for the Tests A and B, which indicates that System 1 had the lowest corrosion rate and exhibited the best anti-corrosion durability.



Figure 50. Time dependence of creepage for coated panels in Test A.

For Tests A and B, System 2 showed the second smallest slope and System 3 showed the third smallest slope, which indicates that both systems had good anti-corrosion durability. Systems 7 and 8 also showed low corrosion rates in Tests A and B. System 4 showed higher corrosion rates than Systems 2, 3, 7, and 8. In Test B conditions, System 4 had a higher corrosion rate than in Test A conditions. Systems 5 and 6 exhibited poorer anti-corrosion durability than the other systems. Under Test A conditions, Systems 5 and 6 exhibited nearly the same corrosion rate. System 5 however exhibited a lower corrosion rate than System 6 in Test B. Systems 3, 5, and 7 all showed better anti-corrosion performance than Systems 4, 6, and 8, respectively, in Test B. This confirmed that the polyurethane topcoat performed better than the epoxy topcoat under UV/cyclic salt fog condition.



Figure 51. Time dependence of creepage for coated panels in Test B.

### 5.3. Pull-Off Adhesion Test

The adhesion strength of the coatings on steel panels was evaluated according to the standard ASTM D4541 procedures, which use an apparatus known as Pull-Off Adhesion Tester. A portable Elcometer F106-2 apparatus (0-1000 psi scale) was used to apply a concentric load to a single coating surface. In this study, the pull-off adhesion test was conducted both before and after 4,032 hours of Salt-Spray Test or Cyclic Salt Fog/UV Exposure Test. For each coating system, three replicate pull-off tests were conducted following the same standard procedures [127]. When the topcoat got dried completely, the select test area on each coated panel was cleaned using a non-abrasive sponge. The aluminum fixture was cleaned using an abrasive finishing pad first and then cleaned using a non-abrasive sponge. The aluminum fixtures were then adhered on the surface of the dried coating by a thermally curable epoxy adhesive (Product No. 2011, Huntsman Araldite), which can be cured at 24 hours before applying load. When the adhesive dried, the tester was coupled to the fixture and the upper part was turned until the fixture was pulled off [127]. The pull-off strength was read from the scale of the tester directly. The pull-off strength mainly depends on the strength of adhesion bonds between the loading fixture and the test panel surface. The adhesion strength was considered properly measured when the rupture took place at the substrate-primer interface [184]. Figure 52 shows one panel before and after testing.



Figure 52. Photography of a coated panel before and after adhesion test.

Table 13 shows the summary of pull-off test results. After 4,032 hours, all the coating systems exhibited pull-off strength above 500 psi. The worst case was observed on System 6, which lost about 22% of adhesion strength after 4,032-hour UV/cyclic salt fog exposure. All coating systems exposure in Test B showed bigger changes in adhesion strength than in Test A. This indicated that Test B conditions simulate a more serious corrosive environment. Coating systems with epoxy topcoat (T2) exhibited obvious change in adhesion strength in both Tests A and B, especially for Test B condition. This demonstrated that epoxy topcoat (T2) has lower corrosion resistance when exposed to UV. Systems 3 and 7 also exhibited a small change in adhesion strength after 4,032 hours in Tests A and B.

					Chan	ge in	Change in	
	Aver	rage Adhesi	on Strength	n (psi)	Adhesion	Strength	Adhesion	
System					(p	si)	Streng	th (%)
No.	Before Test A	After 4,032-h Test A	Before Test B	After 4,032-h Test B	4,032-h Test A	4,032-h Test B	4,032-h Test A	4,032-h Test B
1	771.5	741.2	771.8	735.5	30.3	36.3	4%	5%
2	756.7	685.2	755	680	71.5	75	9%	10%
3	785.6	745.3	784.5	740.5	40.3	44	5%	6%
4	778.2	710.5	778.8	695.2	67.7	83.6	9%	11%
5	785	685.8	783	661.1	99.2	121.9	13%	16%
6	800	645.6	795	622.4	154.4	172.6	19%	22%
7	580	541.3	578.8	530.6	38.7	48.2	7%	8%
8	582	512.4	580.6	500.1	69.6	80.5	12%	14%

Table 13. Adhesion Strength Test Results Before and After Tests A and B (4,032 Hours)

#### 5.4. Electrochemical Impedance Spectroscopy (EIS) Analysis

EIS was used to further investigate the corrosion-protection performance of the eight two-layer coating systems. A high-performance barrier coating will generate a straight line with unit negative slope (Bode modulus) that represents a pure capacitive behavior in Bode modulus plot of EIS [184, 185]. When the Bode modulus plot showed a deviation from its straight line, the water ingress through the coating occurred and corrosion might be initiated [184].

Impedance of the coating system was recorded across the frequency from 10 kHz to 0.1 Hz. Low-frequency impedance was used to characterize the performance of coating and large low-frequency impedance values normally indicate a high performance barrier coating [184, 186, 187]. In this study, the maximum impedance at low frequency (i.e., 0.1 Hz) was recorded and analyzed for all eight two-layer coating systems by EIS.

Figure 53 shows the Bode plot w.r.t. frequency for all the coating systems before immersion in a 5% of NaCl aqueous solution. All coating systems have about the same unit negative slope in Bode modulus plot of EIS, which demonstrated that all coating systems performed like a pure capacitor before exposure in corrosion environment. In addition, all coating systems almost have the same impedance at 0.1 Hz. This indicated that all coating systems have about the same corrosion resistance before exposure to a corrosion environment.



Figure 1. Bode Plot for All Coating Systems before Exposure to a 5% NaCl Solution

Figure 54 shows the Bode plot w.r.t. frequency for all the coating systems after 4,032-h immersion in 5% of NaCl solution. System 8 exhibited the worst situation because its Bode modulus plot showed an earlier deviation from its straight line portion. System 2, 4, 5, and 6 also showed a deviation from their straight line portion. This indicated that the water ingress through the coating occurred and corrosion products formed. This phenomenon can be explained by the low cohesive strength between the primer and topcoat, especially for the epoxy topcoat (T2). This phenomenon also verified the accelerated laboratory test results. Systems 1, 3, and 7 keep

the straight line in their Bode modulus plot, which indicated that no obvious water ingress through the coating occurred. In other words, no corrosion occurred under the coating.



Figure 54. Bode plot for all coating systems after 4,032-hour exposure to a 5% NaCl solution.



Figure 55. Impedance at 0.1 Hz of coating systems before and after 4,032-hour exposure to a 5% of NaCl solution.

Figure 55 shows the impedance at 0.1 Hz for all coating systems before and after 4,032-h exposure to the 5% NaCl aqueous solution. Systems 2, 4, 5, 6, and 8 have significant decreases in low-frequency impedance after exposure to corrosion environment. In comparison, Systems 1, 3, and 7 have smaller decreases in low-frequency impedance. Low-frequency impedance decreases for Systems 2, 4, 6, and 8 were caused by the lower barrier function of the epoxy topcoat. During the test, epoxy degradation was faster than polyurethane as a topcoat, and water penetrated through the topcoat causing corrosion. The larger decrease of low-frequency

impedance in exhibited System 5 was mainly due to the low corrosion resistance of epoxy-only primer, which could not defer the corrosion propagation once corrosion started at the interface of the primer and steel substrate. The comparison of impedance at 0.1 Hz for all coating systems before and after 4,032-h exposure to the 5% NaCl aqueous solution demonstrated that Systems 1, 3, and 7 still possessed good corrosion-protection performance after long-term exposure to a rather corrosive condition.

# 5.5. Scanning Kelvin Probe Force Microscope (SKPFM) Analysis

The Volta potential difference (VPD) measured by SKPFM is correlated well with the localized corrosion behavior of metals [101–102]. In order to investigate the ICP protection mechanism, the coated samples for eight two-layer coating systems were used to conduct the SKPFM measurement after the salt/fog UV exposure test. Samples of the sizes 1 cm in length by 1 cm in width were prepared by cutting the aforementioned salt/fog UV exposure tested samples. All coating systems were removed from the substrate using an effective solvent for cured epoxy to expose the substrate surface for SKPFM scanning. The anti-corrosion performance of eight two-layer coating systems was investigated by comparing the surface VPD.

SKPFM analysis was conducted and the VPD of surface area about 1 cm from the scribe line was measured for all coating systems. Figure 56 shows the surface VPD for all coating systems. The surface VPD map of Systems 1, 2, 3, and 4 shows fairly uniformly distributed potential across the scanned domain, which indicates that there are negligible detectable anodic sites corresponding to high surface potential or detectable cathodic sites corresponding to low surface potential in the domain. The surface VPD map for System 5 and 6 shows obvious high surface potential and low surface potential, which indicate the anodic sites and cathodic sites, respectively. Systems 7 and 8 show the similar surface VPD map, but has higher VPD than System 4.

Based on the surface VPD map shown in Figure 56, Systems 1 and 3 exhibited the best anticorrosion performance. Systems 2 and 4 also exhibited the good anti-corrosion performance and Systems 5 and 6 exhibited the worst anti-corrosion performance. The comparison of the surface VPD for Systems 3, 4, 7, and 8 indicate that the organic solvent-based epoxy PANi primer gives higher corrosion resistance for steel than water-based epoxy PANi primer. Actually this result is mainly due to the lower adhesion strength of the waterborne epoxy on steel, which is a match with the pull-off adhesion strength test results. Comparing the surface VPD for Systems 5, 6, 7, and 8 one can find that Systems 7 and 8 exhibited lower surface VPD than Systems 5 and 6, which can be attributed to the existence of PANi particles in Systems 7 and 8. Therefore, the surface VPD map for Systems 3–8 can accurately validate the ICP protection mechanism for corrosion on steel.





Figure 56. Scanned VPD of all coating systems.

# 5.6. Scanning Electron Microscope (SEM) Analysis

The technique of SEM can be used to generate a variety of signals at the surface of solid specimens. Based on the generated signals, the information of external morphology (texture), chemical composition, and crystalline structure can be analyzed for the scanned sample [*188*]. In this study, SEM analysis was conducted to investigate the anti-corrosion performance of the coating systems. According to the accelerated corrosion test result, the polyurethane topcoat exhibited the much better UV resistance capacity than epoxy topcoat and thus the polyurethane-topcoat-based coating systems will be recommended as the long-term anti-corrosion performance coating system. Therefore, only polyurethane-topcoat-based coating systems (Systems 1, 3, 5, and 7) will be conducted by SEM analysis further to validate the extent of corrosion at the location where the corrosion product could not be found visually. After conducting a 4,032 h cyclic salt/fog UV exposure test, these four types of coated samples were cut to small samples with the sizes of 2.54 cm by 2.54 cm, with one edge vertically crossing the scribe line. After then, all samples were molded in epoxy with clear color. Figure 57 shows the cured-molded samples.



Figure 57. SEM samples: Curing (left) and cured (right).

Based on the accelerated corrosion test and EIS test described above, the polyurethane topcoat exhibited better UV resistance capacity than the epoxy topcoat. The coating systems using polyurethane as topcoat will be considered as the recommended coating systems for long-term, anti-corrosion performance investigation. To simplify the experiment, the SEM test was conducted only for Systems 1, 3, 5, and 7 to further investigate the anti-corrosion performance of these four coating system. Figure 58 shows the SEM scanned cross section of the interface between the coating system and steel substrate. System 5 shows the additional layer between the primer and substrate, which is the corrosion product formed during the accelerated corrosion test. No addition layer was found for Systems 1, 3, and 7. The SEM test results confirmed the same result with accelerated corrosion tests and EIS tests.



Figure 58. SEM images at the interface between substrate and coatings.

# 5.7. Summary

This chapter focused on making different two-layer coating systems, investigated the anticorrosion performance of a PANi-based primer coating system comparing with other commercial primer coating systems, and recommends the targeted two-layer coating system. An organic solvent-based epoxy was used to fabricate a second PANi-based primer in addition to the existing PANi-based primer made of waterborne epoxy. These two primers and two other commercial ones (a zinc-rich primer and an epoxy-only primer) with two widely used topcoat materials were obtained to make a total of eight two-layer coating systems that are expected to possess comparable or higher anti-corrosion capabilities and longer durability than the conventional three-layer coatings. To evaluate the long-term performance of an ICP-based two-layer coating system for potential use on steels, the ASTM B117 Salt-Spray Test and ASTM D5894 Cyclic Salt Fog/UV Exposure Test were performed to simulate the accelerated corrosion environment. At different service stages of the tests, the Standard Pull-Off Adhesion Test per ASTM D4541 was used to evaluate the adhesion capacity of the coating on the substrate, and the techniques of EIS, SKPFM, and SEM were conducted to evaluate the long-term performance of a total of eight two-coat systems including the ICP-based systems.

Based on the visual inspection of surface deterioration after 4,032-hour testing, the zinc-based systems and the ICP-based systems developed in this study exhibited comparable, long-term, anti-corrosion durability, both providing higher anti-corrosion durability than the epoxy-only primer. Epoxy topcoat has lower corrosion resistance than polyurethane topcoat in a UV condition. All coating systems showed acceptable adhesion strength (above 500 psi) after 4,032 hours of testing. EIS analysis and SKPFM analyses all exhibited the consistent results with two accelerated corrosion tests. SEM analysis on a polyurethane topcoat-based coating system indicated that the epoxy-only coating systems perform badly and also represent that ICP-based coating systems have comparable anti-corrosion performance with zinc-rich-based coating systems. Both the zinc-rich coating systems and ICP-based coating systems exhibited good longterm anti-corrosion performance. The performance of the ICP-based coating systems however relies on the amount of ICP added in primer. It is noteworthy that polyurethane topcoat exhibited higher corrosion protection than the epoxy topcoat under UV exposure. Based on the visual examinations of the surface deterioration pull-off test, EIS, and SKPFM analyses of the eight two-layer coating systems after the 4,032-hour accelerated corrosion tests, System 3; that is, the ICP-based primer (made of non-waterborne epoxy) topcoated by a polyurethane layer is recommended as the best-performance coating system capable of giving comparable long-term performance as the conventional three-layer zinc-rich system. System 7; that is, the ICP-based primer (made of waterborne epoxy) topcoated by a polyurethane layer, also demonstrated superior long-term performance, but with an adhesion strength slightly lower than System 3.

## **CHAPTER 6 FIELD EVALUATION OF BEST-PERFORMANCE COATING SYSTEMS**

Based on the comprehensive laboratory evaluations in the prior two tasks, two two-coat systems, each including a PANi-based primer (mixed in a regular or a water-based epoxy, respectively) and a polyurethane topcoat, were recommended as the best-performance coating systems for field evaluation in this task. A total of six groups of two-coat systems, including the two recommended best-performance systems, are fabricated and subjected to the outdoor-exposure test to investigate their long-term anti-corrosion performance under the service conditions. Two other PANi-based systems, each including an epoxy topcoat, and two zinc-based systems were included in the field evaluation as control systems. Ten replicate samples were fabricated for each type of system, which after fabrication were fixed on a wooden rack inclined at 45 degrees facing south for field testing. Two testing sites were selected in the greater Chicago area, with due consideration of the urban-heat-island effect of the city. Throughout the one-year period of outdoor-exposure evaluation, the weathering durability of the coating systems are evaluated in terms of their surface gloss reduction, color change, adhesion change, and surface deteriorations.

### **6.1. Experimental Design and Preparation**

#### 6.1.1. Sample Preparation

According to the recommendations from the two laboratory-based evaluations, the outdoor exposure test is conducted for the two best-performance coating systems (Systems 3 and 5 in Table 14). In order to study the anti-corrosion capacity of the PANi-based two-layer coating systems, Systems 1, 2, 4, and 6 (see Table 14) were also included in the test scheme as control systems. On a side note, these systems were included in the outdoor test to validate the laboratory-based anti-UV performance of epoxy and polyurethane topcoats, as well as their overall anti-corrosion performance. Systems 3, 4, 5, and 6 each consist of a primer made by mixing the conductive PANi (5 wt.%) into an organic solvent-based or water-based epoxy and a topcoat of polyurethane or epoxy. Systems 1 and 2 were fabricated according to the provider's recommendations.

System Number	Coating Systems	Coating Description	Initial Dry-Film Thickness (µm)
1	ZE/PU	Zinc-rich epoxy/polyurethane	225
2	ZE/E	Zinc-rich epoxy/epoxy	225
3	PANiE/PU	PANi epoxy/polyurethane	225
4	PANiE/E	PANi epoxy/epoxy	225
5	PANiWE/PU	PANi water-based epoxy/polyurethane	225
6	PANiWE/E	PANi water-based epoxy/epoxy	225

Table 2. Two-Layer Coating Systems Included in Field Testing

Z = zinc; E = epoxy; ZE = zinc-epoxy primer; PU = polyurethane topcoat; PANiE = PANi-epoxy primer; PANiWE = PANi-waterborne epoxy primer.

The same type of steel panel, SAE Designation of 1008/1010, as was used in the laboratorybased evolutions of this study was also used in this task for the field testing. Steel panels were acquired from the company Q-Lab at the dimensions of  $51 \times 89 \times 0.81$  mm. Prior to the coating and corrosion study, the panels were ground using the standard 1200 grid paper, cleaned in acetone, and ultrasound-bathed in ethanol for 3 minutes. The panels were then dried in the ambient room condition at temperature of 25°C.

Sitting on each supporting bar of the rack were ten replicate samples made for one of the six coating systems. Following the same procedures used in laboratory, the primer was spin-coated on the cleaned steel surfaces to achieve a dry film thickness of 100  $\mu$ m according to the manufacturer's recommendation. After 24 hours of drying at the ambient room temperature (25°C), the topcoat was spin-coated on top of the primer film to achieve an additional dry thickness of 125  $\mu$ m. A commonly used two-layer coating system for steel bridge repair or maintenance was applied on the backside and edge of all test samples, consisting of a commercial organic solvent-based epoxy used as the primer and a commercial high-performance acrylic polyurethane as the topcoat.

#### 6.1.2. Outdoor Exposure Testing

## 6.1.2.1. Selection of Testing Sites

The selection of field exposure testing sites is an important component of the field-testing scheme, which ought to be representative of the general outdoor conditions of interest. In practice, it is also common to choose exposure sites in extreme climates and compare coating degradation with that occurring in the service environment [136–138]. Located midway between the Continental Divide and the Atlantic Ocean, and 900 miles north of the Gulf of Mexico, the city of Chicago has a climate that is typically continental with cold winters, warm summers, and frequent short fluctuations in temperature, humidity, cloudiness, and wind direction [189]. The climate of Chicago is therefore representative of the large Midwest area of the country and is selected to be one of the testing sites of this project.

Considering the urban-heat-island effect of the interior of Chicago, two testing sites were selected for the testing scheme of this study, with one located in downtown Chicago and the other located in suburban Chicago. Two sets of test samples were prepared and placed on two separate testing racks positioned at the two selected locations. The campus of IIT located in downtown Chicago was chosen to be one of the two sites. The other testing site was located in west suburban Chicago. The urban-heat-island effect of a city could built up a temperature 5.4°F (3°C) warmer in the day time and 22°F (12°C) hotter in the evening than the nearby rural areas. The temperature difference can affect the factors of moisture level, greenhouse gas emissions, and air pollution, which could all play a role in coating degradation.

### 6.1.2.2. Positioning of Samples

According to ASTM G7 [190], test fixtures could be constructed of any material that does not interfere with the test. A dry whitewood (hemlock) was used to build a fixture rack for the outdoor-exposure test of this project. One of the issues concerning an outdoor weathering test is

the selection of a proper exposure angle that has effects on the amount of sunlight to be received by the samples. There have been many different angles chosen in previous studies, from  $0^{\circ}$ (horizontal) to  $90^{\circ}$  (vertical) facing south, north, or any other direction [137].

As mentioned in literature review, the exposure angle of  $45^{\circ}$  facing south has been most frequently used for outdoor testing in order to achieve the maximum solar effect. Accordingly, the wood racks for this outdoor-exposure test were fabricated with an exposure angle of  $45^{\circ}$  w.r.t. ground and facing south. Figure 59 shows the designed (left) and fabricated test rack (right).



Figure 59. Wooden rack for outdoor-exposure testing: Design (left) and fabricated (right).

# 6.2.2.3. Outdoor-Exposure Testing

As designed, all test panels were placed at a  $45^{\circ}$  angle on the wooden racks that directly face south. The air can flow freely on the front surfaces of the samples. The duration of the test currently is designed to be one year for this study, during which the samples of each group are examined monthly by checking the gloss reduction, color change, adhesion change, and surface failures to evaluate the performance of the coating systems. The outdoor-exposure testing was still going on at this time of reporting and the results have been reported quarterly. The researchers expect to continue the field testing beyond the one-year duration until most samples are severely deteriorated. Figure 60 shows coated panels sitting on the test wooden racks.



Figure 60. Coated steel panels during outdoor testing: Urban (left) and rural (right).

## **6.2.** Corrosion Characterization Methods

Many characterization methods are available for evaluating the performance of coating systems, such as by monitoring the changes in physical and chemical properties, surface defects, and rust creepage. Commonly used physical properties include surface gloss, color, and adhesion. In addition, miscellaneous methods such as pencil scratch hardness, dry film thickness (DFT), drying time, and sag resistance can also be found in the literature [14, 135, 136, 143, 191]. Chemical properties used include volatile content and solid content, pigment content, and elemental pigment. Gloss, often used to describe the visual appearance of an object, is the perception of a shiny surface by human eyes [14, 191]. Measured gloss reading can be obtained by comparing the luminous reflectance of a test specimen to that of a standard specimen with the same geometric condition.

The measured gloss readings change as the surface refractive index changes because of the dependency of specular reflectance on the surface refractive index of the specimen [191]. Color is another visual perceptual property of surface by human eyes, which is also an important physical property used to characterize the performance of coating [14, 191]. In addition, adhesion strength, coating defects, and rust creepage are important indicators for characterizing the performance of coating system [136, 137]. In this study, characterization methods or tests such as surface gloss reduction, color change, adhesion change, and surface deteriorations were conducted on the test panels throughout the entire outdoor exposure tests. Initial data of color, gloss, adhesion strength, and coating defects were collected prior to outdoor exposure tests. Performance of all two-coat systems was evaluated in terms of changes in color, gloss, adhesion strength, development of surface defects, and rust creepage at the end of each month.

### 6.2.1. Surface Gloss

Gloss of all of the two-coat systems was measured using a digital gloss meter following ASTM D523-14, Standard Test Method for Specular Gloss. The 60 degree geometry measurements

were conducted on the selected test panels (not scribed) prior to and after outdoor exposure tests [190]. Three gloss readings for each test panel were recorded. Table 15 shows the gloss data for all coating systems before the field exposure test at the two testing sites. The reported gloss of each coating system was the mean of the readings obtained from all test panels that are not scribed.

Coating	Mean Gl	oss (GU)	Standard De	viation (GU)	Coefficient of Variation (%)		
Systems	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	
ZE/PU	69.33	69.33	0.47	0.58	0.68	0.83	
ZE/E	49.00	49.00	0.82	1.00	1.67	2.04	
PANiE/PU	69.00	69.33	0.82	0.58	1.18	0.83	
PANiE/E	48.33	48.67	0.47	0.58	0.98	1.19	
PANiWE/PU	69.33	69.33	0.94	1.15	1.36	1.67	
PANiWE/E	48.83	48.50	0.85	0.50	1.74	1.03	

Table 15. Mean Gloss Data of Samples before Field Exposure Test

Site 1 = Downtown Chicago; Site 2 = Suburban Chicago.

### 6.2.2. Surface Color

Color of all coated samples was measured using a colorimeter following ASTM D2244-15A: Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates [192]. This technique uses the original Commission Internationale de l'Eclairage (CIE) color scales, which are based on the tri-stimulus values X, Y, Z, and chromaticity coordinates x, y. In order to produce more comparable color difference in various regions of color space, a series of weighting factors were considered for each subsequent color scale based on the CIE color scales to provide some degree of uniformity [192]. According to the standard practice, the CIE laboratory color system [CIE  $(L^*, a^*, b^*)$ ] was used for color measurement in this study.  $L^*$ ,  $a^*$ , and  $b^*$  represent the three coordinates of the three-dimensional laboratory color space.  $L^*$  defines where a color falls on a vertical scale from light to dark,  $a^*$ defines where the color falls on the continuum of colors between red and green, and  $b^*$  defines where the color falls on the continuum of colors between blue and yellow. Different values represent different colors for these parameters.  $L^* = 0$  represents black, and  $L^* = 100$  represents diffuse white. Positive values of  $a^*$  indicate green, and negative values indicate magenta. Positive values of  $b^*$  indicate blue, and negative values indicate yellow.

Coating	Mean Color Readings			Standard Deviation			Coefficient of Variation		
Systems	$L^*$	a <sup>*</sup>	$b^*$	$L^*$	a <sup>*</sup>	$b^*$	$L^*$	a <sup>*</sup>	$b^*$
ZE/PU	99.72	0.133	0.367	0.174	0.058	0.153	0.174%	43.30%	41.66%
ZE/E	99.83	0.200	0.267	0.167	0.100	0.115	0.167%	50.00%	43.30%
PANiE/PU	99.77	0.167	0.233	0.159	0.058	0.231	0.160%	34.64%	98.97%
PANiE/E	99.81	0.167	0.233	0.056	0.058	0.231	0.056%	34.64%	98.97%
PANiWE/PU	99.75	0.200	0.133	0.064	0.100	0.058	0.064%	50.00%	43.30%
PANiWE/E	99.74	0.200	0.300	0.056	0.100	0.173	0.056%	50.00%	57.74%

Table 16. Mean Color Readings of Panels in Downtown Chicago Before Field Testing

Table 17. Mean Color Readings of Panels in Suburban Chicago Before Field Testing

Coating	Mean (	Color Rea	adings	Standard Deviation			Coefficient of Variation		
Systems	$L^*$	$a^*$	$b^*$	L	a*	$b^*$	$L^*$	a*	$b^*$
ZE/PU	99.38	0.200	0.433	0.522	0.100	0.115	0.53%	50.00%	26.65%
ZE/E	99.28	0.200	0.433	0.506	0.100	0.058	0.51%	50.00%	13.32%
PANiE/PU	99.64	0.200	0.200	0.231	0.100	0.100	0.23%	50.00%	50.00%
PANiE/E	99.73	0.167	0.300	0.141	0.115	0.200	0.14%	69.28%	66.67%
PANiWE/PU	98.80	0.233	0.133	0.613	0.058	0.058	0.62%	24.74%	43.30%
PANiWE/E	99.15	0.267	0.400	0.954	0.058	0.173	0.96%	21.65%	43.30%

Colors measurements were conducted on the test panels not scribed both before and after the outdoor exposure tests. Three-color readings were obtained for each test panel. Tables 16 and 17 list the color reading for the samples before outdoor testing for the two sites. Color difference  $(\Delta E)$  of the test panels was calculated using the following equation [14, 191]:

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$
(30)

where,  $\Delta L^* = L^*_{end} - L^*_{initial}$ ;  $\Delta a^* = a^*_{end} - a^*_{initial}$ ;  $\Delta b^* = b^*_{end} - b^*_{initial}$ . All values used in the equation were the mean of the data obtained from the test panels.

### 6.2.3. Adhesion Strength

The adhesion strength of the coating on steel panels was evaluated using the standard test ASTM D4541. The portable pull-off adhesion tester Elcometer F106-2 (0–1000 psi scale) was used to apply a concentric load to a single surface. The surfaces of coated test panels were cleaned with water and were lightly roughened using non-abrasive sponge. The base of the aluminum-loading fixture was cleaned using an abrasive finishing pad first and then cleaned using a non-abrasive sponge. The aluminum dolly was affixed to the panel surface by using the thermally curable epoxy adhesive, which was allowed to dry in 24 hours before applying load. The cut through the coating around the edge of the dolly was made after the complete cure of the adhesive (see Figure 61). After that, the tester was coupled to the fixture and the upper part was turned until the

fixture was pulled off. Failure occurs along the weakest plane within the testing system comprised of the fixture, adhesive, individual coating layers, and substrate. The initial adhesion strength and final adhesion strengths of coating systems were read from the scale of the tester directly. The adhesion tests were performed on test panels for both test sites. Table 18 shows the mean adhesion strength of all coating systems before the outdoor exposure test at the two testing sites.



Figure 61. Pull-off adhesion strength testing: Cutter (left) and tested sample (right).

	Mean Adhes	sion Strength	Standard	Deviation	Coefficient of Variation		
Coating	(р	si)	(p	si)	(%)		
Systems	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	
ZE/PU	801.33	799.00	13.80	9.85	1.72	1.23	
ZE/E	817.00	810.33	7.94	6.03	0.97	0.74	
PANiE/PU	816.67	811.33	10.21	11.24	1.25	1.39	
PANiE/E	788.67	790.33	7.57	4.73	0.96	0.60	
PANiWE/PU	596.33	599.67	4.04	2.52	0.68	0.42	
PANiWE/E	594.00	597.33	12.49	7.02	2.10	1.18	

Table 3. Mean Adhesion Strength of Samples Before Field Testing

Site 1: Downtown Chicago; Site 2: Suburban Chicago.

### 6.2.4. Surface Defect Detection

The detection of surface defects was performed following the same procedure described in the laboratory evaluation section of this report. After each month in downtown and suburban Chicago, tested panels were visually examined using ASTM D714, Standard Test Method for Evaluating Degree of Blistering of Paints [174] and ASTM D610, Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces [175]. The reference standards were employed to grade degree of blistering and degree of rusting on the panels. The detection of surface defects was conducted on test panels for both test sites.

### 6.2.5. Rust Creepage Measurement

The rust creepage measurement was performed following the same procedures used in the laboratory evaluation section. After 12 months of outdoor exposure, the rust creepage at the scribe of the tested panels was measured following the ASTM D7087, Standard Test Method for An Imaging Technique to Measure Rust Creepage at Scribe on Coated Test Panels Subjected to Corrosive Environments [183]. According to this standard method, the rust creepage area from the scribe line on the tested panel was traced using a thin tracing pen and a transparent plastic sheet and later the transparent plastic sheet including all scribe creepage trace was scanned with a ruler and saved to an image file. Two traces for each test panel were obtained and the mean creepage distance was reported as the nominal creepage for the coating system. Table 19 shows the mean rust creepage area for all coating systems before the outdoor exposure test at the two testing sites.

~ .	Mean Rus	t Creepage	Standard	Deviation	Coefficient of Variation		
Coating	Area	$(mm^2)$	(m:	$m^2$ )	(%)		
Systems	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	
ZE/PU	10.015	10.010	0.262	0.269	2.61	2.68	
ZE/E	10.080	10.080	0.170	0.170	1.68	1.68	
PANiE/PU	9.880	9.930	0.042	0.042	0.43	0.43	
PANiE/E	10.155	10.160	0.346	0.339	3.41	3.34	
PANiWE/PU	9.875	9.870	0.049	0.042	0.50	0.43	
PANiWE/E	9.950	10.050	0.000	0.071	0.00	0.007	

Table 4. Mean Rust Creepage Area of Samples before Field Testing

# 6.3. Test Results and Analysis

Throughout the one-year outdoor exposure, the performance of all the two-layer coating systems in downtown Chicago and suburban Chicago was evaluated based on the measurements by the aforementioned characterization tests. The evaluation of the results is concluded in the following sections.

# 6.3.1. Gloss Reduction

Surface gloss values of all coated panels were measured and recorded throughout the whole year field exposure period. Table 20 summarizes the mean gloss values for the six, nine, and twelve months of field samples. The table also shows the mean gloss reduction after one year of testing in comparison to the initial gloss values. After one year outdoor exposure, at both field sites the samples with a polyurethane topcoat showed nearly the same level of gloss as the nine-month exposure tested samples and exhibited a small gloss loss comparing to the new samples; while the loss of surface luster on samples with an epoxy topcoat is more obvious comparing to the corresponding new samples. System ZE/PU, PANiE/PU, and PANiWE/PU exhibited very small gloss reduction with a value of 1.30%, 1.56%, and 1.66%, respectively, in both downtown and suburban Chicago sites. System ZE/E, PANiE/E and PANiWE/E exhibited recognizable gloss

reduction with value of 5.08%, 5.07%, and 5.11%, respectively, during the one year exposure in downtown Chicago, which are close to the results observed on the suburban-Chicago samples.

Coating Systems	6 Months Exposure		9 Months Exposure		12 Months Exposure		Mean Gloss Reduction After 12 Months	
	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
ZE/PU	69.13	69.20	68.98	69.06	68.43	68.31	1.30%	1.48%
ZE/E	47.95	48.00	47.28	47.50	46.51	46.67	5.08%	4.76%
PANiE/PU	69.10	68.83	68.95	68.69	68.25	67.90	1.56%	1.59%
PANiE/E	47.57	47.30	47.00	46.90	46.20	46.08	5.07%	4.66%
PANiWE/PU	69.00	69.09	68.91	68.95	68.18	68.08	1.66%	1.80%
PANiWE/E	47.46	47.85	46.82	47.37	46.02	46.42	5.11%	4.94%

Table 20. Mean Gloss Data throughout One-Year Outdoor Exposure Testing

Site 1: Downtown Chicago; Site 2: Suburban Chicago; Unit for Mean Gloss is GU.



Figure 62. Mean gloss reduction for all coating systems tested in downtown Chicago.

Figures 62 and 63 present the time dependence of the mean gloss reduction for all coating systems throughout one-year outdoor exposure in downtown and suburban Chicago. Both figures show an obvious separation in performance that is related to the type of topcoat used. The epoxy-topcoat systems exhibited higher gloss loss with exposure time than the coating systems topcoated by polyurethane. The exposure test started in early summer with strong sunshine effect

in the Chicago area; therefore, more significant gloss reduction occurred for the coating systems with an epoxy topcoat. The coating systems with polyurethane as topcoat shows negligible gloss reduction, confirming that polyurethane possesses higher UV resistance than epoxy. It is noteworthy that the mean gloss reduction rate increased after six months of field testing as the sunshine effect decreased in the Chicago area; however, due to the slower melting of snow in the cold weather, some samples in the suburban Chicago site exhibited slight higher gloss reduction than the corresponding samples tested in downtown Chicago.



Figure 63. Mean gloss reduction for all coating systems tested in suburban Chicago.

## 6.3.2. Color Changes

Color changes of the coating systems after one year of testing were calculated and compared to their initials color readings. Table 21 showed the color changes of all coating systems after one year of outdoor testing. The color changes of the coating systems exhibited similar results as the gloss reduction. System ZE/PU, PANiE/PU, and PANiWE/PU exhibited close and smaller color changes than the other three coating systems with an epoxy topcoat.

Figures 64 and 65 show the time dependence of mean color changes for all coating systems throughout the one year of outdoor exposure in downtown and suburban Chicago. Similar to gloss reduction, color changes for all coating systems also separate into two groups with exposure time due to the different topcoats used. The epoxy-topcoat coating systems exhibited higher color-change rate than the coating systems topcoated by polyurethane. The main reason for this is the lower UV resistance of epoxy topcoat than that of polyurethane topcoat. In addition, all coating systems, especially the coating systems with epoxy as topcoat, show increased color-

change rate after the first three months of testing. This is mainly due to the strong summer sunshine and heavy winter snow and rain activities in Chicago.

Coating	$\Delta L^*$		$\Delta a^*$		$\Delta b^*$		ΔΕ	
Systems	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2
ZE/PU	1.34	1.53	-0.59	-0.27	-1.02	-0.62	1.78	1.68
ZE/E	5.49	5.50	-1.61	-0.92	-2.19	-2.33	6.13	6.04
PANiE/PU	1.75	1.72	-0.41	-0.31	-1.12	-1.16	2.12	2.10
PANiE/E	5.71	5.71	-1.67	-1.41	-2.63	-2.48	6.50	6.38
PANiWE/PU	1.73	1.78	-0.47	-0.48	-1.14	-1.02	2.12	2.11
PANiWE/E	6.18	6.37	-1.69	-1.22	-2.55	-2.09	6.89	6.81

Table 21. Mean Color Change of Panels After One-Year Outdoor-Exposure Testing

Site 1: Downtown Chicago; Site 2: Suburban Chicago.



Figure 64. Mean color change for all coating systems tested in downtown Chicago.



Figure 65. Mean color change for all coating systems tested in suburban Chicago.

## 6.3.3. Adhesion Strength Reduction

Table 22 summarizes the adhesion strength changes in sample panels before and after the one year of outdoor exposure. System PANiWE/E had the highest adhesion strength reduction among all coating systems which has mean adhesion reduction of 2.16% and 1.90% for downtown Chicago and suburban Chicago testing sites, respectively. System ZE/PU and PANiE/PU exhibited the lowest adhesion strength reduction at both testing sites, and System ZE/E, PANiE/E, and PANiWE/PU exhibited the intermediate-level of adhesion strength. This finding can be ascribed to the higher adhesion strength or resistance to adhesion reduction of the organic solvent-based epoxy primer used in System ZE/PU, PANiE/PU, ZE/E, and PANiE/E than the adhesion strength of the water-based epoxy primer used in System PANiWE/PU and PANiWE/E. In addition, the System PANiWE/E exhibited higher adhesion reduction than the System PANiWE/PU because of the lower resistance of epoxy topcoat to UV radiation than the polyurethane topcoat.

Figures 66 and 67 show that the time dependence of mean adhesion reduction for all coating systems throughout one year of outdoor exposure in downtown Chicago and suburban Chicago, respectively. The results from both testing sites exhibited that mean adhesion reduction increased after six month of outdoor exposure test. The reason for this observation is the weather in Chicago area where strong sunshine, heavy rain, and snow occur during the testing period. Under such strong weather effect, both epoxy and polyurethane topcoats degraded fast, which facilitates the ingress of corrosive agents (water, oxygen, and other chemicals) into the topcoat and primer and lead to corrosion occurrence. Such weather effect was especially obvious during the last three months when there was heavy snow in Chicago. A fast decrease of the barrier function of

topcoat might have occurred. In addition, the coating systems with an epoxy topcoat exhibited higher adhesion reduction rates than the coating systems with same primer but polyurethane as topcoat.

Coating Systems	Initial Adhesion Strength (psi)		Final Adhes (p	ion Strength si)	Mean Adhesion Reduction		
	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	
ZE/PU	801.33	799.00	792.43	791.56	1.11%	0.93%	
ZE/E	817.00	810.33	805.25	800.23	1.44%	1.25%	
PANiE/PU	816.67	811.33	807.55	802.85	1.12%	1.05%	
PANiE/E	788.67	790.33	776.12	779.68	1.59%	1.35%	
PANiWE/PU	596.33	599.67	586.76	590.38	1.61%	1.55%	
PANiWE/E	594.00	597.33	581.18	585.96	2.16%	1.90%	

Table 5. Mean Adhesion Strength before and after One Year of Outdoor Exposure

Site 1: Downtown Chicago; Site 2: Suburban Chicago.



Figure 66. Mean adhesion reduction for all coating systems tested in downtown Chicago.



Figure 67. Mean adhesion reduction for all coating systems tested in suburban Chicago.

## 6.3.4. Surface Defects Development

According to ASTM D714, a series of values was specified to indicate the severity of blistering: No. 10 represents no blistering, No. 8 represents the smallest size blister easily seen by unaided eye, and Nos. 6, 4, and 2 represent progressively larger sizes. Figure 68 shows the photos of the tested panels after 12 months of outdoor exposure in downtown Chicago. By visually checking, the tested samples at two testing sites, none of the coated panels showed signs of blistering on the surface of panels. ASTM D610 also specifies a series of values to rank the severity of rusting: Grade 10 represents a rusted surface less than or equal to 0.01%. Grade 9 represents a rusted surface greater than 0.01% and up to 0.03%. Grade 7 represents a rusted surface greater than 0.1% and up to 0.3%. Similarly, none of panels showed rust on the surface of the panels for the samples not scribed. Overall, no tested panels developed surface defects during outdoor exposure in downtown Chicago and suburban Chicago. Table 23 shows the visually checked surface defect results after the 12-month outdoor exposure test.



Figure 68. Photograph of samples at downtown Chicago site after one year of field testing.

~ . ~	Degree of	Blistering	Degree of Rusting		
Coating Systems	Site 1	Site 2	Site 1	Site 2	
ZE/PU	10	10	10	10	
ZE/E	10	10	10	10	
PANiE/PU	10	10	10	10	
PANiE/E	10	10	10	10	
PANiWE/PU	10	10	10	10	
PANiWE/E	10	10	10	10	

Table 23. Assessment of Surface Defects After One Year of Outdoor Exposure

Site 1: Downtown Chicago; Site 2: Suburban Chicago.

# 6.3.5. Rust Creepage Development

Table 24 summarizes the rust creepage development at scribe for all six two-layer coating systems after one year of outdoor exposure. Figure 69 shows the photos of the scribed samples

after one year of field exposure in downtown Chicago. Except System PANiWE/E, none of the coated panels showed signs of rusting on the surface away from the scribe location. By visual checking, the second sample of System ZE/PU exhibits obvious brown color rust around the scribe. The reason for this phenomenon can be poor coating application, poor scribe making, or poor substrate surface treatment.

In addition, System PANiE/PU and PANiWE/PU show negligible brown color materials along and around the scribe and System PANiE/E exhibits little brown color spots along the scribe line. System ZE/E exhibits a little white-colored corrosion product of Zinc along the scribe line with negligible rust creepage development. It is noteworthy that System PANiWE/E shows a tiny crack propagation along the scribe and a few brown color spots around the cracks. Considering the testing results of the 12-month outdoor exposure test, the corrosion and delamination phenomena can be ascribed to the expansion/contraction of the underlying surface relative to that of the coating system. In past three months, the temperature in the Chicago area changed dramatically; thus, all coated panels might be subjected to more severe expansion and contraction.

~ ·	Mean Rust Creepage		Standard	Deviation	Coefficient of Variation		
Coating	Area (mm <sup>2</sup> )		(m	$m^2$ )	(%)		
Systems	Site 1	Site 2	Site 1	Site 2	Site 1	Site 2	
ZE/PU	10.816	10.801	0.240	0.240	0.024	0.027	
ZE/E	10.967	10.927	0.141	0.141	0.014	0.017	
PANiE/PU	10.759	10.784	0.141	0.071	0.014	0.004	
PANiE/E	11.120	11.085	0.283	0.283	0.028	0.032	
PANiWE/PU	10.843	10.818	0.141	0.141	0.014	0.004	
PANiWE/E	11.224	11.276	0.283	0.141	0.028	0.007	

Table 24. Scribe Rust Creepage After One Year of Outdoor Exposure Test

Site 1: Downtown Chicago; Site 2: Suburban Chicago.

Figures 70 and 71 show the rust creepage growth during one year of outdoor exposure test in downtown Chicago and suburban Chicago, respectively. One can find that the rust creepage growth is small, less than 0.1 mm for all coating systems at the end of nine months of outdoor exposure; however, an obvious increase after nine months occurred due to the cold weather and heavy snow in the last three months. It is noteworthy that the rust creepage of panels coated by the System PANiWE/PU show a higher growth rate from the end of six months to the end of nine months in both testing sites; the increase however slows down after nine months of exposure owing to the self-healing function of the PANi material. Once the corrosion was initiated, the PANi was activated and released dopant that formed a complex compound with the corrosion product to defer corrosion propagation. Systems ZE/PU, ZE/E, PANiE/PU, and PANiE/E exhibited similar rust creepage growth trends. System PANiWE/E exhibited a little larger rust creepage growth among all coating systems. The negligible rust creepage development for all samples indicates that the coating systems still possesses good corrosion resistance after one year of outdoor exposure.

### 6.4. Summary

Two two-layer coating systems, each including a PANi-based primer (mixed in a regular or a water-based epoxy, respectively) and a polyurethane topcoat, were recommended as the bestperformance two-layer systems based on the laboratory evaluations in Stage 1. A total of six groups of two-layer coating systems were fabricated and subjected to the outdoor-exposure test to investigate their anti-corrosion durability under the service conditions. Two other PANi-based systems, each including an epoxy topcoat, and two zinc-based systems were also included in the field evaluation scheme as control systems. Ten replicate test panels were fabricated for each coating system and fixed on a wooden rack inclined at 45 degrees and facing south. Two testing sites were selected in the greater Chicago area, with due consideration of the urban-heat-island effect of the city. Throughout the one-year period of outdoor-exposure evaluation, the weathering durability of the coating systems was evaluated in terms of their surface gloss reduction, color change, adhesion change, and surface deteriorations.



Figure 69. Photos of scribed samples after one year of field testing in downtown Chicago. After one year of outdoor exposure testing, it was found that the Systems ZE/PU, PANiE/PU, and PANiWE/PU exhibited smaller gloss reduction and color change than the other three coating

systems, Systems PANiWE/PU and PANiWE/E showed slightly higher adhesion strength reduction than the other coating systems, and that System PANiWE/E exhibited the highest rust creepage growth among all coating systems. The System PANiWE/E also showed slight crack propagation along the scribe, indicating lower resistance to the severe weathering effects. It is noteworthy that the System PANiWE/PU showed increasing rust-creepage-growth rate from the sixth to the ninth month of exposure at both testing sites; the increase however slowed down after nine months of exposure owing to the self-healing function of PANi primer. The adhesion strength reduction and rust creepage growth for all coating systems were small relative to their initial measurements, meaning that all coating systems still exhibited good anti-corrosion performance after one year of outdoor exposure. At both testing sites, the samples with a polyurethane topcoat have roughly the same levels of gloss and color as new samples, while the samples with an epoxy topcoat lost part of their surface luster. This observation, again, confirms that polyurethane has a higher resistance to UV radiation than epoxy under the field service conditions.



Figure 70. Mean rust creepage growth for all coating systems tested in downtown Chicago.


Figure 71. Mean rust creepage growth for all coating systems tested in suburban Chicago.

### **CHAPTER 7 NUMERICAL MODELING OF CORROSION OF DEVELOPED**

### **COATING SYSTEMS**

### 7.1. Introduction

Corrosion-related deterioration of steels and structures may cause varying consequences from environmental contamination and unscheduled shutdowns, to severe personal injuries and fatalities [1]. Some forms of corrosion exhibit negligible visible material loss, but may cause unexpected sudden failure. Pitting corrosion is a common localized corrosion type and is considered to be dangerous since it is hard to detect and predict [194]. The rate of dissolution in pitting corrosion can be greater than that in other forms of corrosion such as uniform corrosion, and structural failure may take place after a very short period. Paint or an organic coating has been commonly used on metal substrates for corrosion prevention [195].

To develop alternative organic coatings with long-lasting corrosion protection, intrinsically conducting polymers (ICPs) with self-healing ability have been developed as novel and useful corrosion inhibiting materials for the protection of metals against corrosion [21, 54, 196–198]. Polyaniline (PANi) and its derivatives have been widely developed and evaluated in corrosion protection coatings due to easy synthesis and transformation between different redox states [17]. However the experimental characterization and assessment of anti-corrosion performance of organic coatings normally are time-consuming and costly in the preparation and testing process, such as the operations of salty spray test, cyclic corrosion test, and outdoor exposure test. As an effective tool for engineering design and analysis, numerical modeling has been widely used in the development and evaluation of corrosion-resistant coatings [199–205].

Brown and Barnard created a finite difference numerical model of localized corrosion to simulate the effects of microstructural variations in Zn-Al Galfan type coatings on the corrosion behavior of cut-edge material. Simulation results from the model shows a comparable result to experimental observations [199]. Thébault et al. investigated the self-healing mechanism of coatings on galvanized steel cut edges by coupling the scanning vibrating electrode technique (SVET) with numerical modeling; the numerical simulation demonstrated that the model of local inhibition indeed generated the results observed from the SVET experiment [200]. Murer et al. created a finite element model for the galvanic coupling in aluminum alloys and conducted experimental validation using the techniques of SVET and microcapillary electrochemical cells. The numerical simulation showed comparable current distributions to the experimental measurement depending on the input conditions and the solved equation [201].

Abodi et al. developed a multi-ion transport and reaction model to simulate the pitting corrosion of aluminum alloys at the microscale. As the authors declared, the model can solve for the electrolyte potential and the concentration distribution of 13 species and simulate polarization curves measured over a microscopic area of the AA2024 alloy surface that contains multiple phases [202]. Cross et al. developed a time-dependent finite element model to simulate the corrosion of zinc and aluminum coatings on a mild steel substrate in de-aerated 0.01 M  $H_2SO_4$  electrolyte. The simulation results were compared with experimental measurements and good agreement between the model predictions and corrosion tests were observed initially for both coatings [203]. Although many research works have been done for modelling the corrosion

behavior of metals, no work has focused on investigating the anti-corrosion performance of ICPbased organic coatings.

This task aims to investigate the corrosion resistance ability of PANi by developing a timedependent finite element model that considers the complex iron microstructure phases and the initiation of pitting corrosion when exposed to an electrolyte solution. Two models are created to simulate the growth of corrosive pit inside the different iron phases, including a PANi-based epoxy primer model and an epoxy-only primer model. The electrical potential and current distribution are generated during the simulation to indicate the corrosion resistance ability of PANi.

### 7.2. Numerical Model

The following numerical model was built to simulate the electrochemical system including a coated steel panel immersed in a specific aqueous electrolyte (3.5% NaCl solution). The model geometry is shown in Figure 72. By checking the electrical potential and current distribution of the modeled domain, the anti-corrosion capability of PANi for steel can be investigated. An epoxy-only primer-coated steel panel was a control model, with the same model configurations.



Figure 2. Geometry of numerical model for studying corrosion of coated steel substrate.

#### 7.2.1. Geometry Definition

The 2D model geometry has the dimensions of 200  $\mu$ m in width and 200  $\mu$ m in height. The toppart domain is a 70- $\mu$ m-deep electrolyte that simulates sea water. The intermediate part is the primer layer, which is either a PANi-based primer or an epoxy-only primer with a thickness of 30  $\mu$ m. The short black bars represent the PANi particle clusters evenly dispersed in the matrix of the primer. The epoxy-only primer does not contain such PANi particle clusters. The line between the top and intermediate parts indicates the electrolyte-primer interface. The bottom part represents the steel substrate consisting of three different metallurgical phases, ferrite, cementite, and a third impurity phase (another phase in steel) with a total height of 100  $\mu$ m. The lines between the phases represent the grain boundaries. The line between the bottom part and the intermediate part represents the interface between the substrate steel and coating primer.

To investigate the anti-corrosion performance of the PANi-based primer on steels, we assume that both the epoxy-only primer and PANi-based epoxy primer have been penetrated through by the electrolyte and that the initiation of localized corrosion has occurred at a spot (due to surface defects, impurities, or damage of protecting coating). Thus, the primer layer can be treated as electrolyte with the same conductivity as the simulated sea water (3.5% NaCl solution). In Figure 72, the semi-circle represents the forefront of the spot with initiated corrosion. The forefront is expected to due to continuing pitting corrosion. The numerical model aims to study how the PANi-based coating would mitigate such corrosion propagation.

## 7.2.2. Governing Equations

#### 7.2.2.1. Electrolyte Solution

The Nernst-Planck Equation is used to model the mass balance for the diluted species in an electrolyte for each species [206]. Focusing on directly investigating the protective performance of PANi on steels, mass transport of the diluted species is not considered in this numerical model. Electroneutrality and negligible concentration gradients of the current-carrying ion were assumed, which lead to the expression of the current density vector in the electrolyte domain given in Eq. 31 [207].

$$\mathbf{i}_l = -F^2 \sum z_i u_{m,i} c_i \nabla \phi_l \tag{31}$$

where,  $\mathbf{i}_l$  denotes the current density vector in electrolyte,  $(A/m^2)$ , *F* is the Faraday constant with the value of 96485 C/mol,  $z_i$  represents the charge number of species,  $c_i$  represents the concentration of the species *i* (mol/m<sup>3</sup>),  $u_{m,i}$  is the mobility of the species *i* (s·mol/kg), and  $\phi_l$  is the electrolyte potential (V).

Based on the assumed constant composition of charge carriers, the electrolyte conductivity is a constant and can be defined as Eq. 32. Accordingly, the current density vector in electrolyte can be rewritten as Eq. 33 [210].

$$\sigma_l = F^2 \sum z_i u_{m,i} c_i \nabla \phi_l \tag{32}$$

$$\mathbf{i}_l = -\sigma_l \nabla \phi_l \tag{33}$$

It is worth noting that Eq. 33 has the same form as Ohm's law. Due to the homogenization, a source or sink term is always considered in the pore electrolyte for the current balance and the electrochemical charge transfer reactions at the interface between an electrode and an electrolyte can be defined as source or sinks term in the porous electrodes. Eq. 34 gives the domain equation for the electrolyte [207].

$$\nabla \cdot \mathbf{i}_l = Q_l \tag{34}$$

where,  $Q_l$  denotes the source term for the electrolyte domain. Similarly, the current conduction in the solid electrode domain also follows the Ohm's law and can be expressed as Eq. 35 and 36 [207].

$$\mathbf{i}_s = -\sigma_s \nabla \phi_s \tag{35}$$

$$\nabla \cdot \mathbf{i}_s = Q_s \tag{36}$$

where,  $\mathbf{i}_s$  denotes the current density vector in the solid electrode phase, (A/m<sup>2</sup>),  $\phi_s$  is the electric potential in the solid electrode (V), and  $Q_s$  denotes the source term for the electrode domain.

#### 7.2.2.2. Electrode Kinetics Expressions

Tafel and Butler-Volmer equations are commonly used in electrochemical kinetics to relate overpotential to the rate of electrochemical reactions [204, 208]. The most general Tafel expression can be given as Eqs. 37 and 38 for anodic and cathodic reaction, respectively [204].

$$i_{loc\ an} = i_{0\ an} \cdot 10^{\eta/A_{an}} \tag{37}$$

$$i_{loc\_cat} = i_{0\_cat} \cdot 10^{\eta/A_{cat}} \tag{38}$$

where,  $i_{loc\_an}$  and  $i_{loc\_cat}$  are the charge transfer current density (A/m<sup>2</sup>) for anodic and cathodic electrochemical reaction, respectively,  $i_{0\_an}$  and  $i_{0\_cat}$  represent the exchange current density (A/m<sup>2</sup>) for anodic and cathodic Tafel expression, respectively,  $A_{an}$  and  $A_{cat}$  are anodic Tafel slope and cathodic Tafel slope respectively,  $\eta$  denotes the activation overpotential (V), which is relating to the rate of the electrochemical reactions and is defined as Eq. 39 [204, 208].

$$\eta_k = \phi_s - \phi_l - E_{eq,k} \tag{39}$$

where,  $\eta_k$  is the activation overpotential for reaction k (V),  $E_{eq,k}$  is the equilibrium potential (also known as reversal potential) for reaction k (V). At the equilibrium potential, the chemical and electrical forces are in balance and the equilibrium potential can be calculated using the Nernst equation shown in Eq. 40 [209].

$$E_{eq} = E^0 + \frac{RT}{zF} \ln(a_A^{z+})$$
(40)

where, *R* is gas constant, 8.314 J/(mol·K), *T* is the temperature (K), *z* is ion species charge, *F* is Faraday's constant, 96485 C/mol,  $E^0$  is the standard electrode potential for unit activity of dissolved metal ions,  $a_M^{Z+}$ , which is defined the equilibrium potential of an electrode reaction when all components are in their standard states and measured against the standard hydrogen electrode (SHE); that is

$$A^{z+} + ze^- = A \tag{41}$$

The current density in the electrolyte in the normal direction is the sum of the charge transfer current density at all electrode reaction and expressed as Eq. 42 [207].

$$\mathbf{i}_l \cdot \mathbf{n} = \sum_k i_{loc,k} + i_{dl} \tag{42}$$

where,  $i_{dl}$  is the current density at the interface between the electrode and electrolyte due to the double layer capacity. We ignore the influence of the current density from the double layer capacity in this study.

When the corrosion occurred, the concentration changes of corroding species could be used to describe the change of the corroding electrodes and the rate of the concentration changes also can be used for denoting the boundary movement velocity of the deforming geometry. Assuming the corrosion occurs along the normal direction to an electrode boundary, we can define the normal mesh velocity (or total corrosion growth velocity) as the sum of the velocity contributions for all species and electrode reactions, per Eq. 43 [207].

$$\frac{\partial \mathbf{X}}{\partial t} \cdot \mathbf{n} = \sum_{i} \frac{M_{i}}{\rho_{i}} \sum_{k} \frac{\nu_{i,k} i_{loc,k}}{n_{k} F}$$
(43)

where,  $\frac{\partial \mathbf{x}}{\partial t} \cdot \mathbf{n}$  represents the total growth velocity in the normal direction to an electrode boundary (m/s),  $M_i$  denotes the molar mass of species *i*, (kg/mol),  $\rho_i$  is the density of species *i*, (kg/m<sup>3</sup>),  $v_{i,k}$  is the stoichiometric coefficients for the species *i* at the reaction *k*,  $n_k$  is the number of participating electrons in the reaction *k*. In this study, we assume the other chemical reactions are negligible and the only anodic reaction for the steel substrate dissolution is:

$$Fe - 2e^- \to Fe^{2+} \tag{44}$$

and oxygen reduction at the neutral or basis solutions is the only cathodic reaction:

$$O_2 + 2H_2O + 4e^- \to 4OH^-$$
 (45)

In addition, we also assume that dissolution reaction occurs at the anode surface and oxygen reduction reaction takes place at the cathode surface. Thus, the anode will exhibit dissolution reaction and propagation inward inside of the steel phase, the cathode surface however is expected to not corrode.

### 7.2.3. Boundary Condition and Meshing

Finite element method (FEM) is used to solve the mathematical equations. Proper boundary conditions are important to obtain reasonable solutions from a FEM model. Figure 73 shows the boundary condition used for solving the equations presented above for the epoxy-only primer.



Figure 73. Schematics of modeled domain and boundary conditions.

For simplification, the surrounding boundaries are set to insulation. As mentioned above, the PANi-based epoxy and epoxy-only primer are saturated and the pitting front as the interface between the saturated primer and steel substrate is set to be an anode and a surface part of the steel away from the interface is set to the cathode. The boundary between the different phases of steel is not constrained and can expand freely by re-meshing the domain during the simulation.



Figure 74. Meshes before and after adaptive mesh refinement for epoxy-only system.

Quadratic elements are used to generate the mesh for the computational domain, which allows the mesh to have smooth topology and the numerical model to deform properly when the mesh changes. The Arbitrary Lagrangian-Eulerian (ALE) method is a popular moving mesh technique that combines the best features of both the Eulerian formulation method and the Lagrangian formulation method. The ALE thus is used here to simulate the growth of the pit corrosion in the steel substrate. In addition, the adaptive mesh refinement technique is used to ensure the best mesh during the time-dependent simulation. Figure 74 shows the mesh before and after automatic adaptive mesh refinement during the simulation. As time proceeds, geometry mesh is continuously refined in order that the FEM solution can converge to obtain the solution of the mathematic model.

### 7.3. Results and Discussion

### 7.3.1. Parameter Determination

The FEM model is built to simulate the growth of pit corrosion inside the steel substrate when coated with an epoxy-only or a PANi-based epoxy primer. When the coating is intact, the PANi-based epoxy primer has the similar barrier function as the epoxy-only primer, which prevents the steel from contacting with the aggressive ion species in electrolyte. This study aims to predict the anti-corrosion performance of PANi when the corrosion initiated by simulating the electrical current and electrolyte potential distribution in the computational domain. To solve the governing equation by FEM and get accurate solution accurate parameters are needed.

Since the primer is penetrated by electrolytes (sea water), it is treated as a type of electrolyte that has similar electrical conductivity as that of the electrolyte on top. To simplify the simulation, we assume that the electrolyte domain and the primer domain have the same electrical conductivity. In this case, the epoxy-only primer is treated the same as the electrolyte (sea water); the PANibased primer domain however is different because of its unique electrochemical properties. The PANi not only changes the electrical conductivity of the primer domain, but also is involved in the electrochemical reaction when corrosion occurs. PANi has a very low electrical conductivity in comparison with sea water, which has an electrical conductivity of 5 S/m, and therefore the effect of PANi on changing the electrical conductivity of the electrolyte is negligible. We assume that the electrical conductivities of the epoxy-only and PANi-based epoxy primer have the same value as sea water; i.e., 5 S/m. The electrical conductivity of iron at 20°C (293K) is about  $1.00 \times$  $10^7$  S/m. Ferrite (also known as  $\alpha$ -Fe) is solid phase in steel with a BCC crystal structure. Cementite (also known as iron carbide) is an interstitial compound of iron and carbon with the formula Fe<sub>3</sub>C. In this study, Ferrite and cementite are modeled as the two phase of steels. We set the electrical conductivity as  $1.00 \times 10^7$  S/m and  $1.07 \times 10^7$  S/m for the Ferrite and Cementite phases, respectively [1]. An impurity phase with a higher potential will be molded as the cathode in this study.

In this study, Tafel expression is used to calculate the charge transfer current density for both anodic and cathodic reactions during each time-dependent analysis step. Thus, equilibrium potential, exchange current density, and Tafel slope for both anode and cathode reactions are important parameters in this model.

The values of equilibrium potential of the electrodes depend on their standard electrode potential and the concentration of dissolved metal ions in the electrolyte. In the microstructure of steels, we assume that the impurity phase has higher equilibrium potential, being cathodic reaction areas. Ferrite and cementite phases, especially at the location of the pitting corrosion, possess more negative equilibrium potentials and therefore are anodic sites. It is noteworthy that the presence of PANi will affect the electrode potentials of both anode and cathode reactions and change the distribution of electrode potential at the interface between the electrode and electrolyte due to the uniformly formed small anode spots when corrosion occurs.

	Domain	Equilibrium Potential	Exchange Current Density	Tafel Slope
		$E_{eq}(\mathbf{V})$	$i_0 (\mathrm{A/cm}^2)$	$\beta$ (mV/dec)
Cathode	Impurity phase	-0.58	$1.0  imes 10^{-7}$	-120
Anode	Cementite phase	-0.90	$1.0  imes 10^{-6}$	50
	Ferrite phase	-1.00	$1.5 imes10^{-6}$	55
	PANi cluster	-1.10	$2.0  imes 10^{-6}$	60
Reference		Self-measured	[209, 213]	[207, 209]

Table 25. Parameters Used in Tafel Equation for Anodic and Cathodic Reactions

The exchange current density is the rate of oxidation and reduction reaction at equilibrium condition at which there is no net current. The value of exchange current density is normally dependent on the nature of the redox reaction, electrode composition, and concentration ratio of oxidized and reduced species [210]. The approximate exchange current density for the hydrogen evaluation reaction on iron at 25°C is about  $10^{-6}$  A/cm<sup>2</sup> [1]. Tafel equation is a common expression for the kinetics of corrosion and has received considerable attention. Tafel slope is the vital parameter to accurately describe the rate of corresponding electrochemical reaction. According to prior experiments and research works, the cathodic Tafel constant is generally about 120 mV for typical cathodic reactions of hydrogen ion reduction or oxygen reduction and the anode Tafel constant is generally in the range of from 30 to 70 mV for metal dissolution reaction [1, 204, 206, 208–211]. Table 25 summarizes the parameters used for the FEM model.

# 7.3.2. Data Analysis

Based on the assumption, boundary condition setting, and input parameters mentioned above, two numerical models, epoxy-only primer and PANi-based epoxy primer model, are simulated for a total of three days. The electrolyte potential and electrical current distribution are generated to investigate the anti-corrosion functionality of PANi. Figure 75 shows the electrolyte potential distribution in the modeled domain at different time for the epoxy-only primer model.



Figure 75. Electrolyte potential distribution in epoxy-only primer model: (a) 0 h, (b) 24 h, (c) 48 h, and (d) 72 h.

As expected, the pitting corrosion grows into the steel substrate indicating iron dissolution. The electrical potential is uniform in the areas away from the corroding pit; also, the difference between the maximum and minimum electrical potential is small. Thus, one can conclude that the entire domain possesses a small potential range except for the corroded pit location, where the highest electrolyte potential exists that *indicates* an anode location. As time goes, the pit corrosion front enlarges and propagates forward. It is noteworthy that the pitting corrosion front grows faster in ferrite phase than in cementite phase. This phenomenon is reasonable because of the lower equilibrium potential of the ferrite phase.



Figure 76. Electrolyte potential distribution in PANi-base epoxy primer model: (a) 0 h, (b) 24 h, (c) 48 h, and (d) 72 h.

Thus, once the electrolyte penetrates through the primer, the steel substrate is exposed to the aggressive environment and corrosion will be initiated and continue. In the FEM model, one can conclude that the epoxy primer loses its corrosion resistance as the electrolyte penetrated the epoxy-only primer and reached the steel substrate surface. The PANi-based primer model exhibits a different electrical potential distribution in the simulated domain. Figure 76 shows the potential distribution in the computational domain at different times for the PANi-based primer model. Comparing with the epoxy-only primer model, the PANi-based primer model exhibits

two major differences for the electrolyte potential distribution: PANi acts as anode as corrosion continues and the corroding pit grows significantly slower.

From Figure 76, PANi located at the interface between the saturated primer and steel substrate shows higher electrical potential that can be ascribed to its conductive property. The behavior of acting as an anode in electrochemical reaction is similar to the galvanic corrosion protection. In this case, PANi supplies electrons to the corrosion reaction to prevent the consumption of iron. By this mechanism, PANi gives corrosion protection for steel even as the primer is penetrated by electrolyte. On the other hand, due to the uniform dispersion of PANi particles in the matrix, the electrical potential is uniformly distributed across the surface of the steel substrate. Once the content of PANi reaches to a high value, surface potential distribution on the steel substrate will be uniform, which will help more effectively protect steel from corrosion.

Another apparent phenomenon can be found from the growth pattern of the corroding pit. As the simulation time increases, the localized corroding pit continues growing toward the inside of the steel; the rate of growth however is much slower than the growth speed of corroding pit in the epoxy-only primer model. This can be ascribed to the addition of the PANi, which acts as anode and has lower electrical potential. The overpotential of localized corrosive pit is lower than that of PANi; thus, PANi is more active in corrosion and will provide electrons for the corrosion kinetic reaction prior to the steel phases.

It is worth noting that PANi did not dissolute during corrosion although it acts as anode. The theoretical reason for this phenomenon is not clear, but could be related to its self-healing properties. Many research works have been done to investigate the corrosion protection mechanisms of conducting polymers such as polyaniline (PANi), polypyrrole (PPy), and polythiophene (PTh) [17, 38, 196]. However, the corrosion protection mechanisms of these conducting polymers are still not understood completely. Some possible corrosion protection [73, 167], controlled inhibitor release [17, 212], electric field formation [17, 42], and formation of a dense, adherent, and low-porosity film [26, 213]. Each proposed hypothesis for the corrosion protection mechanism is self-justification on the basis of the corresponding research works.

The simulated behavior of PANi is closely related to the electric field formation mechanism between PANi and the substrate materials. Iron and PANi are in direct contact, which can generate an electric field to limit the movement of electrons from the steel phases to an oxidizing species, thus preventing or decreasing the corrosion rate [42]. In addition, owing to its redox properties, PANi can easily interchange between oxidation conductive states and reduction-nonconductive states under appropriate conditions. During the redox process, PANi allows for the inserting and expelling of dopant depending on the local corrosion condition and thus preventing the corrosion process [17]. With the release of the doping anions, PANi participates in the reduction reaction and could be re-oxidized by the oxygen, thus exhibiting a self-healing property that depends on the nature of the metal and doping anions [17]. The interchanges between different states of PANi driven by the undergoing redox process well explains its non-dissolution as an anode.



Figure 77. Electrode current densities in epoxy-only primer model.

Figures 77 and 78 show the electrode current densities at different times of simulation for the epoxy-only primer model and the PANi-based primer model, respectively. As expected, both models exhibit the highest electrode current densities at the contact point between the anode and cathode. In addition, electrode current densities decrease and become a stable value at locations away from the contact point of the anode and cathode.

Another important feature shown in Figures 77 and 78 is the time-dependent property of electrode current densities. Both figures show electrode current densities increasing at cathode area and decreasing at anode area as time goes; but the change is negligible, especially at the anode area in the PANi-based epoxy primer model. This phenomenon can be attributed to the different polarization rate of anodic and cathodic half-cell reaction that controls the rate of electron flow [205]. The anodic half-cell reaction is the reversible oxidation reaction of iron, which is related to the activation energy of iron. Although the pitting corrosion is driven by the difference in activation polarization between the two types of iron phases, the difference is small and thus the current density is also small. The cathodic half-cell reaction is also reversible oxygen-reduction reaction, which may contain activation polarization and concentration polarization. As time proceeds, dissolved oxygen in saturated primer increases and leads to higher polarization rate, resulting in increased current density.

In comparison to the epoxy-only primer model, the PANi-based epoxy primer model shows a higher cathodic current density and a lower anodic current density. In addition, the change in electrode current density is negligible over the simulation time. This phenomenon can be ascribed to the addition of PANi in the primer, which acts as anode and provides electrons to the system during the cathodic polarization. Thus, the electrode potential can shift negatively from corrosion potential to a more negative potential, which results in a decrease in anodic current density and an increase in cathodic current density [205]. It is worth noting that the anodic

current density shown in Figure 78 seems to have a constant value at all anodes. This is mainly due to the closed overpotential of the different iron phases and PANi and depends on the exchange current density and equilibrium potential.



Figure 78. Electrode current densities in PANi-based epoxy primer model.

Figures 79 and 80 show the electrolyte current density vector (y component) along the interface of the saturated primer and steel substrate for the epoxy-only primer model and the PANi-based epoxy primer model, respectively. The current density vector in the electrolyte demonstrates an electrolyte current density distribution consistent with the electrolyte potential distribution shown in Figures 75 and 76. Similarly, the highest electrolyte current distribution along the interface of the primer and steel substrate was found at the contact points of the anode and cathode. It is noteworthy that the y component of electrolyte current density vector in Figures 79 and 80 point to the radius direction; thus, the maximum values locate at the center of the anode and cathode areas. In addition, positive and negative values just indicate the direction of the electrolyte current density vector (y component) along the primer-steel interface between the epoxy-only primer model and the PANi-based epoxy primer model, one can conclude that the PANi-based primer exhibits much lower electrolyte current density at anode and small pitting corrosion propagation. These findings well match the results observed from the electrolyte potential distribution.



Figure 79. Electrolyte current vector, y component at interface between primer and steel substrate in epoxy-only primer model/



Figure 80. Electrolyte current density vector, y component at interface between primer and steel substrate in PANi-based epoxy primer model.

# 7.4. Summary

Two microscale numerical models: an epoxy-only primer model and a PANi-based epoxy primer model are developed to investigate the corrosion protection ability of PANi and growth of pitting corrosion in a different iron phase. The main difference between the two models is the addition of PANi, which is an additive and uniformly dispersed in the primer for the latter model. The simplified Nernst-Planck equation is used to model the current density of the simulated electrochemical systems and FEM-based COMSOL software is used to solve the partial differentiation equation. Based on proper simplification and assumption, the electrical potential and current distribution are computed from the simulation to estimate and assess the anti-corrosion ability of PANi.

The electrolyte potential distribution of both models indicates that the pitting grew faster in the epoxy-only primer model than in the PANi-based epoxy primer model over the simulation time. These phenomena demonstrate that epoxy-only primer will lose its anti-corrosion capability once the coating is penetrated by electrolyte; PANi-based epoxy primer however still protects steel against corrosion after being penetrated by electrolyte. In the model simulation, PANi participates in the anodic reaction and supplies electrons to the corrosion reaction and thereby inhibits the pitting corrosion process. In addition, PANi stays stable during the electrochemical reaction due to its self-healing property. Based on the results of electrolyte potential distribution, electrolyte current density vector and electrode current density distribution from the model simulation, one can conclude that the addition of PANi improves the anti-corrosion ability of epoxy primer.

Containing certain assumptions and simplifications, the modeling and simulation produce results consistent with those obtained from the laboratory tests and outdoor exposure test. The numerical results are also comparable with results from other researchers, which further indicates the rationality of this numerical model. The model can be used to improve the understanding of pitting corrosion growth inside the steel microstructure. Based on this preliminary work, a more comprehensive and realistic model, with proper considerations of the transport of reaction species and effects of other relevant physical processes, will be developed to investigate the anti-corrosion performance of PANi-based coatings.

# **CHAPTER 8 CONCULSIONS AND RECOMMMENDATIONS**

## **8.1.** Conclusions

This NCHRP IDEA project developed an intrinsically conducting polymer (ICP)-based, twolayer coating system that possesses unique capacity for long-term corrosion protection of steels. A two-strand waterborne polyaniline: poly (acrylic acid) complex, (or PANi:PAA) was successfully synthesized and utilized to fabricate the primer layer of the proposed two-layer coating system. The techniques of Scanning Kelvin Probe Force Microscopy (SKPFM) and Electrochemical Impedance Spectroscopy (EIS) were used to evaluate the anti-corrosion capability of the PANi-based primer layer. The corrosion potential of substrate surface was analyzed by SKPFM to evaluate the steel-ennobling capability of the primer. The SKPFMmeasured topography, aided with the electronic and ionic conductivities of the primer measured by EIS, was used to evaluate the primer's capabilities for reducing coating delamination and smart self-healing.

A prototype two-layer coating system was then manufactured based on the PANi-based primer and including a polyurethane topcoat. To verify whether the prototype two-layer coating system possesses the expected anti-corrosion capabilities or not, a two-layer polyurethane-over-epoxy coating system was made as the control system. The standard Salt-Spray Test per ASTM B117 and the technique of EIS were used to quantify the coating's anti-corrosion performance.

In the laboratory-based evaluation, a non-waterborne epoxy was used to fabricate a second PANi-based primer, in addition to the existing PANi-based primer made of waterborne epoxy. These two primers and two other commercial primers (a zinc-rich primer and an epoxy-only primer) were based on a total of eight two-layer coating systems using two widely used topcoat materials. The systems, including a PANi-based primer, are expected to have comparable or higher anti-corrosion capabilities and longer durability than the conventional three-layer coatings. To evaluate the long-term performance of the ICP-based two-layer coating systems for potential use on steels, ASTM B117 Salt-Spray Test and ASTM D5894 Cyclic Salt Fog/UV Exposure Test were performed to simulate the accelerated corrosion environment. At different service stages of the tests, the Standard Pull-off Adhesion Test per ASTM D4541 was used to evaluate the adhesion capacity of the coating on the substrate, and the techniques of EIS, SKPFM, and Scanning Electron Microscope (SEM) were conducted to evaluate the long-term performance of the eight two-coat systems.

In the field-based evaluation, a total of six groups of two-layer coating systems were fabricated and subjected to the outdoor-exposure test to investigate their anti-corrosion durability under the service conditions. Two other PANi-based systems, each including an epoxy topcoat, and two zinc-based systems were also included in the field evaluation scheme as control systems. Two testing sites were selected in the greater Chicago area, with due consideration of the urban-heatisland effect of the city. Throughout the one-year period of outdoor-exposure evaluation, the weathering durability of the coating systems was evaluated in terms of their surface gloss reduction, color change, adhesion change, and surface deteriorations. Two numerical models: an epoxy-only primer model and a PANi-based primer model, were developed to investigate the corrosion protection ability of PANi and the growth of pitting corrosion on steel surfaces. Based on the comprehensive laboratory and field evaluation, the following conclusions are reached.

- Coating systems including a PANi-based primer show measurable anti-corrosion capability;
- The anti-corrosion capability of PANi-based primer depends on the amount of PANi included in the primer matrix;
- The matrix material in which PANi is mixed plays an important role in the long-term anti-corrosion performance of the coating system;
- The waterborne epoxy is effective in dispersing PANi nano-particles and has zero VOC; the waterborne epoxy however does not bond to the steel surface as strongly as the regular non-waterborne epoxy;
- The topcoat material also plays an important role in the long-term anti-corrosion performance of coatings. Polyurethane has higher durability than epoxy as a topcoat material.

# 8.2. Recommendations

Two coating systems, each including a PANi-based primer (one using a waterborne epoxy and the other using a non-waterborne epoxy) and a polyurethane topcoat, demonstrated corrosion protection performance comparable to the conventional zinc-rich three-layer system based on one year of field testing. At this reporting time, it is premature to make recommendations as to whether the PANi-based two-layer coating systems can be applied on field steel structures or not, considering the relatively short evaluation period (one year) in the field service condition. There might be more unpredictable occurrences in the long-term field testing of the PANi-based systems, as evidenced by the reduced bonding strength (to steel surface) of the primer made of the waterborne epoxy in the last three months of testing. The research team suggests continuing the testing and observing the samples in the field conditions till the time when most of the samples are deteriorated and definitive conclusions and reliable recommendations can be made.

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