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Program WP19-1017 – An Experimental and Finite Element Modeling Approach to Determining Deterioration of Aircraft Coating Systems: Final Report

STEVEN A. POLICASTRO

RACHEL M. ANDERSON

CARLOS M. HANGARTER

ATTILIO ARCARI

ERICK B. IEZZI

*Center for Corrosion Science & Engineering Branch
Chemistry Division*

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FINAL REPORT

An Experimental and Finite Element Modeling Approach to Determining Deterioration of Aircraft Coating Systems

Steven A. Policastro, Rachel M. Anderson, Carlos M. Hangarter, Attilio Arcari, and Erick B. Iezzi

*Center for Corrosion Science and Engineering, U.S. Naval Research Laboratory,
4555 Overlook Avenue SW, Washington, DC 20375*

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SERDP FINAL REPORT

PROJECT: # WP19-1017

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ABSTRACT

Introduction and Objectives

Exposure to temperature and relative humidity changes, deposition of pollutants and other corrosive ions on a coating surface, along with water from rain and condensation, stress fields, and ultraviolet radiation from sunlight, eventually degrade aircraft coating systems. This deterioration is characterized by a sequential progression of behaviors, including: diffusion of water and dissolved oxygen; transport of electrolyte ions; development of anodic and cathodic regions at the coating substrate interface; onset of electrochemical reactions; chemical and hydrolysis reactions; displacement of polymer-surface bonds by water-surface bonds and accumulation of water to form blisters or the formation of corrosion products at the coating-oxide interface, both of which result in loss of coating-to-surface adhesion. This degradation eventually leads to surface corrosion.

Coating system removal for inspections and mitigation actions are planned prior to the onset of corrosion damage for many commercial and military aircraft. These removal and repainting operations are performed on a time-based, rather than condition-based, schedule and these processes generate large quantities of waste that must be properly handled and can expose workers to toxic materials. Thus, from a maintenance and environmental perspective, there is much interest in reducing the number of aircraft paint removal coating operations to the minimum necessary, preferably basing these decisions on the condition of the coating.

Technical Approach

Our approach focused on developing an improved mechanistic understanding of the roles that environmental exposure and stress play in degrading the corrosion barrier properties of the aircraft topcoat and the entire coating system. The principal means we used for this included analysis of electrochemical impedance spectroscopy data, SEM imaging and compositional mapping, and numerical modeling of electrolyte transport through the coating. Finite element analysis (FEA) was used to both determine stress fields in coating systems near rivet and fastener connections and simulate crack propagation in coatings due to fatigue loading.

Results

The principal results obtained from this program include a polymer aging model for water uptake, a method for deriving impedance matrices for equivalent circuit models for EIS analysis and an algorithm for determining the frequency-dependent impedance of an equivalent circuit model, coating system stress field models that represent a coated aircraft structure, and tensile testing of aged and unexposed coatings to obtain changes in mechanical properties.

Benefits

Synthesis of environmental exposure data, particular water and pollutant accumulation and exposure to UV radiation; with the new models for the rate of water saturation of organic polymers; and the effect of cyclic and high stress loads on the coating system is, as yet, incomplete. Such a full-state model is necessary to be able to accurately predict the state of the coating along with the underlying substrate.

EXECUTIVE SUMMARY

Introduction

Organic coatings are used in a wide variety of environments, including seawater immersion and exposure to the atmosphere, as a method for preventing corrosion. In some cases, coatings are applied in layers over one another to form a structure that performs multiple functions[1,2]. In addition, for metals like aluminum that can form oxides that do not provide good adhesion, a surface pretreatment may be used that alters the oxide film of the aircraft skin material and aids in adhesion of the base coating to the substrate[3,4]. Then the base layer, generally a thin primer coating that binds to the oxide and provides an adherent surface for a topcoat[5], is applied. For structures exposed to atmospheric conditions, this layer provides barrier protection, and may also contain corrosion inhibitor additives. The outermost layer usually consists of a thick topcoat layer that protects the primer and provides coloring using pigments and other filler materials[6].

When properly applied, organic coatings exhibit excellent durability. However, exposure to ultraviolet radiation from sunlight, temperature and relative humidity changes, and deposition of pollutants and other corrosive ions on the coating surface, along with water from rain and condensation, eventually degrade the coating system[7]. The degradation can be evidenced in the color change and loss of gloss, in addition to the formation of flaws, *e.g.*, pits or fissures that can aid in the transport of oxygen and electrolyte to the coating-metal interface, with the subsequent loss of mechanical properties. This deterioration is characterized by a sequential progression of behaviors, including: diffusion of water and dissolved oxygen; transport of electrolyte ions; development of anodic and cathodic regions at the coating substrate interface; onset of electrochemical reactions; chemical and hydrolysis reactions; displacement of polymer-surface bonds by water-surface bonds and accumulation of water to form blisters or the formation of corrosion products at the coating-oxide interface, both of which result in loss of coating-to-surface adhesion. This degradation eventually leads to surface corrosion.

Because of this deterioration progression, coating system removal for inspections and mitigation actions are planned prior to the onset of corrosion damage for many commercial and military aircraft. As the state of the coating and the underlying substrate are usually not known, these removal and repainting operations are performed on a time-based, rather than condition-based, schedule. These processes generate large quantities of waste that must be properly handled and can expose workers to toxic materials. Thus, from a maintenance and environmental perspective, there is much interest in reducing the number of aircraft paint removal coating operations to the minimum necessary, preferably basing these decisions on the condition of the coating.

This report summarizes the results and insights gained from SERDP project WP19-1017. The focus of this work was on understanding changes in the mechanical and chemical properties of organic polymer coatings applied to aluminum substrates that had undergone laboratory aging and outdoor exposures meant to simulate in-service environments.

Objectives

Aircraft maintenance that occurs on time-based intervals does not account for the varying environments that an aircraft sees during operation. As a result, often-unnecessary maintenance is performed due to a lack of information about the specific environmental exposure conditions of that system, and the resulting state of the coating. The proposed goal of this program was to help reduce the cost and unnecessary worker exposure to hazardous materials arising from the paint removal process during programmed depot maintenance for aircraft. A key step towards achieving this goal was to quantify how environmental factors and external stress fields influenced coating system degradation. These factors were evaluated using laboratory experimentation and data analysis, model development including finite element analysis, and outdoor exposure testing.

By developing models that can characterize the damaged state of a military aircraft's coating system as a function of environmental exposure and operations, the results of this program can facilitate improved decision-making regarding maintenance. Eliminating unnecessary maintenance reduces the generation of additional hazardous waste and worker exposure to hazardous materials in paint remover formulations and primers during the repainting process.

Technical Approach

Our approach focused on developing an improved mechanistic understanding of the roles that environmental exposure and stress play in degrading the corrosion barrier properties of the aircraft topcoat and the entire coating system. The principal means we used for this included analysis of electrochemical impedance spectroscopy data, SEM imaging and compositional mapping, and numerical modeling. Finite element analysis (FEA) was used to both determine stress fields in coating systems near rivet and fastener connections and simulate crack propagation in coatings due to fatigue loading.

All experimental tasks used UNS A92024 as the base substrate materials for coating test specimens. The coating systems consisted of a MIL-DTL-81706, Type I (hexavalent chromium) surface pretreatment, followed by MIL-PRF-85582 chromate epoxy primer, and a MIL-PRF-85285 polyurethane topcoat.

The technical approach consisted of four principal sub-tasks. These included the following:

1. *Task 1 – Understanding coating transport mechanisms under simulated field conditions.* Water, aggressive ionic components, and oxygen have been found to travel through barrier coatings and reach the protected substrate, though on different timescales. Hypothesis: Varying humidity and exposure temperatures, such as those found under outdoor and some laboratory exposure conditions, alter the transport rates of electrolyte species through coating systems.
2. *Task 2 – Fatigue cycling under simulated field conditions.* The disparity between accelerated tests and field performance for organic coating systems has been recognized to result in improper ranking of these materials. Moving beyond standard accelerated testing formats that qualitatively or associatively grade coatings or even more advanced statistically correlated coating lifetime predictions, requires resolution of both deterioration mechanisms and kinetics. Mechanical stress contributes to the coating deterioration by direct crack formation at high strain values and by accelerating many of the photochemical and thermochemical deterioration reactions at lower strain values. Hypothesis: Fatigue failure mechanisms are strongly dependent on environmental conditions and the combined

impact of fatigue cycling and environmental conditions results in chemical and physical deterioration that provides a parallel path for electrolyte transport through an aircraft coating system.

3. *Task 3 - Modeling coating system stress fields and crack propagation.* The mechanical behavior of joints due to the applied aerodynamic loads is expected to be one of the principal causes of time-varying deformations of the coating during its service lifetime. Coatings on a component surface are expected to experience stresses and strains below the mechanical strength and elongation at fracture of the coating material. However, aircraft joints during high-g maneuvers or a take-off or landing events, can cause the coating system to distort, elongate or bend. Thus, a need exists to model the stress-strain conditions experienced in service by coatings and to collect experimental evidence for the fatigue behavior of coatings when the components they protect are subjected to representative service loads. Hypothesis: Local stress-strain conditions in coatings, modeled as part of an aircraft component assembly and obtained through finite element analysis methods, cause fatigue deterioration of coatings in service, and affect their performance. Hypothesis: Coupling of mechanical fatigue loads and the deterioration of material properties due to exposure to the environment causes cracking of aircraft coatings.
4. *Task 4 – Outdoor exposure testing and model calibration.* Hypothesis: Development of a cumulative damage model for a coating system exposed to environmental stressors required synthesizing coating system deterioration mechanisms and crack models.

While not specifically identified in the task descriptions, electrochemical impedance spectroscopy (EIS) was the principal tool used for non-destructive assessment of the coated samples in this program. Thus, interpretation of the EIS data and relating the results to physical and chemical changes occurring in the coating required the development of new insights into coating behavior.

Results and Discussion

The principal results obtained from this program include 3 modeling outcomes and 2 experimental methods and results.

1. Polymer aging model for water uptake

Possart and Zimmer described three polymer aging mechanisms based on their work on polyurethanes exposed to high relative humidity environments[8]. They suggested that during the initial water uptake, the water molecules separated weak polymer-polymer hydrogen bonds to form stronger polymer-H₂O hydrogen bonds as well as solvating hydrophilic regions along the polymer chains. This initial phase usually took less than a week to complete. In the second stage of water uptake, dispersed clusters of a mixed phase of water and polymer strands formed throughout the coating. This stage took thousands of hours to complete. They characterized these first two stages as physical aging mechanisms because they were generally reversible by drying out the coating. In the final stage, they observed irreversible chemical aging from the cleavage of the polymer chains via hydrolysis reactions with the water molecules.

In our model, the diffusion coefficients in both coating layers were treated as functions of the polymer type, depth, saturation, and immersion time. Water diffusivity was assumed to be high during the initial period of water uptake into the coating, corresponding to the first physical aging stage. Once this initial water uptake was completed, which took roughly seven days, in our immersion experiments, the diffusion coefficients were altered. That is, once a critical saturation

threshold of the polymer was reached, which we assumed to be around 55% for polyurethane and 45-50% for epoxy, the diffusion coefficient was changed from $D_i^{initial}$ to $D_i(t)$. This decrease was done to account for slower water sorption during the formation of the water-rich and polymer mixed phase.

An expression to simulate the effect of this aging process on water transport was obtained by solving the logistic equation given in (E1),

$$\frac{dD_i}{dt} = kD_i(D_i^{age} - D_i), \quad (E1)$$

subject to the initial condition, $D_i(t = 0) = D_{i,0}$. The subscript, i , in (E1) differentiates between the polyurethane and epoxy layers. The solution to (E1) is given in (E2),

$$D_i(t) = \frac{D_i^{age}}{\left[\frac{(D_i^{age} - D_{i,0})}{D_{i,0}} * e^{-D_i^{age} \frac{t}{\tau}} \right] + 1}, \quad (E2)$$

where we assume the formation of the mixed phase proceeds as an autocatalytic logistic function[9]. In (39), D_i^{age} is the diffusion coefficient at the end of the formation of the mixed water-polymer phase. τ is a characteristic reaction area constant. Values of $\tau \approx 10^{-9} m^2$ worked for this analysis. $D_{i,0}$ represents the diffusion coefficient at the start of the phase formation process. $D_{i,0}$ for both polymers was assumed to be $\approx 0.01 \times D_i^{age}$. A plot of $D_i(t)$ for $T = 5^\circ C$ and $[Cl^-] = 0.01 M$ is shown in Figure E1.

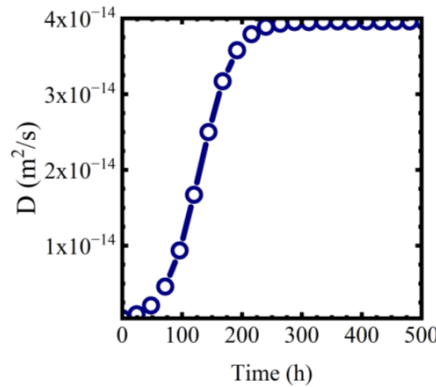


Figure E1. $D_i(t)$ for $T = 5^\circ C$ and $[Cl^-] = 0.01 M$.

Numerical values for the various diffusion coefficients in each polymer are given in Table E1.

Table E1. Variable diffusivity water sorption models.

Model	Summary	$D \left(\frac{m^2}{s} \right)$
Glass-to-gel transition model	D varies as a function of position in the coating and	$D_1^{glass} = 96 \times 10^{-16}$ $D_1^{gel} = 0.96 \times 10^{-13}$

	composition. Glass-to-gel transition of the polymer.	$D_2^{glass} = 80 \times 10^{-16}$ $D_2^{gel} = 0.8 \times 10^{-13}$
Polymer aging model	D varies as a function of position and time. Rapid uptake of water into the polymer followed by a slow polymer relaxation.	$D_1^{initial} = 0.96 \times 10^{-13}$ $D_1^{age} = 0.76 \times 10^{-13}$ $D_{1,0} = 0.01 * D_1^{age}$ $D_2^{void} = 0.8 \times 10^{-13}$ $D_2^{age} = 0.31 \times 10^{-13}$ $D_{2,0} = 0.01 * D_2^{age}$

The saturation function profiles resulting from the polymer aging model are shown in Figure E2 for the model coating system aged in 0.01 M NaCl at $T = 5^\circ\text{C}$. Saturation proceeded much more slowly in this model than in the glass-to-gel transition model, as can be seen by comparing the timestamps on the saturation profiles. The polymer aging model, when coupled with an effective medium theory for changes in the dielectric properties, exhibited the expected behaviors of the water sorption curves for polymers.

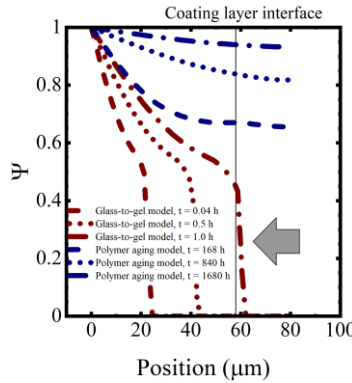


Figure E2. Saturation profiles for the glass-to-gel transition model and polymer aging model.

Thus, to explain features of the water sorption curves for the polymers obtained from the EIS data, we proposed that water uptake by the organic coating system was consistent with the two-stage kinetics mechanism. The first stage, associated with a high diffusivity, resulted in rapid water uptake. In the literature, this mechanism has been associated with the formation of polymer-H₂O hydrogen bonds following separation of polymer-polymer hydrogen bonds.

The second mechanism was then initiated once the volume fraction of water reached a critical threshold. This mechanism, associated with a varying diffusivity modeled using an autocatalytic logistic function, was consistent with the physical aging mechanism that theorizes further water uptake results in the formation of a water-rich and polymer mixed phase.

Capacitance values predicted from the polymer aging and Brasher-mixing models were consistent with trends observed in the experimental data. These results are important for potential industrial applications because polyurethane and epoxy coatings are widely used by commercial and military aviation and on aluminum materials in industrial applications. This modeling approach allows us

to estimate the state of the layers of the coating system using only the type of coating and the exposure conditions, while also providing context for interpreting non-destructive EIS measurements of *in-situ* coatings.

2. Derivation of impedance matrices for equivalent circuit models and an algorithm for determining the frequency-dependent impedance of an equivalent circuit model

The derivation of the impedance matrix for the modified undamaged coating equivalent circuit model starts with Kirchhoff's current law in (E3) for each branch of the circuit,

$$\sum i_k = 0, \quad (E3)$$

$$i_3 = i_1 + i_2, \quad (E4)$$

where, i_3 is the current flowing through R_Ω , i_2 is the current flowing through the CPE, and i_1 is the current flowing through R_1 .

As in most other electrical circuit analysis, the fundamental building block for determining the impedance of a circuit is Ohm's Law. The frequency-dependent impedance of a circuit can be expressed using (E5)[10],

$$e_0 \sin \omega t = (i_0 \sin \omega t + \phi)Z(\omega) \quad (E5)$$

where $\omega = 2\pi f$, f is the oscillation frequency, e_0 is the amplitude of the sinusoidal potential oscillation, i_0 is the amplitude of the current response, and ϕ is the phase shift in the current.

Using (E5), expressions for the sum of the voltage drops through both pathways in the circuit are given in (E6),

$$v_1 = i_3 R_\Omega + i_1 R_1, \quad (E6)$$

$$v_2 = i_3 R_\Omega + i_2 Z_{cpe}.$$

Then using (E4) to substitute for i_3 and collecting terms results in (E7),

$$v_1 = i_1(R_\Omega + R_1) + i_2 R_\Omega, \quad (E7)$$

$$v_2 = i_1 R_\Omega + i_2(R_\Omega + Z_{cpe}).$$

Rewriting the system of equations from (E7) in matrix form results in (E8),

$$\begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} i_1 \\ i_2 \end{bmatrix} \begin{bmatrix} R_\Omega + R_1 & R_\Omega \\ R_\Omega & R_\Omega + Z_{cpe} \end{bmatrix}, \quad (E8)$$

where the impedance matrix is given by (E9),

$$\mathbf{Z} = \begin{bmatrix} R_\Omega + R_1 & R_\Omega \\ R_\Omega & R_\Omega + Z_{cpe} \end{bmatrix}. \quad (E9)$$

The circuit models shown in Figure E3 can be divided into three categories: 2, 3, and 4 pathway models. The circuits from Figure E3a-d are 2 pathway models while the circuits from Figure E3e-g are 3 pathway models, and the circuit in Figure E3h is a 4 pathway model. The number of pathways indicates the number of rows and columns in the conductivity matrices that are

constructed for the impedance calculations and the number of rows and columns in the impedance matrix in (E9) are consistent with a 2-pathway equivalent circuit.

The modified Randles circuit is also a 2-pathway equivalent circuit. The impedance matrix is given in (E10) and was derived using a similar procedure as shown previously.

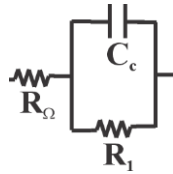
$$Z = \begin{bmatrix} R_{\Omega} + R_1 + Z_W & R_{\Omega} \\ R_{\Omega} & R_{\Omega} + Z_{cpe} \end{bmatrix} \quad (E10)$$

The extended modified REAP equivalent circuit model, introduced in this work, and shown in Figure E3h, is a 4-pathway equivalent circuit. This circuit was derived from the previous equivalent circuits that have been used for analyzing EIS data from coating systems. This circuit is intended to account for effects from non-ideal capacitive behavior and transport of electrolyte species in different coating layers as well as electrochemical processes occurring at the coating-substrate interface. The impedance matrix is given in (E11).

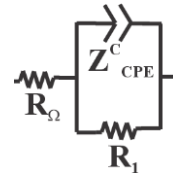
$$Z = \begin{bmatrix} Z_{00} & Z_{01} & Z_{02} & Z_{03} \\ Z_{10} & Z_{11} & Z_{12} & Z_{13} \\ Z_{20} & Z_{21} & Z_{22} & Z_{23} \\ Z_{30} & Z_{31} & Z_{32} & Z_{33} \end{bmatrix}$$

$$\begin{aligned} Z_{00} &= R_{\Omega} + R_t + Z_W^t + R_p + Z_W^p + R_{pre} \\ Z_{11} &= R_{\Omega} + R_t + Z_W^t + R_p + Z_W^p + Z_{cpe}^{pre} \\ Z_{22} &= R_{\Omega} + R_t + Z_W^t + Z_{cpe}^p \\ Z_{33} &= R_{\Omega} + Z_{cpe}^t \\ Z_{01} &= Z_{10} = R_{\Omega} + R_t + Z_W^t + R_p + Z_W^p \\ Z_{02} &= Z_{20} = Z_{21} = Z_{12} = R_{\Omega} + R_t + Z_W^t \\ Z_{03} &= Z_{30} = Z_{13} = Z_{31} = Z_{23} = Z_{32} = R_{\Omega} \end{aligned} \quad (E11)$$

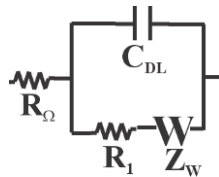
a. Undamaged coating model[11]



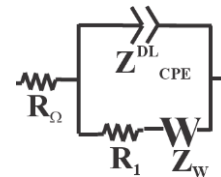
b. Modified undamaged coating model (this work)



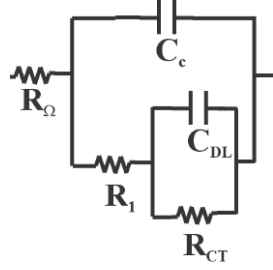
c. Randles model[12]



d. Modified Randles model (this work)

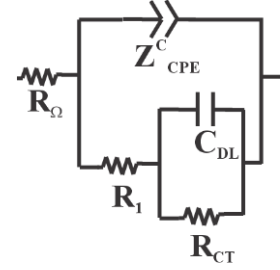


e. Simplified Randles circuit as nested coating defect model[13]

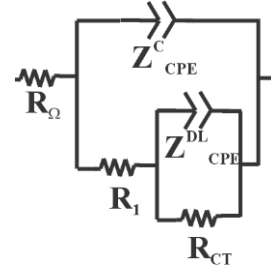


f. model[14]

REAP



g. Modified REAP model[15]



h. Extended modified REAP model (this work, but compare with the equivalent circuits found in [16])

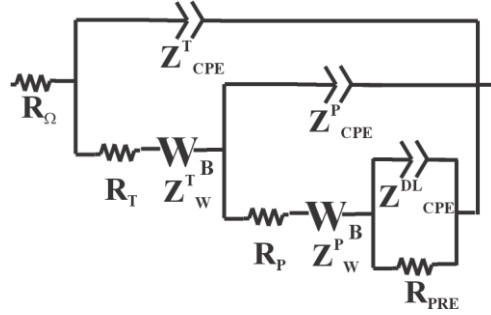


Figure E3. Classification of the various equivalent circuit models used for analyzing EIS data obtained from coatings.

To determine the impedance at each frequency, the following algorithm was employed:

1. The currents flowing in each path of the circuit were calculated from (E12),

$$\mathbf{i} = \mathbf{Z}^{-1}\mathbf{v}. \quad (\text{E12})$$

2. The solution to (E12) was obtained using an LU decomposition algorithm from the `mldivide` function in MATLAB (R2023a, MathWorks) because the conductivity matrices are square matrices with only a few elements.
3. The M individual current components of the $\mathbf{i}$ vector from (E12) were then summed to obtain the total current, i_t , as shown in (E13),

$$i_t = \sum_{m=0}^{M-1} i_m. \quad (\text{E13})$$

4. Regardless of the path through the circuit, the voltage drop across each path must be the same and, for convenience, we assumed $v_m = e_0 = 1.0$. The complex impedance at each frequency was then obtained from (E14),

$$Z(\omega) = \frac{e_0}{i_t} = x + jy, \quad (\text{E14})$$

where x and y are the calculated real and imaginary components of the impedance, respectively, and $j = \sqrt{-1}$.

Thus, a numerical method for calculating the equivalent circuit impedance using matrix algebra was derived and incorporated into a simplex regression algorithm coded in MATLAB. Results from these calculations were compared with outcomes obtained from a commercial EIS analysis software. The new method was generally as accurate as the commercial software.

The principal benefits of these methods include: 1) the capability to incorporate physics-based models into the equivalent circuit analysis technique for analyzing EIS data, which is very difficult to do with commercial software, and 2) improving our understanding how physical processes occurring during environmental exposures of coating systems change the properties of coatings. This last benefit is necessary to improve our understanding of the state of a coating system. While these results were obtained for coating systems exposed to immersion; in principle, we expect these results can be extended to coating systems on other structures exposed to atmospheric conditions, so that they can be evaluated *in-situ* to determine how well they are maintaining corrosion protection.

3. Coating system stress field model to represent a coated aircraft structure

A model consisting of two aluminum plates, each with a 70 GPa elastic modulus, and 20 countersunk fasteners was developed to simulate the local fastener-plate interface displacements. The fasteners between the two plates were modeled using solid elements to capture the full extent of their deformations within the structure. The fastener material was stainless steel with an elastic modulus of 210 GPa. The fastener and fastener holes were countersunk with an angle of 100 degrees, and a countersunk head height of 1.73 mm. The fastener shank and nut were modeled as a single part. The bolt was simplified as an integral part of the fastener to allow application of the desired amount of force as preload. The coating layer was applied to the aluminum plate at the locations shown in Figure E4. The coating layer has a higher mesh density around fastener #6 to allow for a more refined characterization of the local deformations. The model configuration is shown in Figure E4.

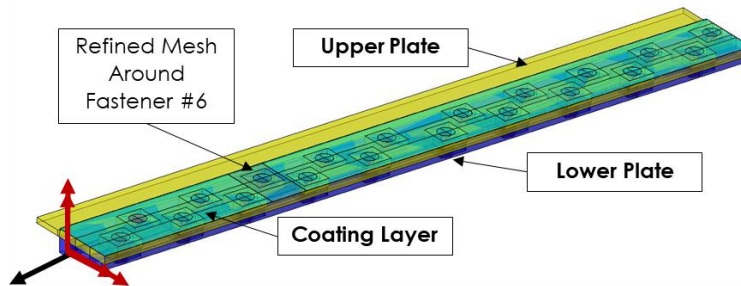


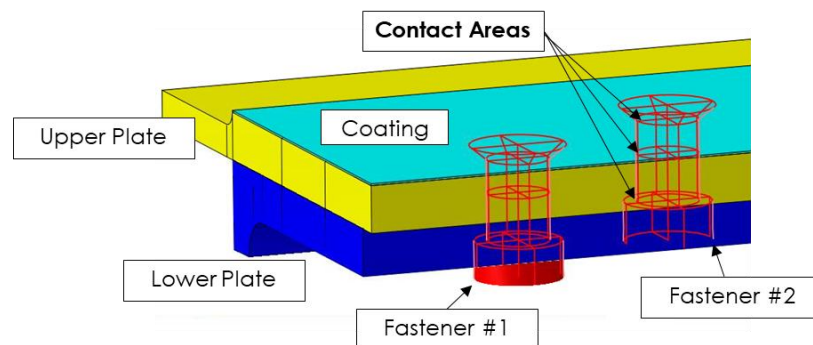
Figure E4. Geometry and components of the finite element model in this work.

The coating system was modeled as a bilayer structure consisting of a primer and topcoat, 25 μm and 100 μm in thickness, respectively. A perfect bonding between the two layers and a perfect bonding of the primer with the aluminum plate and fastener is assumed. Note that aluminum alloy surfaces often receive a pretreatment or conversion coating that anodized the aluminum oxide layer to thicken and to aid in the adhesion between the surface and the primer. The surface pretreatment that would be applied to the aluminum substrate to improve primer adhesion was treated as part of the substrate and was not included in the model.

The analysis was divided into two steps: the first step applied the preload to the fasteners and the second step applied the external loads to the entire model. Two sets of external loads were applied to the model: one which caused the upper plate to be under tension and one which caused the upper plate to be under compression. These types of loads correspond to events, for example, like an aircraft landing or flying through wake turbulence, respectively. The Von Mises stress of the top aluminum plate away from the fasteners obtained for the tension-dominated case was approximately 1/3 of the yield strength, which is assumed to be 450 MPa for this alloy. For simplicity, we refer to “tension-dominated” and “compression-dominated” loads for the rest of the manuscript. These refer to the condition of the upper plate and to define the upper and lower bounds of the deformations obtained, respectively. The loads are identical in magnitude for the two cases but reversed in sign. The applied loads consisted of a combination of two bending moments and an axial force to represent a typical mixed-mode condition of a structural member.

The installation of the fasteners and the application of preloads during the assembly process preceded the coating of the skin panels. This was simulated in the model by deactivating the coating layers during preload. This deactivation step allowed the coating layer to conform to the final shape of the structure without causing any strains or stresses in the coating. This initial “inactive” state was included to ensure that the strains and stresses in the coating were only caused by the external loads. The net result was that the coating layer adhered perfectly to the contours of the fastened structure, including the small geometrical details around fastener heads and skin.

The areas between the fastener head and countersunk hole surface, between the fastener shank and hole surface, and between the nut and bottom plate surfaces were in contact, as shown in Figure E5. The contact properties were defined in the model as non-penetration in the perpendicular direction to the contact surface, and with friction in the tangential direction. The latter used a static coefficient of friction of 0.61 for clean and dry steel[17]. The areas between the upper and lower plate were also modeled with contact, defined as non-penetration in the perpendicular direction to the contact surface, and with friction in the tangential direction. The static coefficient of friction was 1.05, representative of clean and dry aluminum surfaces[17].



E-10

Figure E5. Detail of the model in this work with defined contact surfaces between fasteners, top, and bottom plates.

A sub-modeling strategy was used to refine the results around a single fastener: the displacements resulting from the application of the loads were used as boundary conditions for a sub-part of the model, specifically the coating layer on top of fastener #6. This allowed for significant mesh refinement near the region of interest without paying a large penalty in terms of computational time. The analysis was performed using Abaqus and CAE on an HPE SGI 8600 high-performance computing cluster.

We used the properties obtained from the tensile testing of the different coating layers to study the expected strains in the primer and topcoat layers of the coating system. The substrate materials were assumed to be able to withstand the applied deformations without failing. The next section includes a failure criterion to model the occurrence of cracking during the studied loading cases, given the observed fracture stresses and strains from tensile testing.

The primer layer was modeled as a linear elastic material with an elastic modulus obtained by analysis of the tensile tests. The topcoat was modeled as an elastic-plastic material with its initial modulus and yield stress obtained from analysis of the tensile tests. The plastic behavior was modeled with kinematic hardening. That is, the models used calculated stress-strain data as a reference for an elastic-plastic regression to find the points needed by the kinematic hardening model. The plasticity model used for modeling the topcoat material was based on the Von Mises yield criterion, given in (E15),

$$f(\boldsymbol{\sigma} - \boldsymbol{\alpha}) = \sqrt{\frac{3}{2}(\mathbf{S} - \boldsymbol{\alpha}^{dev}) : (\mathbf{S} - \boldsymbol{\alpha}^{dev})} = \sigma_y, \quad (\text{E15})$$

where $\boldsymbol{\sigma}$ is Cauchy stress and $\mathbf{S}$ is the stress tensor in the deviatoric space. $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha}^{dev}$ are the back stress and the back stress in the deviatoric space, respectively, σ_y is the yield strength. The plastic flow always follows a direction perpendicular to the yield surface, as shown in (E16),

$$\dot{\boldsymbol{\epsilon}}^{pl} = \frac{\partial f(\boldsymbol{\sigma} - \boldsymbol{\alpha})}{\partial \boldsymbol{\sigma}} \dot{\bar{\boldsymbol{\epsilon}}}^{pl}, \quad (\text{E16})$$

where $\dot{\boldsymbol{\epsilon}}^{pl}$ is the plastic strain rate, $\dot{\bar{\boldsymbol{\epsilon}}}^{pl}$ is the equivalent plastic strain rate defined as $\dot{\bar{\boldsymbol{\epsilon}}}^{pl} = \sqrt{\frac{2}{3} \dot{\boldsymbol{\epsilon}}^{pl} : \dot{\boldsymbol{\epsilon}}^{pl}}$ [18]. The linear kinematic hardening model defines the back stress rate of change in (E17) as,

$$\dot{\boldsymbol{\alpha}} = C \dot{\bar{\boldsymbol{\epsilon}}}^{pl} \frac{1}{\sigma_y} (\boldsymbol{\sigma} - \boldsymbol{\alpha}) + \frac{1}{C} \boldsymbol{\alpha} \dot{C}, \quad (\text{E17})$$

where C is a hardening parameter and in its simplest form describing the slope of the stress-plastic strain response of the material for a uniaxial tensile test[19]. This model, employing the measured mechanical properties of the coating system, allowed us to model coating cracking in response to the aircraft loading scenarios.

4. Tensile testing of aged and unexposed coatings

The results of the tensile samples in comparison to the unexposed full stacks and topcoat are shown in Figure E6. The test results for the full coating system were not conclusive. They showed a wide

range of maximum stresses and ultimate strains. The initial elastic modulus was generally consistent, however the behavior at strains higher than 0.005 differed significantly among the three exposed samples. The strains at failure were consistently lower than previously measured for the full coating system. The tensile testing of the topcoat material showed a significant decrease in the tensile properties after exposure, with both a reduction in elastic modulus and a significant reduction in ultimate strain. The modulus averaged 722 MPa, a reduction of 14.7%, while the strain at failure averaged 2.04%, a reduction of 46.3% with respect to the unexposed conditions. All tensile curves were consistent as shown in Figure E6b.

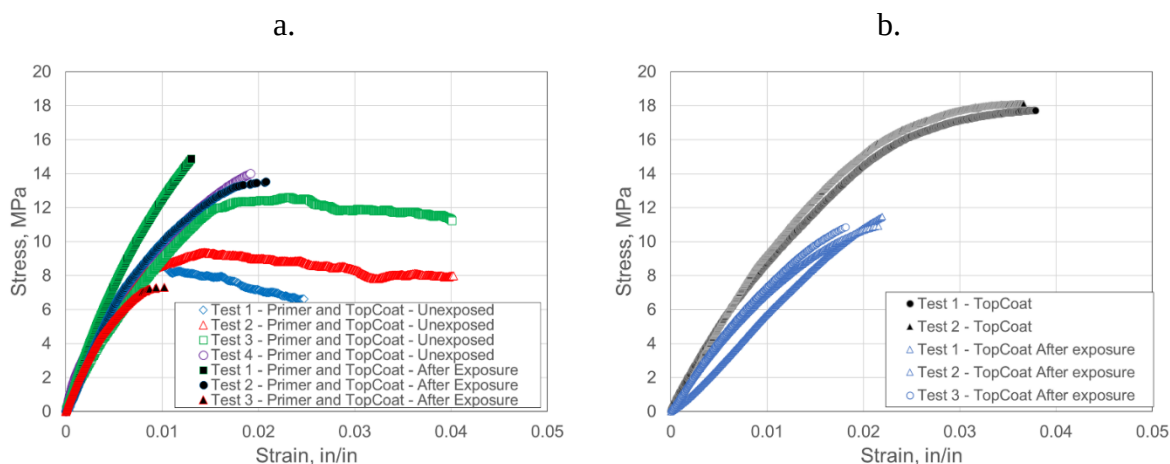


Figure E6. Tensile testing of (a) full system of primer and topcoat coating after exposure to atmospheric environment for 5736 h and comparison with unexposed tensile testing results, and tensile testing of (b) topcoat material coating after exposure to atmospheric environment for 5736 h and comparison with unexposed tensile testing results.

5. Analysis of EIS measurements of stressed and unstressed coatings on atmospheric test racks in Fleming Key, FL

Analysis of the EIS data was performed by fitting the data with the modified REAP equivalent circuit model, shown in Figure E7, using the analytical software suite (Echem Analyst, Gamry) provided by the potentiostat manufacturer. In all cases, R_{Ω} was assumed to be 4Ω due to the experimental approach taken for measuring the impedance. Fits were done using the simplex fitting algorithm included with the software to ensure convergence.

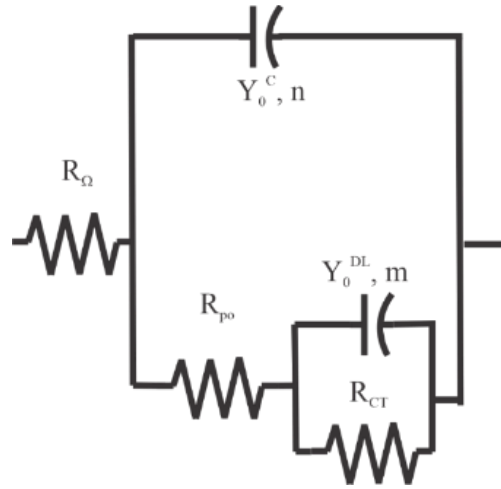


Figure E7. Modified REAP model[15] used to analyze the EIS data from the coatings.

Examples of the calculated impedance obtained from the fit parameters in comparison with the data are shown in Figure E8.

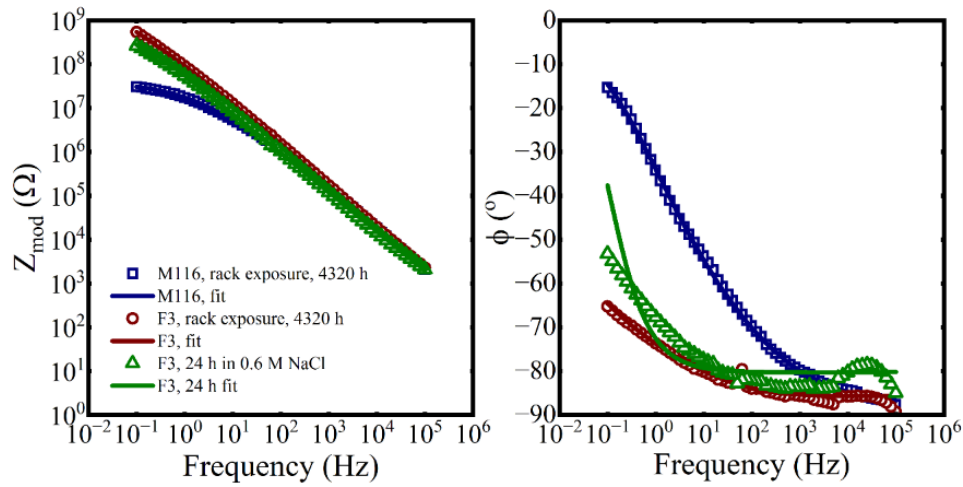


Figure E8. Comparison of the fit with EIS data. $X_{F3}^2 = 4.7 \times 10^{-4}$, $X_{F3,24h}^2 = 110 \times 10^{-4}$

Fit parameters for the unstrained coatings mounted on the atmospheric exposure racks with and without sea spray as a function of time are shown in Table E2. These values are shown in contrast to an immersed coating.

Table E2. Comparison of fit parameters for unstrained samples mounted on atmospheric exposure racks with (M116) and without sea spray (N119) and an immersed coating (I118) over time.

Parameter	Sample ID and Exposure Time (h)				
	M116		N119		I118
	0	4320	0	10272	3120
R_{Ω} (Ω)	4	4	4	4	4
R_{po} (G Ω)	5.7	0.04	4.8	2570	0.78
R_{ct} (M Ω)	9.15	0.02	0.019	207	0.82
$Y_0^{DL}(nF \cdot s^{n-1})$	1.48	12.9	2.37	1.01	5.35
m	0.562	0.537	0.589	0.602	0.594
$Y_0^C(nF \cdot s^{n-1})$	2.28	1.05	1.23	1.77	1.78
n	0.950	0.978	0.968	0.950	0.958

Table E3. Comparison of fit parameters for unstrained samples mounted on atmospheric exposure racks with (M116) and without sea spray (N119) and an immersed coating (I118) over time.

Parameter	Sample ID and Exposure Time (h)		
	4320	F3	I118
		24*	3120
R_{Ω} (Ω)	4	4	4
R_{po} (G Ω)	15.4	3.16×10^{-5}	0.78
R_{ct} (M Ω)	30.4	404	0.82
$Y_0^{DL}(nF \cdot s^{n-1})$	1.32	283	5.35
m	0.561	0.747	0.594
$Y_0^C(nF \cdot s^{n-1})$	1.40	3.37	1.78
n	0.952	0.892	0.958

* Indicates the previously exposed coating was immersed in 0.6 M NaCl for 24 h immediately prior to making the EIS measurement.

For the immersed coating and the coatings exposed to seawater spray, R_{po} decreased as a function of exposure time, as expected, because of water ingress into the coating. In contrast, for the coating exposed to just the ambient conditions, R_{po} increased over the duration of the exposure. This is likely due to long-term curing of the coating from sun exposure, resulting in improved barrier properties of the overall coating system. Also of note, the exponent, m , on the constant phase element that captures the dielectric properties of the double-layer at the coating substrate interface shows a strong diffusion effect, with values near 0.5 for many of the exposure conditions. This is consistent with a transport mechanism dominating the reaction at the substrate-coating interface. Likewise, the exponent, n , on the constant phase element that captures the dielectric property of the coating is close to 1.0, which suggests that the coating system is behaving like an ideal capacitor. The fit parameters for the fatigued, fully supported coatings are shown in Table E3.

These values differ in several ways from the ones reported in Table E2. For the fatigued coatings, R_{po} increased over the course of the exposure period, as did the ambient exposure coating. However, the increase was only 6% of the increase seen in the ambient exposure coatings, suggesting that the additional curing may have been counteracted by damage from the fatigue loading. In addition, after exposure to 0.6 M NaCl solution in the laboratory for 24 h, R_{po} exhibited 5 orders of magnitude decrease. While the $23\times$ decrease in the goodness of fit parameter, illustrated visually in the plots shown in Figure 75 in the main report, suggests that the Modified

REAP model is no longer the best choice to fit this data, the decrease in R_{po} suggests rapid ingress of electrolyte into the coating. A possible cause for this ingress is cracking by the topcoat or primer in response to fatigue loading.

SKP results, shown in the main report, provide additional support the EIS data suggesting that exposure to sunlight on the atmospheric exposure racks provided additional curing to the polymers, as the work function for the coating was higher than the work function for the unexposed coating. However, there are several areas in the work function plot for the fatigued coating system where the work function plunges 700-800 meV, approaching that of pure aluminum. This suggests that the fatigue loads damaged the coating, which is consistent with the EIS data for the fatigued coatings.

While SEM images of the coating cross-section shown in the main report did not provide evidence of coating cracking, they did reveal cracks in the pretreatment layer, which would allow electrolyte transported through the coating system to eventually reach the unprotected substrate. Fatigue loading, perhaps unsurprisingly, increased the linear density of the cracks. In the unstressed sample, pretreatment cracking occurred on the order of 2.5×10^{-3} cracks/ μm . In the fatigued sample, pretreatment cracking occurred on the order of 18.5×10^{-3} cracks/ μm , a $7.4\times$ increase.

Likewise, fatigue loading of the unsupported primer coating showed that the epoxy primers used in these aircraft coatings are susceptible to fatigue cracking, though those cracks occurred at lower strain levels versus the coatings on aluminum panels because they were unsupported by a substrate.

The key takeaways from this investigation suggest that exposure of the coating system to ambient weather conditions without stress can initially result in improved barrier properties for the coating due to enhanced curing of the polymer. Exposure of the unstrained coating system to atmospheric and sea spray conditions, even for short durations, can result in degradation that is similar to that experienced by immersed coatings. Lastly, fatigue loading of unsupported and supported coatings can result in organic coating and pretreatment cracking that speeds up water ingress, substrate corrosion, and resulting coating failure.

Implications for Future Research and Benefits

Two principal future research directions suggest themselves at the conclusion of this program: one focused on theory and modeling development and one focused on implementation and improving the TRL of the technology. In the modeling direction, the synthesis of the environmental exposure data, particular water and pollutant accumulation and exposure to UV radiation; with the new models for the rate of water saturation of organic polymers; and the effect of cyclic and high stress loads on the coating system is, as yet, incomplete. Such a full-state model is necessary to be able to accurately predict the state of the coating along with the underlying substrate. In the implementation direction, once the full state model has been validated, an in-situ EIS measurement device, coupled with aircraft sensors to detect local corrosive environments and aircraft loads, would be able to provide the maintainer with an accurate assessment of the state of the coating system. Such output could be in the form of red/yellow/green assessment, as was suggested by the interim rating scheme, but the red/yellow/green categories would then be founded on a stronger physics basis than simply the coating impedance at 0.1 Hz.

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1. OBJECTIVE

Aircraft maintenance that occurs on time-based intervals does not account for the varying environments that an aircraft sees during operation. As a result, often-unnecessary maintenance is performed due to a lack of information about the specific environmental exposure conditions of that system, and the resulting state of the coating. The proposed goal of this program was to help reduce the cost and unnecessary worker exposure to hazardous materials arising from the paint removal process during programmed depot maintenance for aircraft. A key step towards achieving this goal was to quantify how environmental factors and external stress fields influenced coating system degradation. These factors were evaluated using laboratory experimentation and data analysis, model development including finite element analysis, and outdoor exposure testing.

Our approach focused on developing an improved mechanistic understanding of the roles that environmental exposure and stress play in degrading the corrosion barrier properties of the aircraft topcoat and the entire coating system. Finite element analysis (FEA) was used to both determine stress fields in coating systems near rivet and fastener connections and simulate crack propagation in coatings due to fatigue loading. Our final task will focus on the development of process models that can be used to predict the current state of the coating system, based on its exposure and fatigue history.

All experimental tasks will use UNS A92024 (aluminum alloy 2024-T6) as the base substrate material for panels or other test specimens. For galvanic corrosion testing, the galvanic couples are formed from UNS A92024 and UNS S13800 (PH 13-8 Mo stainless steel) precipitation-hardened stainless-steel bolts and UNS A92117 (aluminum alloy 2117-T4) rivets. The coating systems will consist of a MIL-DTL-81706, Type I (hexavalent chromium) or Type II (no hexavalent chromium) surface pretreatment, followed by MIL-PRF-85582 chromate epoxy primer and a MIL-PRF-85285 polyurethane topcoat.

The technical approach consisted of four principal sub-tasks. These included the following:

1. *Task 1 – Understanding coating transport mechanisms under simulated field conditions.* Water, aggressive ionic components, and oxygen have been found to travel through barrier coatings and reach the protected substrate, though on different timescales. Hypothesis: Varying humidity and exposure temperatures, such as those found under outdoor and some laboratory exposure conditions, alter the transport rates of electrolyte species through coating systems.
2. *Task 2 – Fatigue cycling under simulated field conditions.* The disparity between accelerated tests and field performance for organic coating systems has been recognized to result in improper ranking of these materials. Moving beyond standard accelerated testing formats that qualitatively or associatively grade coatings or even more advanced statistically correlated coating lifetime predictions, requires resolution of both deterioration mechanisms and kinetics. Mechanical stress contributes to the coating deterioration by direct crack formation at high strain values and by accelerating many of the photochemical and thermochemical deterioration reactions at lower strain values. Hypothesis: Fatigue failure mechanisms are strongly dependent on environmental conditions and the combined impact of fatigue cycling and environmental conditions results in chemical and physical deterioration that provides a parallel path for electrolyte transport through an aircraft coating system.

3. *Task 3 - Modeling coating system stress fields and crack propagation.* The mechanical behavior of joints due to the applied aerodynamic loads is expected to be one of the principal causes of time-varying deformations of the coating during its service lifetime. Coatings on a component surface are expected to experience stresses and strains below the mechanical strength and elongation at fracture of the coating material. However, aircraft joints during high-g maneuvers or a take-off or landing events, can cause the coating system to distort, elongate or bend. Thus, a need exists to model the stress-strain conditions experienced in service by coatings and to collect experimental evidence for the fatigue behavior of coatings when the components they protect are subjected to representative service loads. Hypothesis: Local stress-strain conditions in coatings, modeled as part of an aircraft component assembly and obtained through finite element analysis methods, cause fatigue deterioration of coatings in service, and affect their performance. Hypothesis: Coupling of mechanical fatigue loads and the deterioration of material properties due to exposure to the environment causes cracking of aircraft coatings.
4. *Task 4 – Outdoor exposure testing and model calibration.* Hypothesis: Development of a cumulative damage model for a coating system exposed to environmental stressors required synthesizing coating system deterioration mechanisms and crack models.

While not specifically identified in the task descriptions, electrochemical impedance spectroscopy (EIS) was the principal tool used for non-destructive assessment of the coated samples in this program. Thus, interpretation of the EIS data and relating the results to physical and chemical changes occurring in the coating required the development of new insights into coating behavior.

By developing models that can characterize the damaged state of a military aircraft's coating system as a function of environmental exposure and operations, the results of this program can facilitate improved decision-making regarding maintenance. Eliminating unnecessary maintenance reduces the generation of additional hazardous waste and worker exposure to hazardous materials in paint remover formulations and primers during the repainting process.

2. BACKGROUND

To delay the onset of corrosion on aircraft, exterior metal surfaces are covered in a corrosion prevention organic coating. Organic coating systems provide a reservoir of corrosion inhibitors and establish an electrolyte barrier between the atmosphere and the airframe structure[1,2]. These coating systems include a surface pretreatment*, a primer containing a sacrificial inhibitor additive†, and a topcoat that provides corrosion barrier properties and visual camouflage. Understanding and modeling how these coating properties change as a function of exposure to the service environment in-flight and on the ground would decrease maintenance costs and improve planning for Programmed Depot Maintenance (PDM).

Coatings

Coatings can be defined as pigmented liquids which, when applied to a surface in a thin layer, such as shown in Figure 1, convert to a solid film via a curing process. The three main components of

* MIL-DTL-5541F (2006), MIL-DTL-81706B (2004)

† MIL-PRF-85285E (2012), MIL-PRF-23377K (2012)

a coating are the vehicle or matrix, the pigments and fillers, and any additives for additional functionality.



Figure 1. Spray application of a coating to an aircraft surface

The matrix consists of the binder and any diluents or solvents in which the binder is dissolved. The binder provides the film-forming component of the coating. It can be made from natural or synthetic resins; that is, highly viscous liquids composed of organic polymers with reactive end units that harden during the curing process. Examples of resins include alkyds, acrylics, vinyl-acrylics, vinyl acetate and ethylene, polyurethanes, polyesters, melamine resins, silanes, siloxanes, oils, and epoxies.

The two resins of interest in this report are polyurethanes and epoxies. A polyurethane refers to a polymer composed of organic units joined by urethane links, such as shown in Figure 2.

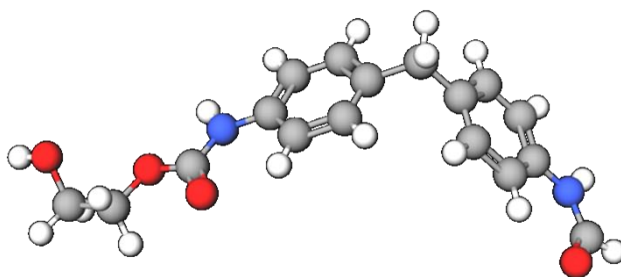


Figure 2. Polyurethane with organic units linked by urethane groups, -NH-(C=O)-O- .

Polyurethane polymers are commonly formed by reacting di- or tri-isocyanate with a polyol. Polyurethanes are used as surface coatings and sealants. In addition, because they are less susceptible to UV damage, they are frequently employed as a topcoat to protect the inner epoxy layer in aircraft coating systems.

Epoxy can refer either to the cured solid film or the epoxy resins that contain epoxide functional groups, as shown in Figure 3. Epoxies can be used as the basis for coatings or adhesives.

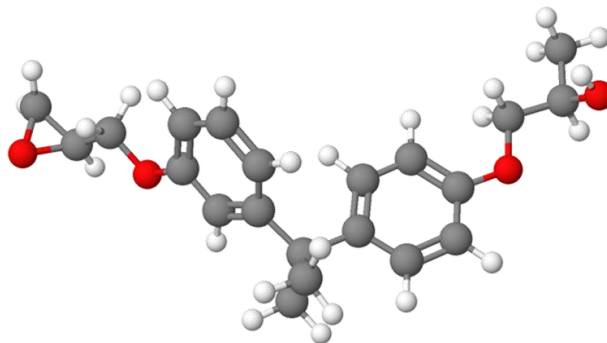


Figure 3. Base epoxy resin. The structure can be repeated up to 15 times.

Binders are generally cured using either a thermoplastic or thermoset process. In thermoplastic curing, no chemical reaction occurs. Instead, the binder solidifies either through a glass transition process or evaporation of the solvent leads to agglomeration of the binder particles. In thermoset curing, polymerization reactions occur during the curing process that cross-link the polymers, via catalyzed reactions or oxidation as the solvent evaporates, to form the solid film. Epoxy resins can be cured by reacting with other epoxy resins or with curing agents such as amines, acids, phenols, alcohols, or thiols. The curing process for epoxies is generally exothermic and can release substantial amounts of heat.

Solvents or diluents refer to volatile chemicals with low vapor pressures that evaporate relatively easily. They are used to dissolve the monomer backbone of the binder to control the viscosity of the coating during application.

Pigments refer to organic or inorganic powders incorporated into the binder to provide coloration to the cured film. Fillers are generally low-cost pigments that provide specific functions, such as supporting the cured film structure, adding volume to the liquid coating, or thickening the cured film.

Additives are generally added in smaller concentrations than the other components but can have significant impacts on the behavior of the coating. Additives can include catalysts, adhesion promoters, UV stabilizers, biocidal agents, and, of interest to this report, corrosion prevention, to include hexavalent chromium, trivalent chromium, and magnesium compounds, among others.

Coating systems

Coating systems are used in a wide variety of environments, including seawater immersion and exposure to the atmosphere, as a method for preventing corrosion. A coating system refers to the layers of coatings that are applied over one another to form a structure that performs multiple functions, which cannot be provided by a single coating. For example, an aircraft coating system can consist of a surface pretreatment that anodizes the oxide layer of the aircraft skin material and aids in adhesion of the base coating to the substrate; a barrier primer layer that contains a sacrificial inhibitor additive; and a topcoat layer that protects the primer and provides coloring using pigments and fillers.

A coating system refers to layers of coatings overlaid on one another. Taken together, the coating system performs multiple functions that cannot be provided by a single coating. For example, a coating system on Navy aircraft consists of a surface pretreatment that can contain a corrosion inhibitor and aids in adhesion of the coating system to the substrate, a primer coating containing a

sacrificial inhibitor additive, and a topcoat that protects the primer and provides visual camouflage through the use of pigments and fillers, as illustrated in Figure 6.

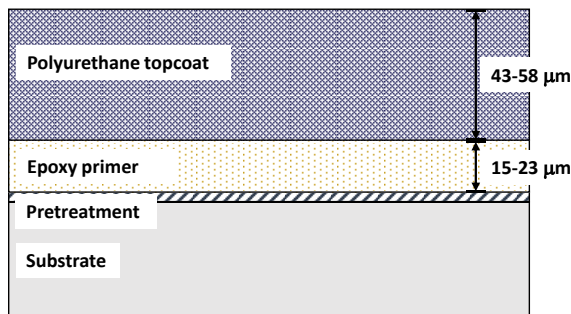


Figure 4. Illustration of a three-layer aircraft coating system consisting of pretreatment, primer, and topcoat.

Coating system deterioration

Exposure of the coating system to environmental conditions that include temperature extremes, ultraviolet (UV) radiation from sunlight, and changing humidity levels, can degrade the polymer at the topcoat's surface. This degradation can then lead to color change and loss of gloss in addition to the formation of flaws (e.g., pits, fissures) that can aid in the transport of oxygen and electrolyte. Several prior SERDP programs were undertaken to understand this degradation process.

In SERDP Project PP-1133[20], Mechanisms of Military Coating Degradation, an extensive characterization plan was developed and carried out to examine breakdown mechanisms in multiple coating systems at exposure sites in Florida and Arizona. The environmental factors that were found to contribute the most to color and gloss change were UV exposure[21,22], temperature changes, and moisture. The outcome of that program was the development of several linear regression models for the different coating systems that correlated surface color changes with changes in measured electrochemical impedance spectroscopy (EIS) parameters to give an indication of the coating system's status. However, the models for each coating system differed – with different sites requiring different models for some coatings – without indicating how the model parameters ought to vary if, for example, the coating system traveled between the different environments.

Following this effort, SERDP Project WP-1674, Dynamic Multivariate Accelerated Corrosion Test Protocol, pursued a two-fold operational approach[23]. The first task in this project focused on developing an accelerated test protocol – including designing a modified environmental chamber – that could replicate at an accelerated rate, the corrosion processes observed in field exposures for uncoated and scribed coated panels. The second task focused on developing a cumulative corrosion damage model to predict mass loss for uncoated panels using a Monte Carlo approach to determine coefficients for various shape functions that related the monitored environmental variables to the measured corrosion mass loss to minimize errors and provide a cumulative damage prediction. However, a limitation with this corrosion model is that it was developed using only UNS G10100 steel panels and thus would not provide any predictive capability for corrosion of aluminum alloys like UNS A92024 or UNS A97075. While there were coated panels included as part of this effort, there was no clear quantification of damage or initial development of a modeling approach for this more complex system.

Lastly, SERDP Project WP-201710, Corrosion Monitoring System to Reduce Environmental Burden and Corrosion Maintenance Costs[24], was established to collect the necessary environmental and corrosion data to train a corrosion algorithm to link environmental parameters to observations of corrosion in order to improve predictions for condition-based maintenance plus (CBM+) and potentially eliminated the need for on-board sensors.

With the previous investment in understanding coating degradation mechanisms, accelerated corrosion testing, and in predicting corrosion, our goal is to leverage the results and approaches of the previous work and apply them at a more granular level to improve understanding and prediction of coating degradation. Given that the coating system covers most of the complex surface of the entire aircraft, we suggest the following framework to categorize the aircraft coating system:

1. Coating system only covers a single material, such as the skin of the aircraft, and is uniform thickness.
2. Coating system spans a junction between two different components, such as the skin and a fastener and has varying thicknesses.

This framework allows us to incorporate the results from earlier projects as well as suggest additional areas of investigation. For example, one important factor that was not previously addressed by a SERDP project is the role that fatigue cycling may play in coating degradation. Time-varying loads arising from flight operations, applied to the coating system, concentrate stresses at the coating flaws and drive the formation of micro-cracks. The micro-cracks grow to form cracks under additional fatigue loads and the presence of thermal stresses. We expect these cracks to facilitate the ingress of aggressive ions to the metal surface that aid in driving corrosion.

In addition, locations where the coating has to span gaps between skin and fastener are expected to be inherently weaker because there is less substrate support. These areas experience high service loads that can deform the coating system via the mechanical contact between the aircraft structure and the coating. The effects of temperature excursions due to sunlight exposure and high-altitude flight further subject the coating system to thermal stresses[25,26]. Differential moisture absorption can cause additional stresses at the interface between coating and substrate[27].

Of particular interest is corrosion driven by galvanic incompatibilities between the aircraft skin and fasteners because these forms of corrosion can have faster reaction kinetics than self-corrosion processes. Materials for fasteners can range from rivets made of higher strength, or corrosion resistant, aluminum alloys to threaded fasteners such as screws and nuts and bolts made from high-strength materials like precipitation-hardened steels or stainless steels. It has been found that galvanic corrosion between noble metal fasteners and aluminum alloy aircraft panels is a critical source of the corrosion damage found on aircraft[28–30].

3. MATERIALS AND METHODS

Sample preparation and immersion

Bare aluminum alloy 2024-0 panels (Q-Lab Corporation), with dimensions 7.62 cm × 15.24 cm × 0.05 cm, were anodized (Almag Plating) on each side of the panel to thicken the native aluminum oxide and cap the oxide to enhance adhesion between the surface and the primer layer[31]. The following coating steps were performed according to the coating manufacturer's specifications. The panels were spray coated with a water reducible epoxy primer (44GN008A; PPG Industries) that complied with the coating performance specification MIL-PRF-85582, Type II, Class C1, and included a barium chromate-based corrosion inhibitor, using high-volume, low-pressure (HVLP) spray equipment[32]. After 24 h, dry film thickness (DFT) measurements indicated the primer was 15.24-22.86 μm thick. Each panel was then coated with a gray (FED-STD-595 #36375) polyurethane topcoat (99GY003; PPG Industries) that complied with the coating performance specification MIL-PRF-85285, Type IV, using HVLP spray equipment[33]. After curing for 24 h, DFT measurements indicated the topcoats were within a range of 43.18-58.42 μm thick. The coating system was then allowed to further cure at ambient conditions, *i.e.*, 20-22 °C, 40-60% R.H., for a minimum of 14 d before immersion. Figure 5 shows a cross-section diagram of the coating system.

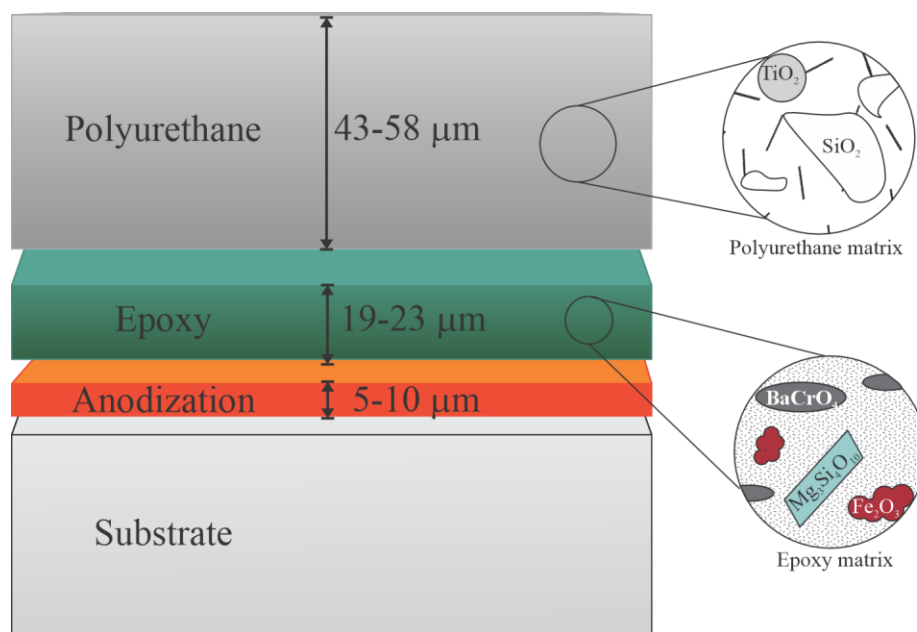


Figure 5. Organic polymer coating system consists of a surface pretreatment layer, a primer layer, and a topcoat layer. Layer thicknesses are approximately to scale while the substrate thickness is not. Schematic sketch of the organic polymer matrices and principal filler particles in each layer.

Once curing was completed, electrical attachment was made to each panel and the electrical connection was then sealed using an epoxy adhesive (50112 ClearWeld, J-B Weld). Electrolyte solutions were mixed using Type I, ultra-pure, ≥18 MΩ-cm water (Milli-Q) and 99% pure, ACS grade, NaCl crystalline powder (Fisher Chemical).

Laboratory aging conditions

Sets of coated panels were exposed to a variety of laboratory aging conditions. Coated coupons, with three replicate coupons per exposure condition, were immersed in the following solutions maintained at the specified temperature:

- Immersion in 0.01 M NaCl and saturated NaCl solutions at $T = 5^{\circ}\text{C}$ and 60°C
- Immersion in 3.2 M NaCl at 25°C

These immersion conditions were selected to simulate the chemistry of an equilibrated thin film electrolyte in atmospheric exposure conditions ranging from 99% to 70% RH in direct sunlight. Test coupons with coatings were placed in glass beakers that were filled with 1.5 L of the specified solution. Beakers with saturated NaCl solutions contained excess salt to ensure saturation. The beakers were covered with mylar sheets to prevent activity changes from evaporative water loss and placed in water baths to maintain the specified temperature. In Phase I of the laboratory exposures, the immersion times lasted for approximately 3192 h. In Phase II of the laboratory exposures, the immersion times lasted for 6840 h.

Additional coated samples were also exposed to environmental stressors that were intended to simulate atmospheric exposures. They included neutral salt spray per ASTM B-117[34] and accelerated artificial weathering in a QUV spray system using a custom aging cycle. Coated panels placed in the QUV spray chamber were either unstressed, elastically loaded with a static stress of 34.5 MPa or 69 MPa, or plastically deformed with 2% strain. The curved sample mounts that applied the static deformations were 3D printed using ABS thread to provide thermal and UV-radiation durability. Example panel mounts are shown in Figure 6. A minimum of three replicate coated panels were exposed to each of the aging conditions. The details of each environment cycle are:

- Unstressed and stressed coupons with applied static loads of 34.5 MPa, 69 MPa, and 2% strain while exposed to 12 hours of UV light at an intensity of 1.46 W/m^2 , followed by 9 hours of condensation at 45°C , then 3 hours of darkness.
- Exposure to ASTM B117-19 salt spray testing with some exposure to below-freezing conditions.

These exposures lasted approximately 3192 hours.

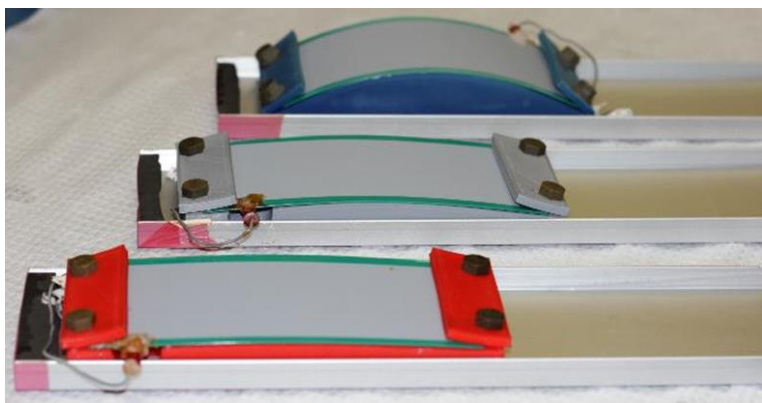


Figure 6. Panel mounts to apply static loads to the coating system. From bottom to top: 34.5 MPa load, 69 MPa load, 2% strain.

Preparation of free film samples

Samples of primer, topcoat, and full coating system were applied to the outer surface of polyvinyl fluoride (PVF) films (DuPont, Holliston, MA) to allow testing of free films of the coatings in tension. For primer samples, the films were spray coated, using high-volume, low-pressure (HVLP) spray equipment, with a two-part water reducible epoxy (44GN008A; PPG Industries, Pittsburgh, PA), which included a barium chromate-based corrosion inhibitor, that complied with the coating performance specification MIL-PRF-85582E, Type II, Class C1. For topcoat samples, PVF films were coated, using HVLP spray equipment, with a two-part gray (FED-STD-595 #36375) polyurethane topcoat (99GY003; PPG Industries, Pittsburgh, PA) that complied with the coating performance specification MIL-PRF-85285, Type IV, Class H. For full coating system samples, the primer was first applied to the PVF film and allowed to cure for a minimum of 24 h before the topcoat was applied. All samples were cured for 24 h, before dry film thickness (DFT) measurements were made to determine sample thickness. The layer thicknesses were consistent and representative of typical aircraft coatings. The primer layers were 25 μm thick, the topcoat layers were 100 μm thick, and the full system samples, composed of a single primer and topcoat layer, were 125 μm thick. All samples were then allowed to further cure at ambient conditions, *i.e.*, 20–22 °C, 40–60% R.H., for a minimum of 14 d before exposure testing.

Outdoor exposure testing

The coating samples were left on the release paper and mounted to moisture resistant high-density polyethylene (HDPE) sheets (McMaster-Carr, Robbinsville, NJ), using threaded nylon fasteners with the sample sandwiched between nylon washers (McMaster-Carr, Robbinsville, NJ), as shown in Figure 7b. The HDPE sheets with samples attached were mounted such that the samples were inclined at a 45° angle from vertical on the atmospheric exposure racks at Fleming Key, FL. They were continuously exposed to atmospheric conditions for 5736 h. The 45-degree angle exposure rack was designed to maximize irradiation by UV light as well as allowing rainwater to run-off easily.

An image of the exposure rack, with coating samples mounted, is shown in Figure 7a. The image includes primer, topcoat, and full coating system samples. The two single layers of primer are shown in the bottom right corner of the exposure panel. Unfortunately, none of the primer samples survived the exposure period. The epoxies used for aircraft coating systems are brittle once cured and are susceptible to UV damage. The combination of weathering and UV degradation resulted in multiple brittle fractures and only small pieces of the primer samples were found attached to the nylon fasteners at the end of the exposure period. At the completion of the exposure period, the full coating system and the topcoat samples were shipped back for machining of tensile samples. The topcoat and full coating system were cut into rectangular tensile samples, with the same geometry used for the unexposed materials.

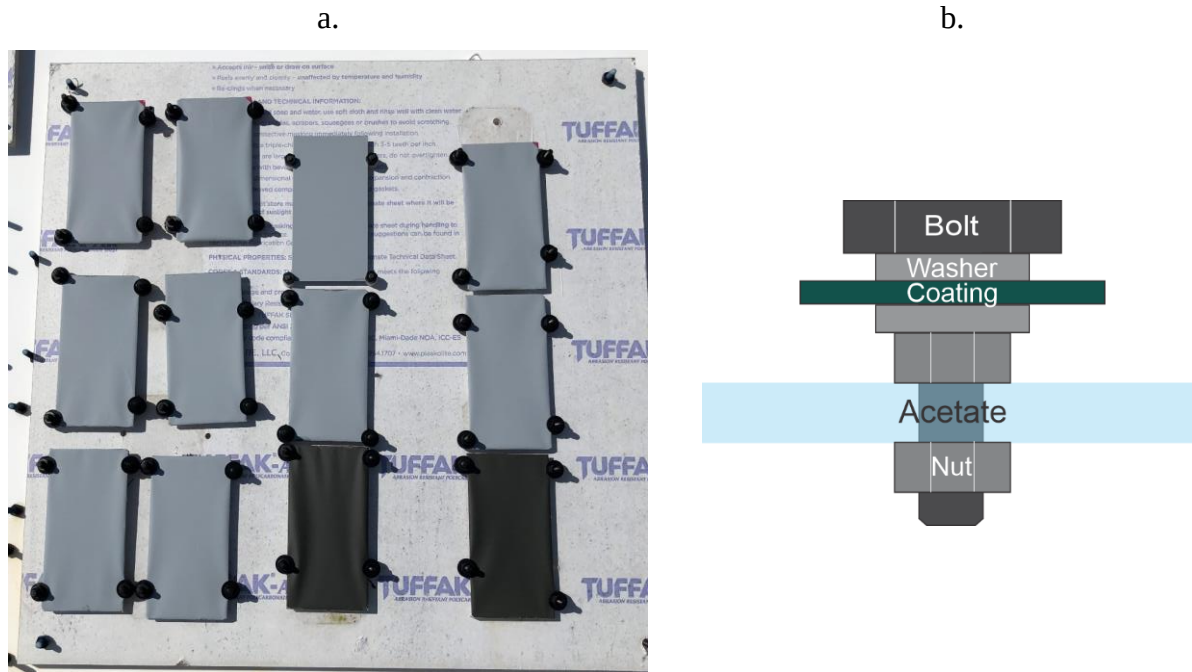


Figure 7 – Atmospheric exposure of primer, topcoat, and full coating system samples at Fleming Key, FL.

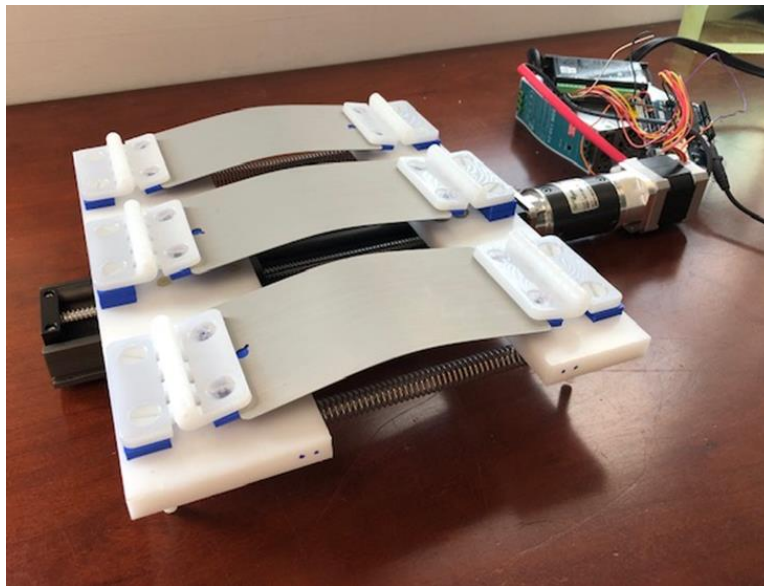


Figure 8. Flexing apparatus to apply loads to coated aluminum 2024-0 alloy panels. The linear motion lead screw was actuated by a NEMA 17 stepper motor with a 50:1 gear reduction with 2 lateral springs used for mechanical advantage. The stepper motor and drive, 12 V DC power supply, and Arduino board, are shown in the upper right of the image.

Fatigue testing of fully supported primer and topcoat

Coated aluminum 2024-0 alloy panels were installed on an in-house designed and manufactured mechanical testing system. The mechanical testing system allowed three test coupons to be mounted and tested simultaneously, as shown in Figure 8, with a custom loading profile.

The load profile was programmed into the Arduino Nano control board[35]. The custom load profile used for the testing is shown in Figure 9. Tension loads were applied to the aluminum 2024-0 alloy panels, and thus to the coatings, by pulling the lower mount point toward the upper one by driving a lead screw with a stepper motor. The load was relaxed by applying the opposite torque to the lead screw.

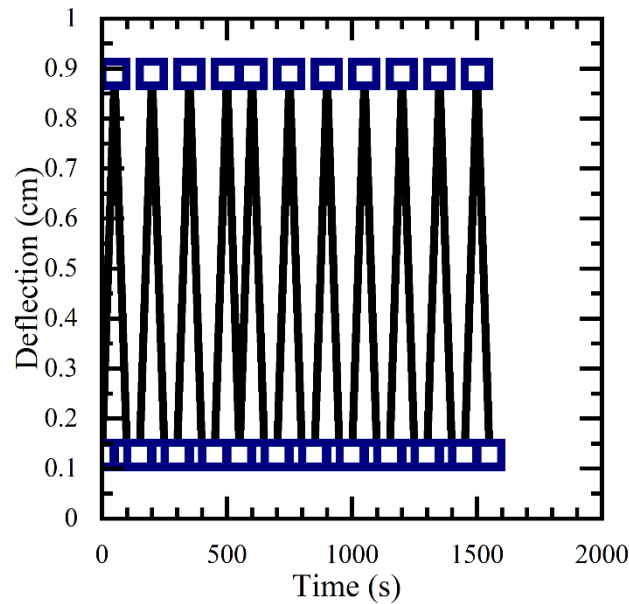


Figure 9. Load spectrum for the aluminum 2024-0 alloy panels tested at NRL-KW; deflections are for the center part of the flexed panels; the spectrum was repeated continuously during more than 6 months of exposure. Total exposure time was 4320 hours for a total of 103680 cycles.

Because the fatigue test coupons would be aged on the atmospheric exposure racks, the Arduino Nano controller, power supply, and stepper motor were housed in a NEMA box rated for outdoor exposures, as shown in Figure 10.

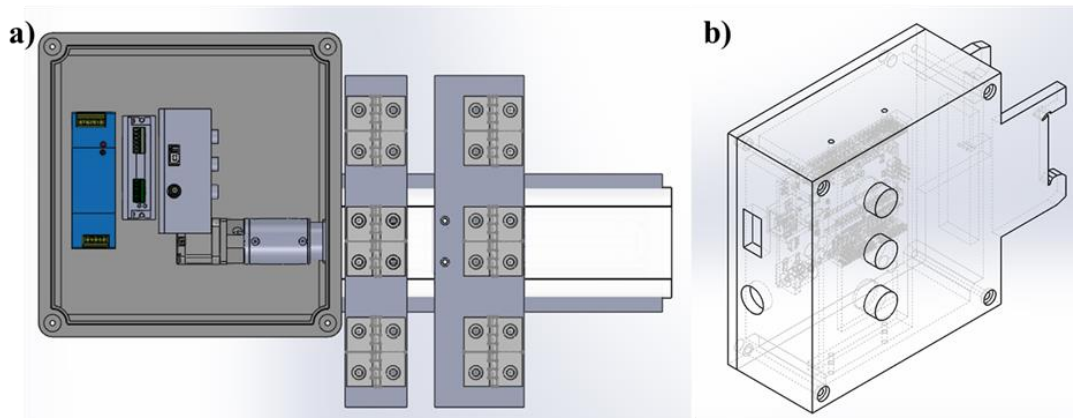


Figure 10. a. Configuration of control modules in NEMA Box for outdoor exposure, and b. 3D Printed DIN Rail mount and control buttons for Arduino board.

Overall placement of the test panels and controllers is shown in Figure 11a, while Figure 11b shows a closeup of the final configuration for fatigue testing the coated panels.

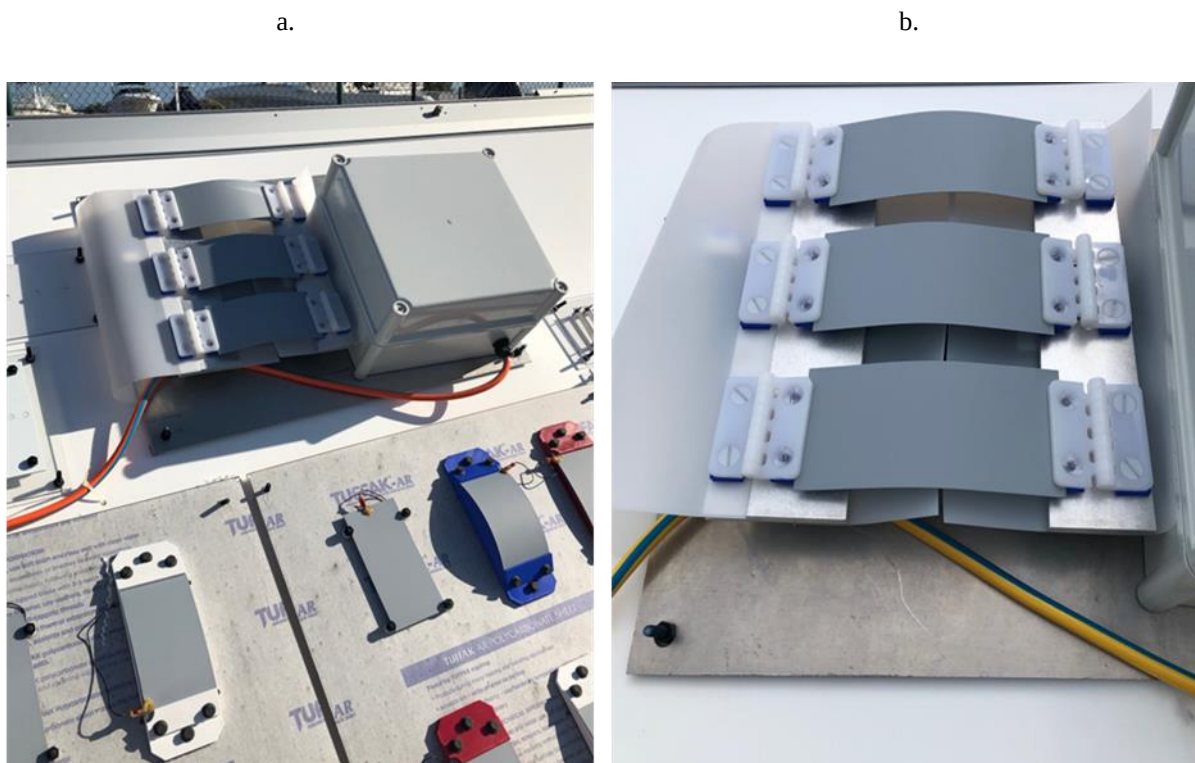


Figure 11. Deployment of the apparatus for outdoor exposure for flexing aluminum 2024-0 alloy panels on a 45° inclined exposure rack on Fleming Key, FL.

EIS measurements

Each coated panel coupon was washed with Type I, ultra-pure, ≥ 18 M Ω -cm water (Milli-Q) and dried with laboratory-supplied nitrogen. A cylindrical-bodied glass vessel (PTC1; Gamry) was mounted to the center of the test coupon using a Viton rubber O-ring to seal the glass cell to the coating surface and a metal clamp to secure the vessel and O-ring to the surface for EIS testing. The exposed area of the coating system was 14.6 cm². The glass vessel was filled with 40 mL of 0.6 M NaCl, and a 3D printed plastic stopper with ports for a glass saturated calomel electrode (SCE) reference electrode (Gamry) and graphite rod counter electrode was used to cap the vessel. The counter and reference electrodes were installed through the plastic stopper so that the distance between the counter and reference electrodes and the working electrode surface was constant for each measurement. The entire assembly was placed inside a Faraday cage to minimize external electrical interference. For the stressed panels, the paint test cell was installed in a 3D-printed mount with the appropriate curvature to match the deformation of the stressed panel. The mount was sealed to the coating and the paint test cell was sealed to the mount using Viton rubber O-rings. The entire apparatus was secured using four stainless-steel bolts.

The EIS measurements were made using a potentiostat (Interface 1000; Gamry) in the potentiostatic configuration with the potential modulated ± 10 mV_{RMS} about the stable potential of the system. The frequency modulation for the potentials ranged from 100 kHz to 100 mHz. The frequency values were spaced logarithmically, 10 points per decade, and averaged over 4 cycles at each frequency. The stationary criterion was met with the ± 10 mV_{RMS} perturbation and linearity of the coupon response to the potential modulation was confirmed using the Kramers-Kronig transform utility provided with the analysis software (Echem Analyst; Gamry).

Fatigue testing of unsupported primer coatings

While fatigue testing is commonly done for structural metals, composites, and polymeric materials following standard guidelines[36], no standard exists for coated panels or coatings more generally. To study the resistance to fatigue of the primer materials, a new sample design was developed to concentrate the strain experienced by the coating system, while allowing the use of conventional testing machines. A panel was modified by cutting a notch/slot at its center to allow the formation of an area of higher deformation at the center of the panel and a pattern of holes around the center notch. As shown in Figure 12a, the center notch was 0.16 cm in height and 3.3 cm in length. A pattern of holes was machined at the four corners of a bounding box around the center notch. The holes were in the shape of ovals, 1.91 cm long and with a radius of 0.32 cm on either side, as indicated in Figure 12a.

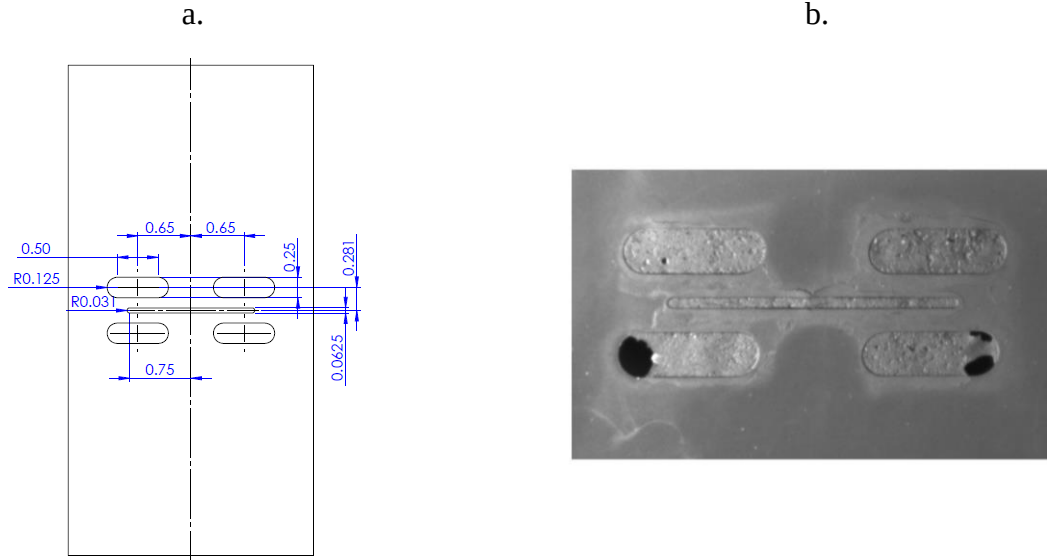


Figure 12 – a. Schematic diagram of the coating fatigue test panel developed to measure fatigue life of primer. b. Image of the center portion of the fatigue test panel before testing. Note that the black areas on the lower cutouts show where the coating cracked during curing.

The pattern was defined by studying the application of a remote uniform traction on the panel. Because of the designed center slot, the displacement at the center corresponds to an applied strain to the primer that depends on the applied loads. When the applied remote traction on the panel is 6.9 MPa, the stress at the edges of the 4 slots is 24.8 MPa and the stress at the ends of the center notch is 10.3 MPa. The strain for the coating across the center slot is 0.4%.

The four slots at the corners of the bounding box around the center slot were designed to reduce the stress concentration at the edges of the center slot, as shown in Figure 12b. The slot was a significant stress concentrator for the aluminum panel; therefore, the four-slot pattern reduces the stress at the edges of the center slot and the chance of fatigue crack initiation in the aluminum at its edges. The stresses at the edges of the center notch were reduced significantly by the presence of the four corner slots, with the center displacement only minimally affected.

The machined panel was coated with primer and the center slot was filled with primer during the spray process by using a backing of a polyvinyl fluoride (PVF) film for the panel. This was done because the cured organic polymer coating has poor adhesion to the PVF film[37], which would allow the PVF film to be removed from the back of the panel once the coating had cured, leaving behind a free-standing region of the cured coating.

The panel was then tested by a servo-hydraulic machine by gripping the unmachined part of the sample with flat hydraulic grips and applying a sinusoidal load. One panel was tested at a maximum load of 267 N and minimum load of 89 N and at a testing frequency of 1 Hz. Given the dimensions of the panel, a load of 267 N corresponded to a traction of 6.9 MPa and a strain in the primer of 0.4%. The number of cycles to failure was defined as the time when a crack was observed at the center of the slot. The sample was illuminated from the back and a camera positioned at the other side to monitor the occurrence of cracking, as illustrated in Figure 13, by taking 1 image every 100 seconds.

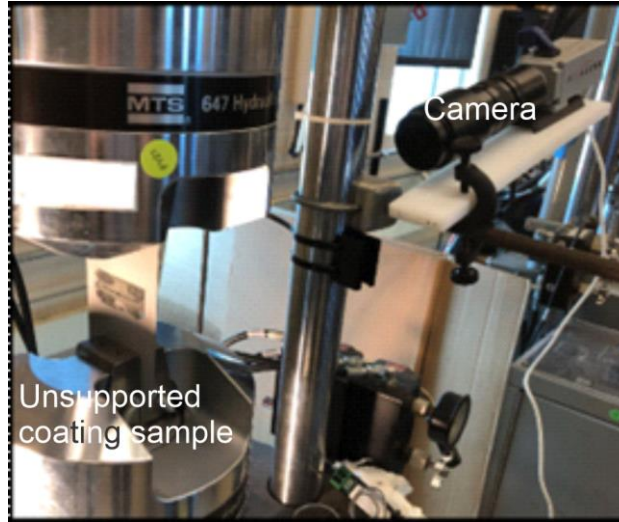


Figure 13 – Coating fatigue test panel developed to measure fatigue life of primer. Test setup using a digital camera scope to observe crack propagation.

Scanning Kelvin Probe (SKP) measurements

Fatigued, exposed, and unexposed coatings were equilibrated for over 1 h at 95% RH and room temperature in a controlled humidity chamber housing a scanning Kelvin probe instrument (RHC 2020, KP Technology) with a 50 μm gold tip mounted to the scanning head, as shown in Figure 14.

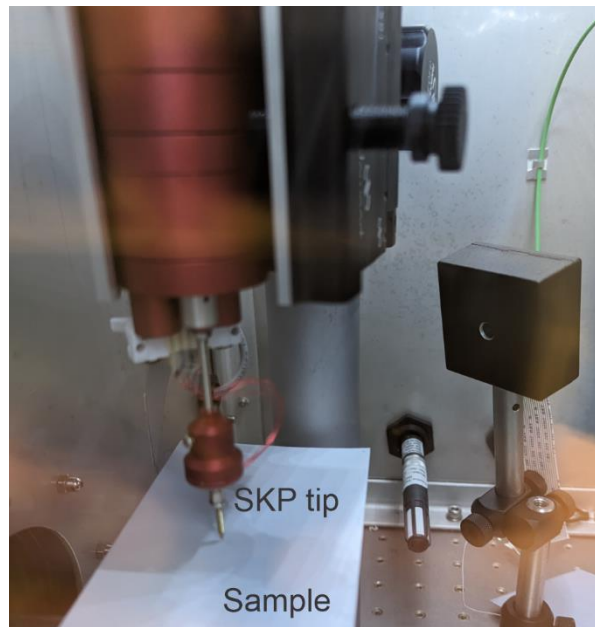


Figure 14. Placement of the coating sample in the SKP chamber.

Following equilibration, the Al-Au standard was area scanned (2 mm x 12 mm) across the interface to ensure the instrument was calibrated. The work functions are obtained from (1),

$$\Phi_{\text{sample}} = V_{\text{cpd}} + \Phi_{\text{tip}}, \quad (1)$$

where ϕ_{tip} is obtained from (2),

$$\Phi_{tip} = \Phi_{Au} - V_{cpd}, \quad (2)$$

and $\Phi_{Au} = 5100$ meV[38], and V_{cpd} is obtained from an equilibration of the tip in the environment. Φ_{tip} from (2) is then used in (1) to obtain Φ_{sample} . The calculated work functions for the calibration sample are shown in Figure 15. From the literature, $\Phi_{Al} = 4080$ meV[38], which closely matched the average work function over the aluminum portion of the standard, so the instrument was assumed to be calibrated.

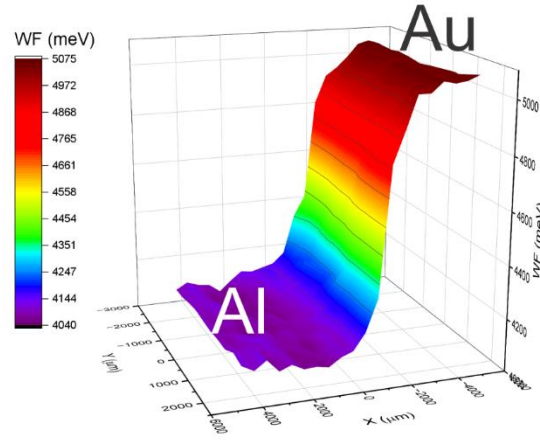


Figure 15. 2 mm x 12 mm area scan across the interface on the Al-Au SKP standard showing that the instrument was calibrated.

Tensile Testing of Primer and Topcoat Materials

The PVF films were cut into 2.54 cm-wide samples to allow the coating samples to be detached and positioned in the testing machine. A Testometric load frame (Testometric, Rochdale, U.K.) with a 250 kgf load cell was set up to allow the gripping of 2.54 cm-wide strips of the materials. Both the applied loads and displacements were measured during the test [39]. The elastic properties for the various coating samples were determined before and after atmospheric exposure. The tensile testing setup is shown in Figure 16.



Figure 16. Test configuration for measuring the elastic properties of the different coating samples.

It was very difficult to avoid breaking the epoxy samples while handling them for mounting in the load frame and applying the grips. Observations from the data that were collected indicated an elastic behavior followed by brittle fracture of the sample. The results for the testing of the topcoat were consistent and showed an initial linear behavior followed by continuous decrease in instantaneous modulus until final failure near 4% strain. The complete coating system demonstrated an initial elastic behavior, with similar modulus as measured for the topcoat alone, up to a point where a maximum load was measured, and the deformations started to increase significantly. Failure occurred around 4% strain for 2 of the 3 tests performed and around 2.5% for the other test.

SEM imaging

Scanning Electron Microscopy (SEM) samples were created by shearing 1 cm by 3 cm small coupons from several of the test panels. The small coupons were mounted edge-upward in EpoFix (Struers) epoxy with a 1:1 ratio by weight of conductive nickel filler added (Buehler). SEM images were obtained using a Quattro-S environmental SEM (Thermo Scientific) in high vacuum mode, operating at either 10 kV for imaging or 20 kV for EDS data collection.

Color change measurements

A portable spectrophotometer (MiniScan EZ 4500, HunterLab) was used to monitor the color changes in the topcoat in response to the laboratory aging processes. The instrument is a fixed geometry, 45:0 device, with the light source set at 45° from vertical and the detector set directly overhead. This setup is appropriate for measuring the color of the matte topcoat surface. Following calibration with the supplied black glass and white tile standards, the color measurement was obtained by pressing the sample port against the topcoat so that the sample completely covered the port to prevent contamination of the measurement from ambient room lighting.

4. USING MACHINE LEARNING TECHNIQUES TO ESTIMATE INITIAL MODEL PARAMETERS

Introduction

One technique that can be used to measure and monitor changes in coatings due to environmental exposures is electrochemical impedance spectroscopy (EIS)[40,41]. This is because of the presence of water and electrolyte in the coating system. In EIS, a small, oscillating, excitation signal is overlaid on a constant potential or current that is applied to the test system and the magnitude and phase of the system's response is measured[10]. If a sinusoidal potential with a frequency, ω , and amplitude, E_0 , is applied to the coating system, the current response of the system will be a sinusoid at the same frequency but with a phase shift, ϕ , and amplitude I_0 . The impedance $Z(\omega)$ of the system can then be expressed as,

$$Z(\omega) = \frac{E_0 \sin \omega t}{I_0 \sin \omega t + \phi} \quad (3)$$

The excitation signal is kept small so the system's response can be kept linear or nearly linear. The response of the system to the excitation signal can then be interpreted to reveal physical or chemical changes.

One approach to analyzing impedance spectroscopy is to fit the data with an equivalent circuit model to obtain estimates of the circuit components' parameters[42,43]. A common equivalent circuit model used to analyze the EIS data for an organic coating on a metal electrode is given in Figure 17. In this model, R_1 represents the ohmic resistance of the electrolyte, R_2 represents the resistance of the coating, C_1 represents the dielectric behavior of the coating system, R_3 represents the polarization resistance of the substrate metal surface, and C_2 represents the double-layer capacitance.

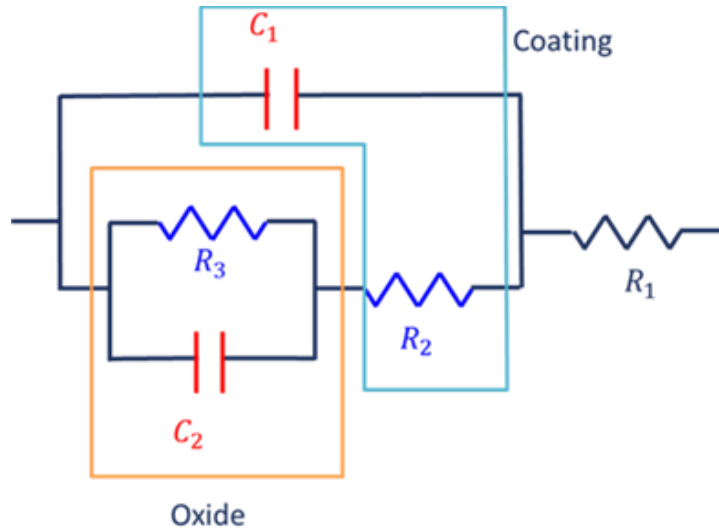


Figure 17: Equivalent circuit model used to analyze EIS data obtained from an organic coating system on a metal surface: R_1 = solution resistance; R_2 = coating system resistance; C_1 = coating system capacitance; R_3 = metal polarization resistance; and C_2 = double-layer capacitance.

The impedance for the equivalent circuit provided in Figure 17 can be calculated from (4). This equation can be derived using combinations of equations for the impedance of a resistor, capacitor, and a parallel resistor-capacitor circuit, given in (5) to (7), respectively.

$$Z(\omega) = \left[R_1 + \frac{R_2 + (\omega R_3 C_2)^2 R_2}{(1 - \omega^2 R_3 C_2 R_2 C_1)^2 + \omega^2 (R_3 C_2 + R_3 C_1 + R_2 C_1)^2} \right] - j \left[\frac{\omega [R_3^2 C_2 (1 + \omega^2 R_2^2 C_1 C_2) + C_1 (R_2 + R_3)^2]}{(1 - \omega^2 R_3 C_2 R_2 C_1)^2 + \omega^2 (R_3 C_2 + R_3 C_1 + R_2 C_1)^2} \right] \quad (4)$$

$$Z_R = R \quad (5)$$

$$Z_C = \frac{1}{j\omega C} \quad (6)$$

$$Z_{||} = \frac{R}{1 + (\omega RC)^2} - j \frac{\omega R^2 C}{1 + (\omega RC)^2} \quad (7)$$

Parameter values for circuit elements in an equivalent circuit model can be obtained using nonlinear regression methods. However, these methods are frequently sensitive to the initial values used and simple heuristic approaches to selecting the initial parameter estimates can result in the regression algorithm failing to provide a good fit to the data in a least-squares sense[44]. Given a sufficiently large training dataset, however, machine learning models offer a path forward for obtaining initial estimates that have a high probability of obtaining a good, least-squares, fit to the data.

Machine learning (ML) refers to the subset of artificial intelligence algorithms that construct models based on a sample dataset, known as training data, to make predictions[45]. ML algorithms, which learn from datasets in which the outcome of the experiments in the training dataset is known, are called supervised learning algorithms[46]. The relatively recent widespread availability of machine learning frameworks, such as TensorFlow[47], Keras[48], and PyTorch[49], for example, has led to the employment of machine-learning-based methods to address a wide variety of materials science and engineering problems[50] that include corrosion phenomena in both marine and atmospheric environments[51–53]. Some of these methods include Bayesian probabilistic approaches, genetic algorithms, decision trees, and artificial neural networks[54].

Of these, artificial neural network (ANN) methods have been investigated as a means of assessing coating integrity for several decades. For example, Hack and Matteson[55] used EIS data from epoxy-polyamide coatings on steel panels exposed to ASTM Standard D1141 seawater. They classified all sample coatings as “good coatings”, *i.e.*, Z_{mod} for the coating at oscillation frequencies below 0.1 Hz exceeded 10 GΩ and “bad coatings”, *i.e.*, Z_{mod} for the coating at oscillation frequencies below 0.1 Hz was below 1 MΩ. They evaluated several ANNs, with different numbers of hidden layers, to predict if a coating was good or bad. Each ANN also used different parts of the available impedance data. Their best-performing models did not require phase data to make good predictions but did require impedance data at oscillation frequencies below 10 Hz.

Lee and Mansfeld[56] also used ANNs that were trained using theoretical impedance data and then used to predict coating quality for various coating systems on steel substrates exposed to natural seawater for over a year at the NRL site in Key West, FL. They used three quality distinctions: good, intermediate, and poor; that were based off the value of the pore resistance, R_{po} , of the coating system. For good coatings, $R_{po} \geq 5 \times 10^{10} \Omega$ and for bad coatings, $R_{po} \leq 5 \times 10^6 \Omega$. Kumar and Buccheit[57] used ANNs to relate EIS data collected from conversion coatings immersed in 0.5 M NaCl for 24 hours to conversion coatings that were exposed to ASTM Standard B117 salt spray testing for 1500 hours.

More recently, Mousvivard and colleagues[58] used a combination of an ANN and a neuro-fuzzy inference system to model the corrosion current density for a Zr-based conversion coating on galvanized steel. Zhu and colleagues [59] trained a support vector machine method to determine the best equivalent circuit model to use for analyzing a given set of EIS data. Lastly, Bongiorno and colleagues[60] trained ML models to fit representative EIS data as well as select an equivalent circuit model to fit to the EIS data.

These selected examples help to illustrate a trend away from using ML models as a qualitative replacement for expert classification and toward more quantifiable predictions. In addition, all these example studies used quantitative elements of the impedance datasets as features for training the ML models. In keeping with the quantitative approaches taken by these other studies, the goal of this work was to develop two supervised ML models that could be employed in a sequence to optimize the selection of initial parameter values. These values were then employed by a nonlinear regression algorithm to fit an equivalent circuit model to EIS data obtained from an organic coating system applied to an aluminum substrate.

Results

Representative examples of the EIS data, as Z_{mod} vs. frequency, are shown in Figure 18. Figure 18a shows data for coated coupons immersed in a 0.01 M NaCl solution at 60°C over the course of 3192 h. Figure 18b shows EIS data for a coated coupon exposed to condensation at 45°C and UV light with an intensity of 1.45 W/m². Figure 18c shows EIS data for a coated coupon exposed to the salt spray solution in the ASTM Standard B117-19 spray testing at 35°C. Figure 18d shows EIS data for a coated coupon exposed to condensation at 45°C and UV light with an intensity of 1.45 W/m².

Representative examples of the Kramers-Kronig fit residuals for the coupon shown in Figure 18a, at $t = 0$ hours, and $t = 3192$ hours, are plotted in Figure 19. The small residual values and their distributions about zero indicate a linear system response in the EIS measurements of the coating systems.

While only a subset of all EIS measurements obtained are plotted, there are several key features that should be noted. The generally sigmoidal shapes of the Z_{mod} curves on the log-log plots are indicative of reactive elements present in the system. In fact, the measured EIS response for the coating systems at $t = 0$ hours was principally dominated by a single capacitor response, as can be seen in the phase vs. frequency plots in Figure 18 at $t = 0$ hours. Over the duration of the exposure to the test conditions, however, the impedance response of the coating systems changed. As the capacitive response declined, the influence of other circuit elements could be observed. At longer times, the sigmoidal shape of the response became more pronounced at lower oscillation frequencies. For these reasons, the equivalent circuit shown in Figure 17 was selected as the equivalent circuit model to fit the EIS response for the coating systems.

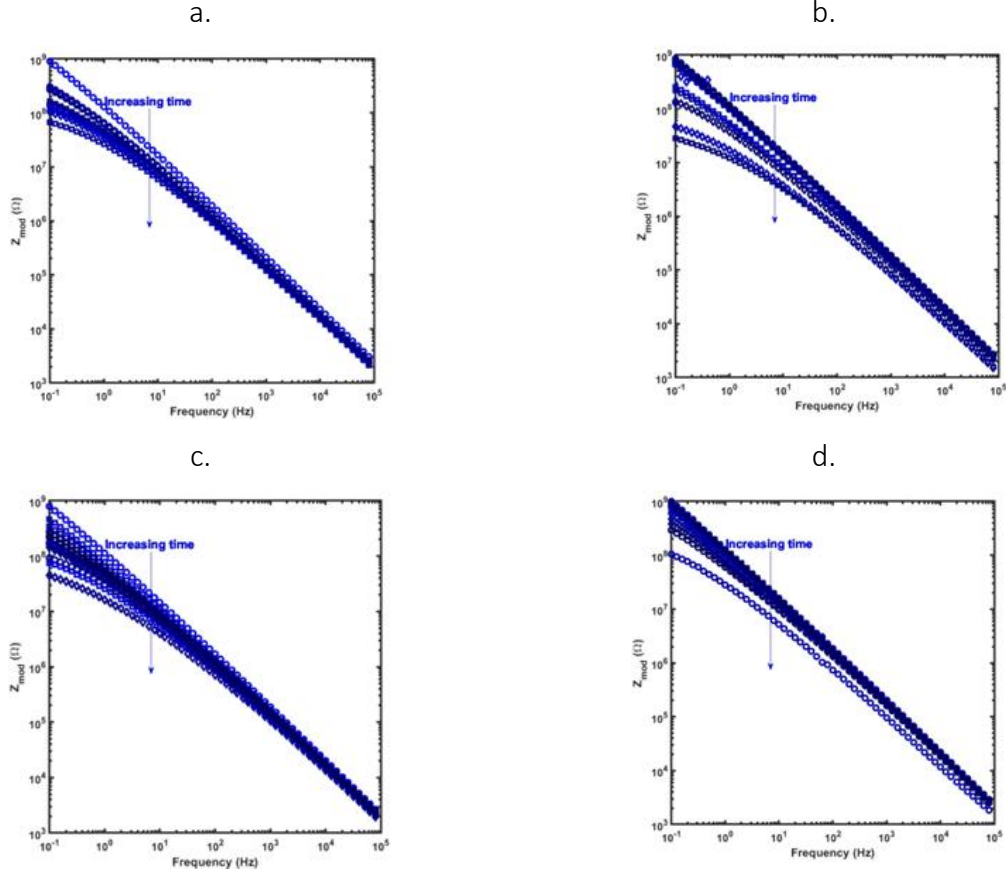


Figure 18: Z_{mod} vs frequency for coating systems exposed to the indicated environmental conditions for 3192 hours. a. Immersion in 0.01 M NaCl at 60°C. b. Exposed to condensation at 45°C and UV light. c. Exposed to 0.5 M NaCl spray at 35°C. d. Exposed to condensation at 45°C, UV light, and 34.5 MPa loading.

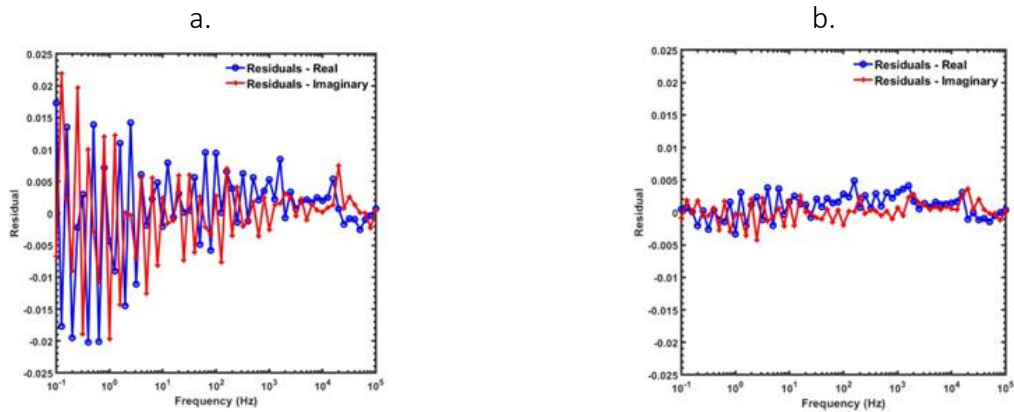


Figure 19: Real and imaginary residuals from the Kramers-Kronig analysis of the EIS data for the coated coupon in 0.01 M NaCl at $T = 60^\circ\text{C}$ at a. $t = 0$ hours and b. $t = 3192$ hours.

The analysis of the impedance data for all coating systems under all exposure conditions formed the basis for the training dataset that was used by the ML methods.

Calculations

As discussed by Walter[61] and Schwake and colleagues[62], graphical analysis of the EIS data can be used to obtain estimates of the equivalent circuit element parameter values. However, the predominant method for obtaining these values is to use a nonlinear regression algorithm to fit the equivalent circuit response to the measured EIS response of the system. For the analysis in this paper, a Levenberg-Marquardt algorithm was implemented.

Derivation of the Nonlinear Regression Algorithm

Equations (4) to (7), which were used to calculate the impedance of an equivalent circuit, can be nonlinear in their parameters. The general approach for obtaining estimates of the parameters that provide the best fit is to directly minimize the objective function. In our case, the objective function was defined to be the difference between the measured impedance, Z^D , of the coating system and the equivalent circuit impedance, Z^M , at each of the N measurement frequencies, ω_i . The equivalent circuit impedance was also a function of the k total resistor and capacitor parameter values, θ_j .

$$\epsilon_i = Z^D(\omega_i) - Z^M(\omega_i, \theta_j) \quad (8)$$

The error sum of squares that needed to be minimized is given by (9),

$$S(\theta) = \sum_{i=0}^{N-1} (\epsilon_i)^2 \quad (9)$$

In a Gauss-Newton approach[63], the Taylor series of Z^M is taken through the linear terms:

$$\langle Z^M(\omega_i, \theta_j + p_{GN}) \rangle = Z^M(\omega_i, \theta_j) + \sum_{j=1}^k \left(\frac{\partial Z_i^M}{\partial \theta_j} \right) (p_{GN})_j \quad (10)$$

The correction vector, p_{GN} , can then be obtained by solving (11),

$$(J^T J) p_{GN} = J^T (Z^D - Z^M) \quad (11)$$

where the Jacobian matrix, J , is given by (12),

$$J = \left(\frac{\partial Z_i^M}{\partial \theta_j} \right), i = 0, 1, \dots, N-1; j = 1, 2, \dots, k \quad (12)$$

And, the new parameter estimates are obtained from (13), with the k initial parameter estimates designated as, $\phi_{0,k}$,

$$\theta_{i+1,k} = \theta_{i,k} + p_{GN} \quad (13)$$

In the gradient-descent method[64], the correction vector, p_g , is determined by (14),

$$p_{g,k} = - \left(\frac{\partial S}{\partial \theta_1}, \frac{\partial S}{\partial \theta_2}, \dots, \frac{\partial S}{\partial \theta_k} \right)^T \quad (14)$$

The modified Levenberg-Marquardt[65,66] algorithm represents a compromise between the gradient-descent and Gauss-Newton methods for fitting a nonlinear model to the data. In this approach, the correction vector, p_{LM} , is obtained from (15),

$$(J^T J + \lambda D)p_{LM} = J^T(Z^D - Z^M) \quad (15)$$

where D represents the diagonal of the $J^T J$ matrix and λ is a Lagrange multiplier that serves as a damping factor.

Two values of λ : λ_1 and λ_2 , are used in each iteration of the algorithm. λ_1 was set equal to the current value of λ and an estimate of the fit parameters, $\theta_{i,k}$, was calculated. λ_2 was obtained by reducing λ by a specified factor. In our algorithm, λ was reduced by a factor of 2, and a new estimate of the fit parameters, $\theta_{i+1,k}$, was obtained. $S(\theta_i)$ and $S(\theta_{i+1})$ were calculated for the two sets of fit parameters. The set of θ values that reduced the error the most was accepted and that value of λ was kept for the next iteration.

If neither set of fit parameters fulfilled $S(\theta_{i+1,k}) < S(\theta_{i,k})$, then λ was increased by a factor of 3 and the iteration tried again. The value of λ acted to shift the algorithm behavior between the gradient descent approach and the Gauss-Newton method. When the value of λ was large, the algorithm approached the gradient descent method and when the value was small, the algorithm approached the Gauss-Newton method.

Formation of ML Training and Testing Sets

Despite the effectiveness of the Levenberg-Marquardt algorithm in fitting nonlinear models to data, the initial parameter estimates, $\theta_{0,k}$, that start the iteration sequence given in (13), play a significant role in how many iterations the algorithm will take to converge, or even if convergence is possible. Selecting initial estimates that maximize the chance for convergence and minimize the number of iterations of the regression algorithm are the objectives of the machine-learning methods.

The training set was created by coding the modified Levenberg-Marquardt nonlinear regression algorithm in C# and fitting the equivalent circuit model from Figure 17 to all EIS data. The number of iterations to reach convergence that the algorithm used, or if it failed to converge, was included in the output. Following Marquardt(Marquardt, 1963), convergence was reached if both (16) and (17) were true.

$$S(\theta_{i+1,k}) \leq S(\theta_{i,k}) \quad (16)$$

$$\frac{|p_{LM,k}|}{|\theta_{i,k}| + \tau} \leq \delta \quad (17)$$

where $\tau = 1.0 \times 10^{-3}$ and $\delta = 1.0 \times 10^{-8}$.

The two states for failed convergence were: State 1 – the algorithm reached the maximum iteration count without meeting the conditions in (16) and (17) or State 2 – The Lagrange multiplier parameter, λ , exceeded $\lambda_{\max}$. If the algorithm reached either state, the number of regression

iterations was set equal to the maximum iteration count and the convergence parameter was set to false.

It was found that convergence occurred more frequently if the ohmic resistance of the solution, parameter R_1 , in Figure 17, was set at a constant value. Thus, it was not included in the θ vector in the regression algorithm. To create the initial parameter estimates for R_2 , R_3 , C_1 , and C_2 , the following procedure was employed.

For each of the N oscillation frequencies:

- Starting from the high frequencies and working toward the low frequencies, $R_{2,0}$, was set equal to the real portion of the impedance at frequency, f_{high}
- $C_{1,0}$ was set equal to $\frac{1}{2\pi f_{high}|Z_{imag}(f_{high})|}$
- Starting from the low frequencies and working toward the high frequencies, $R_{3,0}$ was set equal to the real portion of the impedance frequency, f_{low}
- $C_{2,0}$ was set equal to $\frac{1}{2\pi f_{low}|Z_{imag}(f_{low})|}$

This procedure resulted in 61 unique initial estimates of the starting parameters for each of the 740 EIS data files. The final two methods for establishing initial parameter estimates involved setting $R_{2,0}$, $R_{3,0}$, $C_{1,0}$, and $C_{2,0}$ to constants that were unrelated to the measured impedance values.

These initial parameter estimates were then used to calculate the equivalent circuit impedance for each of the data sets for each test coupon. The nonlinear regression fits and data were imported into a relational database using a relational database management system (MariaDB, MariaDB Foundation). The database was accessed using a custom web application developed with Razor and Entity Framework Core (Microsoft Corporation). Six different data sets, corresponding to the different sets of exposure conditions, and one combined data set were extracted from the database to form the basis of the training and testing sets. An example of one of the rows from an extracted data set is provided in Table 1.

Table 1: Example entry from the Q data set including the column headers.

Run	$R_{1,0}(\Omega)$	$R_{2,0}(G\Omega)$	$C_{1,0}(nF)$	$R_{3,0}(\Omega)$	$C_{2,0}(nF)$	Iterations	Converged?
0	76.86	0.23	2.0	76.86	0.71	25429	TRUE

The characteristics of the different data sets are defined in Table 2.

Table 2: Characteristics of the data sets used to form the training and testing sets.

Data identifier	set	Characteristics
F		Fits to EIS measurements from all test coupons alternated weekly between ASTM B117 test salt spray conditions and placement in a freezer at -5°C
Q		Fits to EIS measurements from all test coupons exposed to 12 hours of UV light at an intensity of 1.46 W/ m ² , followed by 9 hours of condensation at 45°C, then 3 hours of darkness.

U	Fits to EIS measurements from all test coupons exposed to ASTM B117 test salt spray conditions.
S	Fits to EIS measurements from all test coupons exposed to 12 hours of UV light at an intensity of 1.46 W/ m ² , followed by 9 hours of condensation at 45°C, then 3 hours of darkness. All test coupons were statically loaded with different stress states.
I	Fits to EIS measurements from all test coupons immersed in NaCl solutions with varied concentrations and at different temperatures.
C0.8	Random selection from the combined data sets to form a new data set with 80% of the total number of fits. Data set only used for training.
C0.2	Random selection from the combined data sets to form a new data set with 20% of the total number of fits. Data set only used for testing.

Training and Testing the ML Models

To form training sets for predicting algorithm convergence, the equivalent circuit impedance, Z_{mod} , was obtained using (4) for each set of initial parameter estimates. The l²-norm, v , between the equivalent circuit, Z^M , and the measured Z^D was obtained using (18),

$$\|v\| = \sqrt{\sum_{i=1}^N (Z_i^D - Z_i^M)^2} \quad (18)$$

The run parameter, the l²-norm, and the number of regression iterations performed were the three features that were used to predict the convergence outcome column. Because of the significant difference in the scales of the features, each feature was standardized using (19),

$$X' = \frac{X - \mu}{\sigma} \quad (19)$$

where X' is the standardized feature value, X is the original value, μ is the mean of the feature values, and σ is the standard deviation. The relationships between the normalized features and label for the C0.8 training set are shown in Figure 20. From Figure 20, for initial parameter estimates that resulted in high l²-norm values, the nonlinear regression algorithm generally failed to converge.

Within the ML.Net[67] framework, the machine learning algorithms are called binary classification trainers. Several of these, including logistic regression, support vector machines, and gradient boosted algorithms, were trained to determine which one resulted in the best predictions.

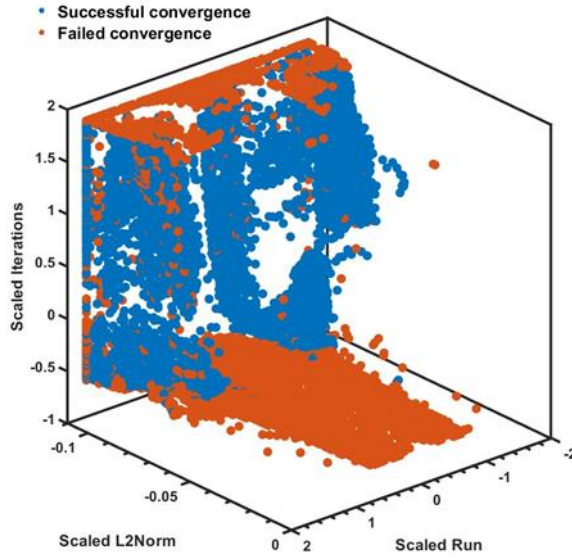


Figure 20: Successful and unsuccessful convergence as functions of the scaled features for the C0.8 training set. Initial estimates that established large l2- norm values generally failed to converge.

The best trainer, *i.e.*, the trainer with the highest accuracy, was a variant of a gradient boosting decision tree trainer, called LightGBM[68]. The accuracy estimates for algorithm convergence for various testing sets from using different training sets are given in Table 3.

Table 3: Accuracy of testing predictions for a given training set.

Training Set	Testing Set					
	F	Q	U	S	I	C0.2
F	1.00	0.93	0.93	0.92	0.94	-
Q	0.97	0.99	0.95	0.93	0.93	-
U	0.96	0.93	0.99	0.93	0.92	-
S	0.96	0.93	0.94	0.99	0.95	-
I	0.97	0.91	0.92	0.92	0.98	-
C0.8	0.97	0.95	0.96	0.96	0.95	0.97

The advantage of using the LightGBM trainer, besides its increased accuracy, was its included probability estimate of its predictions as part of its prediction engine output. These estimates of the probabilities were then used to evaluate the convergence predictions when selecting the initial parameter estimates. As expected, the combined training set, labeled C0.8, provided the highest accuracy of predictions for the testing sets, indicated by the accuracies in the last row in Table 3; though the Q training set also performed surprisingly well.

The rows in the C0.8 training set that corresponded to successful convergence of the nonlinear regression algorithm were then used to train the models to predict the iterations to convergence. For these models, only the standardized run parameters and the l^2 -norm values were used as the features to predict the number of iterations to convergence.

Several regression trainers were evaluated, including a gradient boosting decision tree trainer for regression, a stochastic dual coordinate descent trainer, a gradient descent trainer, and a random forest decision tree trainer. The random forest decision tree trainer, called FastTree – Tweedie Regression, provided the most accurate predictions. For this algorithm, the boosting in the FastTree method used a Tweedie Compound Poisson distribution[69]. The distribution of convergence iterations, shown in Figure 21, displayed characteristics of an exponential dispersion distribution[70], which likely contributed to the success of this algorithm.

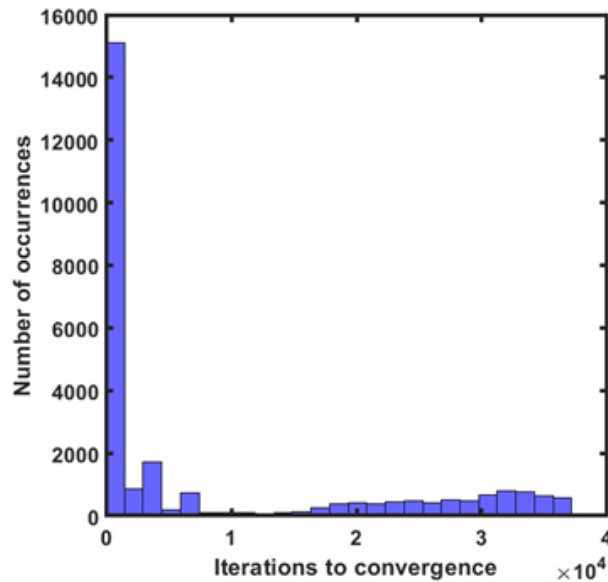


Figure 21: Distribution of iterations needed for convergence for the nonlinear regression algorithm. The large number of occurrences on the extreme low-end of the distribution and the long tail to the high end are characteristic of the Tweedie Compound Poisson distributions.

However, even though the FastTree – Tweedie Regression trainer was the most successful, the R^2 value for its predictions, with the number of “trees” formed set equal to 1000, was only 0.716. The relatively low accuracy of the predictions is likely due to the highly nonlinear dependence of the convergence iterations on the run and l^2 -norm values that may be alleviated by increasing the size of the training set with additional data.

The code from both ML models was incorporated into the original nonlinear regression application. The first ML model was employed to determine the initial parameter sets that offered the highest probabilities of convergence. These initial parameter sets were passed to the second ML model, which predicted the number of iterations necessary for the nonlinear regression algorithm to converge. This iterations-to-convergence value and predicted best-performing initial parameter set were then submitted to the modified Levenberg-Marquardt algorithm to fit the EIS data.

Discussion

The 740 individual EIS measurements were submitted both to the original nonlinear regression algorithm and to the algorithm employing the two ML models. The datasets were fit on a desktop computer with 64 GB of RAM and an AMD Ryzen 7 3700X CPU. While the 8-core CPU could support up to 16 threads, the ML models were not thread-safe. Thus, all code executed on individual cores. A comparison of the execution times showed that, by using the ML models, the nonlinear regression algorithm could run through 372 the datasets in 87 s, while without the ML models, the process required 4657s. Thus, using the ML models offered ~53x improvement in execution time.

However, there was a loss of accuracy with the algorithm using the ML models. The models' predicted iteration count and initial parameter set often failed to meet the convergence criteria for the algorithm – and did so more frequently than the original algorithm. A comparison of an example convergence-failure fit with a successfully converged fit, shown in Figure 22 suggests that even though the first fit did not meet the convergence criteria, it still provided a reasonable estimate of the equivalent circuit parameters.

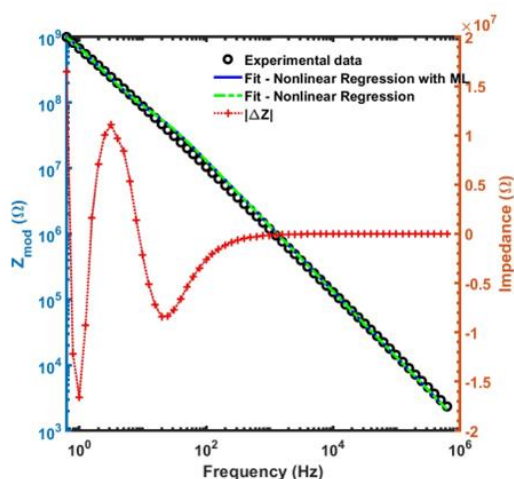


Figure 22: Z_{mod} vs. frequency data overlaid with equivalent circuit models on the left axis. One fit algorithm used the ML models to provide the initial estimate, and the other fit algorithm did not. The difference between the two fits as a function of frequency is shown on the right axis.

The largest difference between the model impedance that did converge and the one that did not, plotted on the right axis in Figure 22, was roughly 1.7%.

Conclusions

EIS data was obtained from measurements of an aircraft coating system that had been applied to aluminum alloy test coupons and exposed to a variety of laboratory conditions that were designed to simulate atmospheric exposures. The impedance of the coating systems was measured weekly over the course of 3000-plus hours. The impedance data was then fit using a modified Levenberg-Marquardt nonlinear regression algorithm. Each fit resulted in four parameters that corresponded to circuit element values in the coatings equivalent circuit.

63 sets of initial values were created for each of the electrochemical impedance spectroscopy datasets and then the fit was attempted for each set of initial values. The outcome of the fit attempt and the number of iterations in the attempt were recorded and used to create the datasets to be used

with the supervised ML models. Using the ML.Net toolkit, several ML algorithms were trained on the C0.8 dataset. The two best-performing ML models, in a non-linear regression sense, were implemented to provide initial estimates to the fitting algorithm.

The nonlinear regression algorithm with ML models was quantitatively faster at fitting the equivalent circuit model to the EIS data. However, there was a loss of accuracy, as this algorithm often did not converge within the model's predicted number of iterations. However, comparisons between a converged fit using the base algorithm and a fit that had not converged with the ML models' algorithm indicated that the difference between the two fits was below 2%. These results suggest that, provided a large enough training dataset is available, ML models can be used to obtain estimates for initial values for nonlinear models. This can be especially helpful for more complex equivalent circuit models for which initial parameter estimates cannot be easily obtained from straightforward calculations using data points

5. RELATING CHANGES IN ELECTROCHEMICAL PROPERTIES TO BARRIER PROPERTY CHANGES OF AN ORGANIC COATING SYSTEM

Experimental results

EIS data

Two iterations of the laboratory exposures, which varied in duration, were performed. During the first iteration, EIS measurements were made on the test panels approximately every 168 hours over the course of 2184 hours. Representative examples of the data from each of the test conditions are shown in the following plots. Figure 23 shows EIS data obtained from an unstressed coating system exposed to a neutral salt spray over the course of 2184 hours.

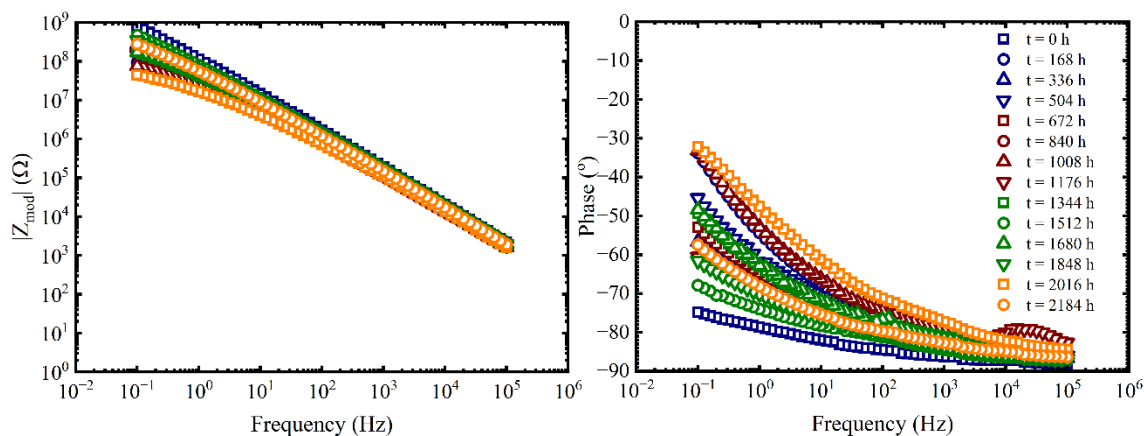
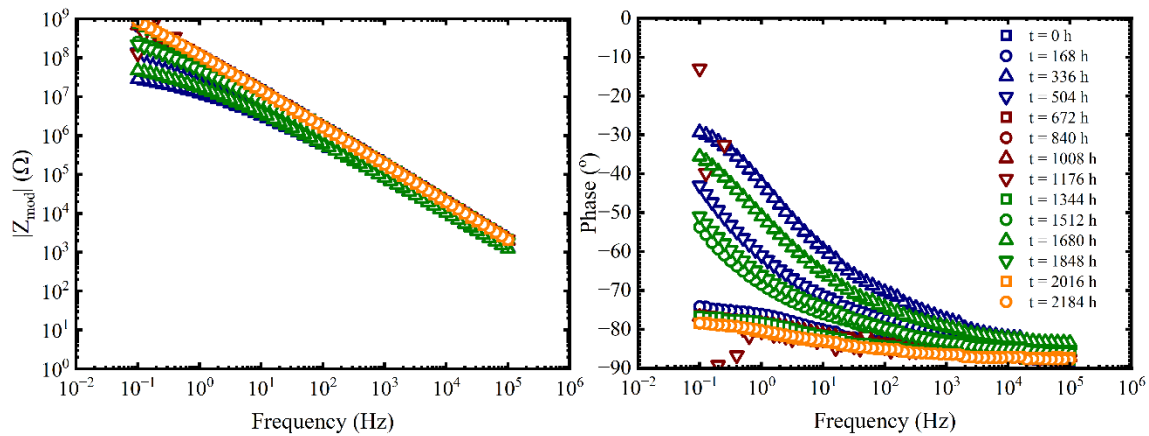


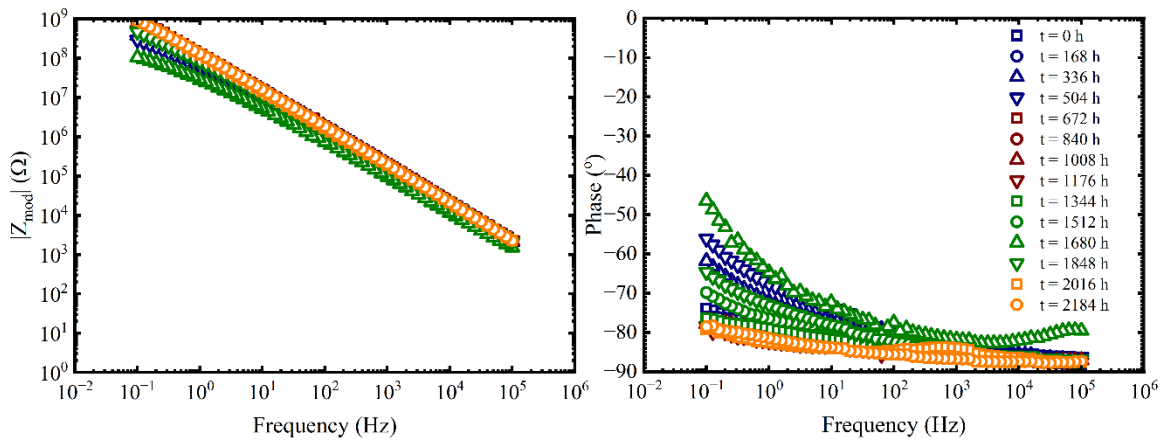
Figure 23. Bode representation of the EIS data, Z_{mod} on the left and phase on the right, obtained from an unstressed coating system aged in ASTM B117 salt spray for 2184 h.

Figure 24 shows EIS data obtained from both stressed and unstressed coating systems exposed to a repeating 24-hour cycle that consisted of: heat + darkness, condensation from a deionized fog, and ultraviolet light aging, that repeated for 2184 hours.

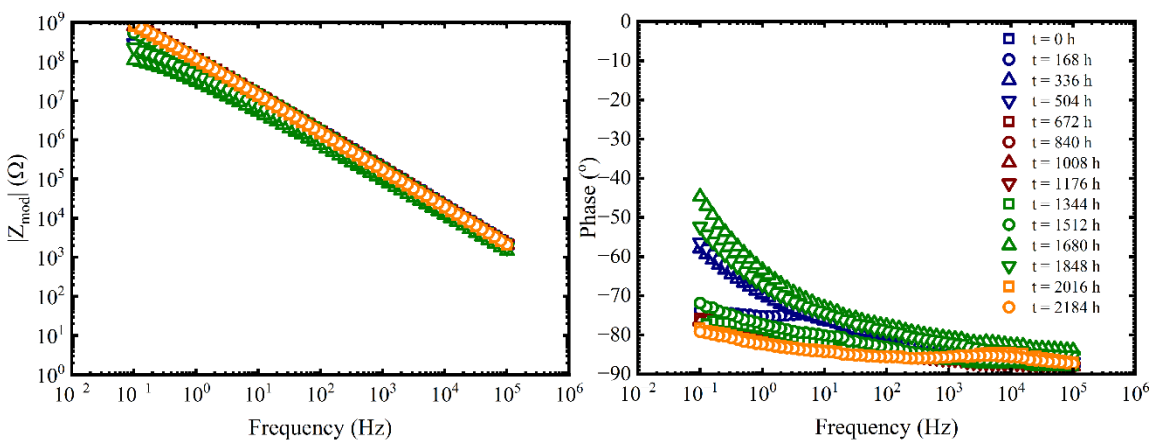
a.



b.



c.



d.

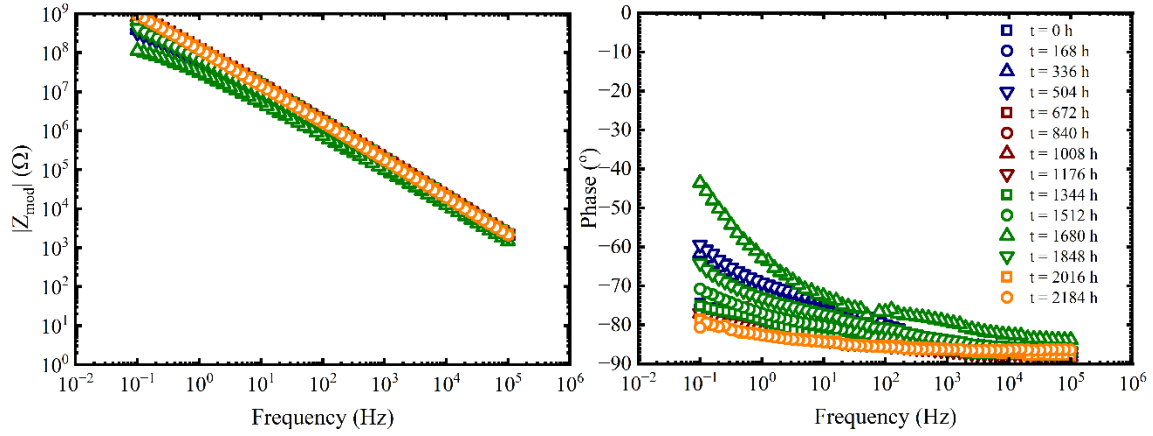


Figure 24. Bode representation of the EIS data, Z_{mod} on the left and phase on the right, obtained from coating systems aged in a QUV spray system under the following repeated conditions: heated at 45°C for 3 hours in darkness, condensation from a deionized water mist for 9 hours at 45°C, followed by 12 hours of UV irradiance at an intensity of 1.46 W/m² a. unstressed coating system, b. coating system stressed at 34.5 MPa, c. coating system stressed at 69 MPa, and d. coating system strained at 2%.

For the second iteration of laboratory aging, the panels were exposed to the same conditions, but the duration was on the order of 6840 hours, with EIS measurements performed at the beginning, approximately midway through the exposure period, and at the end. Figure 25 shows EIS data obtained from an unstressed coating system exposed to a neutral salt spray solution. Figure 26 shows EIS data obtained from both stressed and unstressed coating systems exposed to a repeating 24-hour cycle of heat and darkness, condensation from a deionized fog, and ultraviolet light aging.

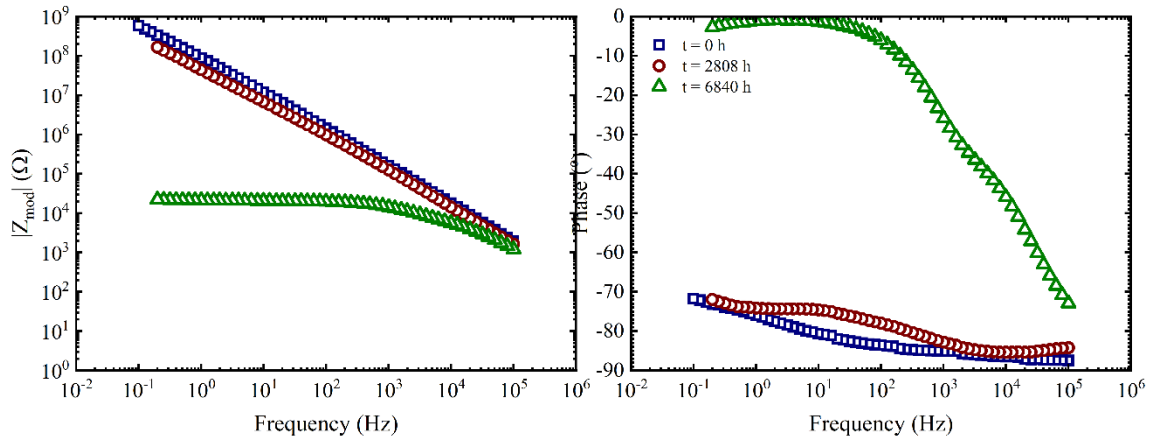
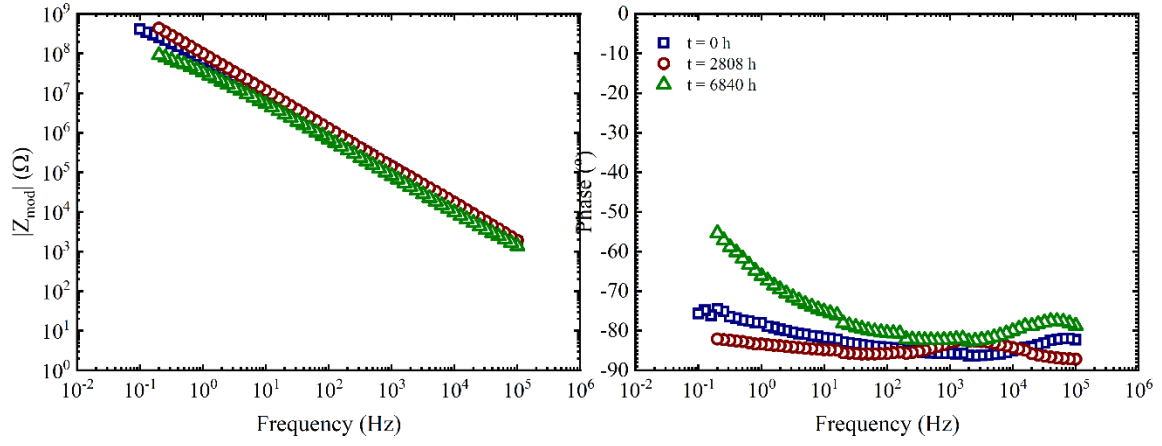
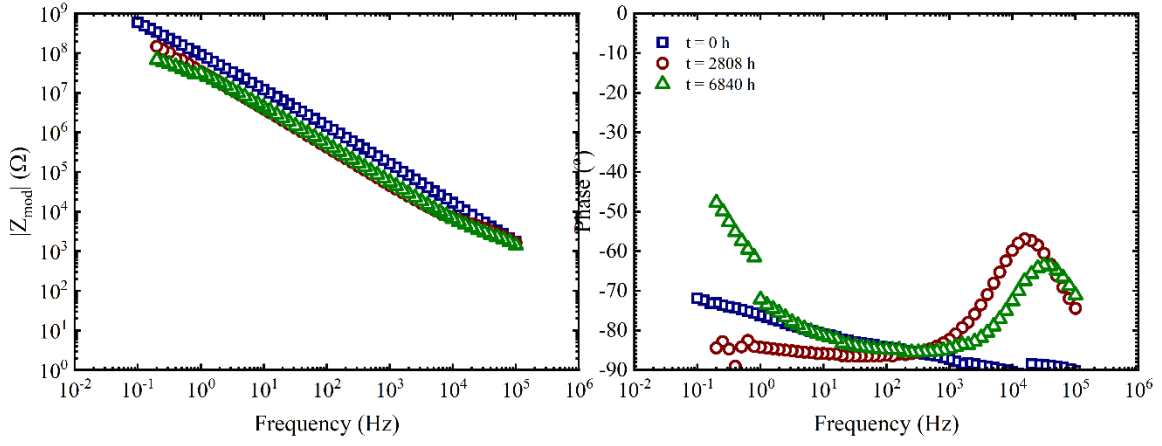


Figure 25. Bode representation of the EIS data, Z_{mod} on the left and phase on the right, obtained from an unstressed coating system aged in ASTM B117 salt spray for 6840 h.

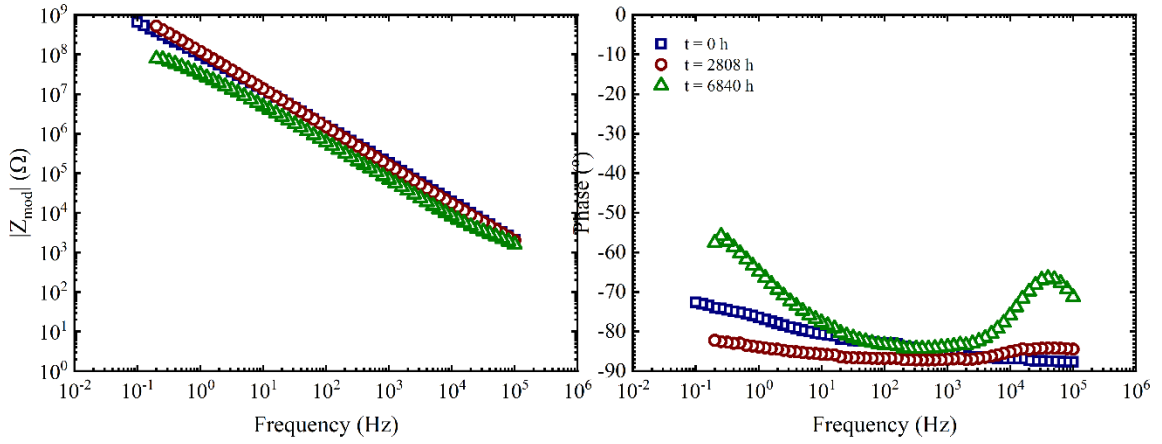
a.



b.



c.



d.

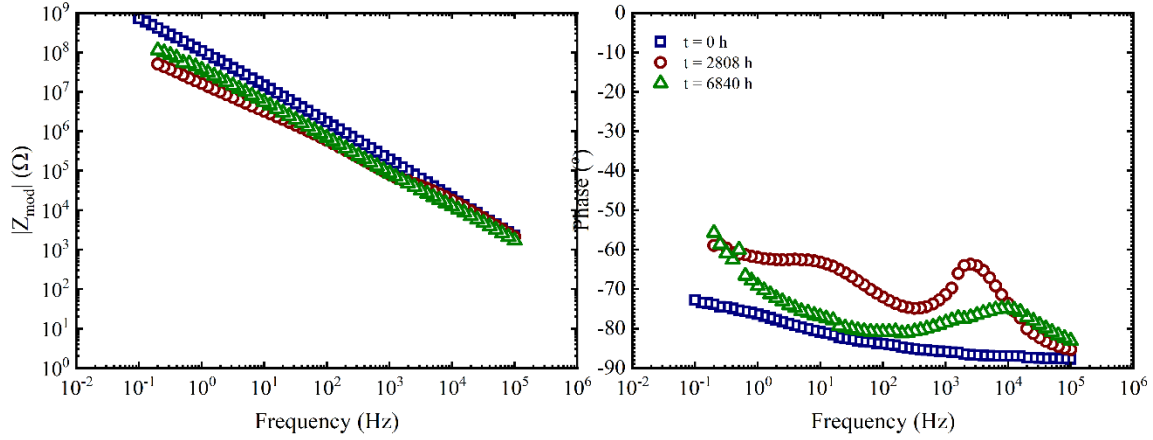


Figure 26. Bode representation of the EIS data, Z_{mod} on the left and phase on the right, obtained from coating systems aged in a QUV spray system under the following repeated conditions: heated at 45°C for 3 hours in darkness, condensation from a deionized water mist for 9 hours at 45°C, followed by 12 hours of UV irradiance at an intensity of 1.46 W/m² a. unstressed coating system, b. coating system stressed at 34.5 MPa, c. coating system stressed at 69 MPa, and d. coating system strained at 2%.

The stationary criterion for EIS analysis was met on the coated coupons with the ± 10 mV_{RMS} perturbation. For these measurements, the linearity of the coating systems' responses to the 28-mV peak-to-peak amplitude of the potential perturbation was confirmed using the Kramers-Kronig transform utility provided with the analysis software (Echem Analyst; Gamry) for the potentiostat. A representative example of the Kramers-Kronig fit residuals is shown in Figure 27 for a panel at three different times. Five Voigt elements per decade were used to obtain each fit. The small residuals indicate that the data is linear, causal, and stable.

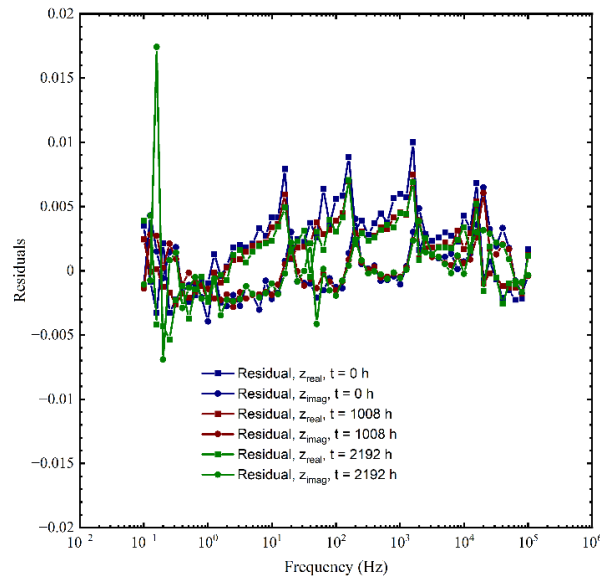


Figure 27. Kramers-Kronig transform residuals for a QUV test coupon at three different exposure times.

The EIS data were plotted on Bode diagrams, with the logarithm of the impedance modulus, $|Z_{mod}|$, and phase angle as functions of the logarithm of the frequency. Analysis was performed by fitting the data with the equivalent circuit models shown in Figure 28 using the analytical software suite (Echem Analyst, Gamry) provided by the potentiostat manufacturer.

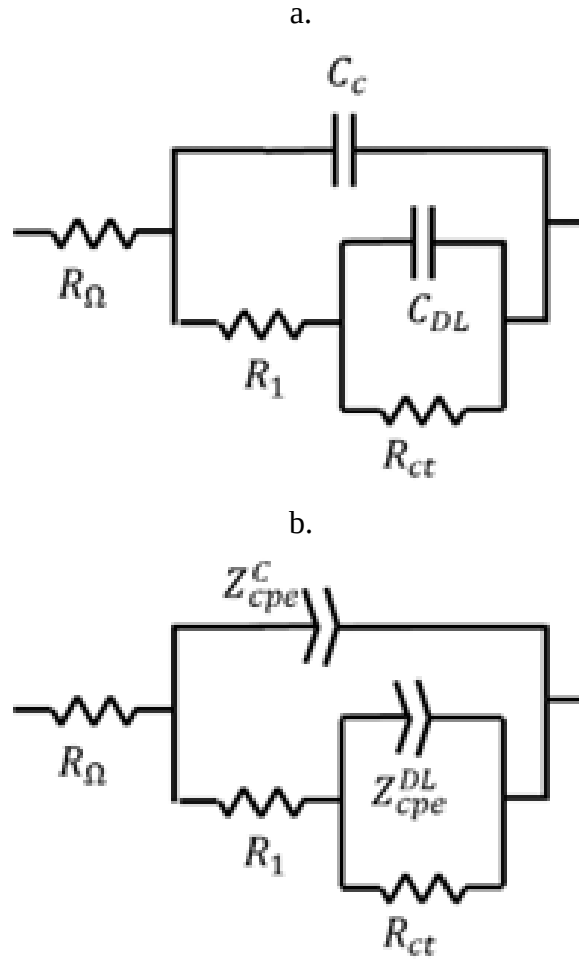


Figure 28. a. Simplified Randles circuit as nested coating defect model(Beaunier et al., 1976; Hack & Scully, 1991). b. Modified REAP model(Duval et al., 2000).

Fit values for the equivalent circuit elements from Figure 28a are provided in Table 4. These values were obtained from the first iteration of laboratory aging of the coating systems. The time intervals selected for analysis corresponded to the intervals for which color change data was available.

Table 4. Fit parameters for the EIS data obtained in the first iteration of laboratory aging.

Conditions	Time (hr)	$R_u (\Omega)$	$R_{ct}(\Omega)$	$C_{DL} (F)$	$R_1 (\Omega)$	$C_c(F)$
UV aging with heat and condensation	0	150.4957	5.67×10^7	8.01×10^{-10}	1.98×10^9	6.28×10^{-10}
	1176	318.528	2.00×10^9	1.02×10^{-9}	1.17×10^8	5.88×10^{-9}
	2184	174.2137	5.46×10^7	8.18×10^{-10}	2.98×10^9	5.07×10^{-10}
	0	2.80×10^4	3.26×10^7	8.41×10^{-10}	2.06×10^9	7.55×10^{-10}
	1176	144.886	2.43×10^7	8.30×10^{-10}	3.08×10^9	5.33×10^{-10}
	2184	73.3005	2.82×10^9	1.13×10^{-9}	9.75×10^9	5.23×10^{-10}
	0	1.65×10^2	2.04×10^7	8.48×10^{-10}	1.95×10^9	7.64×10^{-10}
	1176	1.45×10^2	4.87×10^7	8.10×10^{-10}	3.32×10^9	4.90×10^{-10}
	2184	2.37×10^2	3.45×10^7	9.10×10^{-10}	3.67×10^9	4.94×10^{-10}
Salt spray	0	1.40×10^2	5.06×10^7	8.74×10^{-10}	2.26×10^9	7.10×10^{-10}
	1176	5.29×10^2	6.84×10^6	1.44×10^{-9}	2.16×10^8	3.04×10^{-9}
	2184	1.40×10^4	1.23×10^7	1.14×10^{-9}	3.37×10^8	2.05×10^{-9}
	0	1.60×10^2	3.60×10^7	8.81×10^{-10}	2.30×10^9	6.88×10^{-10}
	1176	1.88×10^3	1.42×10^7	1.04×10^{-9}	4.24×10^8	1.83×10^{-9}
	2184	6.91×10^2	9.12×10^6	1.19×10^{-9}	2.64×10^8	2.33×10^{-9}
	0	1.39×10^2	4.78×10^7	8.78×10^{-10}	2.24×10^9	7.02×10^{-10}
	1176	4.57×10^4	9.17×10^6	1.09×10^{-9}	3.80×10^8	1.96×10^{-9}
	2184	2.98×10^2	7.37×10^6	1.29×10^{-9}	2.42×10^8	2.50×10^{-9}
	0	1.38×10^2	4.60×10^7	9.12×10^{-10}	2.21×10^9	7.24×10^{-10}
	1176	2.34×10^2	1.27×10^6	1.05×10^{-9}	2.26×10^8	1.56×10^{-9}
	2184	2.66×10^3	1.09×10^7	1.21×10^{-9}	2.87×10^8	2.30×10^{-9}
	0	1.87×10^2	3.18×10^7	9.71×10^{-10}	1.76×10^9	8.27×10^{-10}
	1176	6.66×10^3	1.28×10^7	1.09×10^{-9}	5.42×10^8	1.76×10^{-9}
	2184	2.23×10^2	1.18×10^7	1.26×10^{-9}	3.25×10^8	2.16×10^{-9}
	0	1.28×10^2	3.62×10^7	1.08×10^{-9}	1.34×10^9	9.89×10^{-10}
	1176	1.79×10^2	9.56×10^6	1.24×10^{-9}	4.57×10^8	1.94×10^{-9}
	2184	1.33×10^1	7.86×10^6	1.50×10^{-9}	2.29×10^8	2.75×10^{-9}

Destructive sampling

The EIS data from Figure 24d was obtained from the panel shown in Figure 29. This coating system was also one of the panels that was destructively sampled in the region indicated by the dotted line and imaged in the SEM. In several of the strained panels, small pits were observed below cracked regions of the surface pretreatment. This suggests that deionized water condensed from the fog in the UV exposure chamber and diffused through the coating system to reach the pretreated surface. Once the oxide cracked, water that had permeated the coating system was able to reach the unprotected aluminum alloy surface and cause a small amount of corrosion. We did not find these small pits on the unstressed and lower stressed panels.

We also note that we did not observe a pitting corrosion signature in the EIS data from these strained coating systems. This is likely because the barrier properties of the coating system are still sufficiently protective that the corrosion signature was masked by the high resistivities of the coating layers. This is important because it indicates that corrosion can occur beneath, apparently intact, coating systems that have undergone plastic deformation that has cracked the protective oxide layer. Organic polymers are known to allow water ingress from environmental exposure while still maintaining their barrier properties as obtained from EIS measurements.



Figure 29. a. Test panel following 2184 hours of UV and condensation exposure with sampling region highlighted. b. SEM image of a corrosion pit found below a crack in the surface pretreatment on a 2% strained coating system.

Color change

The change in color as a result of the laboratory aging was determined using the change in the CIELAB color space calculation, given in (20),

$$\Delta E^* = \sqrt{(L_0^* - L_1^*)^2 + (a_0^* - a_1^*)^2 + (b_0^* - b_1^*)^2} \quad (20)$$

where ΔE^* is the ASTM D2244-21 color difference, L_i^* is the distance along the lightness axis, a_i^* is the distance along the green-red axis, and b_i^* is the distance along the blue-yellow axis. The average values are provided in Table 5.

Table 5. Color change values

Exposure conditions		CIELAB values			
	Time (h)	L_i^*	a_i^*	b_i^*	ΔE^*
All	0	67.95	-2.22	-3.59	-
Unstressed, UV and condensation	1176	67.19	-2.24	-3.50	0.760
	2184	67.07	-2.26	-3.52	0.877
Stressed, UV and condensation	1176	67.19	-2.23	-3.42	0.774
	2184	67.06	-2.25	-3.42	0.897
Salt spray	1176	67.73	-2.22	-3.63	0.223
	2184	67.60	-2.22	-3.64	0.350

Equivalent circuit fits and analysis

Kosik and collaborators (Kosik, 2003) analyzed EIS data from several coating systems placed at two outdoor exposure sites, in Arizona and Florida, for 97 weeks. One of their coating systems, designated as coating system C, a MIL-PRF-23377, Type II, Class C primer overcoated with a MIL-PRF-85285, Type I topcoat, corresponded most closely to the coating system we evaluated. They developed two response surface models that accepted equivalent circuit element parameter values as input and estimated the CIELAB color change value as an output. Their two models are given in (21) and (22), respectively. Equation (21) corresponds to their Arizona model.

$$\Delta E^* = \alpha_0 + \alpha_1 R_1 + \alpha_2 C_c \quad (21)$$

where α_0 is a constant, α_1 accounts for the increase in the dielectric constant from UV-induced bond breakage in the outer-most 25 μm of the topcoat, and α_2 accounts for the increasing density of the coating system as it continued to cure from thermal energy in the environment.

Equation (22) corresponds to their Florida model.

$$\Delta E^* = \alpha_0 + \alpha_1 R_1 + \alpha_2 C_c + \alpha_3 C_c \quad (22)$$

where α_0 is a constant, α_1 accounts for the increase in the dielectric constant from UV-induced bond breakage in the outer-most 25 μm of the topcoat, α_2 accounts for the increasing density of the coating system as it continued to cure from thermal energy in the environment, and α_3 accounts for the increasing dielectric constant due to water uptake.

The estimated color changes using the Florida and Arizona models and the average equivalent circuit element values from Table 4 and the comparison with the measured values are shown in Table 6.

Table 6. Comparison of measured and predicted ΔE^* values

Conditions	$\Delta E^*_{measured}$	$\Delta E^*_{Arizona}$	$\Delta E^*_{Florida}$
Unstressed, UV and condensation	0.00	0.00	0.00
	0.76	2.77	4.23
	0.88	3.24	0.85
Stressed, UV and condensation	0.00	0.00	0.00
	0.77	3.50	0.97
	0.90	7.65	2.83
Salt spray	0.00	0.00	0.00
	0.22	0.97	0.83
	0.35	1.04	1.09

The Florida model provided better predictions of the color change because it included a term capturing the change in the capacitance due to water uptake, which was present in both laboratory aging processes. As expected from the desert environment, water uptake was substantially less for the coating systems exposed at the Arizona site. Thus, the response surface model from that site did not include any influence from water uptake.

EIS data obtained from the second iteration of laboratory aging of the coating system were fit with equivalent circuit model from Figure 28b. This model was better able to capture the non-ideal capacitance behavior of the coating system because the capacitors were replaced with constant phase elements. Representative values of the fit for the data from Figure 25 are shown in Table 7.

Table 7. Equivalent circuit fit values for a coating system exposed to ASTM B117 salt spray.

Time (h)	$R_u(\Omega)$	$R_P(G\Omega)$	$R_{po}(M\Omega)$	$Y_{0,DL}(nS s^n)$	n	$Y_{0,c}(nS s^m)$	m
0	4	3.04	169.65	0.69	0.552	1.86	0.930
2808	4	2.61	0.00	1.14	0.980	4.05	0.728
6840	4	0.00	0.01	114.62	0.703	3.20	0.930

An examination of the exponent, m , for the constant phase element corresponding to the coating system, shows that, in general, the coating system behaves less like an ideal capacitor as the coating system ages. Plots of the change in m for the UV and condensation-aged coating systems are shown in Figure 30.

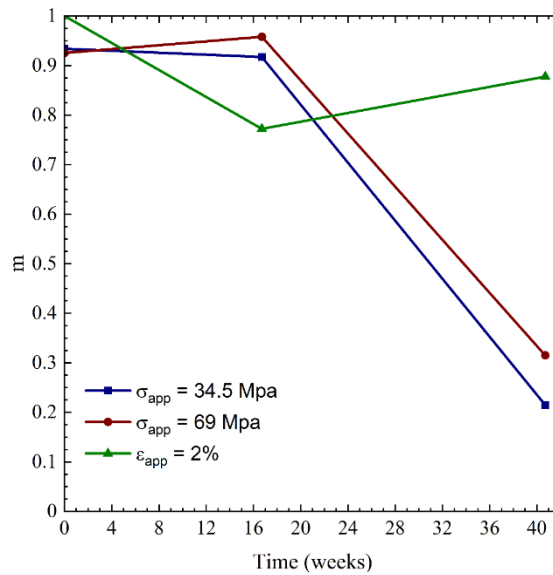


Figure 30. Change in the exponent value for the constant phase element representing the coating system in the modified REAP equivalent circuit.

This result is expected. Water uptake by the coating changes the dielectric properties of the polymer, as well as providing a conductive pathway for ions and dissolved gases in the solution. These conductive pathways through the polymer lower the capability of the coating to separate charged species, thereby reducing its capacitance. In addition, the water uptake is likely not uniform across the coating, favoring areas with less cross-linking or flaws in the coating. This non-uniformity then appears in the EIS response as a non-ideal capacitance.

Conclusions

EIS data, color changes, and some SEM imaging of destructively extracted coating system samples were obtained from a two-layer aircraft coating system that had been applied to pre-treated aluminum alloy test coupons that were then exposed to different laboratory aging processes.

The predicted topcoat color changes as a function of the EIS data were obtained using two response surface models that had been published in the literature. The results showed that the Florida-based response surface model, which included EIS changes from UV exposure, temperature effects, and water uptake, was better at predicting the measured color changes from the laboratory aging processes. The Arizona-based response surface model, which did not contain a water uptake effect, performed worse.

Destructive sampling and SEM imaging of the plastically deformed coatings showed the presence of corrosion below the oxide pretreated layer, which suggested that the strain had ruptured the oxide, though the coating remained nominally intact.

Analysis of the EIS data from the coating systems that had been aged for the longest times indicated that the laboratory aging process used in this work caused the coatings to behave less like ideal capacitors.

6. EXPERIMENTAL AND NUMERICAL INVESTIGATION INTO THE EFFECT OF WATER UPTAKE ON THE CAPACITANCE OF AN ORGANIC COATING

Introduction

To improve the analysis of EIS data obtained from aging coatings, physical models of the degradation process can provide useful initial estimates to fitting routines or provide bounds on equivalent circuit element parameter values. In equivalent circuit models, coatings are usually represented with a resistor element in parallel with a capacitive element. While the range over which capacitance can change is smaller than the range of resistivities, the change in polymer dielectric properties is sensitive to water uptake. Further, it is transport of electrolyte and associated ions or dissolved gases through the coating that ultimately leads to degradation of coating barrier properties or inhibitor exhaustion[72,73]. Thus, the focus of this work is on modeling water uptake in organic polymers found in coating systems.

The prevailing understanding for water uptake by an organic polymer is via a two-stage procedure. During the first stage, transport along defects in the coating that occur because of inhomogeneities in polymer cross-linking or other processes that resulted in damage to the coating[74,75]. And the second stage occurs via network relaxation processes plasticized by water[76].

In contrast to the proposed first stage process, Li and co-workers[77] examined water uptake in six different epoxy resins using gravimetric analysis, attenuated total reflectance FTIR (ATR-FTIR) measurements, and positron annihilation lifetime spectroscopy measurements. They found that water diffusion through the epoxy structure was only weakly correlated with the availability of void space, but the saturation concentration was strongly correlated with the availability of polar sites, such as hydroxyl groups, on the polymer chains.

Boubakri and co-authors[78] identified three regions on sorption curves for water uptake in a thermoplastic polyurethane: a Fickian region, region I, characterized by a linear relationship between the absorption ratio and the square root of the immersion time, a pseudo-Fickian region, region II, where the uptake deviated from the Fickian process and the saturation level depended on the immersion temperature, and, lastly, at high immersion temperatures, region III that had an increasing absorption ratio characterized by the formation of microcracks within the coating that eventually led to mechanical failure.

Huacuja-Sánchez and collaborators[79] also examined aging in polyurethanes using gravimetric measurements and ATR-FTIR spectroscopy. They pointed out that, in the second region of the sorption curve, the deviation from the Fickian region resulted in a lower diffusion coefficient and the diffusion coefficient was further dependent on the saturation. They also showed that absorption of water by the polymer disrupted H-H bonds between the polymer chains by forming water-polymer H-bonds.

The goal of this work is to develop numerical models of water uptake by an organic polymer coating system that incorporate physical and chemical processes that give rise to the experimentally observed two-stage kinetics of water sorption in both an epoxy primer and polyurethane topcoat. We incorporate the changing physical and chemical processes by continuously varying the diffusivity of the saturation as a function of polymer type, immersion conditions, time, and saturation. As a check on the model, we demonstrate that it accurately predicts the measured capacitance of the coating system during immersion in various NaCl solutions.

Results

EIS Data

Bode diagrams with impedance modulus, Z_{mod} , and phase angle as functions of the frequency were used to visualize the spectra. Three replicates of baseline EIS measurements were made on a pretreated test panel in 0.6 M NaCl solution. An example of the data is shown in Figure 31.

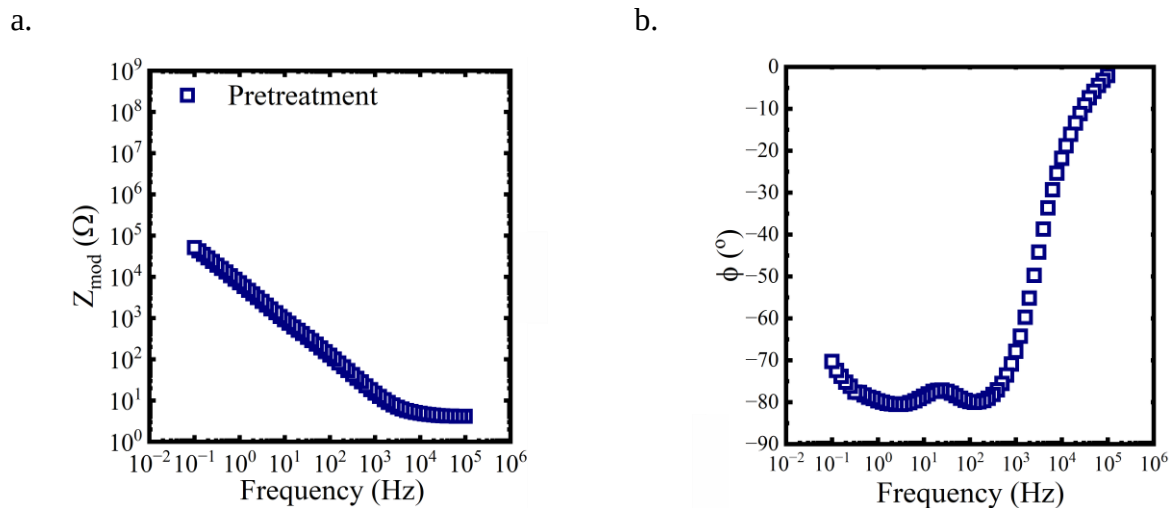


Figure 31. Bode representations of EIS data, a. magnitude and b. phase, for a pretreated panel exposed to a 0.6 M NaCl solution at 25°C.

EIS measurements were made on each panel approximately every 168 h for the first 10 weeks and then at 3192 h at the end of the aging period. While three replicate coated panels were aged in each condition, only EIS data from one of the replicates is shown in each plot in Figure 32 through Figure 34.

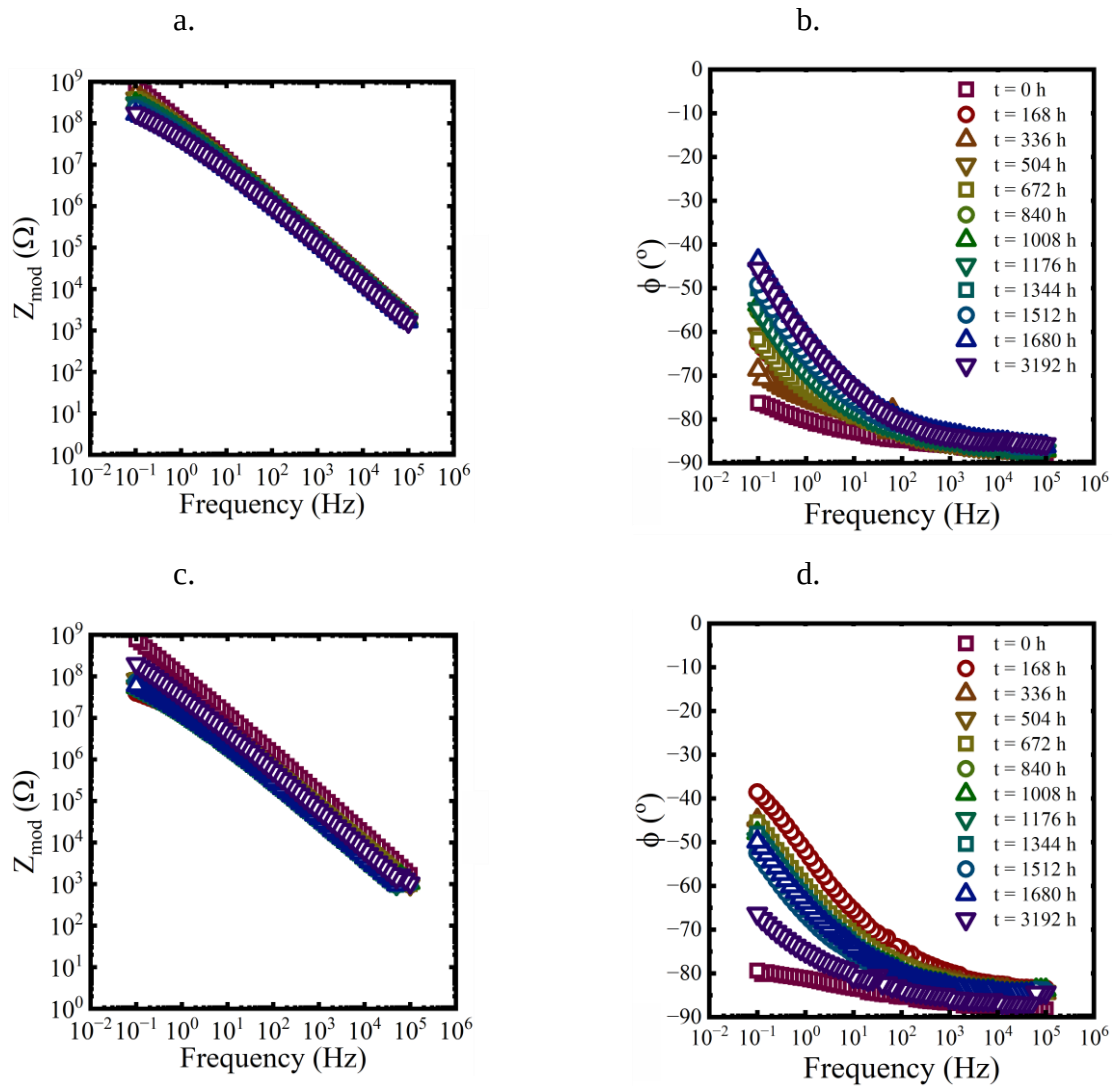


Figure 32. Bode representations of EIS data for a coated panel immersed in a saturated NaCl solution and a 0.01 M NaCl solution at 60°C for 3192 h. a, c. magnitude and b, d. phase.

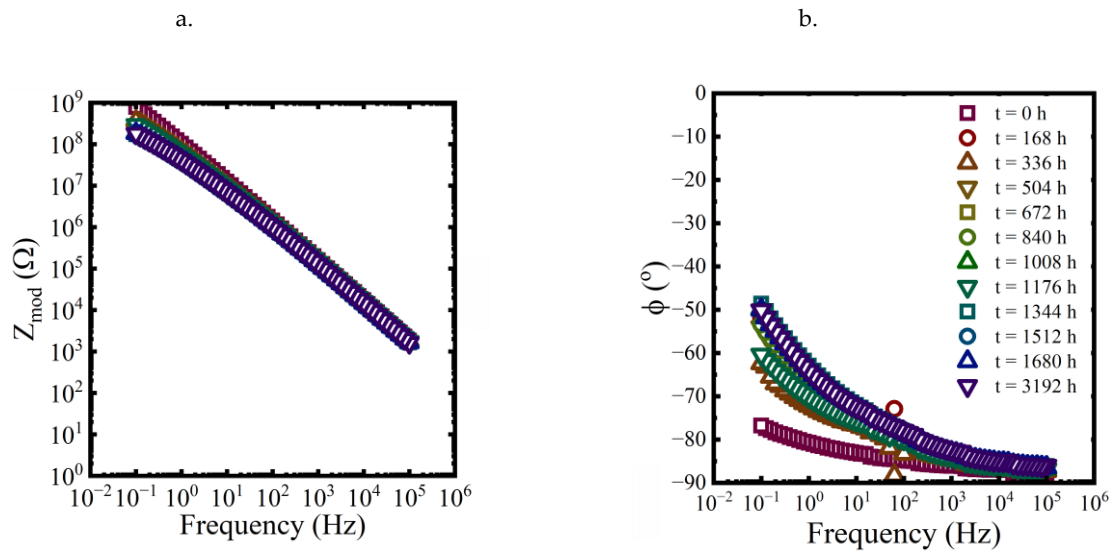


Figure 33. Bode representations of EIS data, a. magnitude and b. phase, for a coated panel immersed in a 3.2 M NaCl solution at 25°C for 3192 h.

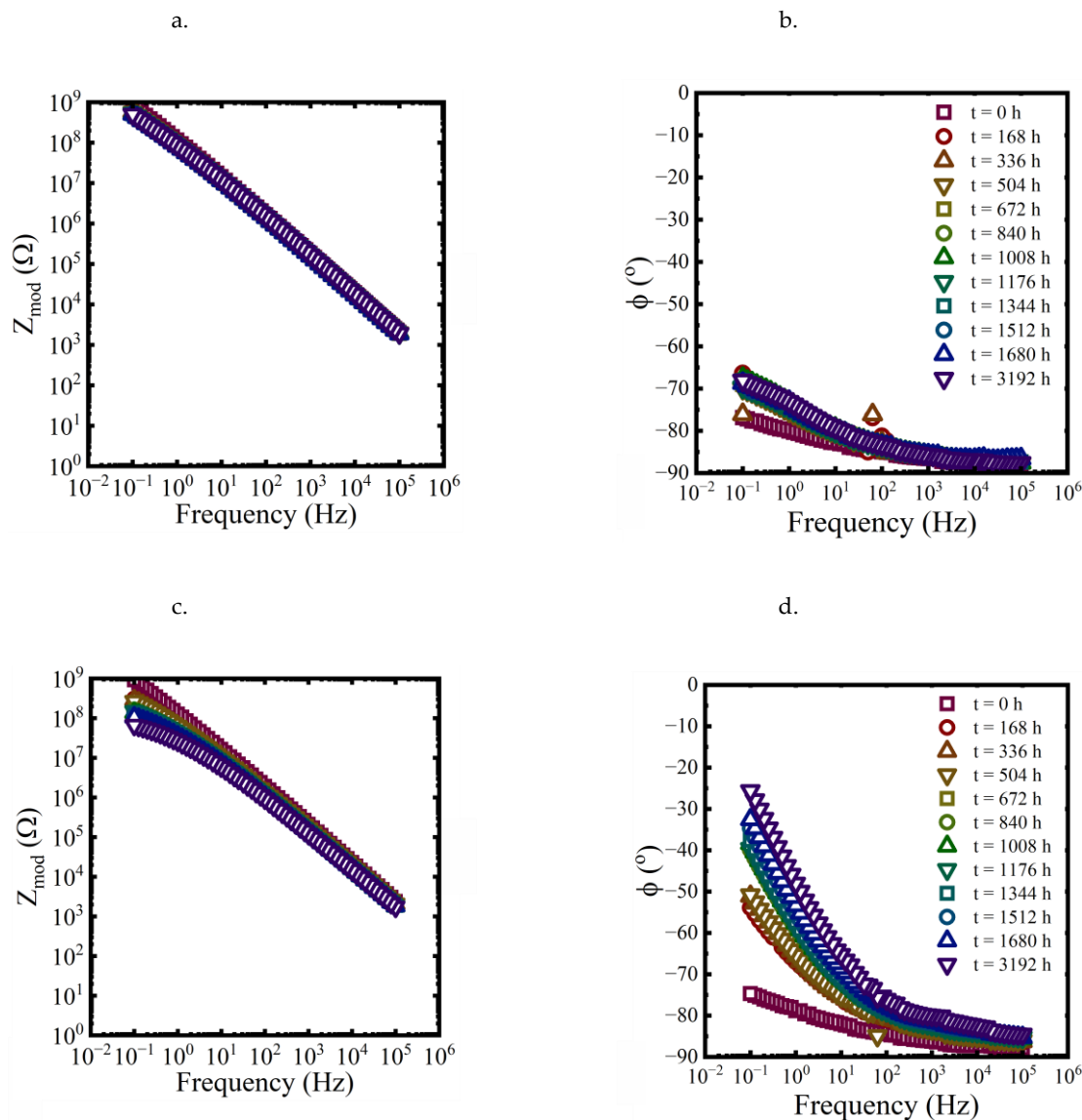


Figure 34. Bode representations of EIS data for a coated panel immersed in a saturated NaCl solution and a 0.01 M NaCl solution at 5°C for 3192 h. a, c. magnitude and b, d. phase.

EIS Analysis

The EIS technique employs a small oscillating excitation signal that is overlaid on a constant potential or current. The amplitude of the excitation signal is kept small to ensure that the system's response to the excitation will remain nearly linear. The measured response of the system to the excitation signal can then be interpreted to reveal changes to the system's physical or chemical properties. Analysis of the measured impedance data usually involves fitting an electrical analog model to the data to obtain estimates of the parameters of the circuit components. These parameter values are then used as proxies for the state of the coating.

The EIS spectra for the pre-treated samples from Figure 31 were analyzed by fitting with a single resistor-single constant phase element (CPE) equivalent circuit (Murray, 1997a) in series with a solution resistance, as shown in Figure 35a. The EIS spectra for the coated panels were analyzed by fitting with a two resistor-two constant phase element (CPE) equivalent circuit [15] in series with a solution resistance, as shown in Figure 35b. This type of equivalent circuit is commonly used to model the EIS response of coatings [14]. R_{Ω} in both circuits indicates the sample-to-reference electrode solution resistance. The behavior of the oxide-electrolyte interface for both the pretreated and coated samples is reflected in the polarization resistance, R_{CT} , in parallel with a CPE impedance, Z_{cpe}^{DL} . The coating system response is reflected in a pore resistance, R_{po} , in parallel with the impedance from a CPE, Z_{cpe}^C .

For non-reactive elements, the impedance is simply the resistance, R . However, reactive elements generally have real and imaginary impedance contributions. For constant phase elements, the impedance is given by (23) [80],

$$Z_{cpe}(\omega) = \frac{1}{Y_0(j\omega)^{m,n}}, \quad (23)$$

where Y_0 represents a proportionality factor, $j = \sqrt{-1}$, ω is the angular frequency, and m , or n , the CPE exponent.

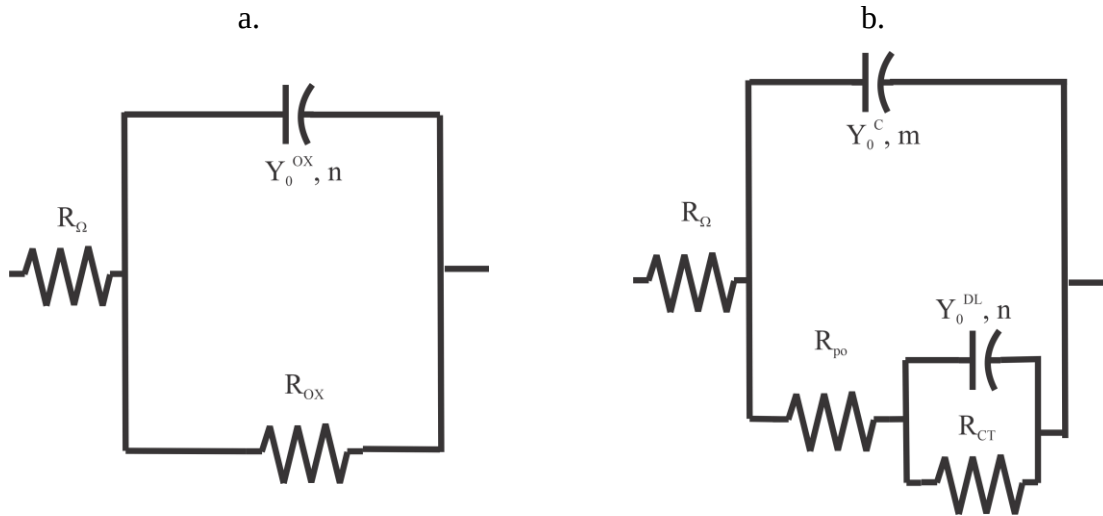


Figure 35. Equivalent circuits used for the EIS analysis. a. two resistors and single CPE circuit. b. three resistors, two CPEs circuit.

To obtain values of the equivalent circuit element parameters, nonlinear regressions were performed using a simplex algorithm [81–83]. Equivalent circuit element parameter values associated with the anodized aluminum oxide are given in Table 8.

Table 8. Equivalent circuit element parameter values for a pretreated panel.

$R_{\Omega}(\Omega)$	$R_{CT}(\text{k}\Omega \cdot \text{cm}^2)$	$Y_0^{DL}(S \cdot s^n \cdot \text{cm}^{-2})$	n
4	76	2.1×10^{-9}	0.895

These were assumed to be the same values for the analysis of EIS measurements of the coated panels. Note that R_{Ω} was a constant for all EIS measurements because we consistently used 40 mL of 0.6 M NaCl to fill the PTC and used a 3D printed cap for the PTC that positioned the reference and counter electrodes at a constant height for each measurement.

Representative equivalent circuit element parameter values are given in Table 9 for a single coating system aged in 0.01 M NaCl at $T = 5^{\circ}\text{C}$ for 3192 h. As expected, the pore resistance, R_{po} , decreased over the course of the immersion as the coating system aged. The decrease in the CPE exponent, m , indicates the coating is behaving less like an ideal capacitor. This change in the exponent has been associated with changing ionic conductivity [84].

Table 9. Equivalent circuit element parameter values for a coated panel immersed in 0.01 M NaCl at $T = 5^{\circ}\text{C}$ for 3192 h.

Time (h)	$R_{po}(\text{G}\Omega \cdot \text{cm}^2)$	$Y_0^C(S \cdot s^n \cdot \text{cm}^{-2})$	m	$C_c(nF \cdot \text{cm}^{-2})$
0	22.6	0.08×10^{-9}	0.946	0.09
168	6.13	0.14×10^{-9}	0.914	0.14
336	5.55	0.15×10^{-9}	0.912	0.14
504	5.26	0.15×10^{-9}	0.909	0.15
840	3.07	0.19×10^{-9}	0.898	0.18
1008	2.63	0.21×10^{-9}	0.893	0.20
1176	2.77	0.21×10^{-9}	0.896	0.19
1344	2.63	0.21×10^{-9}	0.894	0.20
1512	2.34	0.22×10^{-9}	0.891	0.20
1680	2.04	0.23×10^{-9}	0.886	0.21
3192	1.31	0.29×10^{-9}	0.872	0.25

The relationship between Y_0 and an estimated coating capacitance, C_c , for values of m near 1, is given in (24),

$$C_c = \frac{(Y_0^C R_{po})^{\frac{1}{m}}}{R_{po}}. \quad (24)$$

Calculated capacitance values obtained from (24) are shown in the last column of Table 9 for a single panel. The calculation was repeated for all EIS data obtained from all panels exposed to the laboratory aging conditions. These capacitance values are shown in Figure 36 as a function of aging time.

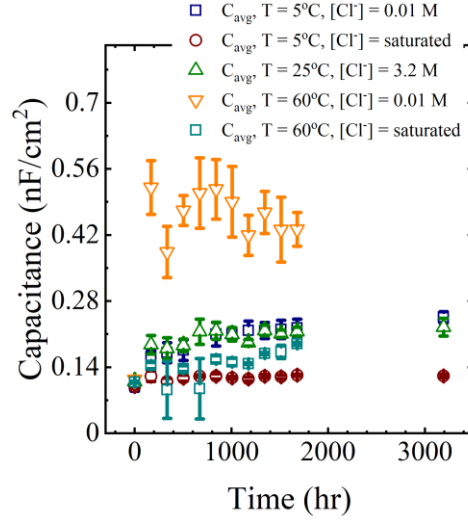


Figure 36. Average coating capacitance values for all aging conditions.

The general trend in the data from all aging conditions indicated a rapid increase in the coating capacitance during the initial few to tens-of-hours of immersion. This corresponded to the region I sorption, as identified by Boubakri and co-authors[78]. At longer times, the changes in the capacitance appeared to stabilize or increase only slowly. This corresponded to region II sorption[78,79]. The changes in the average capacitance at long times were assumed to be due to water sorption by the epoxy layer.

The saturation function, Ψ , of the coating can be described by (25)(Wind & Lenderink, 1996),

$$\Psi(t) = \frac{\phi(t)}{\phi_s} = \frac{\ln\left(\frac{C_c(t)}{C_c^0}\right)}{\ln\left(\frac{C_c^s}{C_c^0}\right)}, \quad (25)$$

which arises because we assume the capacitance of the coating is a function of $\ln \epsilon$, the mixed dielectric constant of the water and polymer[86]. The saturation function, which ranges from 0 to 1, is the ratio between the fraction of available free space within the polymer that is filled with water at time, t , corresponding to $\phi(t)$, and the fraction of available free space that is filled with water at saturation, ϕ_s . $C_c(t)$ is the coating capacitance at time, t ; C_c^0 is the coating capacitance at $t = 0$; and C_c^s is the coating capacitance at saturation.

Discussion

Development of governing equations for polymer saturation

We assume saturation of a polymer coating immersed in solution can be treated as a one-dimensional diffusion process in a plane sheet, subject to the fundamental differential equation of diffusion, as given in (26),

$$\frac{\partial \Psi(x, t)}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial \Psi(x, t)}{\partial x} \right). \quad (26)$$

The initial condition is given in (27),

$$\Psi(x, 0) = 0. \quad (27)$$

A constant Dirichlet boundary condition is assumed at the air-coating interface and a Neumann boundary condition is assumed at the coating-metal interface (C. Yang et al., 2020); both given in (28), respectively,

$$\begin{aligned} \Psi(0, t) &= \Psi_s, \\ \frac{\partial \Psi}{\partial x}(x_2, t) &= 0, \end{aligned} \quad (28)$$

where Ψ_s is the saturated volume fraction of the polymer coating occupied by water for the given conditions. D_i is the diffusivity of the water in the polymer. $x = 0$ corresponds to the coating-electrolyte interface, $x = x_1$ corresponds to the interface between coating layers in later models, and $x = x_2$ corresponds to the coating-substrate interface. At $t = 0$, there is no water present in the coating.

An analytical solution to the diffusion equation in (26), subject to the initial condition given in (27) and the boundary conditions given in (28), and assuming a constant diffusivity is shown in (29)[88],

$$\Psi(x, t) = \Psi_s - \frac{4\Psi_s}{\pi} \sum_{n=0}^{\infty} \left(\frac{(-1)^n}{2n+1} \right) \left(e^{\frac{-D(2n+1)^2\pi^2 t}{4x_2^2}} \right) \left(\cos \frac{(2n+1)\pi x}{2x_2} \right). \quad (29)$$

For a plane sheet, the mass fraction of water uptake can be obtained from (30) (Crank, 1975),

$$\Psi(t) = \frac{M(t)}{M_s} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} e^{\frac{-D(2n+1)^2\pi^2 t}{4x_2^2}}, \quad (30)$$

where $M(t)$ is the amount of water uptake after time, t ; M_s is the amount of water uptake needed to saturate the polymer; and Ψ is the saturation function from (25).

The mass fraction of water in the coating is obtained from (31),

$$M(t) = \rho \phi_s \int_0^{x_2} \Psi(x, t) dx, \quad (31)$$

where ρ is the density of water.

If unknown, the diffusion coefficient, D , can be estimated by using a Newton-Raphson algorithm to find the roots of (32) at a given time,

$$f(t) = \frac{M(t)}{M_s} - \frac{\phi(t)}{\phi_s}, \quad (32)$$

where the first term is given by (30) and the second term by (25). However, for shorter aging times, (30), can be approximated with (33)[85],

$$\Psi(t) \approx \frac{2}{\sqrt{\pi}} \left(\frac{D}{x_2^2} \right)^{\frac{1}{2}} \sqrt{t}. \quad (33)$$

The diffusion coefficient, D , for the initial, region I, water uptake in the polyurethane topcoat was determined from the slope of the linear fit to Ψ vs $\sqrt{t}$. The region II diffusion coefficient was calculated as the mean of the diffusion coefficients, obtained from (30), from 200 to 800 h of immersion. Water uptake by the polyurethane topcoat was assumed to be the dominant process over this duration. The diffusivity for water uptake in the epoxy coating was determined as the mean diffusion coefficient over the final two time periods of the coating aging. It was assumed that the topcoat had reached saturation and water uptake by the primer had become the dominant process. These diffusion coefficients are shown in Table 10.

Table 10. Estimated diffusion coefficients for polyurethane and epoxy from Figure 36.

T (°C)	$[Cl^-](M)$	$D_{polyurethane}^{region I} \left(\frac{m^2}{s} \right)$	$D_{polyurethane}^{region II} \left(\frac{m^2}{s} \right)$	$D_{epoxy}^{region II} \left(\frac{m^2}{s} \right)$
5	0.01	0.41×10^{-13}	0.40×10^{-13}	0.23×10^{-13}
5	Saturated	0.07×10^{-13}	0.05×10^{-13}	0.25×10^{-13}
25	3.20	0.96×10^{-13}	0.76×10^{-13}	0.31×10^{-13}
60	0.01	4.0×10^{-13}	1.3×10^{-13}	0.35×10^{-13}
60	Saturated	2.3×10^{-13}	2.3×10^{-13}	0.19×10^{-13}

The diffusion coefficient for $D_{polyurethane}^{region I}$ at $T = 25^\circ C$ in Table 10 is reasonably consistent with values obtained from the literature. That is, diffusion coefficients for water in polyurethane at $25^\circ C$ span the range from $5.0 \times 10^{-13} m^2/s$ [89] to $15.6 \times 10^{-13} m^2/s$ [79] so our value was approximately 20% lower. For epoxy, the literature suggests $D_{epoxy}^{region I} = 3.5 \times 10^{-13} m^2/s$ [90]. Our estimated value for $D_{epoxy}^{region I}$ at $T = 25^\circ C$ was $0.8 \times 10^{-13} m^2/s$, which was roughly 20% lower than the literature value.

Water sorption models

Water sorption of the polymer coatings assumes that water molecules occupy adsorption sites along the cross-linked polymer chains and transport occurs via exchange between these sites. The coating systems in the laboratory aging conditions were assumed to be saturated when available adsorption sites were filled. For the numerical models, the polyurethane coating was identified as Layer 1 and the epoxy coating was identified as Layer 2.

Constant diffusivity models

These two models were not intended to replicate the water sorption curves. Instead, they were used to provide upper and lower bounds on the coating response. The constant diffusivity models assumed the diffusion coefficients for water uptake in both polymer layers were constant and equal. For these two models, the solution provided by (29) was valid. In the fast water uptake model, $D_{1,2} = 0.96 \times 10^{-13} \text{ m}^2/\text{s}$. For the slow water uptake model, $D_{1,2} = 96 \times 10^{-16} \text{ m}^2/\text{s}$.

Varying diffusivity as a function of depth and polymer type

These models were used to develop and test the numerical methods for solving the diffusion equation with a non-constant diffusivity. They varied the diffusion coefficient as a function of depth, x , and polymer. Numerical solutions were obtained using the Crank-Nicolson[91] discretization of the diffusion equation, given in (34),

$$U_i^{j+1} - \frac{\nu}{2}(U_{i+1}^{j+1} - 2U_i^{j+1} + U_{i-1}^{j+1}) = U_i^j + \frac{\nu}{2}(U_{i+1}^j - 2U_i^j + U_{i-1}^j), \quad (34)$$

where U_i^j is the discretization of the saturation function, Ψ , at node, i , for time-step, j . That is, $U_i^j \approx \Psi(x, t)$ and the time and space variables were non-dimensionalized as, $\nu = \delta\tau/(\delta X)^2$ with $\tau = Dt/x_2^2$, and $X = x/x_2$.

For the step-change model, the diffusion coefficient was assigned using a step function between layers 1 and 2, as shown in Figure 37a, where $D_1 = 0.96 \times 10^{-13} \text{ m}^2/\text{s}$ and $D_2 = 0.8 \times 10^{-13} \text{ m}^2/\text{s}$. At the interfacial point, s ,

$$\frac{\partial U_{s,j}}{\partial t} = -\frac{D_1}{\delta x}(U_s - U_{s-1}) + \frac{D_2}{\delta x}(U_{s+1,j} - U_{s,j}), \quad (35)$$

which assumed the flux of water leaving Layer 1 was exactly equal to the flux of water entering Layer 2. At the interface, the saturation was assumed to be equal for layers 1 and 2. Numerically solving this equation required modifications to the discretized equation in (34). The modified version is shown in (36),

$$\begin{aligned} U_i^{j+1} - \frac{\nu_-}{2}(U_{i+1}^{j+1} - U_i^{j+1}) + \frac{\nu_+}{2}(U_i^{j+1} - U_{i-1}^{j+1}) \\ = U_i^j + \frac{\nu_-}{2}(U_{i+1}^j - U_i^j) + \frac{\nu_+}{2}(U_i^j - U_{i-1}^j), \end{aligned} \quad (36)$$

where, $\tau = \max(D) t/x_2^2$, $\nu_- = \nu D_{i-1}$ and $\nu_+ = \nu D_{i+1}$.

In the sigmoidal model, the diffusion coefficient as a function of depth, x , in the coating system was determined using (37),

$$D(x) = \frac{D_{1,0} - D_{2,0}}{2} \tanh\left(\frac{x}{w}\right) + \frac{D_{1,0} + D_{2,0}}{2}, \quad (37)$$

where $D_{1,0} = 0.96 \times 10^{-13} \text{ m}^2/\text{s}$ and $D_{2,0} = 96 \times 10^{-16} \text{ m}^2/\text{s}$, as shown in Figure 37b. The distance, w , small in comparison to the thickness of the coating layers, was the distance over which D varied.

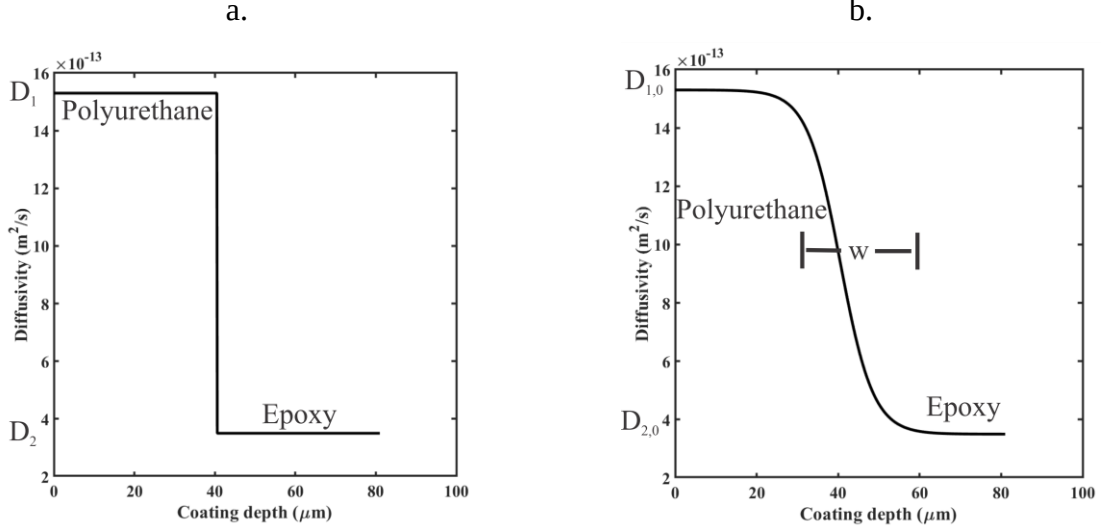


Figure 37. Notional diffusion coefficient profiles for a. step-change model and b. sigmoidal variation model for water uptake in coating layers 1 and 2.

Saturation function profiles resulting from these water uptake models, for a simulated coating system aged in 0.01 M NaCl at $T = 5^\circ\text{C}$ for approximately 1 h, are shown in Figure 38. As expected, coating saturation occurred most quickly in the high diffusivity model and most slowly in the low diffusivity model. The interface between the coating layers disrupted the saturation process, slowing it down because of the lower diffusion coefficients in the epoxy layer. The sigmoidal function for the diffusion coefficient resulted in a slightly faster saturation versus the step change in diffusivity.

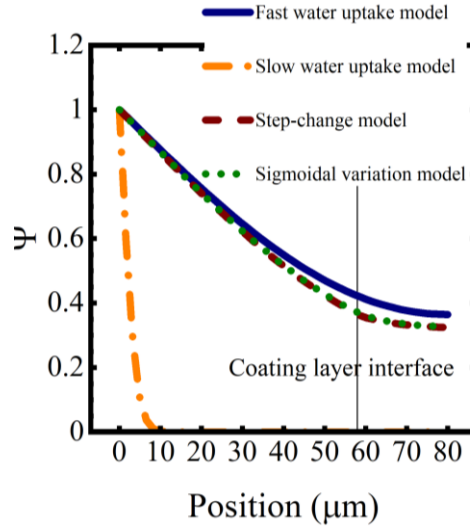


Figure 38. Saturation profiles for the constant and varying by polymer-type diffusivity models after one hour of water sorption.

Thus, these four simple water uptake models helped establish the numerical framework that was used for the more complex models with variable diffusivities summarized in Table 11 and discussed in the following sections.

Table 11. Complex variable diffusivity water sorption models.

Model	Summary	$D \left(\frac{m^2}{s} \right)$
Glass-to-gel transition model	D varies as a function of position in the coating and composition. Glass-to-gel transition of the polymer.	$D_1^{glass} = 96 \times 10^{-16}$
		$D_1^{gel} = 0.96 \times 10^{-13}$
		$D_2^{glass} = 80 \times 10^{-16}$
		$D_2^{gel} = 0.8 \times 10^{-13}$
Polymer aging model	D varies as a function of position and time. Rapid uptake of water into the polymer followed by a slow polymer relaxation.	$D_1^{initial} = 0.96 \times 10^{-13}$
		$D_1^{age} = 0.76 \times 10^{-13}$
		$D_{1,0} = 0.01 * D_1^{age}$
		$D_2^{void} = 0.8 \times 10^{-13}$
		$D_2^{age} = 0.31 \times 10^{-13}$
		$D_{2,0} = 0.01 * D_2^{age}$

Glass-to-gel transition model

This model represents the classic case of diffusion of a liquid into a glassy polymer with a steep concentration gradient that results in an initial water uptake proportional to $\sqrt{t}$ but water uptake behind the concentration gradient is proportional to t [92–94]. For our system, the diffusion coefficients in both coating layers were treated as functions of polymer type, depth, and concentration. Diffusivities were initially low for water transport through the cured, glassy polymer. However, once the saturation surpassed a threshold level, the diffusivity values were then smoothly *increased*, using a form of (37) to transition the diffusion coefficient from the glass to gel value. The threshold saturation corresponded to the transition of the polymer from a glassy state to a gel-like state. The diffusion coefficients for the gel-states and glass-states for the two polymers are given in Table 11. As a simplification, we assumed the transition between the glassy and gel states was similar for both polymers[95].

The initial uptake of water into the coating occurred as Type I diffusion. This is the classic Fickian diffusion that exhibits a dependence on $\sqrt{t}$. However, once the transition to the gel state was completed, water transport took place as Type II diffusion. In Type II diffusion, the increase in saturation is dependent on t [96,97]. The arrow pointing at the near-vertical saturation curve in Figure 40 indicates the transition between Type I to Type II diffusion.

In this simulation, complete saturation of the coating occurred within a few hours, which was not consistent with the observations of the immersed coating systems, where the capacitance was still changing after 1000-1500 h, as seen in Figure 36. Thus, despite its more complex behavior, the polymer glass-to-gel transition model also did not replicate the observed sorption curves for polymer coatings.

Polymer aging model

Possart and Zimmer described three polymer aging mechanisms based on their work on polyurethanes exposed to high relative humidity environments[8]. They suggested that during the initial water uptake, the water molecules separated weak polymer-polymer hydrogen bonds to form stronger polymer-H₂O hydrogen bonds as well as solvating hydrophilic regions along the polymer chains. This initial phase usually took less than a week to complete. In the second stage of water uptake, dispersed clusters of a mixed phase of water and polymer strands formed throughout the coating. This stage took thousands of hours to complete. They characterized these first two stages as physical aging mechanisms because they were generally reversible by drying out the coating. In the final stage, they observed irreversible chemical aging from the cleavage of the polymer chains via hydrolysis reactions with the water molecules.

In our model, the diffusion coefficients in both coating layers were treated as functions of the polymer type, depth, saturation, and immersion time. Water diffusivity was assumed to be high during the initial period of water uptake into the coating, corresponding to the first physical aging stage. Once this initial water uptake was completed, which took roughly seven days, in our immersion experiments, the diffusion coefficients were *decreased*. That is, once a critical saturation threshold of the polymer was reached, which we assumed to be around 55% for polyurethane and 45-50% for epoxy, the diffusion coefficient was changed from $D_i^{initial}$ to $D_i(t)$. This decrease was done to account for slower water sorption during the formation of the water-rich and polymer mixed phase.

An expression to simulate the effect of this aging process on water transport was obtained by solving the logistic equation given in (38),

$$\frac{dD_i}{dt} = kD_i(D_i^{age} - D_i), \quad (38)$$

subject to the initial condition, $D_i(t = 0) = D_{i,0}$. The subscript, i , in (38) differentiates between the polyurethane and epoxy layers. The solution to (38) is given in (39),

$$D_i(t) = \frac{D_i^{age}}{\left[\frac{(D_i^{age} - D_{i,0})}{D_{i,0}} * e^{-D_i^{age} \frac{t}{\tau}} \right] + 1}, \quad (39)$$

where we assume the formation of the mixed phase proceeds as an autocatalytic logistic function[9]. In (39), D_i^{age} is the diffusion coefficient at the end of the formation of the mixed water-polymer phase. τ is a characteristic reaction area constant. Values of $\tau \approx 10^{-9} m^2$ worked for this analysis. $D_{i,0}$ represents the diffusion coefficient at the start of the phase formation process. $D_{i,0}$ for both polymers was assumed to be $\approx 0.01 \times D_i^{age}$. A plot of $D_i(t)$ for $T = 5^\circ C$ and $[Cl^-] = 0.01 M$ is shown in Figure 39.

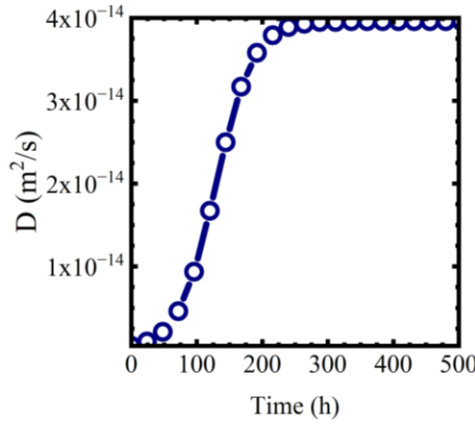


Figure 39. $D_i(t)$ for $T = 5^\circ C$ and $[Cl^-] = 0.01 M$.

Numerical values for the various diffusion coefficients in each polymer are given in Table 11. The saturation function profiles resulting from the polymer aging model are shown in Figure 40 for the model coating system aged in 0.01 M NaCl at $T = 5^\circ C$. Saturation proceeded much more slowly in this model than in the glass-to-gel transition model, as can be seen by comparing the timestamps on the saturation profiles. The polymer aging model, when coupled with an effective medium theory for changes in the dielectric properties, exhibited the expected behaviors of the water sorption curves for polymers.

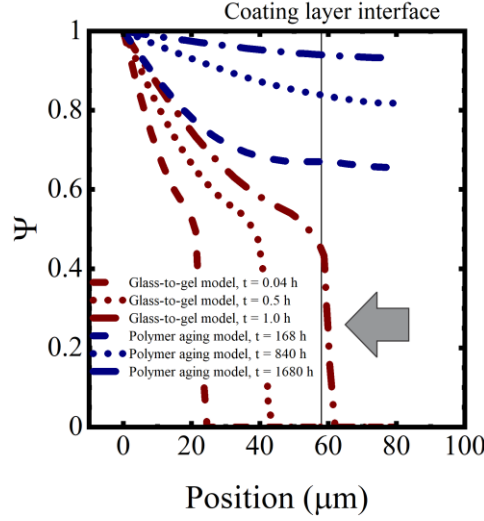


Figure 40. Saturation profiles for the glass-to-gel transition model and polymer aging model.

Estimating capacitance from changes in dielectric properties

As was seen in Figure 36, water uptake by the polymer generally increased the capacitance of the coating. The capacitance of a parallel plate capacitor with a dielectric material separating the plates is obtained from (40),

$$C = \frac{\epsilon_i \epsilon_0 A}{d}, \quad (40)$$

where $\epsilon_0 = 8.85 \times 10^{-12} \text{ A}^2 \text{ s}^4 \text{ m}^{-3} \text{ kg}^{-1}$, A is the exposure area, d is the separation between the oppositely charged plates, and ϵ_i is the dielectric constant of the material. Values of ϵ_i for materials of interest to this work include water, $\epsilon = 80.1$; hydrated Al_2O_3 , $\epsilon = 11.5$ [98]; epoxy, $\epsilon = 3.6$ [99]; and polyurethane, $\epsilon = 6.19$ [100].

To obtain the capacitance of a parallel plate capacitor in which dielectric properties of the material change throughout its depth, we can envision sectioning the dielectric material into thin slices such that each slice has a constant capacitance. The capacitor is then assumed to behave as a series combination of the individual thin-slice capacitors.

The capacitance of each slice is calculated by assuming the contributions to the dielectric constant of that slice follow the Brasher-mixing law[101–103]. The total capacitance is then the sum of the individual capacitances, as given in (41),

$$\frac{1}{C_c(t)} = \frac{1}{A \epsilon_0 \epsilon_{\text{polymer}}} \sum_{n=1}^N \frac{\Delta x}{\exp((\Psi_n) \phi_s \ln \epsilon_{H_2O})}, \quad (41)$$

where N is the number of slices of thickness Δx , and Ψ_n is the saturation function in each slice, n , and is obtained from the solution to the diffusion equation, (26).

Predicting coating capacitance from the polymer aging and Brasher-mixing model

Thus, modeling the polymer aging process and evolving coating capacitance consisted of performing the following steps:

- Assign the diffusion coefficient for water sorption in each polymer layer using the constant values provided in the polymer aging entry in Table 11 or from (39), depending on the saturation level. The change in diffusion coefficients across the polymer layer interface was calculated using (37).
- Determine the saturation in both polymer layers by numerical solution of the Crank-Nicolson discretization of the diffusion equation given in (36), subject to the initial condition given in (27), the boundary condition given in (28), and the continuity condition given in (35).
- Calculate the coating capacitance from (41).

The calculated values could then be compared against the capacitances obtained from the EIS data. Example comparisons are shown in Figure 41 for the different immersion conditions:

- Immersion in 0.01 M NaCl at $T = 5^\circ\text{C}$ or $T = 60^\circ\text{C}$
- Immersion in 3.2 M NaCl at $T = 25^\circ\text{C}$
- Immersion in saturated NaCl at $T = 5^\circ\text{C}$ or $T = 60^\circ\text{C}$

The model predictions for the capacitance were closer to the EIS values for the lower temperature solutions because the experimental data from the solutions at 60°C had significantly more variability than at lower temperatures.

While there are discrepancies between individual data points and the model values, the overall capacitance trends from the polymer aging and Brasher-mixing model presented here are consistent with the sorption behavior observed in the data. That is, at shorter times, region I of the capacitance curve is a function of Fickian diffusion. At longer times, in region II of the capacitance curve, water sorption occurred as a pseudo-Fickian process, which we suggest was governed by the rate of formation of the water-rich and polymer mixed phase.

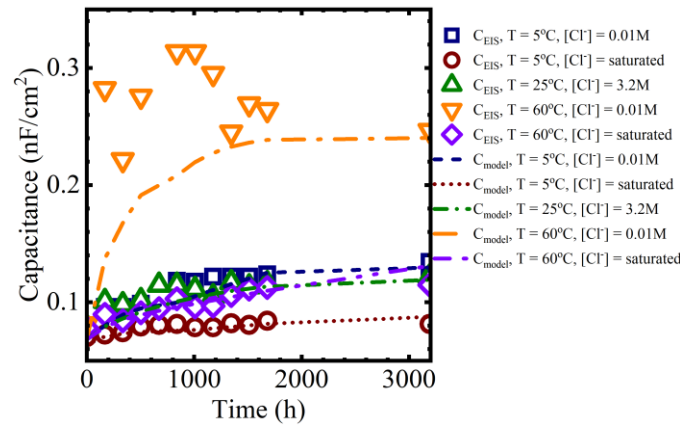


Figure 41. Coating capacitance values obtained from equivalent circuit fits compared to values obtained from the polymer aging and Brasher-mixing model.

These results are consistent with the physical aging mechanisms proposed by Possart and Zimmer[8]. They suggested that irreversible chemical aging of the polymers during water uptake does occur, but that cleavage of the polymer chains themselves is very slow.

These comparisons between model predictions and EIS data indicate that EIS measurements taken at different exposure intervals, over a wide enough frequency range to allow determination of the coating capacitance, can be used to track the saturation of the coating[94,104]. The degree of saturation can then be used to estimate the degree of physical aging in the polymer. We suggest this approach permits a quantifiable measure of the state of the coating, which can then be included as a specific data point in an assessment of the state of the coating to determine if it is still maintaining its protective function. In addition, and independent of any chemical aging processes degrading the polymer chains, saturation of the polymer results in water at the polymer-metal interface, which has been shown to negatively impact coating adhesion to the substrate[105]. Examining and analyzing EIS data to detect water at the polymer-metal interface is a topic for future work.

Summary and Conclusions

EIS data were obtained from measurements of an organic polymer coating system consisting of a polyurethane topcoat overlaid on epoxy primer that had been applied to pre-treated aluminum alloy test coupons that were then immersed in various NaCl solutions at different temperatures for more than 3000 h. A two resistor-two constant phase element (CPE) equivalent circuit model was used to fit the EIS data obtained from the coating systems at approximately 168-hour intervals. Parameters from the equivalent circuit model fits were used to estimate changes in the coating capacitance over the course of the immersions.

Numerical solutions of the one-dimensional diffusion equation were developed that used increasingly complex models of the diffusion coefficient for water sorption in the coating system. To explain features of the water sorption curves for the polymers obtained from the EIS data, we proposed that water uptake by the organic coating system was consistent with the two-stage kinetics mechanism. The first stage, associated with a high diffusivity, resulted in rapid water uptake. In the literature, this mechanism has been associated with the formation of polymer-H₂O hydrogen bonds following separation of polymer-polymer hydrogen bonds.

The second mechanism was then initiated once the volume fraction of water reached a critical threshold. This mechanism, associated with a varying diffusivity modeled using an autocatalytic logistic function, was consistent with the physical aging mechanism that theorizes further water uptake results in the formation of a water-rich and polymer mixed phase.

Capacitance values predicted from the polymer aging and Brasher-mixing models were consistent with trends observed in the experimental data. These results are important for potential industrial applications because polyurethane and epoxy coatings are widely used by commercial and military aviation and on aluminum materials in industrial applications. This modeling approach allows us to estimate the state of the layers of the coating system using only the type of coating and the exposure conditions, while also providing context for interpreting non-destructive EIS measurements of *in-situ* coatings.

7. INCORPORATING PHYSICS-BASED MODELS INTO EQUIVALENT CIRCUIT ANALYSIS OF EIS DATA FROM ORGANIC COATINGS

Introduction

EIS data provides only indirect evidence of the state of an organic coating system and one of the challenges with using EIS data is assigning the correct physical interpretation to the impedance. Analyses are usually performed using equivalent circuit models with the circuit element parameter values providing insight into the state of the coating.

EIS data analysis for organic coatings has traditionally focused on determining coating resistance or capacitance as a means of assessing the state of the coating. Lee and Mansfeld[56] suggested classifying coatings as good, intermediate, or bad if the pore resistance of the coating ranged from 50-500 $G\Omega \cdot cm^2$, 50-500 $M\Omega \cdot cm^2$, or 0.1-5 $M\Omega \cdot cm^2$, respectively. They based this classification on three-layer coating systems of various types applied to steel coupons and immersed in seawater for up to two years[106,107]. This approach for characterizing the state of a coating system is the most widely used.

However, for commercial aircraft coating systems, like the one studied in this work, the impedance response is dominated by the coating capacitance during most of its life cycle [72]. Water uptake by the polymer that forms the coating binder changes the dielectric properties of the coating because the dielectric constant of the polymer-water-air system is assumed to correspond to some ratio of the values, as seen in (42)[108],

$$\epsilon_i = \epsilon_p \frac{V_p}{V} \epsilon_{H_2O} \frac{V_{H_2O}}{V} \epsilon_0 \frac{V_0}{V}, \quad (42)$$

where ϵ_i is the dielectric constant of the polymer-air-water system, ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-12} A^2 s^4 m^{-3} kg^{-1}$), and V_i/V is the volume fraction occupied by a particular component. It is then assumed that changes in the dielectric constant are observed in the EIS data analysis as a change in the capacitance of the coating, though this represents an ideal scenario that does not always hold in practice[94]. The inherent assumption in the capacitance assessment is that water uptake by the polymer results in dissolved oxygen and aggressive electrolyte ion species at the coating-substrate interface. However, Scully[109] found little correlation between capacitance changes and coating deterioration for epoxy polyamide coated steel panels immersed in ASTM standard seawater for over a year, which suggests that assessments of the state of the coating based only on capacitance are unreliable.

In this work, our focus is on incorporating multiple parameters from the EIS data analysis to determine the state of the coating system. These parameters include resistance and capacitance information along with the transport of electrolyte constituents, such as water and dissolved O_2 , through the coating. We propose and test a more complex equivalent circuit model for analyzing EIS data from two-layer organic coating systems. We hypothesize this model will result in improved fits to the EIS data, using the corrected Akaike Information Criterion statistic to compare equivalent circuit results instead of the more common mean-squared error statistic. Thus, the more complex equivalent circuit model with improved fitting will provide an improved understanding of the state of the coating. We also show that the governing equations that give rise to the impedance behavior provide good initial parameter estimates that can be used in the fitting procedure.

Theory and calculations

Review of equivalent circuit modeling for organic coatings

The following literature review briefly summarizes important developments in the use of equivalent circuit models for analyzing EIS data obtained from organic coatings. One of its goals is to draw the reader's attention to the increasing complexity in the equivalent circuit models used to analyze the behavior of coatings. This complexity is seen in the addition of circuit branches and circuit elements to subsequent models as researchers sought improved understanding of features seen in the data from coatings.

The classic review articles by Mansfeld[42] and Murray[110] on using EIS to evaluate coatings were based around employing the *simplified Randles circuit as nested coating defect model* to interpret the electrochemical response of barrier organic coatings exposed to corrosive electrolytes. This equivalent circuit model, shown in Figure 42e, is made up of two building blocks: the undamaged coating circuit model and the simplified Randles circuit model. 1. To maintain consistency with earlier literature, we used the classification scheme shown in Figure 2 to identify equivalent circuit models for interpreting EIS data obtained from coatings. "Modified" describes a version of a circuit model where ideal capacitors have been replaced with constant phase elements. "Simplified" refers to an alteration from the base circuit where the diffusion element has been removed and "extended" refers to the addition of new circuit elements to a base circuit.

The *undamaged coating circuit* model is shown in Figure 42a. For undamaged coatings, the electrochemical response to an EIS perturbation can be modeled as a resistor-capacitor circuit in series with a resistor. This circuit contains a capacitive element, C_c , arising from the dielectric nature of the coating, in parallel with a resistance, R_1 , that corresponds with the resistivity of the polymer to electrolytic conduction[11]. The resistance indicated by R_Ω captures conductance losses in the solution between the reference electrode and the coating surface.

Exposure of the coating system to the service, or test, environment initiates solution transport through the coating. Pathways for solution transport traditionally have been assigned to the existence of coating defects, such as holidays, or micro-porosity within the polymers that make up the coating system. Wind and Lenderink[85], in their study of the pseudo-Fickian diffusion of water in polymers, noted that it is generally assumed that water permeation into an organic coating occupies the free space between the polymer chains. Coating capacitance is then a measure of the changing mixture of the different dielectric constants of polymer, free space, and water. Once the water reaches the metal-coating interface, the physical system changes again. Beaunier[13] was one of the first to propose that the electrochemical response from a coating defect could be modeled by the addition of a second RC element. This second RC element contains both the charge transfer resistance, R_{ct} , for faradaic processes occurring at the metal-solution interface, and the electrical double-layer capacitance, C_{dl} . These processes, along with diffusion of the reacting species, are contained in the *Randles circuit model*[12], shown in Figure 42c. The *simplified Randles model* omits the diffusion process as a contributor to the impedance.

The *simplified Randles circuit as nested coating defect model*, Figure 42e, has been used extensively to interpret EIS data obtained from organic coatings on metal substrates as a means of assessing the state of the coating[111,112]. However, to address some of the shortcomings from the assumption that the electrical double-layer within the defect acted as a perfect capacitor, Kendig and colleagues substituted a constant phase element (CPE) for the double layer capacitance. This model was called the *Rapid Electrochemical Assessment of Paint (REAP) model*

and is shown in Figure 42f [14]. Eventually, the capacitor elements representing both the double-layer and the coating were replaced by CPEs to improve agreement between modeled and measured spectra[15], resulting in the *modified REAP model*, shown in Figure 42g.

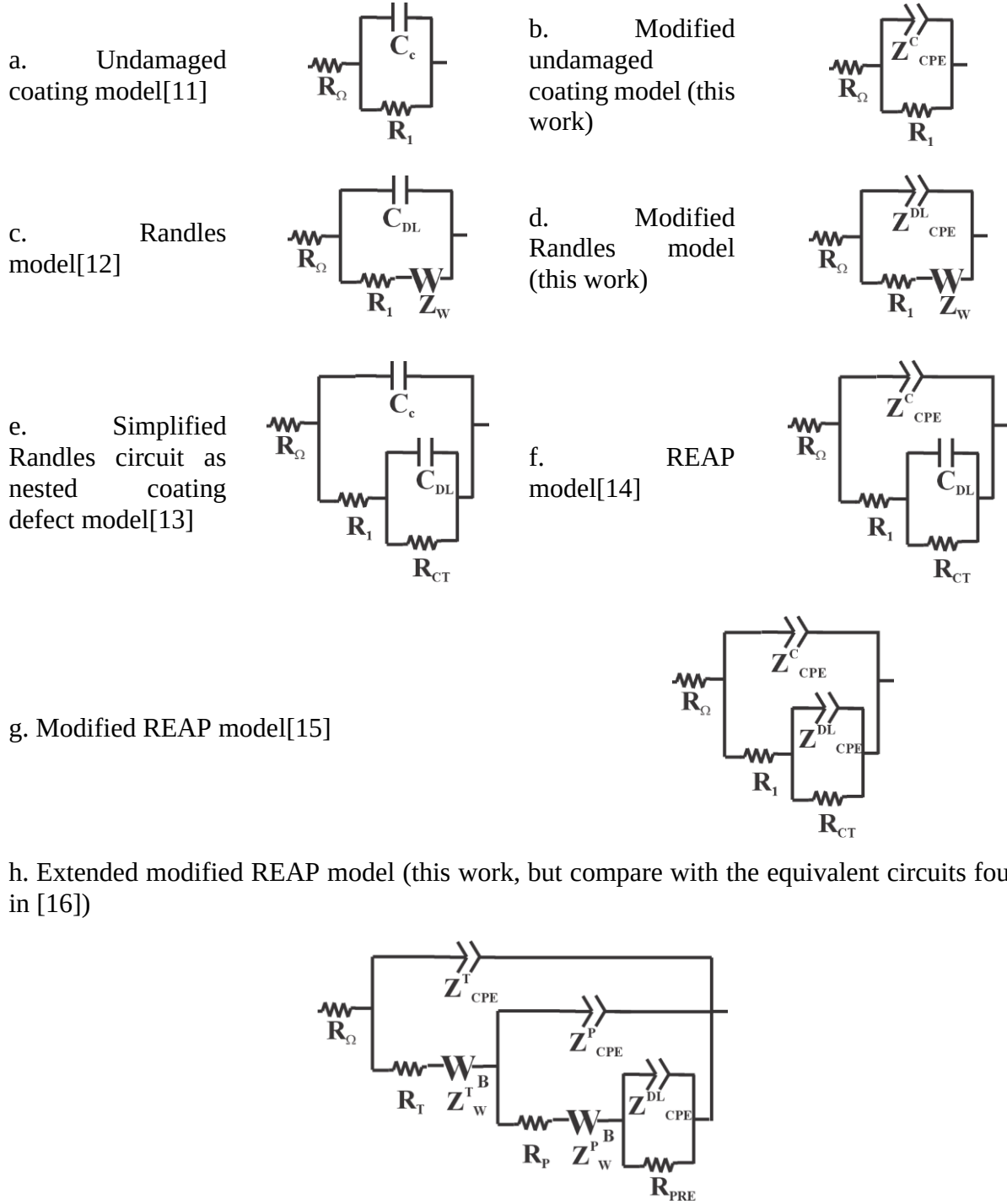


Figure 42. Classification of the various equivalent circuit models used for analyzing EIS data obtained from coatings.

The simplified Randles circuit as nested coating defect model, and its descendants, the REAP and modified REAP models, have displayed remarkable longevity as the predominant circuits for evaluating EIS data from organic coatings. This suggests that the relatively simple formulations of these models still represent much of the physical and chemical processes that give rise to the responses measured by EIS experiments. However, excluding the influence of transport processes limits the usefulness of these models for determining the state of the two-layer aircraft coating systems that was studied in this work.

Thus, we propose the *extended modified REAP model*, Figure 42h, founded on the REAP and modified REAP circuits. Like the REAP and modified REAP models, it includes resistive and capacitive elements, in the form of CPEs, but on separate circuit paths for each coating layer. It also includes bounded Warburg elements to represent transport of electrolyte constituents. We hypothesize the extended modified REAP model will provide better insight into the state of a two-layer organic coating system than the other, earlier, models.

Water-uptake by the polymers that make up the coating layers is assumed to underlie the coating behavior that gives rise to most of the equivalent circuit elements seen in the EIS data. Accordingly, in a previous work[113], we developed a numerical model of water uptake by a polymer using the variations in coating dielectric properties over the course of immersion time. That model incorporated expressions for the diffusion coefficient of water uptake as functions of the degree of water saturation of the coating, immersion time, and immersion temperature. We employed that diffusion model in this work as part of the physics-based models for the equivalent circuit element parameters.

Dispersion relations for equivalent circuit model elements

Analysis of EIS data using equivalent circuits requires expressions for the dispersion relations for the equivalent circuit elements. These are, in general, straightforward. However, incorporating assumptions about the underlying physical or chemical processes that give rise to the circuit element behavior can provide initial parameter estimates or bounds on the parameter values for the regression algorithm.

Capacitance and constant phase element models

The impedance for a capacitor that consists of flat, parallel, oppositely charged surfaces, as a function of the angular frequency, ω , is given by (43),

$$Z_c(\omega) = \frac{1}{Cj\omega}, \quad (43)$$

where C is the capacitance obtained from (44).

$$C = \frac{\epsilon_i \epsilon_0 A}{d}, \quad (44)$$

where A is the exposure area and d is the separation between the oppositely charged regions.

Constant phase elements (CPEs) are generally characterized as non-ideal capacitors because the phase angle of their response is a constant shift that is less than 90° . While the underlying mathematical basis for the CPE, arising from a distribution in the dielectric behavior of the material as a function of frequency[114], has long been accepted, the mechanisms that give rise to this behavior have been debated. There have been many attempts at understanding the physical basis for CPE behavior in the electrical double layer at the metal-electrolyte interface. Proposed

explanations have ranged from microscopic surface roughness[115] causing differences in capacitance, to phenomena arising from anisotropic fields within the double-layer itself[116,117], to changes in oxide properties arising from different grain orientations of the underlying metal[118]. Hirschorn and colleagues showed that a resistivity distribution within a film can give rise to CPE behavior[119]. Schalenbach and co-authors related the resistivity distribution to ion movement in response to the decaying electric field in the double-layer, and the capacitance contributions of the CPE to charge separation and water molecule polarization[120].

The physical basis for the CPE response from organic polymer coatings has been proposed to arise from a different mechanism. The Concept of Mismatch and Relaxation (CMR) for ion migration in disordered structures by Funke and colleagues[84,121] has been proposed by Abouzari and co-authors to give rise to CPE behavior[122] for polymer coatings.

The impedance as a function of frequency for a CPE is given by (45)[80],

$$Z_{cpe}(\omega) = \frac{1}{\xi(j\omega)^\alpha}, \quad (45)$$

where ξ represents a proportionality factor and α is the CPE exponent. The relationship between ξ and C , for values of α near 1, if the capacitor or constant phase element is part of an RC circuit, is given in (46),

$$\xi = \frac{(CR_1)^\alpha}{R_1} \quad (46)$$

where C is the capacitance from (44), and R_1 is the resistance of the resistive element.

The capacitance of a polymer changes as a function of water saturation. Prior work has theorized that water uptake by polymers occurs via two principal mechanisms[78]. The first mechanism is a Fickian diffusion process in which water molecules migrate and adsorb at polar sites along the polymer chains[77]. It corresponds to region I on a saturation curve, which is characterized by a steep slope indicating rapidly changing properties with time. The second mechanism is a non-Fickian transport process in which water clusters form and lead to a mixed polymer and water phase[8,79]. This corresponds to region II on a saturation curve, which is characterized by a very shallow slope. This indicates the coating properties are changing very slowly with time.

Assuming the polymer can be sectioned into thin slices such that each slice has a constant capacitance, The capacitance of each slice is calculated by assuming the dielectric constant of each slice follows the Brasher-mixing law [101]. The overall capacitance can then be obtained as a series combination of individual thin-slice capacitors, as given in (47),

$$\frac{1}{C_c(t)} = \frac{1}{A\epsilon_0\epsilon_{polymer}} \sum_{n=1}^N \frac{\Delta x}{\exp((\Psi_n)\phi_s \ln \epsilon_{H_2O})}, \quad (47)$$

where N is the number of slices of thickness Δx , ϕ_s is the volume fraction of water occupied at saturation, and Ψ_n is the saturation function of each slice, n , and is obtained from the solution to the diffusion equation, (48),

$$\frac{\partial \Psi(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D_{polymer} \frac{\partial \Psi(x,t)}{\partial x} \right), \quad (48)$$

with an initial condition where there is no water present in the coating, a constant Dirichlet boundary condition at the air—coating interface and a Neumann boundary condition at the coating—metal interface [87]. The diffusivity of the water in the polymer is assumed to change as the mechanism for water uptake changes, with a functional form as given in (49),

$$\begin{aligned} \text{Saturation Region I: } D_{polymer}(t) &= D_I \\ \text{Saturation Region II: } D_{polymer}(t) &= \frac{D_{II}}{\left[\frac{(D_{II} - D_0)}{D_0} * e_0^{-D_{II} \frac{t}{A_0}} \right] + 1}, \end{aligned} \quad (49)$$

where D_I is a constant diffusivity in region I of the saturation curve. D_{II} is the diffusivity in region II of the saturation curve at the end of the mixed water-polymer phase formation and D_0 is the diffusion coefficient at the start of the phase formation process. A_0 is a characteristic area. The expression for the change in diffusivity in (49) is in the form of an autocatalytic logistic function[9]. Solutions of diffusion equation with a diffusivity given by (48) can be obtained numerically. Details of the solution are provided elsewhere[113] with the values for Ψ_n then included in (47) to obtain the capacitance.

Resistance models

The impedance for a resistor, Z_R , is dependent on the conductive geometry as indicated in (50),

$$Z_R = R = \frac{\rho l}{A}. \quad (50)$$

The solution resistance, R_Ω , was estimated from (51), using the experimental cell geometry for the distance between the reference electrode and the surface, l , and the cross-sectional area, A , and the resistivity of the solution, ρ_{Cl^-} ,

$$R_\Omega = \frac{\rho_{Cl^-} l}{A}. \quad (51)$$

For NaCl solutions at a given temperature and $[Cl^-]$ concentration, the resistivity was estimated using a Padé approximant model given in (52)[123],

$$\rho_{[Cl^-]} = \left[\frac{(0.0480 + 0.0034T) + (6.7545 + 0.2392T)[Cl^-]}{1.0 + (0.2065 + 0.0013T)[Cl^-]} \right]^{-1}, \quad (52)$$

where T is the temperature in Celsius and c_{Cl^-} is the chloride concentration in mol/L.

For $T = 25^\circ C$, $[Cl^-] = 0.6 M$, $A = 14.96 cm^2$, and $l = 4 cm$, the value obtained from (52), was 3.92Ω . When compared with the high-frequency impedance data shown in Figure 44a and b for the as-received and pre-treated alloys, 4.07Ω and 4.16Ω , respectively, the calculated value from the model differed from the EIS analysis value by less than 6%.

The model for the resistance of the polymer coatings employed several simplifying assumptions to abstract the complex physical processes occurring within the polymer. For water uptake in the first region of the saturation curve, the resistance of the polymers was assumed to function as two

resistors in series: the wetting or saturated polymer and the dry polymer. This is represented in (53),

$$R_{t,p} = \frac{\rho_e d_e}{A} + \frac{\rho_p d_d}{A}, \quad (53)$$

where d_e corresponded to the depth of water penetration, ρ_e was the resistivity of the electrolyte solution, ρ_p was the resistivity of the polymer, and d_d was the remaining depth of the polymer. The two depths are related to one another by (54),

$$d_d = L - d_e, \quad (54)$$

where L was the coating layer thickness. The resistivity of the epoxy and polyurethane was obtained from the functional fits plotted in **Figure 43a** and **b**, respectively. The models for the resistivity changes as a function of water uptake follow the approach taken by Lutz and co-workers[90] with data from the literature [90,100].

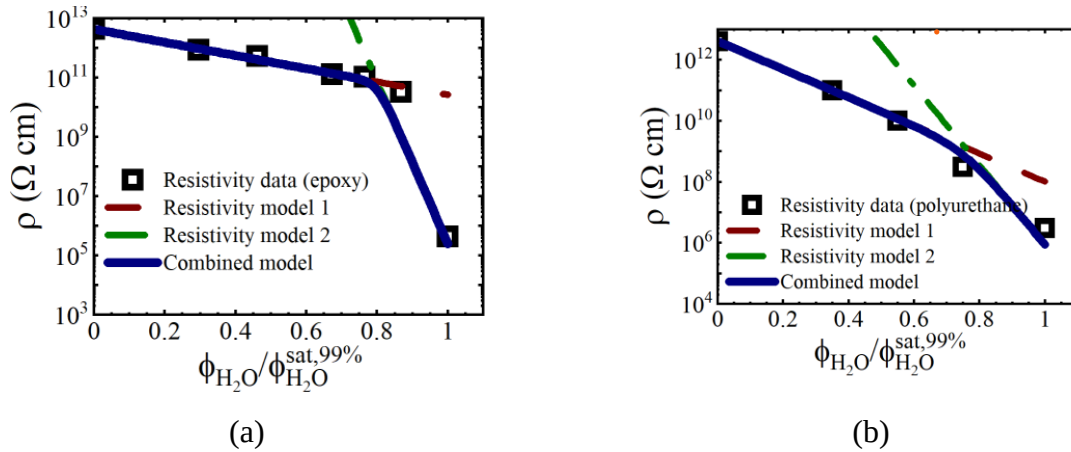


Figure 43. Modeled volume resistivity for (a) epoxy and (b) polyurethane as a function of the ratio of water content.

Both volume resistivity models are exponential decay functions of the form given in (55),

$$\rho = \frac{(c_1 e^{-c_2 \Psi})}{a_1 e^{-a_2 \Psi} + e^{-b \Psi}}, \quad (55)$$

where the saturation function, $\Psi = \phi_{H_2O}/\phi_{H_2O}^{\text{sat},99\%}$ and the parameter values, given in Table 12, were obtained from regression fits to the data points.

Table 12. Parameter values for calculating volume resistivity.

Parameter	Epoxy	Polyurethane
a_1	5.32×10^{-21}	4.08×10^{-7}
a_2	5.10	10.61
b	63.34	30.07
c_1	3.40×10^{45}	4.08×10^{31}
c_2	68.44	40.67

Diffusion impedance models

The resistance values obtained from (55) were assumed to dominate the in-phase impedance response until continuous electrolyte pathways exist between the coating-electrolyte interface and coating-oxide interface. Once these pathways were established, we assumed that the mass transport impedance, arising from the transport of electrolyte species became the principal contributor to the resistance. This impedance is obtained using (56)[124], for the bounded Warburg element,

$$Z_W(\omega) = \frac{\sqrt{2}\sigma}{\sqrt{j\omega}} \tanh\left(\frac{\delta\sqrt{j\omega}}{\sqrt{D}}\right) \quad (56)$$

where σ is the Warburg coefficient. Values for σ were obtained from (57),

$$\sigma = \frac{RT}{\sqrt{2}(zF)^2 A} \left[\frac{1}{c_O^b \sqrt{D_{eff,O}}} + \frac{1}{c_R^b \sqrt{D_{eff,R}}} \right] \quad (57)$$

where c_O indicates the concentration of the oxidized species, c_R is the concentration of the reduced species, $D_{eff,i}$ is the effective diffusivity of the oxidized or reduced species, A is the exposure area, Faraday constant, $F = 96485$ C/mol, z is the ionic charge, and c_i^b represents the bulk solution concentration.

If we assume a redox reaction at the primer-pretreatment interface is the principal contribution to the Warburg coefficient then, in this case, the likely redox reactions are either oxygen reduction or water reduction. In the case of oxygen reduction, dissolved oxygen needs to diffuse from the bulk electrolyte, through the coating, to the oxide-coating interface, where it is reduced to form hydroxide ions. For water reduction, the water molecules participating in the water uptake process are reduced at the oxide-coating interface. While the second mechanism provides a simpler explanation, our data is insufficient to distinguish which redox reaction is occurring.

This approach differs slightly from the analysis performed by Skale and colleagues [125]. In this earlier work, a Dirichlet boundary condition was assumed at the coating-substrate interface, so the diffusion impedance was modeled as a semi-infinite Warburg element. However, to solve (48), our approach assumed a Neumann boundary condition at the oxide-coating interface, which results in a bounded Warburg element for the diffusion impedance. This is similar to the equivalent circuit models developed by Volmajer and colleagues[126] for the analysis of EIS data obtained during

curing epoxy coatings. In our case, the presence of the two different organic polymers that make up the coating system also required the addition of a second bounded Warburg element circuit.

The average diffusivity of the electrolyte constituents inside the coating is assumed to differ from the bulk diffusivity in the electrolyte. In our case, we assumed the transport of the electrolyte components occurred only along the polymer chains. Thus, the complex shapes of filler and pigment particles, from the cross-section of the coating system shown in Figure 46, formed a solid matrix and the polymer regions were assumed to consist of a mix of solid and void space. We used the continuum approximation given in (58)[127] to relate the notional porosity of the polymer film to a Darcy-equivalent, D_{eff} [128],

$$D_{eff} = \frac{\epsilon D_b}{\tau} \quad (58)$$

where ϵ is a measure of the porosity, D_b is the bulk diffusivity value, and, from the Bruggeman relation[129], $\tau = 1.0/\sqrt{\epsilon}$. This empirical approach does neglect interactions between the electrolyte ions and the polymer structure[130]; however, it simplifies the effective diffusivity model.

Derivation of conductivity matrices for equivalent circuit models

The derivation of the impedance matrix for the modified undamaged coating equivalent circuit model starts with Kirchhoff's current law in (59) for each branch of the circuit,

$$\Sigma i_k = 0, \quad (59)$$

$$i_3 = i_1 + i_2, \quad (60)$$

where, i_3 is the current flowing through R_Ω , i_2 is the current flowing through the CPE, and i_1 is the current flowing through R_1 .

As in most other electrical circuit analysis, the fundamental building block for determining the impedance of a circuit is Ohm's Law. The frequency-dependent impedance of a circuit can be expressed using (61)[10],

$$e_0 \sin \omega t = (i_0 \sin \omega t + \phi)Z(\omega) \quad (61)$$

where $\omega = 2\pi f$, f is the oscillation frequency, e_0 is the amplitude of the sinusoidal potential oscillation, i_0 is the amplitude of the current response, and ϕ is the phase shift in the current.

Using (61), expressions for the sum of the voltage drops through both pathways in the circuit are given in (62),

$$\begin{aligned} v_1 &= i_3 R_\Omega + i_1 R_1, \\ v_2 &= i_3 R_\Omega + i_2 Z_{cpe}. \end{aligned} \quad (62)$$

Then using (60) to substitute for i_3 and collecting terms results in (63),

$$\begin{aligned} v_1 &= i_1 (R_\Omega + R_1) + i_2 R_\Omega, \\ v_2 &= i_1 R_\Omega + i_2 (R_\Omega + Z_{cpe}). \end{aligned} \quad (63)$$

Rewriting the system of equations from (63) in matrix form results in (64),

$$\begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} i_1 \\ i_2 \end{bmatrix} \begin{bmatrix} R_\Omega + R_1 & R_\Omega \\ R_\Omega & R_\Omega + Z_{cpe} \end{bmatrix}, \quad (64)$$

where the impedance matrix is given by (65),

$$\mathbf{Z} = \begin{bmatrix} R_\Omega + R_1 & R_\Omega \\ R_\Omega & R_\Omega + Z_{cpe} \end{bmatrix}. \quad (65)$$

The circuit models shown in Figure 42 can be divided into three categories: 2, 3, and 4 pathway models. The circuits from Figure 42a-d are 2 pathway models while the circuits from Figure 42e-g are 3 pathway models, and the circuit in Figure 42h is a 4 pathway model. The number of pathways indicates the number of rows and columns in the conductivity matrices that are constructed for the impedance calculations and the number of rows and columns in the impedance matrix in (65) are consistent with a 2-pathway equivalent circuit.

The modified Randles circuit is also a 2-pathway equivalent circuit. The impedance matrix is given in (66) and was derived using a similar procedure as shown previously.

$$\mathbf{Z} = \begin{bmatrix} R_\Omega + R_1 + Z_W & R_\Omega \\ R_\Omega & R_\Omega + Z_{cpe} \end{bmatrix} \quad (66)$$

The extended modified REAP equivalent circuit model, introduced in this work, and shown in **Figure 42h**, is a 4-pathway equivalent circuit. This circuit was derived from the previous equivalent circuits that have been used for analyzing EIS data from coating systems. This circuit is intended to account for effects from non-ideal capacitive behavior and transport of electrolyte species in different coating layers as well as electrochemical processes occurring at the coating-substrate interface. The impedance matrix is given in (67).

$$\mathbf{Z} = \begin{bmatrix} Z_{00} & Z_{01} & Z_{02} & Z_{03} \\ Z_{10} & Z_{11} & Z_{12} & Z_{13} \\ Z_{20} & Z_{21} & Z_{22} & Z_{23} \\ Z_{30} & Z_{31} & Z_{32} & Z_{33} \end{bmatrix}$$

$$\begin{aligned} Z_{00} &= R_\Omega + R_t + Z_W^t + R_p + Z_W^p + R_{pre} \\ Z_{11} &= R_\Omega + R_t + Z_W^t + R_p + Z_W^p + Z_{cpe}^{pre} \\ Z_{22} &= R_\Omega + R_t + Z_W^t + Z_{cpe}^p \\ Z_{33} &= R_\Omega + Z_{cpe}^t \\ Z_{01} &= Z_{10} = R_\Omega + R_t + Z_W^t + R_p + Z_W^p \\ Z_{02} &= Z_{20} = Z_{21} = Z_{12} = R_\Omega + R_t + Z_W^t \\ Z_{03} &= Z_{30} = Z_{13} = Z_{31} = Z_{23} = Z_{32} = R_\Omega \end{aligned} \quad (67)$$

Algorithm for determining the frequency-dependent impedance of an equivalent circuit model.
To determine the impedance at each frequency, the following algorithm was employed:

1. The currents flowing in each path of the circuit were calculated from (68),

$$\mathbf{i} = \mathbf{Z}^{-1}\mathbf{v}. \quad (68)$$

2. The solution to (68) was obtained using an LU decomposition algorithm from the `mldivide` function in MATLAB (R2023a, MathWorks) because the conductivity matrices are square matrices with only a few elements.
3. The M individual current components of the $\mathbf{i}$ vector from (68) were then summed to obtain the total current, i_t , as shown in (69),

$$i_t = \sum_{m=0}^{M-1} i_m. \quad (69)$$

4. Regardless of the path through the circuit, the voltage drop across each path must be the same and, for convenience, we assumed $v_m = e_0 = 1.0$. The complex impedance at each frequency was then obtained from (70),

$$Z(\omega) = \frac{e_0}{i_t} = x + jy, \quad (70)$$

where x and y are the calculated real and imaginary components of the impedance, respectively, and $j = \sqrt{-1}$.

Procedure for fitting model impedance to EIS data

Fits to the experimental data were obtained by a simplex regression algorithm[81,83] coded in MATLAB (R2023a, MathWorks). The regression algorithm minimized the value of the mean squared error (MSE) between model results and experimental data. The error calculation was dependent on both the number of data points measured and the number of parameters, as given in (71)[82],

$$MSE = \frac{\left[\sum_{i=1}^N \left(\left(\frac{u_i - x_i}{x_i} \right)^2 + \left(\frac{v_i - y_i}{y_i} \right)^2 \right) \right]}{N-k}, \quad (71)$$

where $u_i + jv_i$ represents one of N complex data points, $x_i + jy_i$ represents a complex point obtained from the model, and k represents the number of parameters in the model.

The regression procedure was executed in the following manner:

1. Bound the upper and lower fitting parameter values to prevent non-physical results, such as negative resistances.
2. Use the simplex method to perform the regression of the equivalent circuit model to the data.
 - Generate a set of 1000 vertices in the k parameter space.

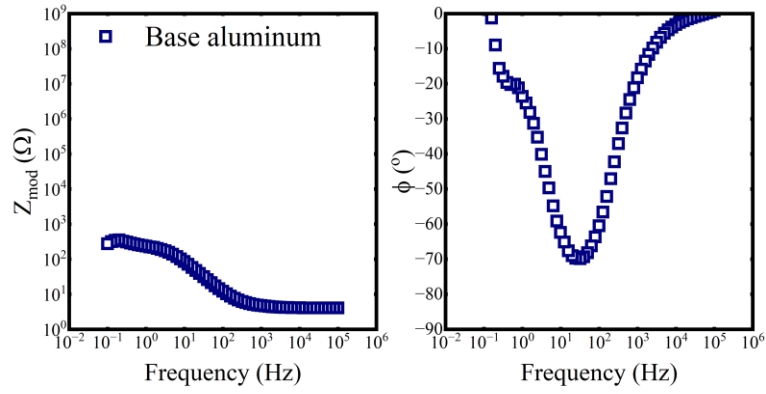
- The first vertex uses the initial estimate parameter set.
 - The second vertex consists of the lower bound of parameter values.
 - The last vertex consists of the upper bound of parameter values.
 - The remaining vertices consist of randomly generated values spanning the range between the upper and lower bounds[82].
3. Calculate the MSE for each vertex.
 4. Create the first simplex from the $k+1$ vertices that have the lowest MSE.
 5. Start the regression and iterate using reflection, contraction, or extension on the vertex with the highest MSE in the simplex to keep or reject that vertex. This forms a new simplex.
 6. Continue iterating until the convergence criterion is satisfied or the number of iterations exceeds the maximum allowed.
 7. Repeat the regression 32 times. Because of the randomly formed middle vertices, this can result in different vertices in the initial simplex, which can result in a slightly different convergence. Of the 32 outcomes, select the parameter values from the simplex that resulted in the lowest MSE.

Results

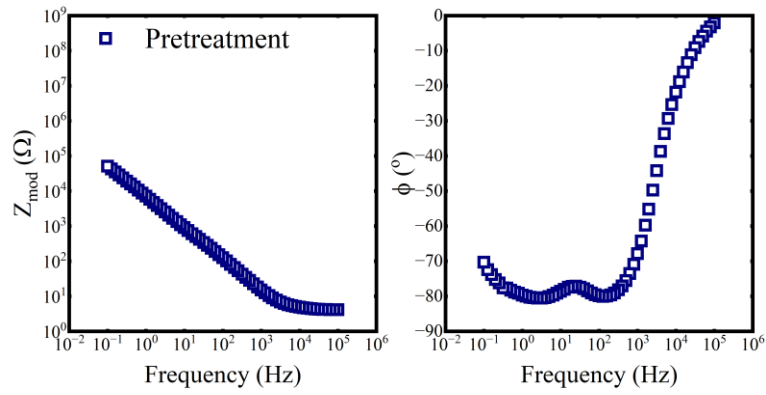
EIS measurements of the initial coating layers

EIS measurements were made on as-received aluminum alloy panels, pretreated panels, primer-only panels, and coating system panels prior to immersion. Representative examples of these results are plotted on Bode diagrams, with the logarithm of the impedance modulus, Z_{mod} , and phase angle, ϕ , as functions of the logarithm of the frequency in Figure 44. Nyquist plots are also frequently used for representing EIS data for many biological systems, especially when employing graphical analysis methods[131–133]. However, in the case of commercial coating systems, with impedance values in the $M\Omega$ to $G\Omega$ range, high-frequency features of the data are obscured because Nyquist plots use linear scales.

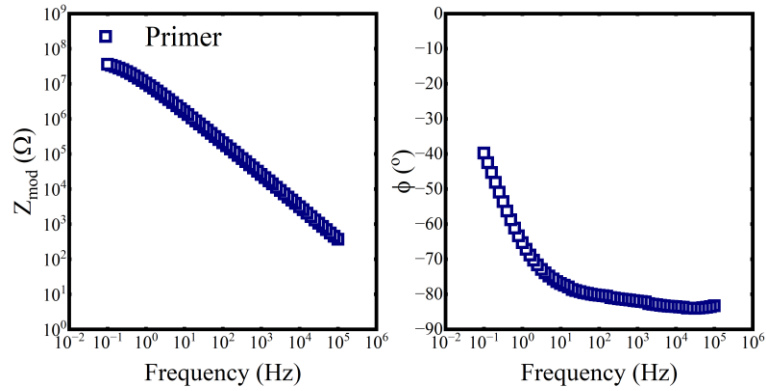
As-received



Pretreatment



Primer plus pretreatment



Topcoat, primer, plus pretreatment

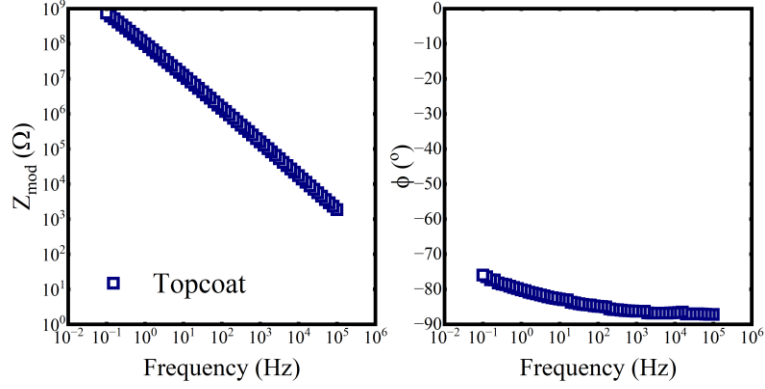
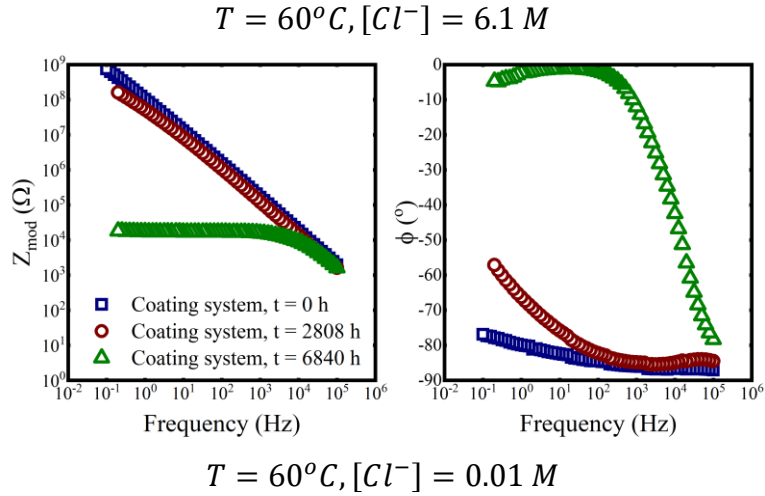
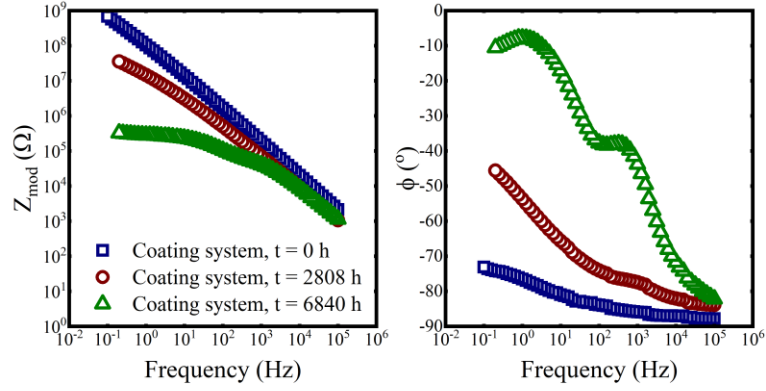


Figure 44. Bode representations of the EIS data, magnitude (left) and phase (right), from: (a) UNS A92024 coupon in the as-received state. (b) UNS A92024 coupon that received a surface anodization pretreatment. (c) Pre-treated UNS A92024 coupon coated with an epoxy primer and allowed to cure for 14 days. (d) Pre-treated UNS A92024 coupon coated with an epoxy primer and polyurethane topcoat and allowed to cure for 14 days. All EIS measurements were made in 0.6 M NaCl and at $T = 25^{\circ}\text{C}$.

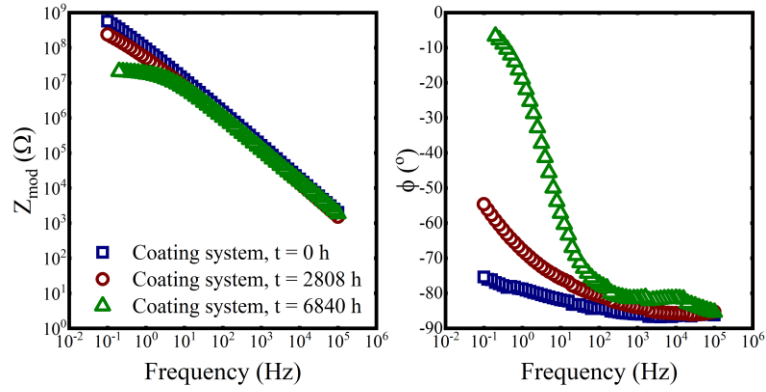
EIS measurements of the immersed coatings

EIS measurements were made at the start of the exposure, $t_{\text{immersion}} = 0$ h; approximately halfway through at $t_{\text{immersion}} = 2808$ h; and at the end of the exposure period, $t_{\text{immersion}} = 6840$ h. Representative examples of the data for all immersion conditions are shown in Figure 45. The EIS data is plotted using the Bode representation with Z_{mod} and the phase angle plotted versus the oscillation frequency.

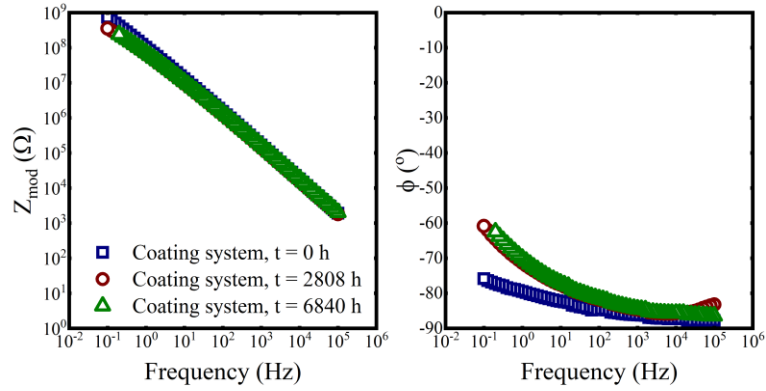




$T = 25^\circ C, [Cl^-] = 3.2 M$



$T = 5^\circ C, [Cl^-] = 6.1 M$



$T = 5^\circ C, [Cl^-] = 0.01 M$

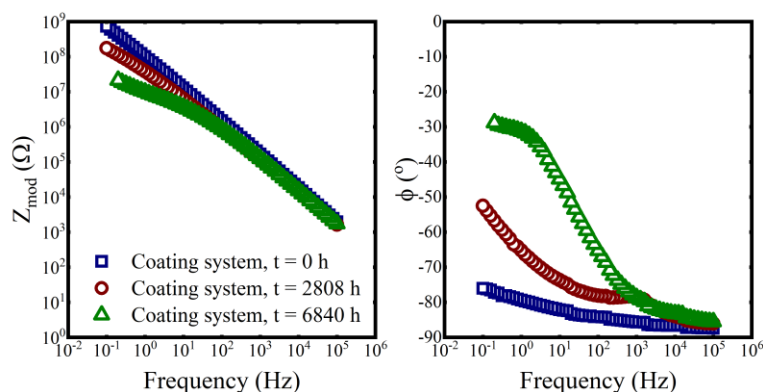


Figure 45. Bode representations of EIS data, magnitude (left) and phase (right), from the coating system. Immersion times are in hours. Results from 1 of 3 replicates are depicted. (a) $T = 60^{\circ}\text{C}$, $[\text{Cl}^{-}] = 6.1\text{ M}$. (b) $T = 60^{\circ}\text{C}$, $[\text{Cl}^{-}] = 0.01\text{ M}$. (c) $T = 25^{\circ}\text{C}$, $[\text{Cl}^{-}] = 3.2\text{ M}$. (d) $T = 5^{\circ}\text{C}$, $[\text{Cl}^{-}] = 6.1\text{ M}$. (e) $T = 5^{\circ}\text{C}$, $[\text{Cl}^{-}] = 0.01\text{ M}$.

The EIS data was analyzed by fitting to the various equivalent circuit models found in Figure 1 using the EIS Analysis software suite written in MATLAB (Version R2023a, MathWorks). The parameters from the models were then correlated with the physical and chemical processes occurring in the coating systems.

The stationary criterion for EIS analysis was met on the coated coupons with the $\pm 10\text{ mV}_{\text{RMS}}$ perturbation. For these measurements, the linearity of the coating systems' responses to the 28-mV peak-to-peak potential perturbation was confirmed using the Kramers-Kronig transform utility provided with the analysis software (Echem Analyst; Gamry) for the potentiostat.

SEM analysis

Figure 46 shows a cross-section of the coating system with the individual layers identified. The EDS line scan shows the relative concentrations of the various elements and provides an indication of the fillers and additives in each coating layer. The chromate inhibitor additives are found only in the primer. In this sample, the polyurethane topcoat had an average thickness of $41.9 \pm 3.0\text{ }\mu\text{m}$ while the epoxy primer had an average thickness of $19.9 \pm 3.7\text{ }\mu\text{m}$. The pretreatment layer had an average thickness of $7.9 \pm 1.6\text{ }\mu\text{m}$. The complex structures of the individual coating layers justified the representation of the diffusivities as effective diffusion coefficients, dependent on the tortuosity and porosity of the polymers.

Attempts to determine the sodium and chloride concentrations between the two layers, and among samples immersed in the different solutions, were inconclusive. The line scans of these elements did not show clear trends, which is likely due to the depth of the interaction volume from the electron beam.

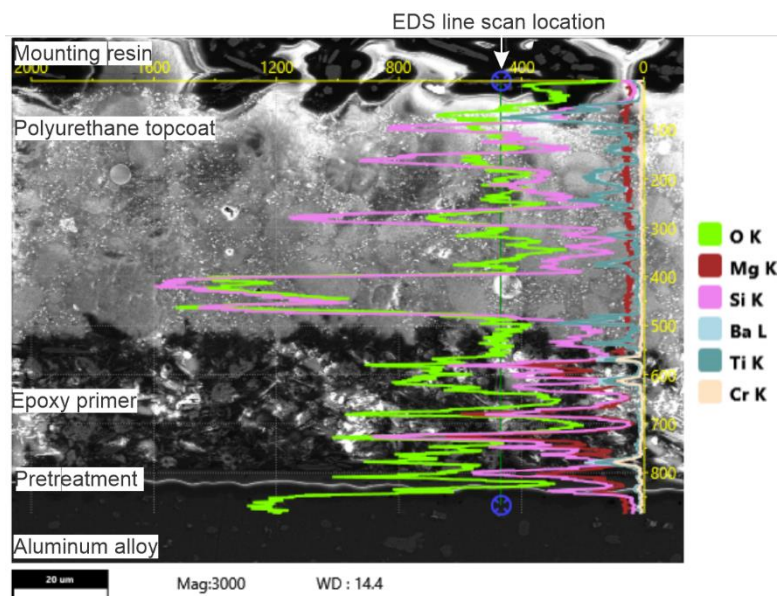


Figure 46. Cross-section of the organic coating system with individual layers identified. The EDS line scan, with endpoints identified with circles, through-thickness of the coating system suggests the complex structure of the coating with various additives and fillers, to include talc, silicon dioxide, titanium dioxide, and barium chromate. The horizontal axis of the composition plot is in units of counts and the vertical axis is in units of scan points, which were spaced at $0.1\ \mu\text{m}$ intervals. Note, however, that the counts for each element at each point in the scan are the results of averaging over the electron interaction volume of the coating and substrate.

3.4 Fits using the modified undamaged coating circuit

The modified undamaged coating circuit model replaced the capacitor in the single RC circuit of the undamaged coatings model with a constant phase element. This circuit, from Figure 42b, was fit to the as-received oxide data, shown in Figure 44a. The fit values and MSE are given in Table 13. Table 13 also shows values obtained from fitting the data using a commercial software package (Echem Analyst Ver. 7, Gamry) and the included CPE equivalent circuit model. MSE values are included for comparison because that is the statistic the commercial software used to determine goodness of fit. The predicted impedance values for the modulus and phase for the two models are plotted in Figure 47 along with the measured data.

Table 13. Equivalent circuit parameter values for the as-received oxide at $T = 25^\circ\text{C}$ and $[\text{Cl}^-] = 0.6\text{ M}$.

Parameter	Equivalent circuit model used for the analysis	
	Modified undamaged coating	CPE model – commercial software
$R_1 (\Omega \cdot \text{cm}^2)$	3875	4338
$\xi \left(\frac{\mu\text{F}}{\text{cm}^2} \cdot \text{s}^{\alpha-1} \right)$	11.6	19.5
α	0.990	0.891
$R_\Omega (\Omega)$	3.92	4.01
MSE	0.362	0.861

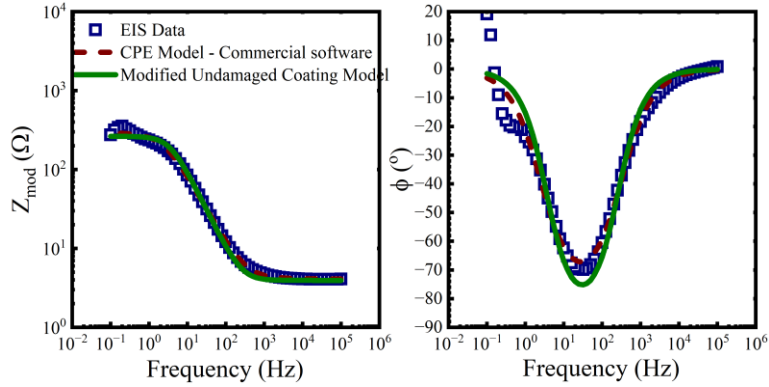


Figure 47. Bode representations of EIS data, magnitude (left) and phase (right), and the predicted responses from the equivalent circuits' fits for the as-received oxide.

Comparing the circuit element values between the two models in Table 13 and visually in Figure 47 suggests that both approaches for modeling the impedance of the equivalent circuit result in similar outcomes.

Fits using the modified Randles circuit

While the modified undamaged coating circuit model was effective at fitting the EIS data from the as-received AA2024, it resulted in poor fits for the other baseline EIS data shown in Figure 44b-d. For these fits, we used the modified Randles circuit model. Parameter values for this circuit were obtained by using the impedance matrix in (66) and the fitting procedure to analyze the EIS data from the pretreated layer, the primer coating, and the topcoat.

The fit values for the circuit parameters are provided in. also shows values obtained from fits using a commercial software package (Echem Analyst Ver. 7, Gamry) and the included CPE with diffusion circuit model. Comparisons for the predicted impedance values for the modified Randles model and CPE with diffusion equivalent circuit model are plotted in Figure 48.

Again, comparing the circuit parameter values between the two modeling approaches in suggests that both approaches arrive at similar outcomes. However, there is a shortcoming with both

approaches. The upper and lower bounds on the parameter values used in the simplex regression algorithm were arbitrarily selected rather than arising from our understanding of the physical and chemical processes at work in the coating system.

Table 14. Equivalent circuit parameter values for the coating layers at $T = 25^\circ\text{C}$ and $[\text{Cl}^-] = 0.6\text{ M}$.

Equivalent circuit model used for the analysis						
	<i>Modified Randles circuit</i>			<i>CPE with diffusion commercial software</i>		
Material	Oxide	Primer	Topcoat	Oxide	Primer	Topcoat
$R_1\text{ (M}\Omega\text{)}$	0.0056	230	0.01	0.0042	240	0.04
$\xi\text{ (nF} \cdot s^{\alpha-1}\text{)}$	25000	4.0	1.0	24000	7.7	1.2
α	0.91	0.99	0.97	0.91	0.95	0.96
$\sigma\left(\frac{\text{M}\Omega}{\sqrt{s}}\right)$	0.16	0.01	900	0.23	0.004	2180
MSE	0.02	0.25	0.04	0.001	0.16	0.001

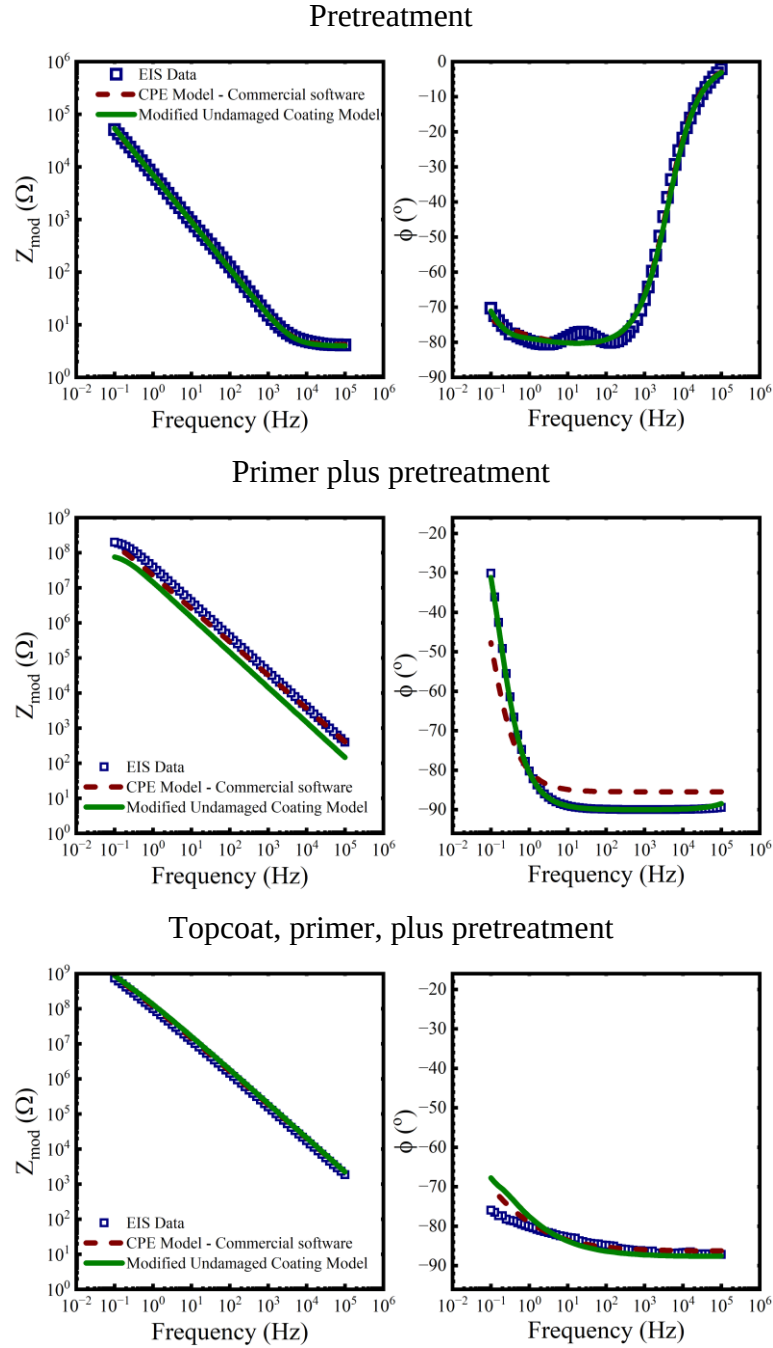


Figure 48. Bode representations of EIS data, magnitude (left) and phase (right), and the predicted responses from the equivalent circuits' fits for (a) the pretreated panel, (b) the primer, (c) the coating system.

Fits using the extended modified REAP circuit

The expressions in (45) (58)- allowed us to estimate initial values for some of the circuit elements from these physics-based models. Thus, the first step in the nonlinear regression procedure was modified to the following:

- Create an initial estimate of the equivalent circuit parameters from the physics-based models. For the baseline measurements of the as-received and pretreated samples, the charge-transfer resistance was treated as a fit parameter. These values became the initial guesses for those parameters in this procedure.
- Solve the diffusion equation for water saturation for the given immersion time with diffusion coefficients obtained from (49).
- Use (47) and (55) to estimate the coating layers' capacitance and resistance, respectively.
- Estimate the impedance of the Warburg elements from (56). We assumed the dissolved oxygen diffusivity and concentration were functions of temperature and chloride concentration and allowed the diffusion length to vary as a fit parameter.

Figure 49 shows an example comparison between the impedance obtained from the physics-based models' initial parameter estimates and the impedance after the regression.

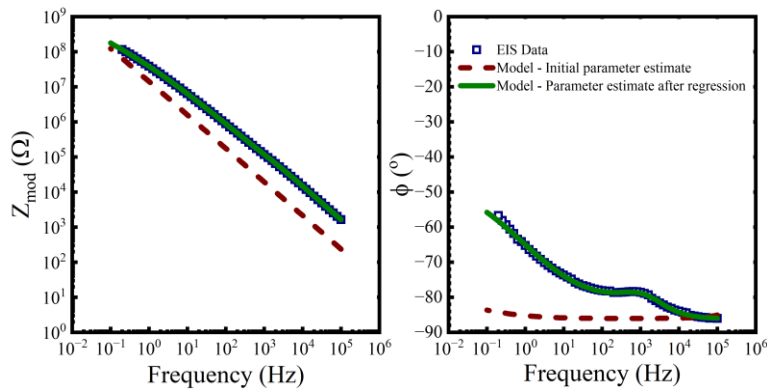
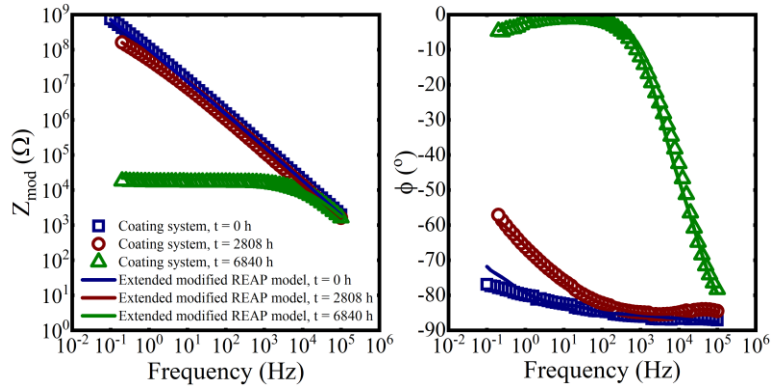


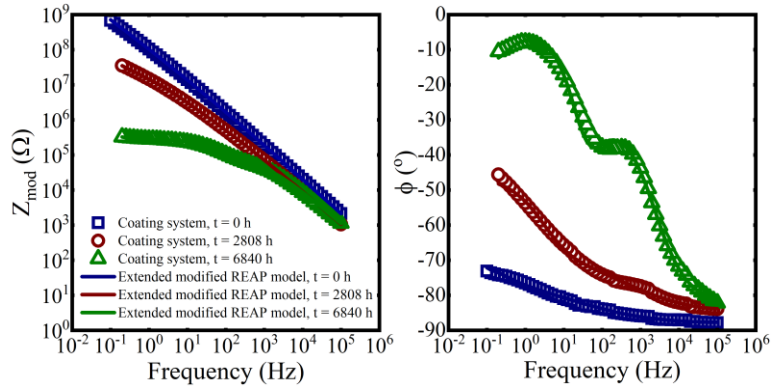
Figure 49. Bode representations of EIS data, magnitude (left) and phase (right) for a coated panel immersed in 0.01 M NaCl at 5°C for 2808 h, and the predicted responses from the initial parameter values and the converged parameter values.

The results of fits using the extended modified REAP model for all immersion conditions are shown in Figure 50.

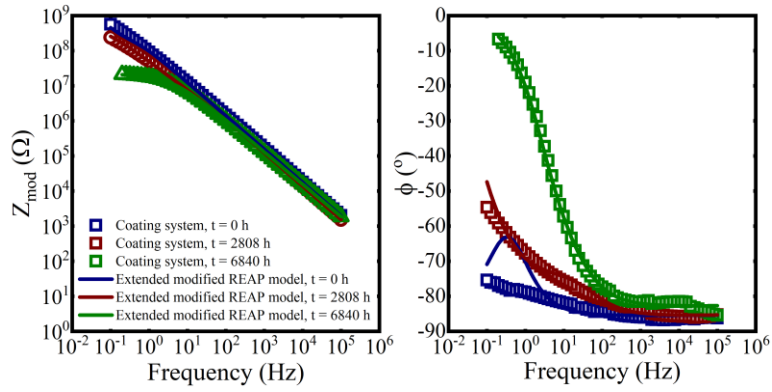
$T = 60^{\circ}C, [Cl^{-}] = 6.1 M$



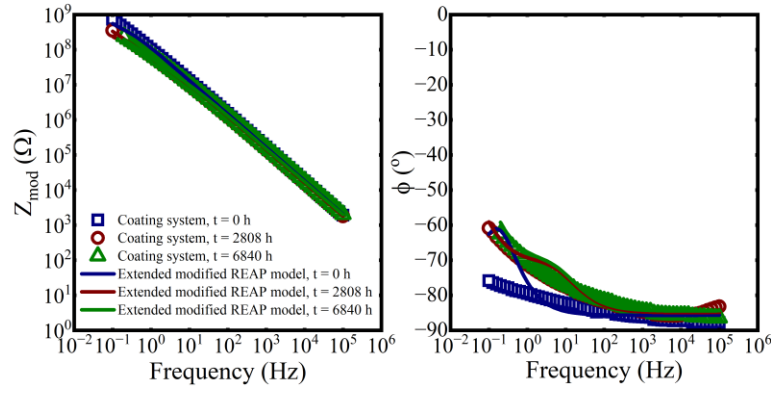
$T = 60^{\circ}C, [Cl^{-}] = 0.01 M$



$T = 25^{\circ}C, [Cl^{-}] = 3.2 M$



$T = 5^{\circ}C, [Cl^{-}] = 6.1 M$



$$T = 5^{\circ}\text{C}, [\text{Cl}^{-}] = 0.01 \text{ M}$$

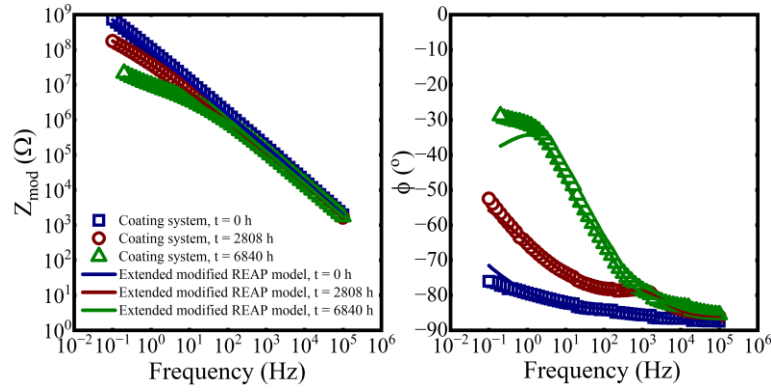


Figure 50. Extended modified REAP equivalent circuit fits to EIS data. (a) $T = 60^{\circ}\text{C}$, $[\text{Cl}^{-}] = 6.1 \text{ M}$. (b) $T = 60^{\circ}\text{C}$, $[\text{Cl}^{-}] = 0.01 \text{ M}$. (c) $T = 25^{\circ}\text{C}$, $[\text{Cl}^{-}] = 3.2 \text{ M}$. (d) $T = 5^{\circ}\text{C}$, $[\text{Cl}^{-}] = 6.1 \text{ M}$. (e) $T = 5^{\circ}\text{C}$, $[\text{Cl}^{-}] = 0.01 \text{ M}$.

An example of the parameter values for the coating system immersed in 3.2 M NaCl at 25°C for 2808 h is shown in Table 15.

Table 15. Equivalent circuit parameter values for the coating layers at $T = 25^\circ\text{C}$ and $[Cl^-] = 3.2\text{ M}$.

Layer	Parameter	Value
Electrolyte	$R_\Omega (\Omega)$	3.93
Topcoat	$R_T (\text{k}\Omega \cdot \text{cm}^2)$	16.0
	$\xi^T \left(\frac{pF}{\text{cm}^2} \cdot s^{\alpha-1} \right)$	66.8
	α_T	0.99
	$\sigma_T \left(\frac{\Omega \cdot \text{cm}^2}{\sqrt{s}} \right)$	212.4
	$D_{eff}^T \left(\frac{\text{m}^2}{s} \right)$	4.93×10^{-13}
Primer	$R_P (\text{M}\Omega \cdot \text{cm}^2)$	28.9
	$\xi^P \left(\frac{pF}{\text{cm}^2} \cdot s^{\alpha-1} \right)$	90.9
	α_P	0.85
	$\sigma_P \left(\frac{\text{G}\Omega \cdot \text{cm}^2}{\sqrt{s}} \right)$	3.0
	$D_{eff}^P \left(\frac{\text{m}^2}{s} \right)$	3.08×10^{-15}
Pretreatment	$R_{pre} (\Omega \cdot \text{cm}^2)$	149.6
	$\xi^{DL} \left(\frac{pF}{\text{cm}^2} \cdot s^{\alpha-1} \right)$	304
	α_{DL}	0.90
	MSE	0.006

As expected, the CPE parameter values for both coating layers are consistent with water uptake by the polymers. The water uptake increases the dielectric constants for both materials above their dry values, which results in a higher capacitance.

The R_T and R_P values, approximating the pore resistances of the coating suggest that continuous electrolyte paths exist from the solution to the coating-oxide interface. However, the bounded

Warburg coefficient value, σ_p , for the epoxy primer suggests that the primer is still providing good barrier protection for the substrate.

The effective diffusion coefficient listed in Table 15 for the topcoat is consistent with literature values of the diffusion coefficient for water molecules in a polyurethane ($5.0 \times 10^{-13} \text{ m}^2/\text{s}$) [89]. This value, in combination with the Warburg coefficients, suggests relatively easy transport for all electrolyte species through the polyurethane topcoat at this point in the immersion, as diffusion of O_2 and H_2O molecules is higher than the other species. In contrast, D_{eff}^P in the primer layer is much lower than the expected water diffusion coefficient in epoxy ($3.5 \times 10^{-13} \text{ m}^2/\text{s}$) [90]. Instead, D_{eff}^P is more consistent with Na^+ or Cl^- ion transport ($3.1 \times 10^{-15}, 4.7 \times 10^{-16} \text{ m}^2/\text{s}$), respectively [109]. This suggests that, for the epoxy primer, electrolyte ion transport is the principal charge carrier.

While the charge-transfer resistance at the oxide-coating interface is low, the CPE coefficient and exponent indicate the anodized pretreatment is still stable. This is consistent with the fit results for the diffusion coefficients. It has been suggested that Na^+ ion transport is the principal ionic charge carrier in coatings, and it is the chief contributor to charge balance at cathodic sites at the coating-substrate interface[134]. It is likely that Na^+ and Cl^- ions are still migrating through the coating and have not reached sufficient concentration to disrupt the thickened oxide.

Discussion

Justification for using the extended modified REAP model.

Each equivalent circuit model from Figure 42 was fit to an experimental data set obtained from a coating system immersed in 0.01 M NaCl at 60°C for 2808 h. This coating system exhibited a large change in Z_{mod} over the duration of the immersion, as shown in Figure 50b, so it was deemed to be a good candidate by which to evaluate the candidate equivalent circuit models. The models were regressed to the data set using the simplex regression algorithm using similar initial guesses. The outcomes of the fits are shown in Figure 51.

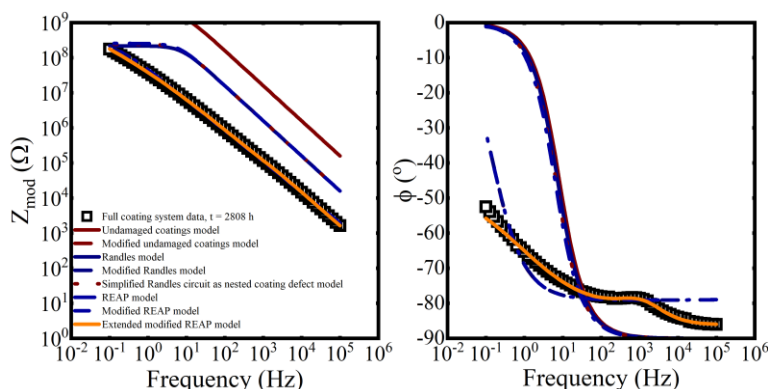


Figure 51. Bode representations of EIS data, magnitude (left) and phase (right), from a coating system immersed in 0.01 M NaCl at $T = 60^\circ\text{C}$ for 2808 h. Fits were obtained using different equivalent circuit models.

The calculated MSEs for the fits in Figure 51, along with the number of independent parameters, k , are shown in Table 16. The last circuit listed corresponds to 29 Voigt elements, a resistor and capacitor in parallel with one another. Because there are 2 parameters to a Voigt element, a resistance and capacitance, this represents the maximum number of circuit elements that could be fit to the data. We assume this also sets the minimum MSE value.

Table 16. MSE and AICc values for the various equivalent circuits fit to the same data.

Circuit Name	MSE	k	AICc
Undamaged coatings model	3.82	2	589.85
Modified undamaged coatings model	0.13	3	173.79
Randles model	130.64	5	1021.75
Modified Randles model	0.13	6	181.11
Simplified Randles circuit as nested coating defect model	140.66	4	1030.36
REAP model	149.24	5	1037.99
Modified REAP model	0.13	6	181.39
Extended modified REAP model	0.005	16	-216.79
Voigt elements model	6.0×10^{-6}	58	6578.69

The MSE results for the circuits based around the undamaged coating model have similar values and are quite high, indicating that the fits are poor. This is due to two reasons:

1. The inability of the capacitance to capture deviations from -1 in $\Delta \log Z_{mod} / \Delta \log f$ that arise because the coatings and oxide functioned as imperfect capacitors.
2. The lack of a diffusion-influenced impedance element in these models.

In purely numerical terms, the presence of CPE and Warburg elements increases the number of parameters available for the regression routine, thereby reducing the MSE. Pursuing the lowest MSE value, however, illustrated by an equivalent circuit consisting entirely of Voigt elements, provides little physical insight into the state of the coating. So, rather than basing model selection for fitting the coating data on the MSE, we used the corrected Akaike information criterion[135] (AICc) as the statistic for this selection. The corrected AIC helps to account for model overfitting due to small sample sizes. The AICc can be calculated by (72)[136],

$$AICc = k + (N(2\pi * MSE) + 1) + \left(\frac{2k^2 + 2k}{k - N - 1} \right). \quad (72)$$

In (72), as the number of data points, $N \rightarrow \infty$, $AICc \rightarrow 0$ and the expression reverts to the classic AIC statistic.

The AICc values for the equivalent circuit fits are given in the last column of Table 16. Like the MSE, lower values are better in terms of evaluating the model. The corrected AIC statistic severely penalizes the Voigt elements circuit but suggests the extended modified REAP circuit does not overfit the data while still providing a low MSE.

Imposing physical constraints in the regression algorithm.

The regression algorithm outlined in section 4.2.3 used physics-based equations to obtain starting values for the fits but the constraints on the parameter values were minimal. Specifically, negative parameter values were rejected, and resistance values were capped at $10^{10} \Omega$. However, from a physical standpoint, including circuit elements such as the CPE and Warburg that can represent more complex behavior in the coating than resistors and capacitors, suggests that additional constraints can be obtained from our understanding of coating behavior. That is, we can impose the following physical constraints on the system:

- Coating layer resistance, while initially high, is expected to drop rapidly during immersion because of water uptake, as shown in (55).
- Inversely, coating capacitance, while initially low, will increase as a function of water saturation, as suggested by (47).
- The Warburg elements will impact the impedance once a continuous diffusion path exists for the reactive species in the solution.

These constraints result in the fits shown in Figure 52 and the time-series values shown in Table 17.

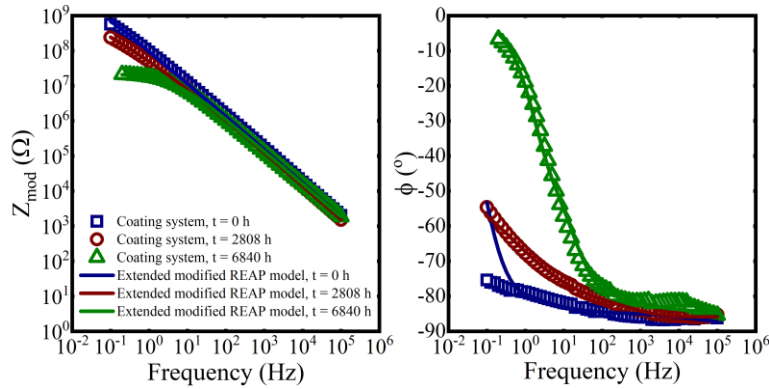


Figure 52. Bode representations of EIS data, magnitude (left) and phase (right), from a coating system immersed in 3.2 M NaCl at $T = 25^\circ\text{C}$. The fits were obtained with physics-based constraints.

Table 17. Parameter values from fits to the EIS data using physics-based constraints.

Time (h)	$R_{coating} (\text{M}\Omega \cdot \text{cm}^2)$	α_T	α_P	$\sigma_{coating} \left(\frac{\text{G}\Omega \cdot \text{cm}^2}{\sqrt{s}} \right)$
0	507	0.99	0.90	-
2808	28.7	0.98	0.85	3.22
6840	3.0×10^{-3}	0.97	0.85	2.47

The fits using the physics-based constraints are roughly 10% worse in their MSE values versus the base constraints. However, the change in parameter values over exposure time is more consistent with expectations. That is, we expect the pore resistance of the coating, $R_{coating} = R_{topcoat} + R_{primer}$, to decrease and the coating layers, in the form of CPE exponent values, to act as less-ideal capacitors but with increasing dielectric constants, in response to water uptake. Likewise, as

the coating becomes saturated, the diffusion length, δ , for reactive species such as dissolved oxygen is expected to decrease.

The values shown in Table 17 are consistent with these expectations, whereas, in the case of fitting with the base constraints, the changes in parameter values over time were not consistent. Thus, trends in the behavior of the coating because of immersion are harder to detect. The inconsistency in the parameter values likely occurs because different combinations of parameters values can result in similar fits and, without the physics-based constraints, the simplex algorithm can't reject non-physical outcomes. These differences in parameter values resulting from the different fitting constraints does argue for using physics-based models for the parameter values when possible.

Summary and Conclusions

The new extended, modified REAP equivalent circuit was derived from previous equivalent circuits that have long been used for analyzing EIS data from coating systems. The new circuit accounted for effects from non-ideal capacitive behavior and transport of electrolyte species. It was demonstrated to provide more useful fits to EIS data obtained from coated panels immersed in NaCl solutions at different concentrations and different temperatures than the earlier models.

The AICc statistic was used to evaluate the fit results from several equivalent circuits to an example EIS data set. The extended modified REAP circuit had the lowest AICc score, which indicated that it provided the best fit, in a regression sense, with little over-fitting. This result justified the use of the extended modified REAP circuit to analyze the EIS data from the coatings immersed in NaCl solutions.

Physics-based models for water uptake, coating resistance, and diffusion resistance were introduced and used to provide initial parameter estimates based on time of exposure to the immersion conditions. In addition, physics-based upper and lower bounds to the circuit parameters were introduced and, while they slightly increased the MSE of the fit, the evolution of the circuit parameters was more consistent with expectations on the behavior of the coating to immersion.

Lastly, a numerical method for calculating the equivalent circuit impedance using matrix algebra was derived and incorporated into a simplex regression algorithm coded in MATLAB. Results from these calculations were compared with outcomes obtained from a commercial EIS analysis software. The new method was generally as accurate as the commercial software.

The principal benefits of these methods include: 1) the capability to incorporate physics-based models into the equivalent circuit analysis technique for analyzing EIS data, which is very difficult to do with commercial software, and 2) improving our understanding how physical processes occurring during environmental exposures of coating systems change the properties of coatings. This last benefit is necessary to improve our understanding of the state of a coating system. While these results were obtained for coating systems exposed to immersion; in principle, we expect these results can be extended to coating systems on other structures exposed to atmospheric conditions, so that they can be evaluated *in-situ* to determine how well they are maintaining corrosion protection.

8. TENSILE PROPERTIES OF AIRCRAFT COATING SYSTEMS AND APPLIED STRAIN MODELING

Introduction

Aircraft skins generally consist of aluminum alloys sheets or extrusions fastened using steel fasteners to other aluminum alloy structures, such as spar, ribs, or stiffeners. Countersunk fasteners are used on surfaces exposed to airflow, *e.g.*, fastening wing skins to the underlying structure. Localized attack at fasteners-skin interfaces has been reported as particularly important for aircraft skins [137]. This attack occurs when the galvanic couple between the dissimilar metals in the fastener-skin junction is exposed to electrolyte. Thus, corrosion has been found to occur on and around the countersunk surfaces of the aluminum skin [138,139]. Exfoliation corrosion is often observed as the first step in corrosion damage of the skin, progressing away from the sides of the fastener borehole, parallel to the skin surface, and eventually leading to fatigue crack initiation and propagation [140]. Exfoliation occurs as a first step because the aluminum skin has an inherent microstructural directionality due to the crystalline grain orientations formed during the forging process. Preventative measures, such as wet installation of fasteners in addition to specific surface preparation of the mating components, are employed. However, time and wear of the surfaces degrade this protection, leading to galvanic interactions and the start of corrosion damage.

Coating systems designed for aircraft structures are tasked with providing the principal means of corrosion protection, but they perform multiple functions to do so. They act as a barrier against direct contact with the atmospheric environment and inhibit corrosion when coating breaching occurs. They provide adherence to multi-material interfaces, which includes physical gaps between surfaces, and maintain resiliency to deformations. In addition, aircraft coatings must sustain corrosion protection in a wide range of environmental conditions, ranging from arid environments to sea salt spray, and are subjected to significant temperature fluctuations. Exposure temperatures range from sub-freezing ($-95^{\circ}\text{C}/-64^{\circ}\text{F}$) when aircraft fly at high altitude, to near-boiling ($93^{\circ}\text{C}/200^{\circ}\text{F}$ in some cases), depending on geographical location at low altitude and speed at high altitude. When coatings fail to provide adequate protection against electrolyte intrusion, corrosion damage follows.

Once coating damage is detected, repairs are labor-intensive and time-consuming. Typical options include stripping and re-application of the coating system to the structure. For small areas of metallic surfaces, paint is removed by hand using medium grade abrasives. For larger areas, chemical paint removal is still the most widely used method [137], though laser ablation is gaining wider acceptance. Once the coating is removed, the metal area is reworked to eliminate all traces of corrosion. In the last step, a new coating system is applied.

We propose that the relative motion of the coated skin and fastener head is the main cause of highly localized deformations at fastener-skin interfaces. We developed a Finite Element Model (FEM) to identify the high deformation areas in the coating near a fastener under a complex loading mode and quantify the magnitude of the applied strains. The skin-fastener interface is a potential failure point for a coating system bridging the gaps forming when loads are applied. However, the critical stress-strain condition that leads to coating failure and cracking needs to be quantified by experimental testing of the materials in the coating system. This stress-strain condition may be changed by the environment, *e.g.*, exposure to UV light and temperature fluctuations from flight operations, which can lead to premature cracking and coating failure [141–144]. Similarly, to fully capture the time scale of coating degradation and crack formation, fatigue behavior of the coating

materials needs to be quantified. Fatigue testing of coating system materials subjected to low cycle fatigue loads has not been previously reported.

In this work we investigate the coating deformations at a fastener-skin interface by numerical methods using a representative structural configuration and we quantify the elastic properties of coating system components to determine the onset of cracking. The manuscript is laid out in the following manner: the experimental methods for measuring the elastic properties of the polymer coatings, before and after atmospheric exposure are described. The FEM results and the calculated strains at the fastener-skin interface are presented. The elastic properties of the polymers are used as inputs for the fracture model to inform the model and determine the critical fracture stress. A crack propagation model is then used to study the progression of a crack through the coating layers, starting from the primer, and propagating through the topcoat using the elastic properties for the coating layers.

Theory

Coating System Stress Field Model

A model consisting of two aluminum plates, each with a 70 GPa elastic modulus, and 20 countersunk fasteners was developed to simulate the local fastener-plate interface displacements. The fasteners between the two plates were modeled using solid elements to capture the full extent of their deformations within the structure. The fastener material was stainless steel with an elastic modulus of 210 GPa. The fastener and fastener holes were countersunk with an angle of 100 degrees, and a countersunk head height of 1.73 mm. The fastener shank and nut were modeled as a single part. The bolt was simplified as an integral part of the fastener to allow application of the desired amount of force as preload. The coating layer was applied to the aluminum plate at the locations shown in Figure 53. The coating layer has a higher mesh density around fastener #6 to allow for a more refined characterization of the local deformations. The model configuration is shown in Figure 53.

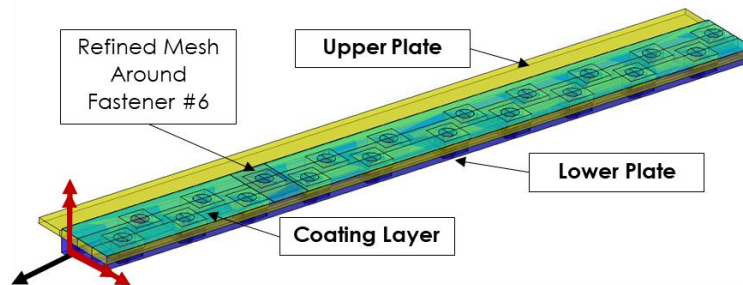


Figure 53. Geometry and components of the finite element model in this work.

The coating system was modeled as a bilayer structure consisting of a primer and topcoat, 25 μm and 100 μm in thickness, respectively. A perfect bonding between the two layers and a perfect bonding of the primer with the aluminum plate and fastener is assumed. Note that aluminum alloy surfaces often receive a pretreatment or conversion coating that anodized the aluminum oxide layer to thicken and to aid in the adhesion between the surface and the primer. The surface pretreatment that would be applied to the aluminum substrate to improve primer adhesion was treated as part of the substrate and was not included in the model.

The analysis was divided into two steps: the first step applied the preload to the fasteners and the second step applied the external loads to the entire model. Two sets of external loads were applied to the model: one which caused the upper plate to be under tension and one which caused the upper plate to be under compression. These types of loads correspond to events, for example, like an aircraft landing or flying through wake turbulence, respectively. The Von Mises stress of the top aluminum plate away from the fasteners obtained for the tension-dominated case was approximately 1/3 of the yield strength, which is assumed to be 450 MPa for this alloy. For simplicity, we refer to “tension-dominated” and “compression-dominated” loads for the rest of the manuscript. These refer to the condition of the upper plate and to define the upper and lower bounds of the deformations obtained, respectively. The loads are identical in magnitude for the two cases but reversed in sign. The applied loads consisted of a combination of two bending moments and an axial force to represent a typical mixed-mode condition of a structural member.

The installation of the fasteners and the application of preloads during the assembly process preceded the coating of the skin panels. This was simulated in the model by deactivating the coating layers during preload. This deactivation step allowed the coating layer to conform to the final shape of the structure without causing any strains or stresses in the coating. This initial “inactive” state was included to ensure that the strains and stresses in the coating were only caused by the external loads. The net result was that the coating layer adhered perfectly to the contours of the fastened structure, including the small geometrical details around fastener heads and skin.

The areas between the fastener head and countersunk hole surface, between the fastener shank and hole surface, and between the nut and bottom plate surfaces were in contact, as shown in Figure 54. The contact properties were defined in the model as non-penetration in the perpendicular direction to the contact surface, and with friction in the tangential direction. The latter used a static coefficient of friction of 0.61 for clean and dry steel[17]. The areas between the upper and lower plate were also modeled with contact, defined as non-penetration in the perpendicular direction to the contact surface, and with friction in the tangential direction. The static coefficient of friction was 1.05, representative of clean and dry aluminum surfaces[17].

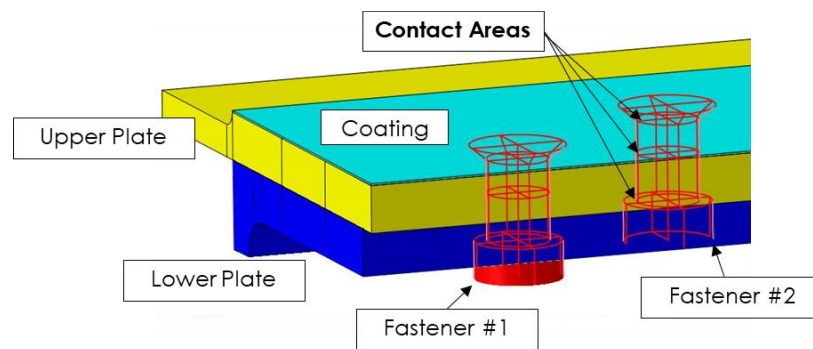


Figure 54. Detail of the model in this work with defined contact surfaces between fasteners, top, and bottom plates.

A sub-modeling strategy was used to refine the results around a single fastener: the displacements resulting from the application of the loads were used as boundary conditions for a sub-part of the model, specifically the coating layer on top of fastener #6. This allowed for significant mesh refinement near the region of interest without paying a large penalty in terms of computational

time. The analysis was performed using Abaqus and CAE on an HPE SGI 8600 high-performance computing cluster.

We used the properties obtained from the tensile testing of the different coating layers to study the expected strains in the primer and topcoat layers of the coating system. The substrate materials were assumed to be able to withstand the applied deformations without failing. The next section includes a failure criterion to model the occurrence of cracking during the studied loading cases, given the observed fracture stresses and strains from tensile testing.

The primer layer was modeled as a linear elastic material with an elastic modulus obtained by analysis of the tensile tests. The topcoat was modeled as an elastic-plastic material with its initial modulus and yield stress obtained from analysis of the tensile tests. The plastic behavior was modeled with kinematic hardening. That is, the models used calculated stress-strain data as a reference for an elastic-plastic regression to find the points needed by the kinematic hardening model. The plasticity model used for modeling the topcoat material was based on the Von Mises yield criterion, given in (73),

$$f(\boldsymbol{\sigma} - \boldsymbol{\alpha}) = \sqrt{\frac{3}{2}(\mathbf{S} - \boldsymbol{\alpha}^{dev}):(\mathbf{S} - \boldsymbol{\alpha}^{dev})} = \sigma_y, \quad (73)$$

where $\boldsymbol{\sigma}$ is Cauchy stress and $\mathbf{S}$ is the stress tensor in the deviatoric space. $\boldsymbol{\alpha}$ and $\boldsymbol{\alpha}^{dev}$ are the back stress and the back stress in the deviatoric space, respectively, σ_y is the yield strength. The plastic flow always follows a direction perpendicular to the yield surface, as shown in (74),

$$\dot{\boldsymbol{\epsilon}}^{pl} = \frac{\partial f(\boldsymbol{\sigma} - \boldsymbol{\alpha})}{\partial \boldsymbol{\sigma}} \dot{\bar{\boldsymbol{\epsilon}}}^{pl}, \quad (74)$$

where $\dot{\boldsymbol{\epsilon}}^{pl}$ is the plastic strain rate, $\dot{\bar{\boldsymbol{\epsilon}}}^{pl}$ is the equivalent plastic strain rate defined as $\dot{\bar{\boldsymbol{\epsilon}}}^{pl} = \sqrt{\frac{2}{3} \dot{\boldsymbol{\epsilon}}^{pl} : \dot{\boldsymbol{\epsilon}}^{pl}}$ [18]. The linear kinematic hardening model defines the back stress rate of change in (75) as,

$$\dot{\boldsymbol{\alpha}} = C \dot{\bar{\boldsymbol{\epsilon}}}^{pl} \frac{1}{\sigma_y} (\boldsymbol{\sigma} - \boldsymbol{\alpha}) + \frac{1}{C} \boldsymbol{\alpha} \dot{C}, \quad (75)$$

where C is a hardening parameter and in its simplest form describing the slope of the stress-plastic strain response of the material for a uniaxial tensile test [19].

Coating Cracking Model

A model was developed to include a fracture criterion for both the primer and topcoat layers based on the experimental fracture stress obtained in tensile testing. For the primer layer, failure occurred when the maximum principal stress calculated in the analysis was higher than a value of 32.0 MPa. For the topcoat layer failure occurred when the principal stress was higher than 18.0 MPa. An enrichment function that allowed the elements to break upon satisfying the failure criterion was included by making use of the extended finite element method (XFEM) implementation in Abaqus. The use of XFEM allowed us to simulate the initiation and propagation of a crack.

Results

Tensile Testing of Unexposed Coatings

Tensile test results for unexposed topcoat and full coating system are shown in Figure 55.

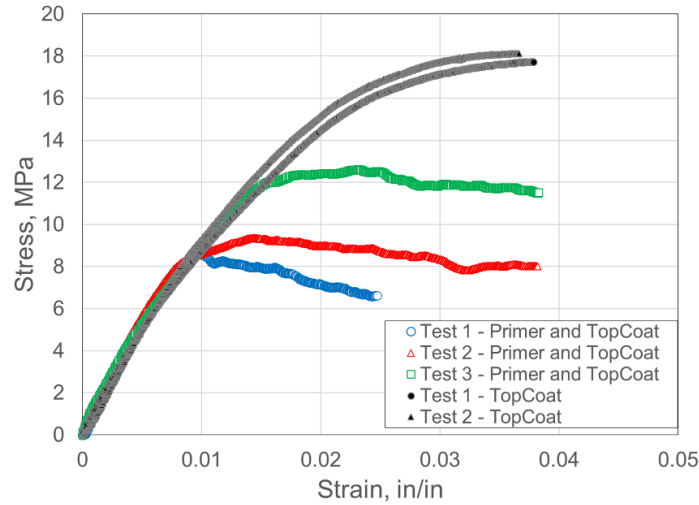


Figure 55. Tensile test results for unexposed topcoat and full coating system samples. Test results for the unexposed primer samples are not included.

The elastic moduli for the topcoat and the full coating system were determined by linear interpolation of the stress and strains, based on a 5.08 cm gauge length and with thicknesses as indicated above. The values are reported in Table 18, along with the estimated value of elastic modulus for the primer material.

Table 18. Average values from tensile test results for primer and topcoat materials and for the full coating system.

Coating Layer	Elastic Modulus (MPa)	Fracture Strain (%)
Full coating system	1,028.6	3.5
Topcoat	846.0	3.8
Primer (estimated from Eq. 1)	3,102.7	-

The elastic modulus of the primer layer was estimated from interpolation of the elastic modulus of the coating system and a modulus for the topcoat layer as calculated from the tensile tests of the topcoat free film. The resulting force for the sample with primer and topcoat is assumed to be given by the expression in (76),

$$F_c = \varepsilon E_1 A_1 + \varepsilon E_2 A_2, \quad (76)$$

where F_c is the force applied to the coating system, and the applied displacements are $\delta_1 = \delta_2 = \delta_c$ and $\varepsilon = \delta_c/L$, with $L = 5.08$ cm. This implies that both primer and topcoat are subjected to equal displacement during the test, and they are perfectly bonded at their interface. The modulus obtained by calculations for the primer is in line with values reported in the literature for epoxies[145–147].

It is interesting to note that the full coating system shows elastic-plastic characteristics as a combination of higher modulus of the primer and higher toughness of the topcoat. The modulus of the coating system is higher than the modulus of the topcoat alone and the failure strain is significantly higher than the failure strain of the primer, while still within the range of the failure strain for the topcoat.

Tensile Testing of Aged Coatings

The results of the tensile samples in comparison to the unexposed full stacks and topcoat are shown in Figure 56. The test results for the full coating system were not conclusive. They showed a wide range of maximum stresses and ultimate strains. The initial elastic modulus was generally consistent, however the behavior at strains higher than 0.005 differed significantly among the three exposed samples. The strains at failure were consistently lower than previously measured for the full coating system. The tensile testing of the topcoat material showed a significant decrease in the tensile properties after exposure, with both a reduction in elastic modulus and a significant reduction in ultimate strain. The modulus averaged 722 MPa, a reduction of 14.7%, while the strain at failure averaged 2.04%, a reduction of 46.3% with respect to the unexposed conditions. All tensile curves were consistent as shown in Figure 56b.

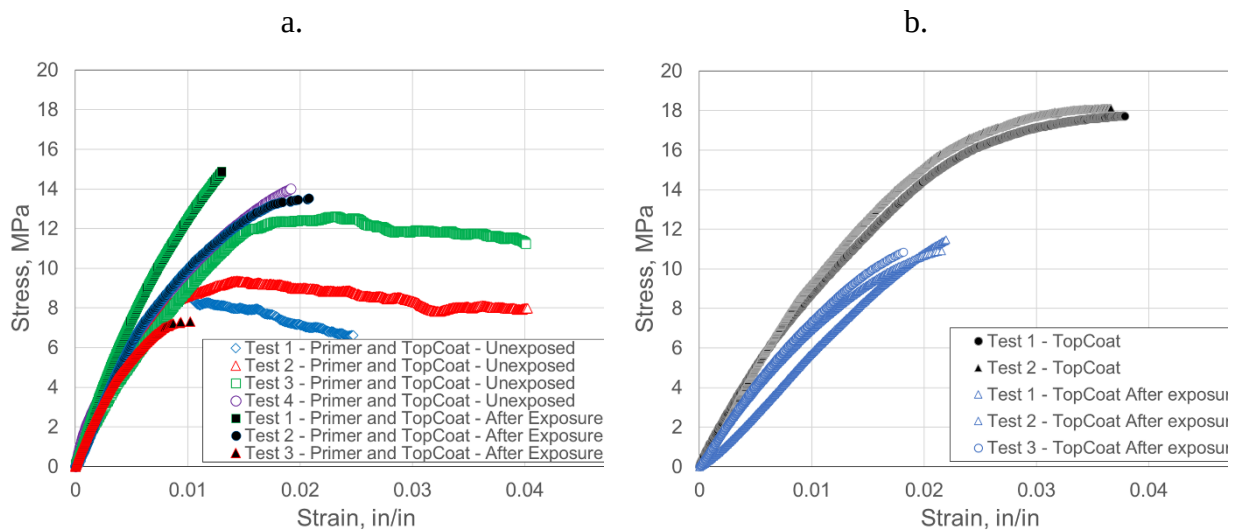


Figure 56. Tensile testing of (a) full system of primer and topcoat coating after exposure to atmospheric environment for 5736 h and comparison with unexposed tensile testing results, and tensile testing of (b) topcoat material coating after exposure to atmospheric environment for 5736 h and comparison with unexposed tensile testing results.

Model Results

A summary of the input for both materials with material properties obtained from the tensile behavior from Figure 55 are shown in Table 19.

Table 19. Elastic input for the constitutive relation of primer and topcoat materials in the model developed.

Coating Layer	Elastic Modulus (MPa)	Poisson's Ratio
Primer	3,102.0	0.37
Topcoat	846.0	0.4

The stress, σ , plastic strain, ϵ_p , which are inputs for the elastic-plastic behavior of the topcoat using the kinematic hardening model discussed earlier are shown in Table 20.

Table 20. Elastic-plastic input for the kinematic hardening constitutive relation of the topcoat materials in the model developed.

Stress (MPa)	Plastic Strain (mm/mm)
13.79	0
15.169	0.002
16.548	0.0055
17.2375	0.0096
17.927	0.0138

The model names corresponding to the different interference fit and preload conditions analyzed are summarized in Table 21.

Table 21. Summary of test conditions and model identification. Each model is tested for a coating thickness of 0.125 mm, 0.25 mm, and 0.5 mm.

Fastener Fit / Strain	Preload	Model Name
Interference / $5 \times 10^{-4} \frac{mm}{mm}$	50% - Low	1a
	75% - Medium	1b
	100% - High	1c
Interference / $15 \times 10^{-4} \frac{mm}{mm}$	50% - Low	2a
	75% - Medium	2b
	100% - High	2c
Neat fit / No fastener-to-hole strain	50% - Low	3a
	75% - Medium	3b
	100% - High	3c

Our results show that high strains are experienced at the location where the relative displacement between the fastener head and the aluminum plate is highest. A larger relative displacement is obtained when tension-dominated loads were simulated, while a lower, but still significant, displacement was predicted for the case of compression-dominated loads.

The main deformations that determine the strains in the coating layer for the two loading cases studied are related to the relative motion of fastener head and countersunk surface of the plate. This motion is shown in Figure 57 for the case of 75% preload and the highest interference fit modeled. The displacements are increased 10 and 50 times respectively for illustrative purposes. The relative displacements of fastener and skin in the y-direction, as indicated in the figure, are -1.1×10^{-2} mm and 3.5×10^{-3} mm, respectively. In the first case, the deformation of the structure causes the countersunk bore to move upwards relative to the head of the bolt; the opposite occurs in the second case. The different magnitudes cause a significant difference in the strains in the coating for the two load cases. The assembly variables studied, and the preloads applied to the fasteners, further influence the relative motion of fastener head and skin, determining different levels of strain in the coating, albeit with less significant effects.

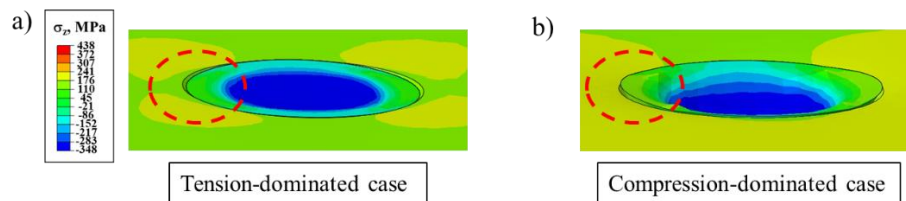


Figure 57. Exaggerated relative motion between fastener head and plate surface for a. tension-dominated loading case and b. compression-dominated loading case.

The results from the finite element analysis (FEA) of the fastened plates and of the sub-modeling of the coating at the fastener-plate interface are presented in the following figures. The data are shown as the average strain at the primer and topcoat layers when different conditions are simulated: a) a different preload of the fastener, Figure 58, b) a different interference fit condition between the fastener and the skin hole, Figure 59, c) a different loading condition, Figure 60.

The maximum strains occur along a circular contour in the primer and topcoat corresponding to the fastener head diameter. The data are extracted from the finite element model along a circular path that includes the highest strains. The resulting strains in the coating obtained around the fastener head for the case of a tension-dominated load in Figure 58 show a steep saddle profile for all cases of preload modeled. A 2% higher maximum strain was obtained on average for the case with the lowest preload. The maximum strains are near 10% for the primer, indicating that primer failure is expected to occur at the interface when tension-dominated loads are applied. The topcoat layer results are not affected significantly by the changes in the preload level. The principal strains on average are near 5% and failure might occur at the location of the highest strains. Plastic deformation is calculated by the model for the topcoat layer for all strain levels higher than 2.1% principal strain. This occurs because of the constraints on the topcoat layer and the value of the other two principal strains (not shown here). The ratio of maximum and minimum principal strains is -0.8 for the topcoat for the tension-dominated case.

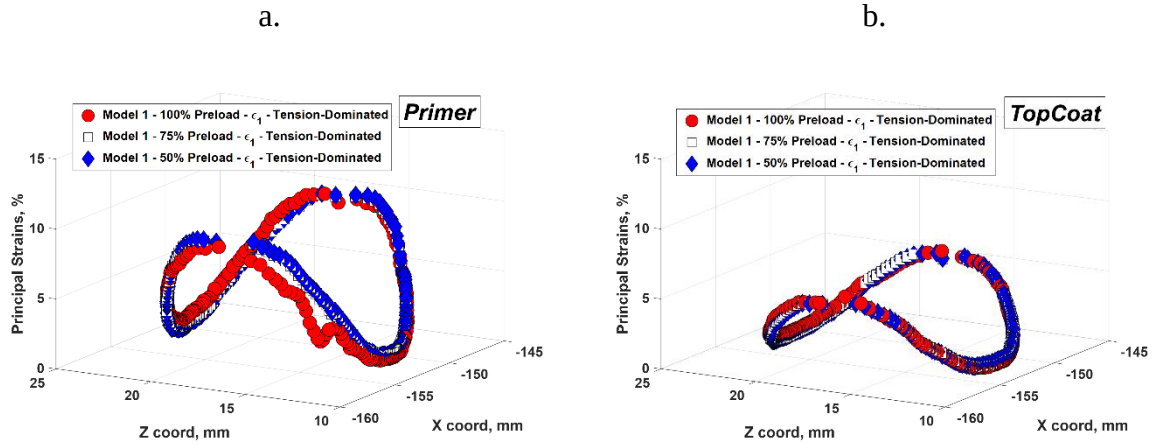


Figure 58. Resulting strain at fastener-skin interface in the a. primer and b. topcoat layer of a coating system for tension-dominated loads and as a function of fastener preload: model 1a, 1b, and 1c.

Figure 59 shows the results for models 1, 2, and 3, all representing a preload condition of 75% and differing by interference fit level. The principal strain values for the primer and topcoat are very similar among the models. The primer results show principal strains 2% higher for the case of Model 3b (no interference fit); the topcoat results also show 5% higher principal strains for Model 3b. This confirms the generally beneficial effect of interference fit fasteners.

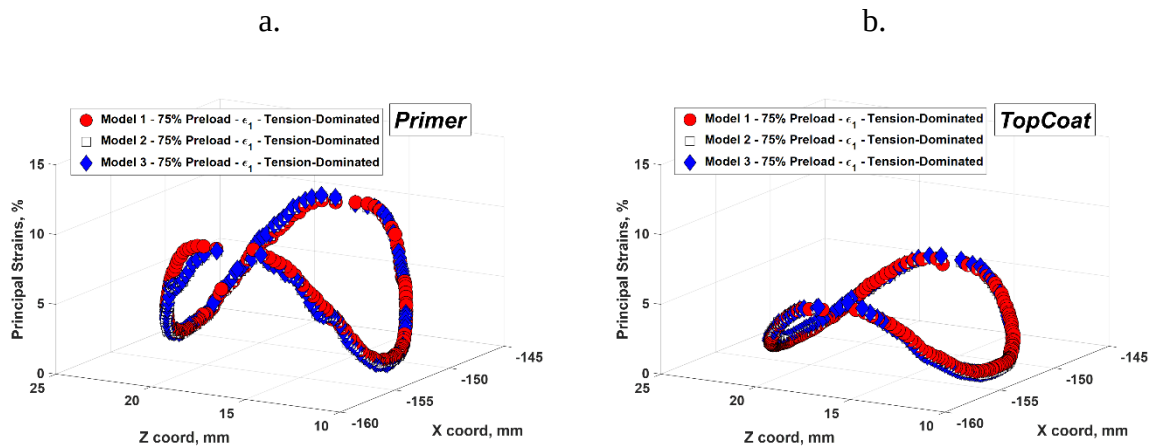


Figure 59. Resulting strain at fastener-skin interface in the a. primer and b. topcoat layer of a coating system for severe loading condition and for different levels of fastener interference fit models 1b, 2b, and 3b.

Figure 60 compares the results of Model 1b for two loading conditions, a tension-dominated, and a compression-dominated load. The principal strains show very significant differences both in maximum strains calculated and in the distribution of the strains along the circular path that corresponds to the head of the fastener. The strains for the compression-dominated load are around 2.6% for the primer and 1.2% for the topcoat. For both materials the relative difference between the minimum and maximum principal strains are much lower for the compression-dominated case than for the tension-dominated case: for the latter the ratio of the highest to the smallest principal

strain is 10.0 for the primer and 19.7 for the topcoat, and for the former the ratio of the highest to lowest principal strains is 4.7 and 1.8 respectively for the primer and topcoat.

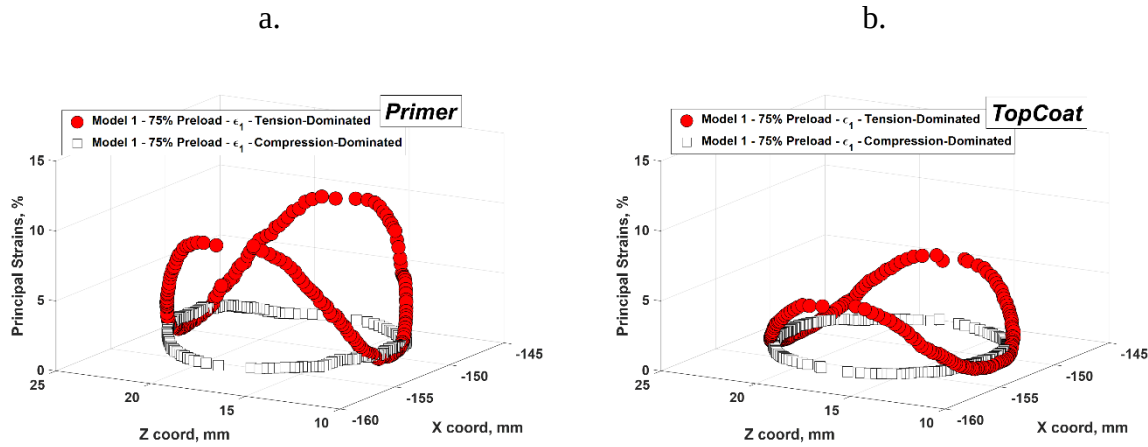


Figure 60. Resulting strain at fastener-skin interface in the a. primer and b. topcoat layer of a coating system for tension-dominated and compression-dominated loads for model 1b.

Coating Failure Models – Fracture in Unexposed Coatings

In this section, the failure of the coating layer is analyzed as a function of the deformations calculated. The two load cases, representing a tension- and compression-dominated conditions for the upper plate, are modeled for one condition of preload (75%) and interference fit ($15 \times 10^{-4} \text{ mm/mm}$). The results for the tension-dominated loads are presented in Figure 61.

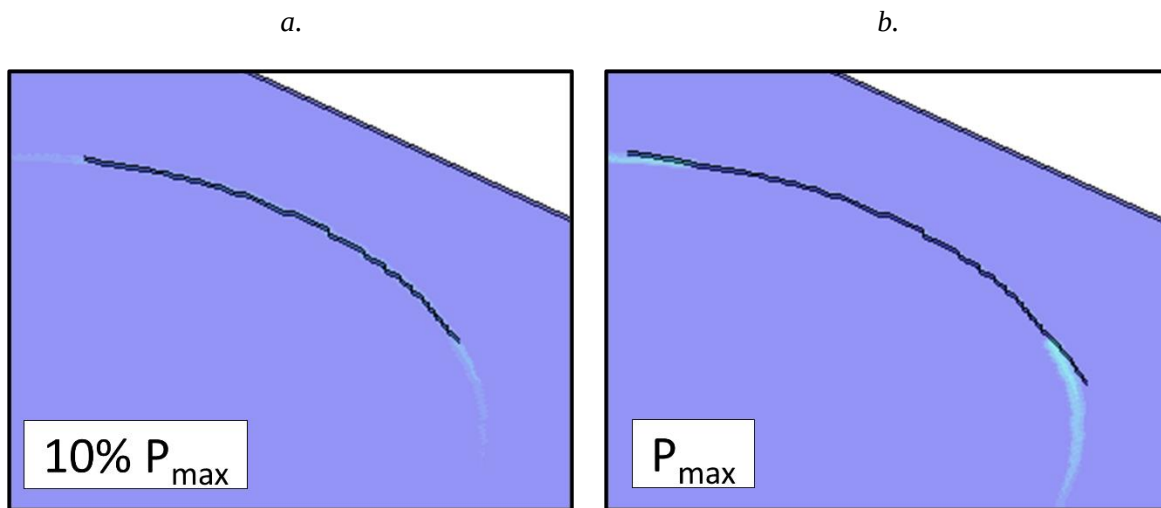


Figure 61. a. Cracking of primer layer at 10% of maximum applied load, and b. crack propagation through the primer along the critical path of highest strain at maximum applied load. Loads are obtained from simulation of tension-dominated event.

The principal strain contour plots for the primer layer are shown for 10% of the maximum applied tension load, and for the maximum applied load, $P_{\max}$. The crack initiates at the point of highest strain and propagates following the contour of strain concentration identified in Figure 58. Initial fracture occurs at the primer interface with the metal skin and progresses towards the outside layer of the coating system.

The interface crack breaches the primer layer between 10 and 15% of the maximum load, with the crack continuing to propagate along the perimeter of the fastener. In Figure 61 a) and b) the crack front crosses both the bottom and top face of the primer, and this is visualized by two distinct crack lines in the figure.

Figure 62 shows the beginning of the fracture of the topcoat layer, occurring at 55% of $P_{\max}$, with crack initiation occurring only at the highest strain location and along the interface with the primer only. The crack front is visualized in the figure as a single crack line, showing that it has not breached the entire topcoat layer. The topcoat layer is not fully breached until the load reaches 95% of $P_{\max}$. The fracture of the topcoat is localized in only a few areas around the perimeter of the fastener. In Figure 65 this can be visualized by the appearance of small sections of a second crack line on the top surface of the topcoat.

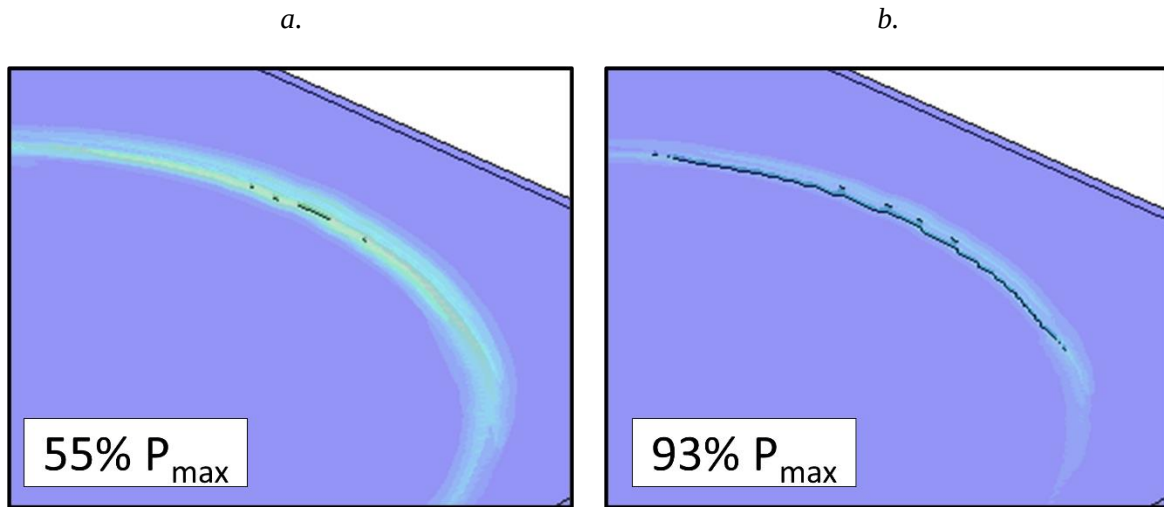


Figure 62. a. Cracking of topcoat layer at 55% of maximum applied load by propagation of the primer crack. b. Propagation of the crack along the critical path of highest strain with only minimal breaching of the topcoat layer observed near maximum applied load. Loads are obtained from simulation of tension-dominated event.

The results for the case of compression-dominated case are shown in Figure 63. Cracking does not occur in the primer until the applied loads reach 50% of the maximum. The applied strains are lower for the compression-dominated condition, but they are enough to cause fracture of the primer layer. For the tension-dominated case the ratio of maximum and minimum principal strains in the primer is -0.76, and for the compression-dominated case the ratio is -1. The latter is closer to a pure shear loading mode causing a reduction in the effective properties and a later occurrence of fracture based on a maximum principal stress criterion [148]. For the compression-dominated case,

the strain distribution is more uniform around the fastener and not specifically concentrated at two opposite edges of the fastener, as shown in Figure 60. The crack in the primer follows the entire contour of the fastener head.

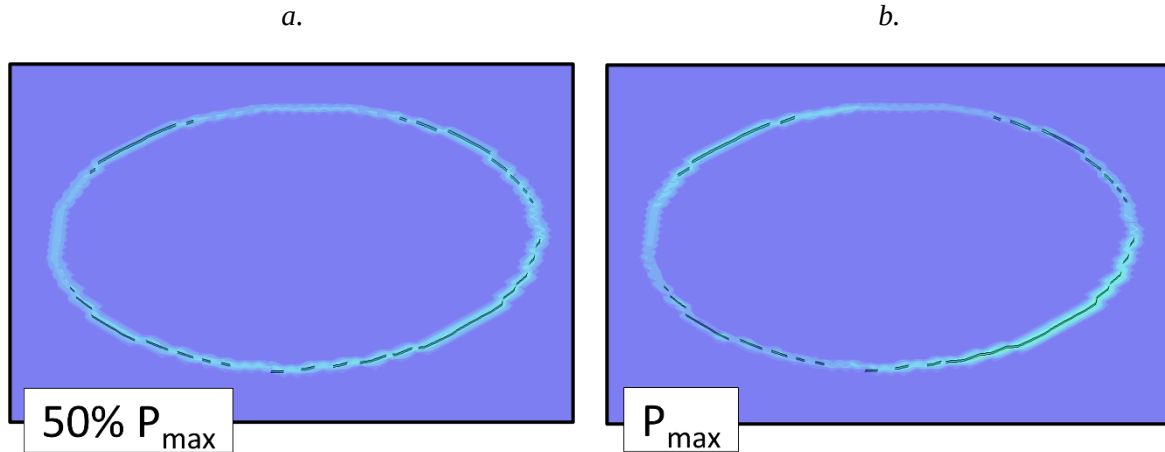


Figure 63. a. Cracking of primer layer at 50% of maximum applied load, and b. crack propagation through the primer along the critical path of highest strain at maximum applied load. Loads are obtained from simulation of compression of the upper plate in Figure 53.

The topcoat layer is not breached by the crack in the primer as the loads are not significant enough to deform the topcoat layer and initiate a crack. Also, the energy released by the cracking occurring in the primer reduces the applied strains in the topcoat to below a critical level. Figure 64 shows the contour of the strain in the topcoat, with the maximum of the scale reaching 1%. Most of the strains in the topcoat are reduced to below 1%, with maximum values only reaching approximately 0.7% strain. Because of the reduced strains in the topcoat, the fracture does not propagate through the topcoat layer.

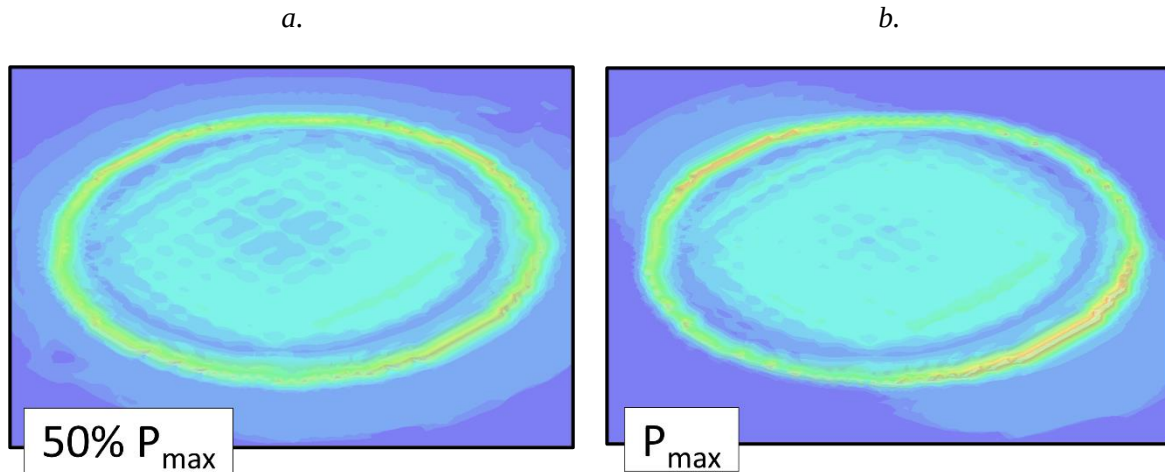


Figure 64. a. Straining of topcoat layer at 50% of maximum applied load. b. Strain of the topcoat layer observed at maximum applied load. Loads are obtained from the compression-dominated case.

Coating Failure Models – Fracture in Aged Coatings

In this section, we investigate the loads that cause cracking of the topcoat layer by exercising the model presented previously with the properties of the topcoat layer after long term exposure to atmospheric environment. Given the measured properties, the failure of the topcoat layer is expected to occur at a lower ratio of the maximum load during the loading cycles presented in Figure 62. Considering the testing of the full system was not conclusive enough to support an estimation of the primer properties after long term exposure, and considering the elastic modulus of the full stack was generally consistent with the unexposed measured values, the primer properties used previously were not changed in the model. The loads from a tension-dominated event are used as input to the model and the cracking of the topcoat layer is monitored to calculate the load when cracking is initially observed in the topcoat layer and the loads when the topcoat layer is fully cracked.

Figure 65 shows that the initial occurrence of cracking in the topcoat layer occurs at approximately 38% of the maximum load caused by a tension-dominated event. A large extent of cracking comparable to the one obtained near the maximum load when the unexposed coating properties were used, occurs at 67% of maximum load. Both results when compared to Figure 62 indicate the expected early cracking due to the degradation of properties in the topcoat layer measured experimentally.

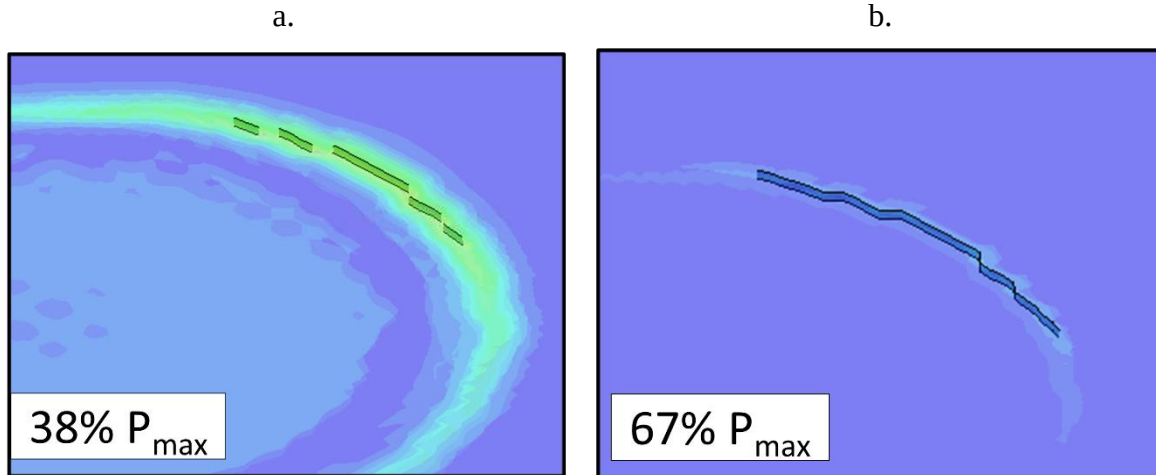


Figure 65. a. Initial cracking of topcoat layer at 38% of maximum applied load by propagation of the primer crack and full breaching of the topcoat layer. b. Propagation of the crack along the critical path of highest strain of the topcoat layer observed near 67% of maximum applied load. Loads are obtained from simulation of tension-dominated event and the cracking of the coating is symmetric around the fastener hole.

Figure 66 shows the contour of the strain in the topcoat for the compression-dominated load case, with the maximum of the scale reaching 1% and the material properties of the topcoat layer after long term exposure to the atmospheric environment. The results are similar to the results with unexposed coating properties shown in Figure 64. Thus, this suggests the local deformations are not sufficient to cause topcoat breaching of the topcoat even with degraded properties after long term exposure. The margin to reach the strain to failure is reduced by approximately a factor of 2.0, with respect to the unexposed condition.

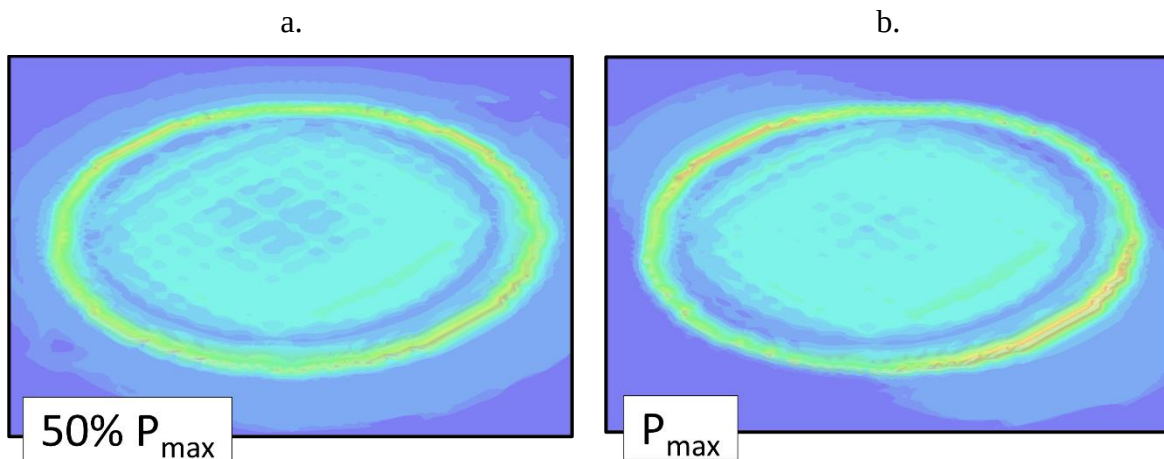


Figure 66 – Results for compression-dominated load case and topcoat layer properties after long term exposure to atmospheric environment. Straining of topcoat layer at 50% of maximum applied load a). Strain of the topcoat layer observed at maximum applied load b).

Coating Failure Models – Fatigue in Aged Coatings

While the previous analysis indicates that a tension-dominated event might cause a direct failure of the coating system at the most critical interface, other locations which represent the majority of the coating areas are subjected to much lower strain levels. Figure 67 a) and b) shows the maximum principal strain in the primer and topcoat layers when subjected to loads from a tension-dominated event. Figure 67 c) and d) shows the maximum principal strains for the compression-dominated case. Large areas of the primer are subjected to strains between 0.4% and 0.2% strain for the case of tension-dominated loads.

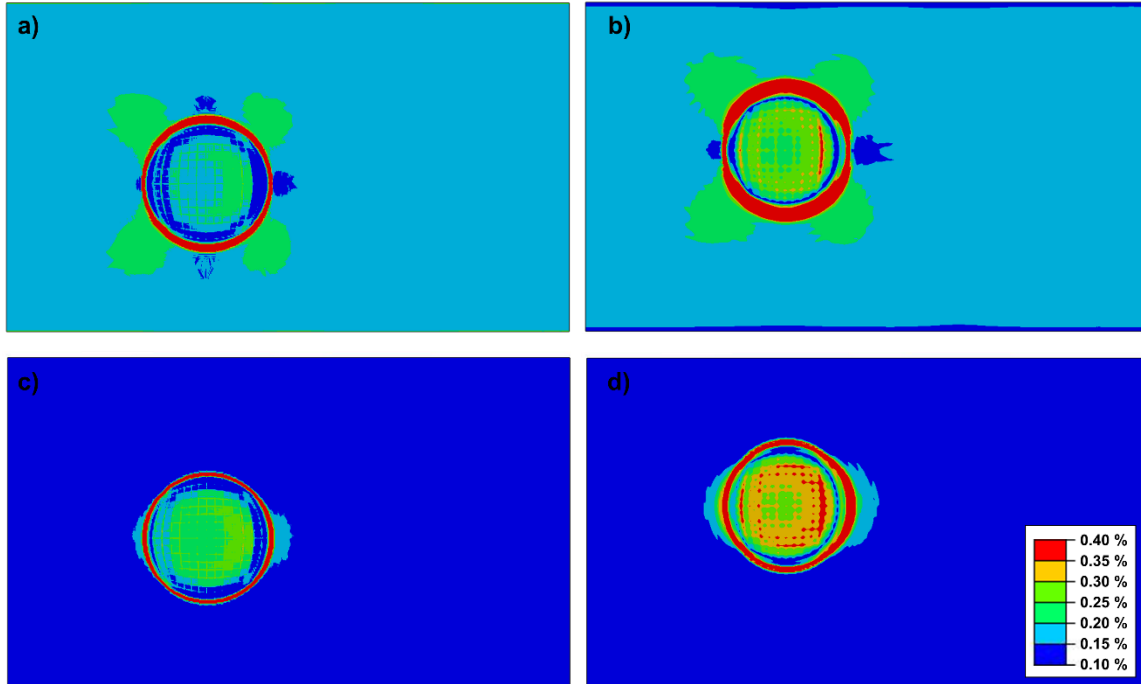


Figure 67 – Maximum principal strain in the primer a) and topcoat b) layers of the coating systems with the application of loads from a tension-dominated event and for the case of compression-dominated loads c) and d). Strain levels are limited to 0.4% maximum and 0.1% minimum.

Thus, a second failure mode for the coating system is crack formation and propagation due to fatigue cycling. The strains are expected to cycle between the maximum values shown in Figure 67 a) through d), and a minimum value corresponding to the mean static loads applied to the structure. However, these static loads are not estimated in this work.

Discussion

The fracture model results indicate that, at a fastener-skin interface, the resulting deformations from both tension- and compression-dominated loads are significant enough to cause fracture of the primer layer. Based on the tensile properties collected, and the fracture analysis performed, we are able to better qualify the extent of fracture in the coating and the likelihood of cracking during the life of a fastened joint exposed to the outdoor environmental conditions.

The load cases studied were proposed to be representative of the life of the joint. However, based on the stress-strain conditions at the critical location for the coating layer, fracture of the primer

occurred at 10% and 50% of the respective maximum of the load cases analyzed. Thus, despite using conservative applied loads, it seems very likely for cracking to occur in the primer early in the life of the structure.

As part of the qualification testing for coating systems, bend tests are used to ensure good adhesion to the substrate [149]. The resulting strains applied during these tests are usually high, thus confirming that mechanical cracking of the full coating system only occurs for severe loading conditions.

In our analysis, cracking of the topcoat was only found at, or above, 55% of the maximum applied tension-dominated loads. This indicates that complete fracture of the coating layer likely only occurs for the most critical load cases at the most susceptible locations. However, atmospheric exposure testing of the full coating system and topcoat materials showed that the topcoat layer is affected significantly after long term environmental exposure. The results show both a reduction in elastic modulus and strain at failure. A reduction in elastic modulus might be due to moisture uptake and increased plasticization[113] and the reduction in failure strain to the exposure to UV light. The results of the analysis indicate that this degradation of the topcoat material properties causes the occurrence of initial and full coating breaching for a lower applied ratio, 38% and 67%, of the maximum loads studied respectively.

As also observed in our analysis, cracking at the interface between the primer and the metal skin causes a reduction in applied strain at the topcoat due to the released energy at fracture. This implies that an already fractured primer might not transfer enough energy to cause fracture of the topcoat at the same level observed in this work during a tension-dominated event. A previous event could establish, for example, a crack extending along the entire perimeter of the fastener head, as shown in Figure 63. This different initial condition is expected to influence the fracture in the topcoat layer by reducing the available energy for fracture.

Conclusions

Free films of primer and topcoat organic polymers were tested in tension to estimate the material properties needed for a mechanical model of a fastener and skin interface coated with a coating system composed of the two polymers. The free films underwent atmospheric exposure testing for 5736 h at the exposure test site in Fleming Key, FL. We measured the change in tensile properties of the coating materials as a result of this exposure. The analysis shows that fracture of the primer is expected to occur upon the application of the tension- and compression-dominated loads. However, fracture of the topcoat is only expected with the application of the full tension load but is not expected to occur otherwise.

Critically, exposure of the coatings to the atmospheric environment caused a deterioration in the topcoat mechanical properties, with a 14.7% reduction in modulus and a 46.3% reduction in strain at fracture. The analysis with degraded properties identified an earlier occurrence of cracking for the topcoat when subjected to tension-dominated loads with respect to the case with unexposed properties, but no difference for the case of compression-dominated loads.

9. EFFECTS OF ENVIRONMENTAL EXPOSURE ON MECHANICAL AND BARRIER PROPERTIES OF AN AIRCRAFT COATING SYSTEM

Introduction

Organic coatings are used in a wide variety of environments, including seawater immersion and exposure to the atmosphere, as a method for preventing corrosion. In some cases, coatings are applied in layers over one another to form a structure that performs multiple functions[1,2]. In addition, for metals like aluminum that can form oxides that do not provide good adhesion, a surface pretreatment may be used that alters the oxide film of the aircraft skin material and aids in adhesion of the base coating to the substrate[3,4]. Then the base layer, generally a thin primer coating that binds to the oxide and provides an adherent surface for a topcoat[5], is applied. For structures exposed to atmospheric conditions, this layer provides barrier protection, and may also contain corrosion inhibitor additives. The outermost layer usually consists of a thick topcoat layer that protects the primer and provides coloring using pigments and other filler materials[6].

When properly applied, organic coatings exhibit excellent durability. However, exposure to ultraviolet radiation from sunlight, temperature and relative humidity changes, and deposition of pollutants and other corrosive ions on the coating surface, along with water from rain and condensation, eventually degrade the coating system[7]. The degradation can be evidenced in the color change and loss of gloss, in addition to the formation of flaws, *e.g.*, pits or fissures that can aid in the transport of oxygen and electrolyte to the coating-metal interface, with the subsequent loss of mechanical properties. This degradation eventually leads to surface corrosion.

This report focuses on understanding changes in mechanical and chemical properties of organic polymer coatings applied to aluminum substrates that have been exposed to outdoor environments for up to 5000 h. In addition, a sample configuration and test methodology are proposed to directly measure the fatigue properties of an unsupported primer and initial results are presented.

Results

EIS measurements of fully supported primer and topcoat

EIS measurements were made on the coating systems that had been applied to the aluminum alloy 2024-0 test coupons at the completion of the exposure iteration. Representative examples of the data from the fatigue samples are shown in Figure 23. The EIS data are plotted on Bode diagrams, with the logarithm of the impedance modulus, $|Z_{mod}|$, and phase angle as functions of the logarithm of the frequency.

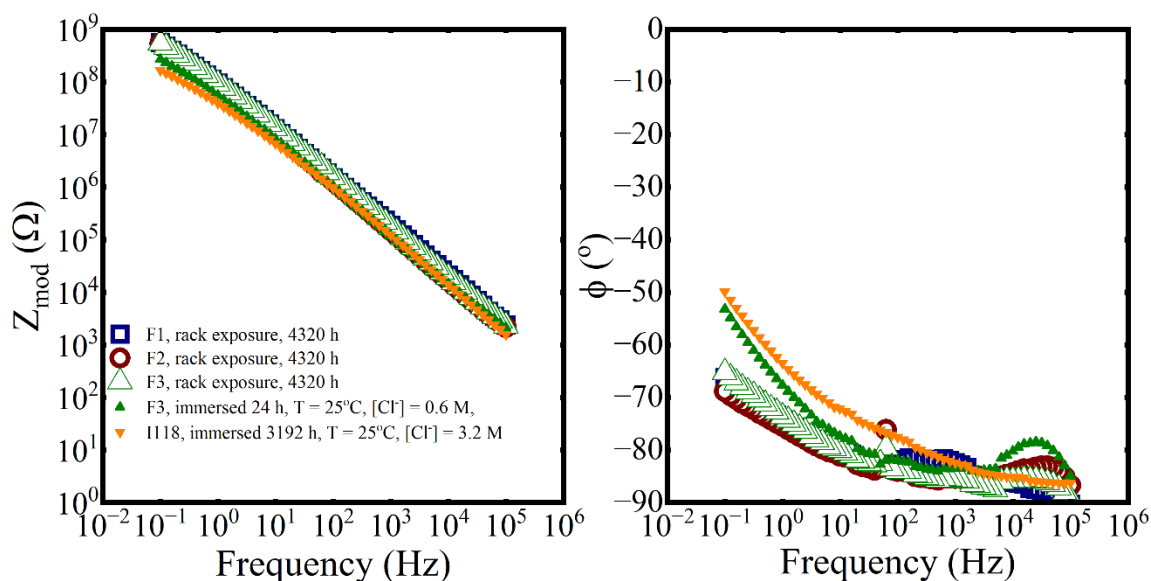


Figure 68. Bode representation of the EIS data, Z_{mod} on the left and phase on the right, obtained from 3 fatigued coating systems on the outdoor exposure racks for 4320 h, with comparison data from a coating immersed in 3.2 M NaCl solution at 25°C for 3192 h. In addition, sample F3 was immersed in 0.6 M NaCl for 24 h after the initial EIS measurement.

Representative examples of the data from the unstrained samples placed on the exposure racks and the unstrained samples placed on exposure racks that were sprayed with seawater for 45 s per day are shown in Figure 69. The EIS data are plotted on Bode diagrams, with the logarithm of the impedance modulus, $|Z_{mod}|$, and phase angle as functions of the logarithm of the frequency.

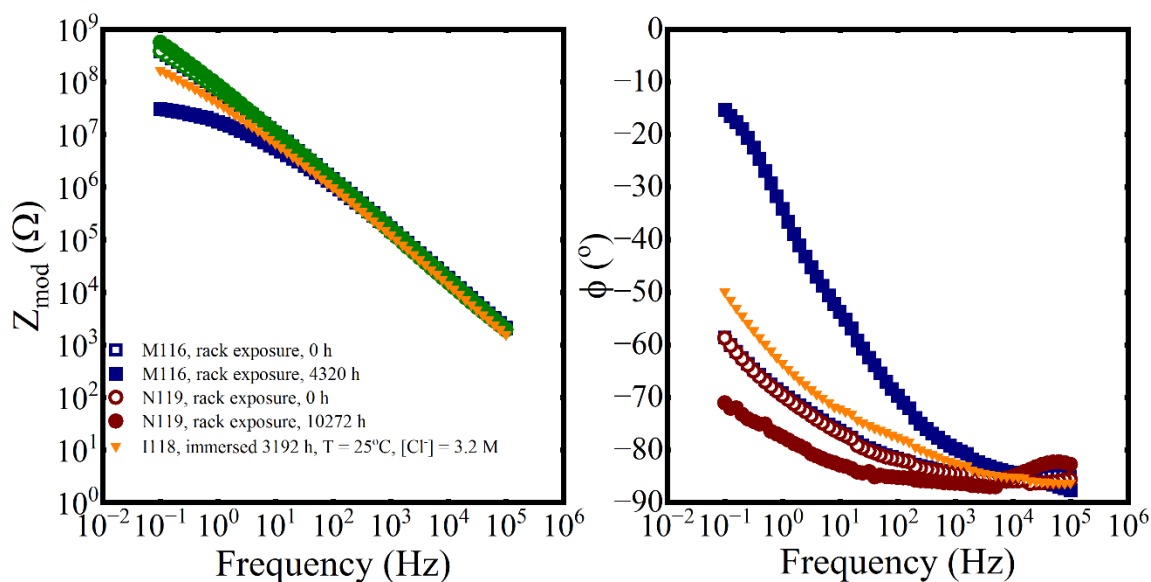


Figure 69. Bode representation of the EIS data, Z_{mod} on the left and phase on the right, obtained from on the outdoor exposure racks for 4320 h and 10272 h, with comparison data from coating immersed in 3.2 M NaCl solution at 25°C for 3192 h.

For the coating systems that did not see seawater spray or immersion, exposure on the test racks resulted in a decrease in the phase angle of the response from mid-to-low frequencies, that suggested the coating was behaving more like an ideal capacitor. In contrast, those coatings that were immersed or exposed to salt spray experienced a decrease in their barrier properties.

Fatigue testing of unsupported primer coating

Crack initiation occurred in the middle of the sample where the strain was highest. Figure 70a and b show the center notch before and after fatigue crack initiation, respectively. The number of cycles to crack initiation for the panel tested was 64140. Interface cracks on the sides of the center notch location were observed at the beginning of the test. Figure 70c shows the position of the interface cracks at both sides of the center fatigue crack. Light from the back illumination of the sample was not visible during the test and became visible only when the center fatigue crack initiated in the primer. We believe that for the first panel, the strain at the center of the notch was not affected by the interface cracks at its edges.

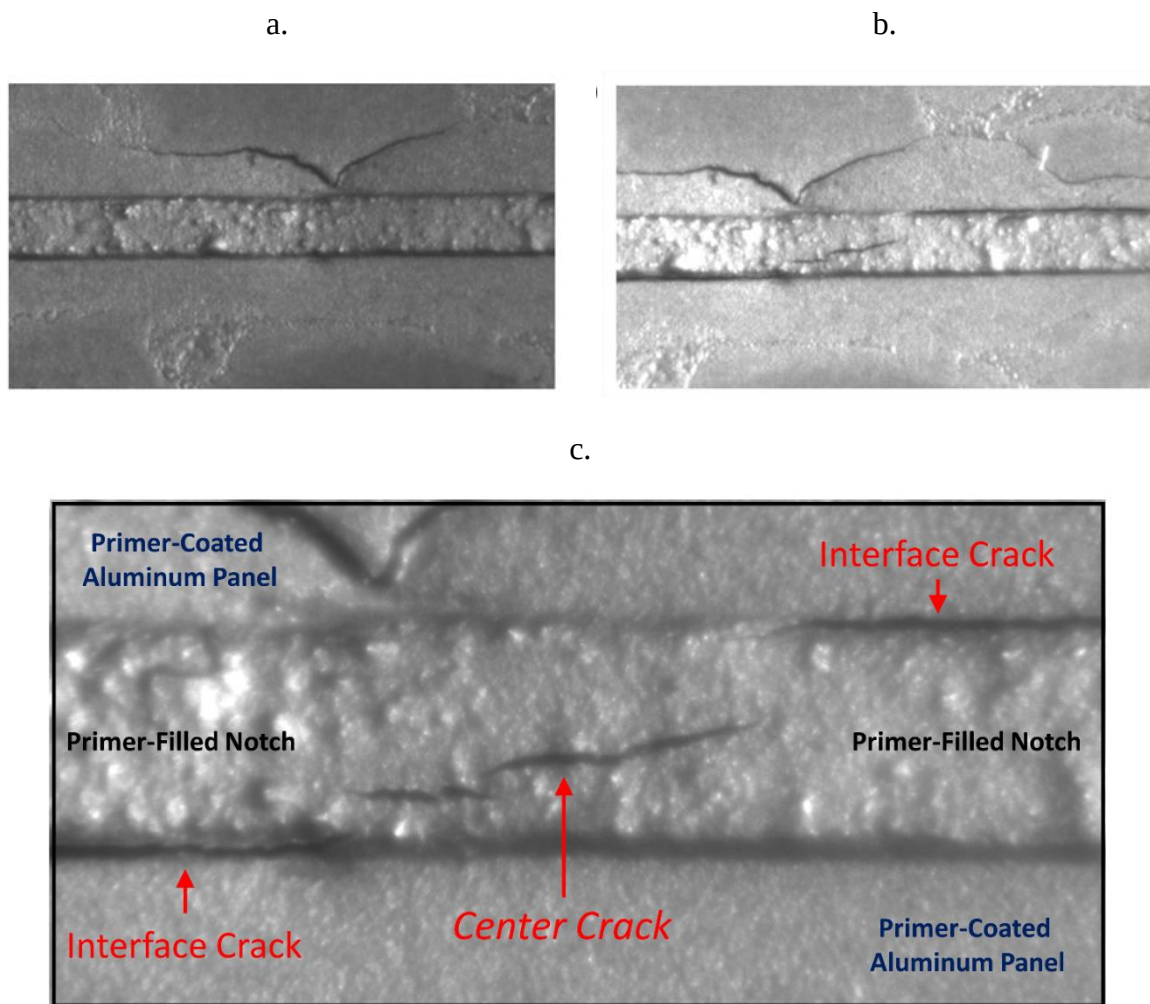


Figure 70. Images showing the center notch of the coated aluminum panel tested in fatigue; a. intact center notch area at the beginning of the test, and b. fatigue crack initiation shown in the center of the notch after 64140 cycles. c. Higher magnification image of the center notch of the coated aluminum panel tested in fatigue in this work. The epoxy primer initiated a fatigue crack for an applied maximum strain of 0.4% and minimum strain of 0.13%.

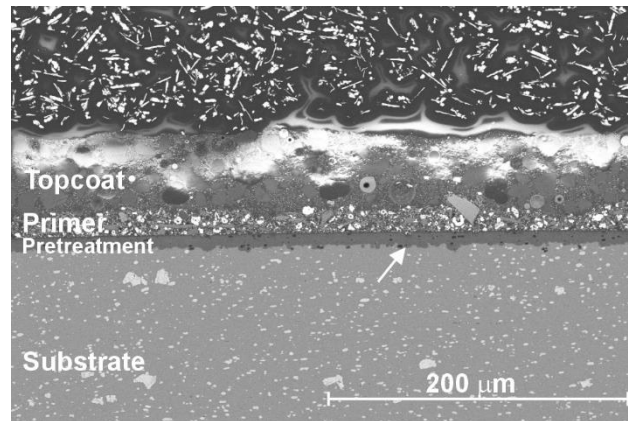
While the fatigue testing was only successful for a single specimen, the sample design and test technique show promise for future work. The number of cycles for the appearance of a fatigue cracks is reasonable for a brittle polymeric material, compared to fatigue results for neat epoxy resins[146,147].

A second panel was also tested in fatigue. However, through-thickness cracks were present in the coating, sufficient to allow light to penetrate through the sample, prior to testing. The panel did not show any fatigue crack initiation at the same applied loads for up to 1 million cycles. The test was stopped as it was likely that the presence of the through-thickness interface cracks reduced the strain at the center notch to very low levels.

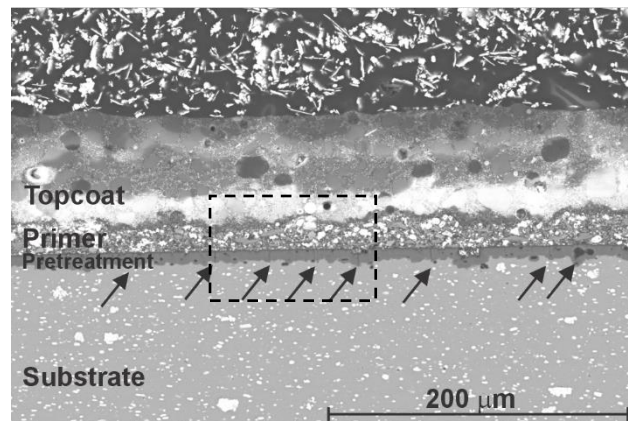
Scanning electron microscopy (SEM) imaging

Longitudinal cross-section samples were destructively removed from a fully supported fatigued coating and an unstressed coating that had been mounted to the atmospheric exposure racks for a similar amount of time. These samples were imaged in an SEM at high vacuum (JSM-IT710HR, JEOL). While coating cracks were not observed in the SEM images, cracking of the pretreated layer could be seen, and it occurred at a higher frequency in the fatigued coating system. This is consistent with earlier results[150].

a.



b.



c.

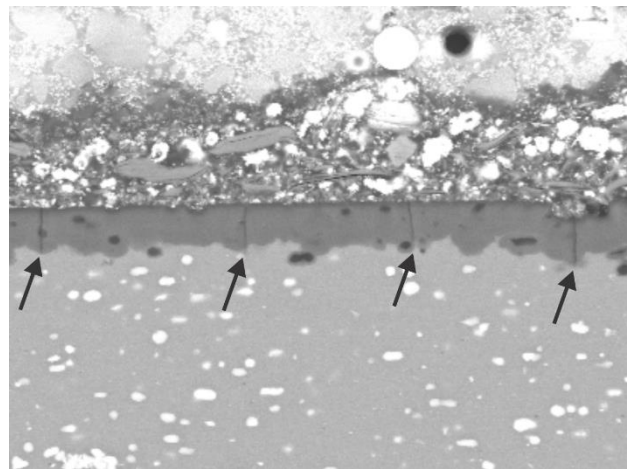


Figure 71. Cross-section images of a. an unstressed coating system, b. a fatigued coating system, and c. magnified view of the region outlined by the dashed box in b. to highlight the cracks in the pretreatment layer. Arrows indicate the presence of through-thickness cracks in the pretreatment layer.

SKP results

During equilibration of the coatings, the SKP tip was brought to within approximately 60 μm of the coating surface and the contact potential difference between the SKP tip and the substrate through the coating was monitored at a single point for longer than 1 h to ensure the coating system had stabilized prior to performing an area scan. The results for the equilibration of the contact potentials for the tested coatings are shown in Figure 72.

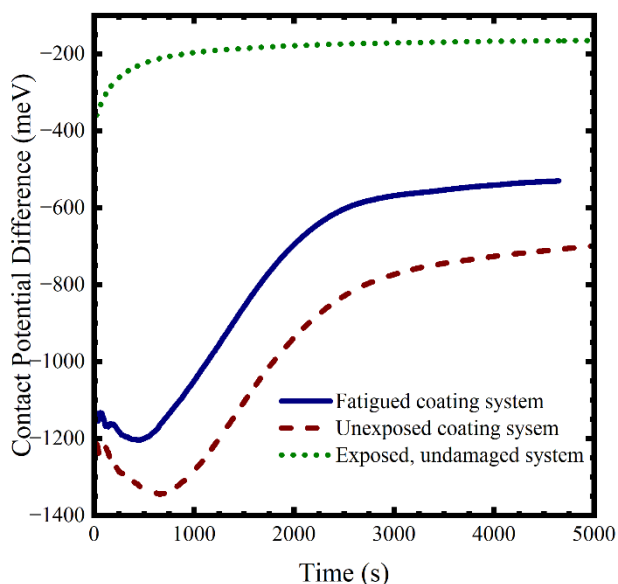


Figure 72. Contact potential differences through the coating systems at a single point as a function of time during the equilibration period.

The calculated work functions for an area scan at the center of the coating samples are shown overlaid in Figure 73.

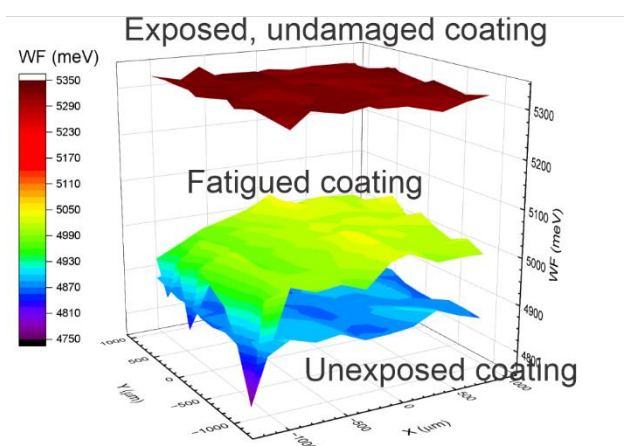


Figure 73. 2 mm x 2 mm area scans at the center of the coating systems for: 1. a fatigued coating in the outdoor environment for 4320 h, 2. An exposed, but mechanically undamaged coating in the outdoor

environment for 4320 h, and 3. a coating applied at the same time as the other samples but stored for the same duration.

Discussion

The stationary criterion for EIS analysis was met on the coated coupons with the ± 10 mV_{RMS} perturbation. For these measurements, the linearity of the coating systems' responses to the 28-mV peak-to-peak potential perturbation was confirmed using the Kramers-Kronig transform utility provided with the analysis software (Echem Analyst; Gamry) for the potentiostat.

Analysis of the EIS data was performed by fitting the data with the modified REAP equivalent circuit model, shown in Figure 28, using the analytical software suite (Echem Analyst, Gamry) provided by the potentiostat manufacturer. In all cases, R_Ω was assumed to be $4\ \Omega$ due to the experimental approach taken for measuring the impedance. Fits were done using the simplex fitting algorithm included with the software to ensure convergence.

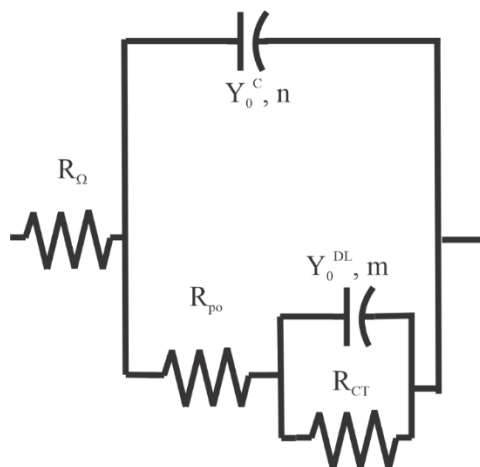


Figure 74. Modified REAP model[15] used to analyze the EIS data from the coatings.

Examples of the calculated impedance obtained from the fit parameters in comparison with the data are shown in Figure 75.

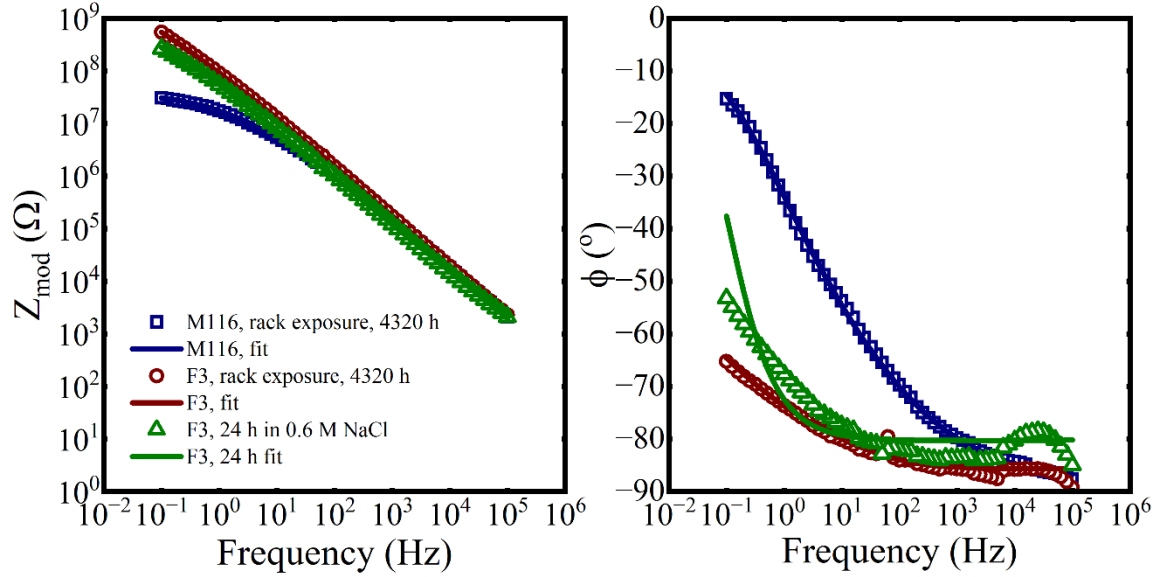


Figure 75. Comparison of the fit with EIS data: $X_{F3}^2 = 4.7 \times 10^{-4}$, $X_{F3,24h}^2 = 110 \times 10^{-4}$.

Fit parameters for the unstrained coatings mounted on the atmospheric exposure racks with and without sea spray as a function of time are shown in Table 22. These values are shown in contrast to an immersed coating.

Table 22. Comparison of fit parameters for unstrained samples mounted on atmospheric exposure racks with (M116) and without sea spray (N119) and an immersed coating (I118) over time.

Parameter	Sample ID and Exposure Time (h)				
	M116		N119		I118
	0	4320	0	10272	3120
R_{Ω} (Ω)	4	4	4	4	4
R_{po} ($G\Omega$)	5.7	0.04	4.8	2570	0.78
R_{ct} ($M\Omega$)	9.15	0.02	0.019	207	0.82
$Y_0^{DL} (nF \cdot s^{n-1})$	1.48	12.9	2.37	1.01	5.35
m	0.562	0.537	0.589	0.602	0.594
$Y_0^C (nF \cdot s^{n-1})$	2.28	1.05	1.23	1.77	1.78
n	0.950	0.978	0.968	0.950	0.958

For the immersed coating and the coatings exposed to seawater spray, R_{po} decreased as a function of exposure time, as expected, because of water ingress into the coating. In contrast, for the coating exposed to just the ambient conditions, R_{po} increased over the duration of the exposure. This is likely due to long-term curing of the coating from sun exposure, resulting in improved barrier properties of the overall coating system. Also of note, the exponent, m , on the constant phase element that captures the dielectric properties of the double-layer at the coating substrate interface shows a strong diffusion effect, with values near 0.5 for many of the exposure conditions. This is consistent with a transport mechanism dominating the reaction at the substrate-coating interface. Likewise, the exponent, n , on the constant phase element that captures the dielectric property of

the coating is close to 1.0, which suggests that the coating system is behaving like an ideal capacitor.

The fit parameters for the fatigued, fully supported coatings are shown in Table 23.

Table 23. Comparison of fit parameters for unstrained samples mounted on atmospheric exposure racks with (M116) and without sea spray (N119) and an immersed coating (I118) over time.

Parameter	Sample ID and Exposure Time (h)		
	4320	F3 24*	I118 3120
R_{Ω} (Ω)	4	4	4
R_{po} ($G\Omega$)	15.4	3.16×10^{-5}	0.78
R_{ct} ($M\Omega$)	30.4	404	0.82
$Y_0^{DL}(nF \cdot s^{n-1})$	1.32	283	5.35
m	0.561	0.747	0.594
$Y_0^C(nF \cdot s^{n-1})$	1.40	3.37	1.78
n	0.952	0.892	0.958

* Indicates the previously exposed coating was immersed in 0.6 M NaCl for 24 h immediately prior to making the EIS measurement.

These values differ in several ways from the ones reported in Table 22. For the fatigued coatings, R_{po} increased over the course of the exposure period, as did the ambient exposure coating. However, the increase was only 6% of the increase seen in the ambient exposure coatings, suggesting that the additional curing may have been counteracted by damage from the fatigue loading. In addition, after exposure to 0.6 M NaCl solution in the laboratory for 24 h, R_{po} exhibited 5 orders of magnitude decrease. While the $23\times$ decrease in the goodness of fit parameter, illustrated visually in the plots shown in Figure 75, suggests that the Modified REAP model is no longer the best choice to fit this data, the decrease in R_{po} suggests rapid ingress of electrolyte into the coating. A possible cause for this ingress is cracking by the topcoat or primer in response to fatigue loading.

The SKP results, shown in Figure 73, provide additional support to the EIS data suggesting that exposure to sunlight on the atmospheric exposure racks provided additional curing to the polymers, as the work function for the exposed coatings were higher than the work function for the unexposed coating. In addition, there are several areas in the work function plot for the fatigued coating system where the work function drops by 200-250 meV, behaving in a similar manner to pure aluminum. This also suggests that the fatigue loads induced damage in the coating, which is also consistent with the EIS results for the fatigued coatings.

While the SEM images did not provide evidence of coating cracking, as seen in Figure 71, they did reveal cracks in the pretreatment layer, which would allow electrolyte transported through the coating system to eventually reach the unprotected substrate. Fatigue loading, perhaps unsurprisingly, increased the linear density of the cracks. In the unstressed sample, pretreatment cracking occurred on the order of 2.5×10^{-3} cracks/ μm . In the fatigued sample, pretreatment cracking occurred on the order of 18.5×10^{-3} cracks/ μm , a $7.4\times$ increase.

Likewise, fatigue loading of the unsupported primer coating showed that the epoxy primers used in these aircraft coatings are susceptible to fatigue cracking, though those cracks occurred at lower strain levels versus the coatings on aluminum panels because they were unsupported by a substrate.

Conclusions

In this work we showed how different outdoor and laboratory exposures resulted in different aging mechanisms that led to substantial changes in the properties of a commercial aircraft coating system. The key takeaways from this investigation suggest that exposure of the coating system to ambient weather conditions without stress can initially result in improved barrier properties for the coating due to enhanced curing of the polymer. Exposure of the unstrained coating system to atmospheric and sea spray conditions, even for short durations, can result in degradation that is similar to that experienced by immersed coatings. Lastly, fatigue loading of unsupported and supported coatings can result in organic coating and pretreatment cracking that speeds up water ingress, substrate corrosion, and resulting coating failure.

We think this combination of fatigue testing of supported and unsupported coatings coupled with SKP and EIS measurements of the coating state during and after exposure provides a useful recipe for future testing and improving our understanding of coating degradation for Navy aircraft.

10. CONCLUSIONS AND IMPLICATIONS FOR FUTURE RESEARCH/IMPLEMENTATION

This project was undertaken to develop an improved theoretical understanding of organic coating system deterioration because of exposure to environmental stressors. This was accomplished by quantifying how static and dynamic environmental conditions influenced coating system deterioration over the duration of laboratory aging conditions and outdoor exposures.

EIS has frequently been used to provide a means to nondestructively evaluate coatings. Two machine-learning models were trained on a set of EIS data obtained from a commercial aircraft coating system applied to test coupons placed in laboratory environments that simulated outdoor exposure conditions. The EIS data was fit with the coatings equivalent circuit model using different initial parameter estimates to form the training datasets. The newly trained models were then included as a preprocessing step in the Levenberg-Marquardt nonlinear regression method for the equivalent circuit model fit. Comparing the outcomes between the original algorithm and the one using the machine-learning (ML) models indicated a ~50x increase in performance.

Several equivalent circuit models were then used to analyze EIS data, and equivalent circuit parameter values were linked to outcomes of physics-based models of the resistivities and dielectric constants of the organic polymers making up the coating system. The fits to the measured EIS data from the equivalent circuit models were compared in how closely they matched the measured data. The physics-based input to the equivalent circuit modeling provided insight into the deterioration of the coating system in response to in-service environmental exposures.

Water uptake by organic coating systems used for corrosion prevention on airframes is one of the principal contributors to the loss of barrier properties of the coating. We used equivalent circuit analyses of EIS data to track changes in coating layer capacitance for a two-layer coating system consisting of an epoxy primer and polyurethane topcoat immersed in NaCl solutions with different concentrations and temperatures. The capacitance curve exhibited two different response regions, consistent with the “two-stage kinetics” mechanisms for water uptake by the polymers. We tested several numerical diffusion models of water sorption and found the most successful to be one that varied the diffusion coefficient as a function of polymer type and immersion time and accounted for physical aging processes in the polymer. We employed the Brasher mixing law along with the water sorption model to estimate the coating capacitance as a function of water uptake. The predicted capacitance of the coating was found to be consistent with the capacitance obtained from the EIS data, which is consistent with theories that water uptake occurs via initial rapid transport followed by a much slower aging process. Thus, both these water uptake processes need to be considered when making EIS measurements to assess the state of a coating system.

A modified version of the rapid electrochemical assessment of paint (REAP) equivalent circuit was developed, along with a method to calculate the impedance of a circuit using matrix algebra. This new equivalent circuit and the calculation method was used to analyze EIS data obtained from a two-layer commercial organic coating system immersed in NaCl solutions with different concentrations and at different temperatures. The matrix calculation method was validated by comparing results obtained from commercial analysis software to this method for two different equivalent circuits and the parameter values are nearly equal. Physics-based models of the equivalent circuit elements were derived and used to obtain both initial estimates for the regressions and physics-based constraints on the model parameters. These models are integrated into the regression procedure and the corrected Akaike information criterion (AICc) is used to

compare fits between the new circuit and classic equivalent circuits. The AICc values indicate the new circuit results in better fits than classic equivalent circuits used for coatings analysis.

While there has been substantial progress in understanding coating degradation and standardized testing has been developed to evaluate coating systems by subjecting them to aggressive weather cycling conditions, the combined effects of exposure conditions and applied deformations are not typically addressed. Here, an aircraft component was modeled to investigate the range of deformations and strains to which an aircraft coating may be subjected, in service. The model focused on the deformations and stresses around a countersunk fastener between the skin and the front spar of an aircraft wing because that is an area that experiences high stresses and strains during landings and flight maneuvers. Results showed that peak strains at the interface of skin or fastener and coating can range from 1% to 10% for severe loading events. Peaks and ranges are a function of coating thickness, preload level of the fastener and level of interference.

To better inform our model of deformations and strains, we experimentally measured the tensile properties of the materials forming a coating system for aircraft structures before and after atmospheric exposure. The materials were deposited on release paper and tested in tension. Samples were tested in the as-deposited condition after curing and after 5736 h of exposure to the atmospheric environment. The material properties for both unexposed and exposed conditions were used in a structural model to identify the applied loads that can lead to cracking of the coating system at a critical fastener-skin interface location. A testing sample and methodology was proposed to directly measure the fatigue properties of the primer and initial results are presented.

Two principal future research directions suggest themselves at the conclusion of this program: one focused on theory and modeling development and one focused on implementation and improving the TRL of the technology. The development of a full-state model for coating degradation that synthesizes environmental exposure data, particular water and pollutant accumulation and exposure to UV radiation, with models for the rate of water saturation of organic polymers, and the effect of cyclic and high stress loads on the coating system is, as yet, incomplete. Such a full-state model is necessary to be able to accurately predict the state of the coating along with the underlying substrate. In the implementation direction, once the full state model has been validated, an in-situ EIS measurement device, coupled with aircraft sensors to detect local corrosive environments and aircraft loads, would be able to provide the maintainer with an accurate assessment of the state of the coating system. Such output could be in the form of red/yellow/green assessment, as was suggested by the interim rating scheme, but the red/yellow/green categories would then be founded on a stronger physics basis than the current state-of-the-art of monitoring the coating impedance at 0.1 Hz.

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