INVESTIGATION OF CORROSION INITIATION AND PROGRESSION UNDER COATING IN ALUMINUM ALLOY 2024-T3 USING THE SCANNING VIBRATING ELECTRODE TECHNIQUE

Thesis

Submitted to

Graduate Engineering & Research
School of Engineering

UNIVERSITY OF DAYTON

In Partial Fulfillment of the Requirements for

The Degree

Master of Science in Chemical Engineering

by

Autumn Marie Buchanan

UNIVERSITY OF DAYTON

Dayton, Ohio

May 2000
INVESTIGATION OF CORROSION INITIATION AND PROGRESSION UNDER COATING IN ALUMINUM ALLOY 2024-T3 USING THE SCANNING VIBRATING ELECTRODE TECHNIQUE

APPROVED BY:

Kevin Myers, D.Sc., P.E.  
Advisory Committee Chairman  
Professor, Chemical Engineering Department

Tony Saliba, Ph.D.  
Committee Member  
Professor and Department Chair, Chemical and Materials Engineering Department

Mohammad Khobaib, Ph.D.  
Committee Member  
Research Engineer, University of Dayton Research Institute

Donald Moon, Ph.D.  
Associate Dean  
Graduate Engineering Programs & Research  
School of Engineering

Blake Cherrington, Ph.D., P.E.  
Dean, School of Engineering
ABSTRACT

INVESTIGATION OF CORROSION INITIATION AND PROGRESSION UNDER COATING IN ALUMINUM ALLOY 2024-T3 USING THE SCANNING VIBRATING ELECTRODE TECHNIQUE

Name: Buchanan, Autumn Marie
University of Dayton, 2000

Research Advisor: Mohammad Khobaib, Ph.D.
Academic Advisor: Kevin Myers, D.Sc., P.E.

For years, aluminum alloys have been the materials of choice for structural components of aircraft because of their high specific strength. However, aluminum alloys, especially those with copper as a major constituent, are susceptible to corrosion. One common approach to preventing corrosion damage is through the use of organic coatings, which provide protection through a complex mechanism of inhibition and barrier functionality. Unfortunately, little is known about the early stages of corrosion initiation under the coating that lead to subsequent failures. In order to gain an understanding of the mechanisms of corrosion initiation and propagation, a reliable evaluation technique that provides information about corrosion initiation and its progression is a necessary tool for coatings research and development. One such tool, the Scanning Vibrating Electrode Technique (SVET), was used in this study to develop a methodology to detect and quantify the early stages of corrosion damage. Corrosion activity was successfully detected by the
SVET on an aluminum 2024-T3 panel with a delaminated coating. SVET testing of panels with intact high-resistance barrier coatings could not reveal corrosion damage under normal testing conditions because of little or no corrosion activity within the time of exposure. To study corrosion initiation and obtain results in a reasonable amount of time, it became necessary to find or develop a method for creating artificial damage. Chemical, mechanical, and electrochemical means of initiating corrosion damage were investigated. Corrosion initiation and its progress under coating were studied in detail and results are discussed here. Imposing an external potential proved to be the most promising way to artificially create damage. A study was further conducted to explore optimum polarization conditions for various coating cure times. The sample with the shortest coating cure (four days) exhibited the best corrosion resistance while the sample with the longest coating cure (eighteen days) exhibited the worst corrosion resistance. There is no clear explanation for this behavior, and more tests should be performed before concrete conclusions are drawn. The three samples did, however, demonstrate similar corrosion mechanisms. Activity at the damage site was initially anodic. With continued exposure, the current density at the damage site switched from anodic to cathodic, possibly due to cathodic copper deposits left behind after aluminum dissolution. With further increases in time, the current density at the damage site changed back again to anodic activity, perhaps because the copper deposits dissolved in the solution since they were no longer anchored to the matrix. A better understanding of the corrosion mechanisms is important because the information can be utilized by coating formulation experts to aid in the development of corrosion resistant coatings.
ACKNOWLEDGEMENTS

This research was sponsored by the Defense Advanced Research Projects Agency-Multidisciplinary University Research Initiative (DARPA-MURI), under Air Force Office of Scientific Research grant number F49620-96-1-0442.

I would like to thank the Ohio Aerospace Institute for their generous grant and the Dayton Area Graduate Studies Institute for their tuition support.

I am grateful to Alan Shipley and Dr. Carol Jeffcoate for their technical advice and guidance concerning the SVET. George Pacinda deserves recognition for supplying the coated panels and for sharing his extensive knowledge of coatings. Also, thanks to Dr. Mohammad Khobaib for his help throughout this research project.

I would finally like to thank my husband, Bob, for his love, support, and understanding throughout the duration of this project.
TABLE OF CONTENTS

ABSTRACT ................................................................................................................ iii
ACKNOWLEDGEMENTS ........................................................................................ v
LIST OF FIGURES .................................................................................................. viii
LIST OF TABLES .................................................................................................... xi
LIST OF ABBREVIATIONS ................................................................................... xii

CHAPTER

1. INTRODUCTION .............................................................................................. 1

2. REVIEW OF RELATED MATERIAL .............................................................. 4
  2.1 BASIC CORROSION PRINCIPLES ......................................................... 4
  2.2 PROPERTIES OF ALUMINUM AND ITS ALLOYS ................................. 6
     2.2.1 Passivity of Aluminum ................................................................. 6
     2.2.2 Alloying Effects ........................................................................... 7
  2.3 COATING PROPERTIES ........................................................................... 9
  2.4 ANODIC POLARIZATION ...................................................................... 13

3. EXPERIMENTAL PROCEDURE .................................................................. 15
  3.1 SAMPLE PREPARATION ......................................................................... 15
  3.2 SCANNING VIBRATING ELECTRODE TECHNIQUE ............................... 17
     3.2.1 Theory ......................................................................................... 17
     3.2.2 Instrumentation ........................................................................... 19
3.2.3 Electrode Preparation ...................................................... 24
3.2.4 Calibration ....................................................................... 26
3.2.5 Advantages of SVET in Corrosion Characterization .... 28

3.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY ...... 29

4. RESULTS AND DISCUSSION ....................................................... 31

4.1 INVESTIGATION OF PRE-EXISTING CORROSION DAMAGE .................................................................................. 31

4.2 INVESTIGATION OF ARTIFICIAL CORROSION DAMAGE ......................................................................................... 36

4.3 POLARIZATION CONDITIONS AND COATING CURE STUDY .................................................................................... 45

  4.3.1 Coating Cure of Four Days: First Experiment .......... 47

  4.3.2 Coating Cure of Eleven Days ........................................ 51

  4.3.3 Coating Cure of Eighteen Days .................................. 55

  4.3.4 Coating Cure of Four Days: Second Experiment ....... 61

5. SUMMARY ...................................................................................... 69

  5.1 FUTURE WORK ........................................................................ 71

BIBLIOGRAPHY ...................................................................................... 72
LIST OF FIGURES

1. Schematic of metal dissolution in the presence of hydrochloric acid.....................5
2. Transport of moisture and oxygen through coating.............................................10
3. Mechanism of blister formation............................................................................12
4. Schematic of increase in corrosion rate with increasing surface potential during anodic polarization.............................................................................................14
5. Schematic of vibrating probe for DC current density mapping .........................18
6. Schematic of SVET system....................................................................................19
7. A typical SVET system setup................................................................................21
8. Schematic of the vibrating probe vibrating in two dimensions: (A) piezoelectric reed producing the vertical component of vibration; (B) and (C) piezoelectric reeds producing the horizontal components; (D) insulated stainless steel electrode with platinized tip (E); (F) end of wire that leads to phase-sensitive detector .....22
9. SVET calibration scheme.......................................................................................27
10. Corrosion damage on Al 2024-T3 panel with organic coating after 2000 hours of Prohesion exposure........................................................................................................32
11. Comparison of impedance behavior .................................................................33
12. Three-dimensional current density map of Al 2024-T3 panel with organic coating....................................................................................................................34
13. Comparison of, (a) two-dimensional surface map with (b) in-situ video image of Al 2024-T3 panel with organic coating .....................................................................................35
14. Current density map of a panel with 10% Harrison’s drop under coating after 75 hours electrolyte exposure.....................................................................................37
15. Current density maps of panel with 10% Harrison’s solution drop under coating after, (a) 85 hours electrolyte exposure, sample scribed prior to scan, and (b) 110 hours electrolyte exposure, CuCl₂ placed in scribe prior to scan ........................................ 38

16. Panel with 10% Harrison’s solution drop under coating after 112 hours total electrolyte exposure, (a) current density map, and (b) corresponding vector overlay .................................................................................................................. 39

17. Current density map of a panel with drop of 0.2% CuCl₂ in Harrison’s solution under coating after 107 minutes total electrolyte exposure .............................................. 41

18. Panel with drop of 0.2% CuCl₂ in Harrison’s solution under coating after seven hours exposure, (a) current density map, and (b) corresponding vector overlay diagram ...................................................................................................... 42

19. Current density map of panel with drop of 0.2% CuCl₂ in Harrison’s solution under coating after 22 hours total electrolyte exposure ............................................. 43

20. Current density map of panel with drop of 0.2% CuCl₂ in Harrison’s solution under coating after 25 hours total electrolyte exposure and potential applied during scan ........................................................................................................ 44

21. Sample with four days of coating cure and 62 hours total electrolyte exposure, polarized to –105 mV, (a) current density map, and (b) corresponding vector overlay diagram ...................................................................................................... 48

22. Current density maps of sample with four days of coating cure after, (a) 64 hours electrolyte exposure, polarized to –105 mV, and (b) 66 hours electrolyte exposure, polarized to –105 mV ......................................................... 49

23. Sample with four days of coating cure and 75 hours electrolyte exposure, polarized to –105 mV, (a) current density map, and (b) corresponding vector overlay diagram ...................................................................................................... 50

24. Sample with eleven days of coating cure and 26 hours electrolyte exposure, polarized to –155 mV, (a) current density map, and (b) corresponding vector overlay diagram .............................................................................................. 52

25. Sample with eleven days of coating cure and 50 hours electrolyte exposure, polarized to –155 mV, (a) current density map, and (b) corresponding vector overlay diagram .............................................................................................. 53

26. Sample with eleven days of coating cure and 64 hours electrolyte exposure, polarized to –105 mV, (a) current density map, and (b) corresponding vector overlay diagram .............................................................................................. 54
27. Vector overlay diagram for sample with eighteen days of coating cure and 28 hours electrolyte exposure, polarized to −550 mV ........................................56

28. Current density maps of sample with eighteen days of coating cure, (a) 55 hours electrolyte exposure, polarized to −500 mV, and (b) 76 hours electrolyte exposure, polarized to −450 mV ..........................................................57

29. Current density maps of sample with eighteen days of coating cure after, (a) 97 hours electrolyte exposure, polarized to −400 mV, and (b) 98 hours electrolyte exposure, polarized to −400 mV ..................................................................................58

30. Sample with four days of coating cure and 23 hours electrolyte exposure, open circuit testing, (a) current density map, and (b) corresponding vector overlay diagram ........................................................................................................62

31. Sample with four days of coating cure and 30 hours electrolyte exposure, polarized to −155 mV, (a) current density map, and (b) corresponding vector overlay diagram ........................................................................................................63

32. Current density maps of sample with four days of coating cure after, (a) 44 hours electrolyte exposure, polarized to −155 mV, and (b) 46 hours electrolyte exposure, polarized to −155 mV ..................................................................................64

33. Current density maps of sample with four days of coating cure after, (a) 49 hours electrolyte exposure, polarized to −155 mV, and (b) 66 hours electrolyte exposure, polarized to −155 mV ..................................................................................66

34. Current density maps and vector overlay of sample with four days of coating cure after, (a) 85 hours electrolyte exposure, polarized to −155 mV, (b) 87 hours electrolyte exposure, polarized to −155 mV, and (c) 87 hours electrolyte exposure, polarized to −155 mV ..................................................................................67
LIST OF TABLES

1. Chemical composition of Al 2024-T3 .................................................................7
2. Cure time between coating application and SVET testing.................................46
3. Immersion times and corresponding polarization values for Panel 1 ..................47
4. Immersion times and corresponding polarization values for Panel 2 ..................51
5. Immersion times and corresponding polarization values for Panel 3 ..................55
6. Immersion times and corresponding polarization values for Panel 4 ...............61
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>alternating current</td>
</tr>
<tr>
<td>Ag</td>
<td>silver</td>
</tr>
<tr>
<td>AgCl</td>
<td>silver chloride</td>
</tr>
<tr>
<td>Al 2024-T3</td>
<td>aluminum alloy 2024-T3</td>
</tr>
<tr>
<td>ASET</td>
<td>Automated Scanning Electrode Technique</td>
</tr>
<tr>
<td>AuKCN</td>
<td>gold potassium cyanide</td>
</tr>
<tr>
<td>CMS</td>
<td>Corrosion Measurement System</td>
</tr>
<tr>
<td>CuCl₂</td>
<td>cupric chloride</td>
</tr>
<tr>
<td>DARPA-MURI</td>
<td>Defense Advanced Research Projects Agency-Multidisciplinary University Research Initiative</td>
</tr>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>ENM</td>
<td>Electrochemical Noise Method</td>
</tr>
<tr>
<td>FRD</td>
<td>Frequency Response Detector</td>
</tr>
<tr>
<td>KCl</td>
<td>potassium chloride</td>
</tr>
<tr>
<td>NaCl</td>
<td>sodium chloride</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>ammonium sulfate</td>
</tr>
<tr>
<td>NDE</td>
<td>Non-Destructive Evaluation</td>
</tr>
<tr>
<td>PSD</td>
<td>Phase-Sensitive Detector</td>
</tr>
</tbody>
</table>
SCC: Stress Corrosion Cracking
SCE: Saturated Calomel Electrode
SVET: Scanning Vibrating Electrode Technique
CHAPTER 1

INTRODUCTION

For decades, aluminum alloys have been the materials of choice for structural components of aircraft. The low specific gravity of aluminum results in high specific strength that makes aluminum alloys the logical selection for weight-critical applications. In addition, well-documented performance characteristics, low fabrication costs, extensive design experience, and established manufacturing methods are all reasons for confidence in and continued use of aluminum alloys into the next century\(^1\).

One major drawback of aluminum alloys, however, is corrosion, a process that is accelerated by an aircraft’s exposure to corrosive materials such as hydraulic fluids, salts, and moisture\(^2\). Based on the environmental conditions encountered, aluminum alloys experience various types of corrosion damage, including general corrosion, galvanic corrosion, pitting corrosion, intergranular corrosion, exfoliation corrosion, and crevice corrosion. Compounding the problems associated with corrosion damage is the age of the aircraft in service\(^2\). The United States Air Force has turned its attention to extending the life of its aging fleet, forcing the existing planes to exceed the service lives for which they were originally designed\(^3\). As these aircraft age, the
importance of detecting and preventing corrosion to maintain structural integrity and airworthiness becomes increasingly imperative.

One common approach to preventing corrosion damage is through the use of organic coatings. Aircraft coatings provide protection through a complex mechanism of inhibition and barrier functionality. In this scheme of corrosion prevention, the surface pretreatment provides passivation of the metal surface, incorporates corrosion inhibitor, and creates a surface topography for maximum primer adhesion. The primer incorporates corrosion inhibitors and serves as an adhesive layer between the metal substrate and the topcoat layers. At mechanically stressed or damaged areas such as fasteners, rivets, expansion joints and scratches, the surface pretreatment/primer system provides active corrosion protection from exposure to environmental factors. The primer is intended to remain intact for over thirty years. The loss of any integrity in such a prevention scheme results in corrosion initiation, mainly due to loss of adhesion. Other factors contributing to corrosion initiation include defects, pores in the primer coating, and degradation of the primer coating, which allows the ingress of environment to substrate. All these factors can be in a broader sense classified under loss of adhesion or exposed substrate at the primer/surface pretreatment interface. Such a loss is a key element in the corrosion initiation process.4

Unfortunately, little is known about the early stages of corrosion initiation under the coating that lead to subsequent failures. This realization, paired with the desire to extend the life of the Air Force’s aging fleet and the need to develop environmentally compliant, durable coating systems, has spurred current research in
the testing and characterization of coatings. In order to gain an understanding of corrosion initiation and propagation, a reliable evaluation technique that provides information about corrosion initiation and its mechanisms is a necessary tool for coatings research and development.

An investigation supported by Defense Advanced Research Projects Agency – Multidisciplinary University Research Initiative (DARPA-MURI) was conducted to study the initiation of corrosion under a protective coating. The primary goal of this study was to develop a methodology to detect and quantify the early stages of corrosion damage using the Scanning Vibrating Electrode Technique (SVET). In general, however, intact high-resistance barrier coatings did not reveal corrosion damage under normal testing conditions. It became necessary, then, to develop a method for creating artificial damage that allowed corrosion to initiate and grow beneath the coating and obtain results in a reasonable amount of time. Chemical, mechanical, and electrochemical means of initiating corrosion were investigated, and imposing an external potential proved to be the most promising way to initiate corrosion in a short period of time. A study was then conducted to explore optimum polarization conditions while simultaneously examining coating cure. The overall goal of the continuing effort is to integrate electrochemical results from SVET with information from other Non-Destructive Evaluation (NDE) techniques. The SVET, which has very high resolution, detects minute corrosion activity on a sample surface. NDE techniques lack high resolution but are available for use in the field. Correlation of data from both techniques would aid in the development of a model to predict the useful life of a coating.
CHAPTER 2

REVIEW OF RELATED MATERIAL

2.1 BASIC CORROSION PRINCIPLES

When a metal is placed in an aqueous environment, three types of behavior can occur: corrosion, passivation, or immunity. If corrosion ensues, dissolution of the metal will result. By definition, corrosion is the destructive attack on a metal by a chemical reaction with the environment that is in contact with the metal. Most commonly, this reaction is an electrochemical one. In fact, the tendency to corrode results from a non-uniform metal composition that leads to anodic and cathodic regions on the surface. For a corrosion reaction to occur, five components are necessary: an anode (metallic region that corrodes), a cathode, electrical contact, an electrolyte (continuous medium), and a cathode reactant (the component, usually oxygen, that reacts with electrons created by the anodic reaction). Removal of one or more of these critical components will thwart the process of corrosion.

For a corroding metal, $M$, the anodic reaction is of the general form:

$$M \rightarrow M^{n+} + ne^- \tag{1}$$

while the corresponding cathodic reaction in acidic conditions, for example, is:
These complementary reactions are shown in Figure 1, a schematic of the dissolution of a metal in an acid solution. The metal, M, is being oxidized, liberating metal ions, M^{2+}, into solution. The metal electrons, e', are consumed by reduction of H^+ to H_2. In this study, however, the aluminum alloy was immersed in neutral or slightly acidic electrolyte. Under these conditions, the cathodic reaction most often encountered is the reduction of dissolved oxygen according to:

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]

The phenomenon of corrosion obeys conservation of charge, meaning that the rate of electron generation must match the rate of consumption.
2.2 PROPERTIES OF ALUMINUM AND ITS ALLOYS

In this section, the properties of aluminum and its alloys are discussed in relation to the corrosion characteristics of aluminum.

2.2.1 Passivity of Aluminum

Thermodynamically, aluminum is a reactive metal with poor corrosion resistance. In reality, however, aluminum and its alloys show relatively high corrosion resistance due to the passive nature of aluminum. Passivity is defined as a condition of corrosion resistance due to the formation of a thin surface oxide film\(^7\). This protective surface film of aluminum oxide forms immediately and grows rapidly when a fresh aluminum surface is exposed to either humid air or water\(^8\). A normal surface film thickness in air is 5 nm. Thicker films are formed in water or at elevated temperatures\(^8\). The oxide film is generally stable over a pH range of 4.0 to 9.0 but dissolves in strong acids and alkalis. It is believed that damage to or breakdown of this passive oxide layer leads to initiation of corrosion damage.
2.2.2 Alloying Effects

Mechanically, pure aluminum is very weak. In order to achieve desirable strength properties necessary for use in the aerospace industry, aluminum is alloyed by the addition of a number of elements. The chemical composition of Al 2024-T3, the aluminum alloy used in this investigation, is listed in Table 1.

Table 1: Chemical composition of Al 2024-T3\(^9\).

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Balance</td>
</tr>
<tr>
<td>Mg</td>
<td>1.2 - 1.8</td>
</tr>
<tr>
<td>Si</td>
<td>0.5</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1</td>
</tr>
<tr>
<td>Mn</td>
<td>0.3 - 0.9</td>
</tr>
<tr>
<td>Fe</td>
<td>0.05</td>
</tr>
<tr>
<td>Cu</td>
<td>3.8 - 4.9</td>
</tr>
<tr>
<td>Zn</td>
<td>0.25</td>
</tr>
</tbody>
</table>

While alloying elements improve the mechanical properties of aluminum, they have a detrimental effect on corrosion resistance. As noted in Table 1, copper is the major alloying element in Al 2024-T3. In the Galvanic Series, copper has a more positive potential than aluminum. As a result, when the copper that is dispersed throughout the aluminum matrix is exposed to a continuous medium (i.e. an
electrolyte) the requirements for corrosion are met, and the potential difference between the two metals cause electrons to flow from aluminum to copper. In this galvanic couple, the more negative element is aluminum, which serves as an anodic site that produces electrons as it dissolves. The more positive element, copper, serves as a reaction site where electrons are consumed. Due to the presence of copper, the 2XXX series of aluminum alloys is particularly susceptible to pitting corrosion, intergranular corrosion, and stress corrosion cracking (SCC).
2.3 COATING PROPERTIES

One of the most common methods to prevent corrosion damage is through the application of organic coating systems. A complete coating system typically consists of a surface pretreatment, primer, and topcoat. While each component of the coating system fulfills a necessary role, the primer is of paramount importance in corrosion prevention and coating adhesion\textsuperscript{10}. The primer protects the metallic substrate by increasing the electrical resistance between the metal surface and the electrolyte, thereby reducing the flow of corrosion current. The primer also inhibits the cathode reaction, as shown in Equation 3 in Section 2.1 above, by diminishing the access of oxygen and moisture to the substrate\textsuperscript{10}.

Even under the best of circumstances, it is almost impossible to completely prevent the access of water and oxygen to the metal. Pinholes, holidays, and other coating defects as well as the general coating film continuum allow the transport of oxygen and moisture\textsuperscript{10}. Most of the coatings are pigmented. In these systems, transport occurs through interstices between pigment particles. In coatings with low pigment, transport takes place at the molecular level through sites such as hydratable polar groups\textsuperscript{10}. Once inside the continuum, the penetrating molecule delves through successive levels of strata until it reaches the metal, as shown in Figure 2. Osmotic and electroendosmotic pressures as well as thermally induced vibrations of the coating molecules facilitate the transport of water and oxygen\textsuperscript{10}. Even if the primer
fails to suppress the cathodic reaction, it does reduce corrosion by resistance inhibition. The ionic resistance of the coating prevents electrical conductance, thereby removing one of the necessary components for corrosive reaction $^{10}$.

![Diagram](image)

**Figure 2:** Transport of moisture and oxygen through coating $^{10}$.

While the primer barrier properties are important, coating adhesion to the metal substrate also deserves consideration. If moisture that has permeated an intact film displaces the coating, water and oxygen dissolved in the water are in direct contact with the metal surface. Because reactive ions in the water layer provide a vehicle for electron transport, all five elements necessary for corrosion are present $^{6}$. Aluminum and hydroxide ions are generated as corrosion proceeds, and an osmotic cell is formed under the coating. The coating acts as a semipermeable membrane, passing water to balance the concentration of soluble materials on either side of the
coating. Osmotic pressure beneath the film increases with time. The build-up of pressure provides enough force to displace the film from the substrate, leading to the formation of a blister. As the blister grows, increasing areas of unprotected substrate are exposed. This results in the formation of additional corrosion products, and the entire process continues. The mechanism of osmotic blistering is shown in Figure 3.

Blistering can also occur by a mechanism referred to by Hare as the "paint remover effect". In this scheme, blistering is not necessarily a result of the dissolution of soluble contaminants on the metal surface. Rather, small molecules penetrate the coating and accumulate at the substrate/coating interface. The presence of these species causes the film to dilate, reducing its adhesion and causing a blister.

It should be obvious, then, that adhesion and barrier properties of the coating are intimately connected in terms of corrosion protection. When barrier properties are satisfactory, lower permeability leads to lower ion concentrations in the solution below the film. As a result, there is less osmotic pressure below the coating. A lower osmotic pressure translates to a lower driving force for increase in water uptake and, hence, less tendency for a blister to grow.
Figure 3: Mechanism of blister formation$^{10}$. 
2.4 ANODIC POLARIZATION

During this investigation, high resistance barrier coatings showed little or no corrosion after the first few weeks of exposure to a laboratory electrolyte. Various chemical, mechanical, and electrochemical means of artificially initiating corrosion damage were examined, and imposing anodic potential was found to be a satisfactory method of creating corrosion damage.

The electrochemical reactions shown in Equations 1 through 3, discussed in Section 2.1, proceed at finite rates, but if there is a deficiency of electrons liberated by the anodic reaction, a positive charge accumulates at the metal/solution interface. This positive potential is called anodic polarization. As the deficiency of electrons becomes greater, the tendency for anodic dissolution becomes greater. In this way, anodic polarization represents a driving force for corrosion\(^7\).

A metal in an aqueous electrolyte solution reaches a steady state potential, \(E_{\text{corr}}\), as shown in Figure 4. This steady state potential depends on the rate at which electrons can be exchanged by the cathodic and anodic reactions. During anodic polarization, the surface potential increases from \(E_{\text{corr}}\) to a new value, \(E^7\). It can be seen from Figure 4 that when the potential is raised to \(E\), the corrosion rate will increase as well.
Anodic polarization requires the use of a potentiostat. The set potential established between the test electrode and a reference electrode is compared with the actual electrode potential. If the two potentials differ, current is made to flow between a counter electrode and the test electrode to re-establish the set potential value.\textsuperscript{11}
CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 SAMPLE PREPARATION

The high strength aluminum alloy 2024-T3 (Al 2024-T3) was selected as the substrate for all the samples prepared in the laboratory. The 3-inch x 3-inch x 0.032-inch aluminum panels were first degreased using a solvent degreaser followed by a hot (120°F) alkaline cleaner. The panels were then rinsed with deionized water and deoxidized in an acid deoxidizer. The samples were rinsed again with deionized water, dried with an air stream, and coated soon after cleaning. The panels were coated using a wire-wound rod and allowed to dry at ambient laboratory conditions. Unless otherwise noted, the primer coating was a water-based epoxy crosslinked with a polyamine curing agent. The wet coating thickness was 2 mils. After coating, the samples were masked with waterproof tape to limit the region exposed to electrolyte. A 5-mm x 5-mm area of the coated substrate was left exposed for testing. After masking the sample, a 1/8” high, 2” diameter slice of acrylic pipe was glued to the masked sample surface to form a cell to hold the electrolyte solution. The glue was allowed to dry for at least 24 hours prior to testing. The cell was filled with regular Harrison’s solution, an electrolyte containing 5.00 grams NaCl and 35.00 grams
(NH₄)₂SO₄ in 1.00 liter of water, immediately prior to each test. Regular Harrison’s solution has a resistivity of 500 ohm-cm and a slightly acidic pH.

It was noted that in most cases, the coating systems performed so well that, under normal immersion, no significant corrosion damage was detected, even after weeks of continuous electrolyte exposure. In order to establish an accelerated test methodology and obtain results in a reasonable amount of time, corrosion damage was intentionally created, allowing the subsequent observation of corrosion progression. Various chemical, mechanical, and electrochemical methods were investigated as a means of artificially damaging the coating and/or the metal substrate to study corrosion initiation. These techniques included placing drops of salt solution under the coating, scribing the sample, and applying an external potential. Sample preparation was slightly different for the panels that contained a drop of salt on bare metal. The aluminum panels were cleaned as described above, then a small drop of salt was placed on the panel using a microsyringe. The drop was allowed to dry at ambient conditions before the sample was coated and prepared for testing as described above.
3.2 SCANNING VIBRATING ELECTRODE TECHNIQUE

The Scanning Vibrating Electrode Technique was the primary tool used in this study to investigate corrosion initiation and its progress under coating. In this section, the theory behind the technique and a description of the instrumentation involved in current density mapping measurements are discussed.

3.2.1 Theory

On a freely corroding surface, direct current (DC) corrosion currents flow due to the presence of anodic and cathodic areas. SVET has been developed to allow in-situ examination of these DC currents associated with localized corrosion activity. SVET current density maps are derived from measurements of potential gradients in solution\textsuperscript{12}. In Figure 5, a schematic of the vibrating probe for DC current density mapping is shown. A single electrode vibrates between two points in solution and measures the changes in potential differences in the solution due to the flow of corrosion currents between the points of vibration excursion. The potential gradient is equal to the voltage difference divided by the distance between the two points of measurement. The current density in the direction of vibration is calculated according to Ohm’s Law, knowing the potential gradient and the solution resistivity\textsuperscript{12}.
Figure 5: Schematic of vibrating probe for DC current density mapping\textsuperscript{12}. 
3.2.2 Instrumentation

A schematic of the SVET system is shown in Figure 6. The equipment was purchased from Applicable Electronics, Incorporated\textsuperscript{13}. Periphery equipment includes a Potentiostat/Galvanostat (Model 263A) and a Frequency Response Detector (FRD) (Model 1025) manufactured by EG&G Princeton Applied Research\textsuperscript{14}.

\textbf{Figure 6:} Schematic of SVET system\textsuperscript{15}. 
The sample is placed on the stage below the video camera and zoom lens. The graphics monitor projects the image captured by the video camera and allows the user to view the sample, properly position the probe, and establish scan boundaries. The video camera can be raised or lowered to focus on the sample surface using keyboard controls. To keep the probe from touching the sample surface, the focus is raised to a pre-determined distance above the surface, and the probe is then lowered to that pre-determined position above the sample. In this study, the probe was maintained at an approximate distance of 75 µm above the surface. Two platinum-blackened wires are also placed in the bath. One wire serves as a ground while the other wire is a reference for the SVET. Automated Scanning Electrode Technique (ASET) software, manufactured by Applicable Electronics\(^{13}\), is used to program the desired scan parameters. A 20 x 20 grid scan was chosen for this study, unless otherwise noted. X and Y probe vibration is turned on prior to testing. Before each scan, a reference measurement is taken at a user-specified location where no corrosion currents are flowing, normally over a completely insulated area such as the masking tape, to obtain a baseline. Following each scan, a video image of the sample is acquired so a vector overlay plot can be created using the ASET software. A typical system setup used in this study is shown in Figure 7. Pictured there are the camera, sample and holder, vibrating probe, calibration point source, grounding wires, and isolation table.
Figure 7: A typical SVET system setup.

The EG&G potentiostat was used for those experiments in which external potential was imposed. An Ag/AgCl reference consisting of a silver wire in a 3M KCl solution saturated with AgCl is placed in the bath to serve as the reference electrode. A platinum wire ring, which serves as the counter electrode, is affixed to the sample cell and placed in the bath. The coated aluminum sample is the working electrode. The desired potential is set using the potentiostat front-panel controls. The camera height is adjusted to focus on the sample, the focus is raised approximately 75 μm above the surface, and the probe is then lowered to that position 75 μm above the sample. Measurements are then taken after specifying the desired scan parameters.

The probe vibrates in two orthogonal directions at the same time, with a different frequency of vibration in each direction. Excitation of two piezoelectric
bimorph reeds produces the two-dimensional vibrations, as shown in Figure 8. Only the vibrations in the Y-direction (vertical) were considered. The electrode vibration converts the DC potential gradient in solution to an alternating current (AC) potential\textsuperscript{15}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Schematic of the vibrating probe vibrating in two dimensions: (A) piezoelectric reed producing the vertical component of vibration; (B) and (C) piezoelectric reeds producing the horizontal components; (D) insulated stainless steel electrode with platinized tip (E); (F) end of wire that leads to phase-sensitive detector\textsuperscript{16}.}
\end{figure}

In order to be electronically processed, the electrode signal is amplified by a factor of 100 in a preamp unit. The signal is then fed to a second amplifier that filters out all signals above 10 kHz and amplifies the signal by another factor of 2 or 20 depending on the gain configuration. Often, the AC signal cannot be measured directly on an oscilloscope because of noise. Lock-in amplifiers (or phase-sensitive detectors, PSDs) are used to extract the signal and convert the probe’s AC signal to a
DC voltage that represents current density$^{12}$. The electrode signal is fed to the PSD along with a reference signal from the oscillators driving the vibrating electrode. If the electrode signal is the same frequency as the reference signal, then it is detected. The PSDs operate at the two frequencies of vibration and detect the magnitude and phase of the electric field and current density components in the two vibration directions. These measurements are combined to give a single two-dimensional current density vector$^{16}$. From the PSD, the signal is fed to an interface board and is finally sent to the computer’s A/D board.
3.2.3 Electrode Preparation

Stainless steel electrodes manufactured by Micro Probe, Incorporated\textsuperscript{17} were used for all measurements. Platinum/Iridium probes may also be used, but stainless steel probes are the most common and least expensive. The probe wires are etched in acid to taper and sharpen the tips to a fine point. The finished probe tip is approximately 10 microns in diameter. The electrodes are coated with parylene to insulate them. Finally, they are electrically arced at the tips.

The manufacturer performs the above steps. Prior to use in the system, however, additional preparation is required. First, the insulation must be scraped off at a distance of 1.5 to 2 centimeters above the probe tip. The probe is then cut with wire cutters at the point where the insulation has been removed, resulting in a final probe length of 1.5 to 2 centimeters. Longer electrodes will whip and vibrate independently of the vibrator. When using stainless steel probes, the scraped end is dipped in full strength phosphoric acid prior to soldering into an R-30 pin. Once soldered, the pin and probe unit is mounted to the vibrator assembly, and the probe is ready to be platinized.

Before measurements can be taken, the probe is electroplated to create a platinum black tip. Platinum deposits in hairlike strands whose ends are connected to the electrode tip\textsuperscript{16}. Plating makes the tip highly capacitive due to the large surface area created by the platinum black plating. When stainless steel probes are used,
a gold-plating step before platinization is necessary to improve adherence of the platinum layer. This is achieved by immersing the electrode tip and a bare platinum wire in AuKCN solution. A current of \(-2\) nA is passed for 5 minutes followed by a current of \(-200\) nA for 1 minute. The probe is removed from the AuKCN solution and placed in a platinum chloride solution. While viewing the electrode in the microscope, a current of \(-200\) nA is passed and the probe is plated for 3 minutes. The current is slowly increased until the tip diameter is approximately 80% of the final desired diameter. The current is turned off and the dial is set to 6.0. One-half second shots of this high current are given until the final tip diameter is reached. The electrode capacitance is checked at this time. The probe test signal is viewed on the oscilloscope, and the tip capacitance is calculated using Equation 5:

\[
\text{tip capacitance} = \frac{\text{gain}}{\text{signal}}
\]

where tip capacitance is in nF, gain is equal to 10 based on system configuration, and signal is equal to the peak-to-peak signal volts\(^{18}\). A good electrode should have at least 2 nF of capacitance.
3.2.4 Calibration

After platinum blackening, the system must be calibrated. It is necessary to calibrate the probe in the solution intended for actual testing. If a different solution is used, a re-calibration step must be performed. Calibration allows the measured potentials to be converted into accurate current densities. Proper calibration is achieved by passing a known current from a current point source (a second, unplated stainless steel electrode) to a solution of known conductivity and making a measurement some known distance away. The distance should be sufficient to insure that the current flow is uniform and representative of that flowing from a point source\(^{15}\). Calibration in both the X and Y directions is performed, as shown in Figure 9. Current density is then calculated according to Equation 6:

\[
\text{current density} = \frac{I}{4\pi r^2}
\]  

(6)

where current density is in \(\mu A/cm^2\), \(I\) is the known current in \(\mu A\) delivered by the current passing electrode, and \(r\) is the distance in cm from the center of probe vibration to the tip of the calibration source\(^{18}\). During normal calibration, a 60 nA current is passed at a distance of 150 \(\mu m\) from the electrode. According to Equation 2, the measured current density should be 21.22 \(\mu A/cm^2\). A watch mode is included in the ASET software to check that the probe is accurately measuring current.
Figure 9: SVET calibration scheme\textsuperscript{18}.
3.2.5 Advantages of SVET in Corrosion Characterization

Several conventional ex-situ techniques have been used to study the corrosion process that occurs under the coating, but these methods have inherent problems\textsuperscript{12}. Polarization is destructive to the sample and averages global effects, Electrochemical Impedance Spectroscopy (EIS) requires imposition of an external voltage, and Electrochemical Noise Method (ENM) is also global rather than local. In addition, none of the above methods can identify the corrosion site. These limitations, coupled with uncertainties in defects due to processing, make comparison of various types of coatings difficult\textsuperscript{12,15,19}.

SVET overcomes some of these limitations. It is an in-situ technique that offers a method of directly observing the progress of corrosion. A video image of the sample is captured after each scan, and calculated current density vectors can be superimposed on the video image to determine the precise location of the current source. A repeat scan function quantifies corrosion progression with time by allowing the user to choose multiple consecutive scans to observe the growth or repassivation of corrosion sources over extended periods of time. Finally, high resolution allows detection of minute corrosion activity on a sample surface.
3.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

An additional characterization technique was used to study the corrosion behavior in delaminated and intact areas of a coated panel. Initial experiments on an aluminum panel with a delaminated coating and underlying corrosion incorporated data from Electrochemical Impedance Spectroscopy (EIS) to supplement the corrosion damage data acquired by the SVET. EIS is an electrochemical technique that can provide a variety of corrosion parameters but was used in this study to evaluate the integrity of the coating. EIS is used to analyze the response of a corroding sample to small-amplitude alternating potential signals of varying frequencies. The time-dependent current response $I(t)$ of an electrode surface to a sinusoidal alternating potential signal $V(t)$ has been expressed as an angular frequency ($\omega$) dependent impedance $Z(\omega)$ as shown in Equation 7:

$$ Z(\omega) = \frac{V(t)}{I(t)} $$

where

$$ V(t) = V_0 \sin \omega t $$

$$ I(t) = I_0 \sin (\omega t + \theta) $$

(7)

(8)

(9)
and $t$ is time and $\theta$ is the phase angle between $V(t)$ and $I(t)^{20}$. Various processes at the surface absorb electrical energy at discrete frequencies. This causes a time lag and a measurable phase angle between the time-dependent excitation and response signals\(^7\).

A variety of instrumentation is needed to conduct and interpret EIS. A function generator applies a range of sinusoidal potential frequencies to a potentiostat. The potentiostat applies the signal to the working electrode (the corroding sample). The electrode response is fed to a digital function analyzer that displays the impedance response and phase angle at each frequency. The data is stored in a computer, and Corrosion Measurement System 100 (CMS 100) software supplied by Gamry Instruments, Incorporated\(^{21}\) is used to manipulate and display the data\(^7\).

Potentiostatic EIS scans were conducted using a CMS 300 electrochemical system manufactured by Gamry Instruments, Incorporated\(^ {21}\). A Saturated Calomel Electrode (SCE) served as the reference, a carbon rod as the counter electrode, and the sample as the working electrode. Regular Harrison’s solution was used as the corroding electrolyte. The initial frequency was 5000 Hz and the final frequency was 0.2 Hz.
CHAPTER 4

RESULTS AND DISCUSSION

4.1 INVESTIGATION OF PRE-EXISTING CORROSION DAMAGE

Initial experiments were conducted on an Al 2024-T3 panel with a delaminated coating and underlying corrosion. The SVET was employed to gain information about conductive pathways present in the coating, while EIS data was collected to supplement the information gathered from SVET. The panel, which was coated with a proprietary organic coating system, was scribed to simulate coating breakdown and placed in a Prohesion chamber for 2000 hours. The Prohesion chamber is a device that imitates environmental conditions by alternating one hour salt fog spray (0.05% NaCl + 0.35% (NH₄)₂SO₄) with one hour of drying. The resulting coating degradation is shown in Figure 10. Large delaminated portions of coating were observed in the region of the scribe. The encircled area, which contained both delaminated and intact coating sections, was tested to measure and compare the property variation in both territories.
Figure 10: Corrosion damage on Al 2024-T3 panel with organic coating after 2000 hours of Prohesion exposure.

Although EIS can provide a variety of corrosion parameters, in this instance it was used to evaluate the integrity of the coating. The intact coating and delaminated coating regions were tested separately. The impedance behavior of the coating is shown in Figure 11. The dashed green line, denoted as 221bulk1.dta, represents the intact portion of the coating while the solid blue line, 221delam.dta, represents the delaminated area in the coating. For aluminum substrates protected by a coating, an impedance value above $10^7$ Ohms indicates a good coating while an impedance value below $10^5$ Ohms indicates a poor coating. At the low frequency end, where only effects of the coating are present, the modulus, or impedance, of the delaminated area is less than $10^4$ Ohms, indicating active corrosion due to poor coating resistance.
Meanwhile, extrapolating the impedance of the intact area at the same low frequency end gives impedance greater than $10^9$ Ohms, indicating good coating integrity and adequate corrosion prevention. EIS measurements demonstrated that there was a definite difference in properties of the delaminated and intact coating portions of the panel, and the data suggested that in the absence of any nicks or scratches, this particular organic coating would offer good protection against corrosion initiation.

**Figure 11:** Comparison of impedance behavior.

The corrosion behavior and coating integrity of the same sample was also evaluated through the use of the SVET. This technique provided a current density map of the sample surface, which gave detailed information about the presence of conductive pathways, the precursor of corrosion under the coating. The sample was
positioned such that approximately half of the scanned region contained delaminated coating while the other half covered intact coating. A 50 x 50 grid scan was chosen for this study. The three-dimensional mapping of the sample surface is shown in Figure 12. The X- and Y-axes represent probe position (in μm) while the Z-axis represents current density (in μA/cm²). Positive current density is anodic and indicative of a corroding site while negative current density is cathodic. From Figure 12, it appeared that the majority of anodic current density occurred in the left half of the sample.

![Three-dimensional current density map of Al 2024-T3 panel with organic coating.](image)

**Figure 12:** Three-dimensional current density map of Al 2024-T3 panel with organic coating.

In order to determine whether the anodic current density corresponded to the delaminated region, the plot was transformed into a two-dimensional surface map and compared with the video image captured immediately after the scan. Both the current density map and the image of the sample are shown in Figures 13(a) and (b). The
video image and two-dimensional surface map represent a 1:1 correspondence. In approximately the center of the in-situ image, a ridge was clearly seen. The portion of the coating to the left was delaminated while the coated area to the right of the ridge remained intact. This analysis confirmed the presence of conductive pathways (anodic current density) in the delaminated region of the sample.

![Figure 13: Comparison of, (a) two-dimensional surface map with (b) in-situ video image of Al 2024-T3 panel with organic coating.](image)

From this study, a means to effectively detect corrosion damage on a panel with a delaminated coating was established using the SVET. EIS results indicated differences in impedance properties between the delaminated and intact coating regions. SVET testing confirmed the difference in properties between the two regions by revealing the presence of conductive pathways in the delaminated portion of the coating.
4.2 INVESTIGATION OF ARTIFICIAL CORROSION DAMAGE

In Section 4.1, the detection of corrosion on a scribed panel with a visibly delaminated coating using SVET was discussed. Panels with intact coatings and no pre-existing corrosion damage were tested using SVET to obtain clues as to the mechanism of corrosion initiation and progression. Unfortunately, little or no corrosion damage was detected in panels with intact high resistance barrier coating, even after prolonged exposure to an aggressive electrolyte. Thus, artificial corrosion damage had to be created to obtain reasonable results in a shorter period of time. The SVET was then used to monitor progression of corrosion with time. Chemical, mechanical, and electrochemical means of creating corrosion damage were investigated.

Placing a small drop of salt solution on the bare Al 2024-T3 surface prior to coating the substrate was investigated as a chemical method of accelerating damage under the coating. A drop of 10% Harrison’s solution was placed on the panel and allowed to dry at room temperature. The panel was then coated with a clear, water-soluble primer (thickness = 26-29 microns). Although the drop of salt solution was not visible below the coating, each sample was masked and positioned on the SVET sample holder such that the location of the salt drop was in the approximate center of the scanned region. A current density map of the sample following 75 hours immersion in Harrison’s solution is shown in Figure 14. The anodic and cathodic
areas were more or less evenly distributed. The drop of salt, which was located in the center of the scanned region, was not distinguishable. Also, the maximum magnitude of anodic current density was only $25 \, \mu A/cm^2$, a value not indicative of an actively corroding surface.

![Current density map of a panel with 10% Harrison's drop under coating after 75 hours electrolyte exposure.](image)

**Figure 14:** Current density map of a panel with 10% Harrison’s drop under coating after 75 hours electrolyte exposure.

Several days of electrolyte exposure failed to reveal any measurable activity at the salt drop site on the panel shown in Figure 14, so a scribe was made in the approximate region of the drop to investigate the effect of mechanical means of creating artificial damage. A two-dimensional surface plot of the panel taken immediately after scribing the sample (85 hours total electrolyte exposure) is shown in Figure 15(a). The anodic current density immediately increased to $100 \, \mu A/cm^2$ in the approximate center of plot where the scribe was placed. While the initial data
were promising in terms of scribing as a means of creating artificial damage, the metal passivated after a few hours and no further changes in current density were apparent. In an attempt to once again increase corrosion activity, CuCl₂ powder was placed in the region of the scribe. A scan was taken immediately after CuCl₂ addition (110 hours total electrolyte exposure). The resulting current density mapping is shown in Figure 15(b). The current density in the region of CuCl₂ addition became increasingly cathodic while the current density in the peripheral region became increasingly anodic. The addition of CuCl₂ to the scribed area created a strong galvanic couple, which allowed active dissolution of aluminum around the scribe.

![Figure 15](image_url)

**Figure 15**: Current density maps of panel with 10% Harrison’s solution drop under coating after, (a) 85 hours electrolyte exposure, sample scribed prior to scan, and (b) 110 hours electrolyte exposure, CuCl₂ placed in scribe prior to scan.

A current density map obtained 2 hours after CuCl₂ addition (112 hours total electrolyte exposure) is shown in Figure 16(a). The two-dimensional map revealed
that the magnitude of both the anodic and cathodic current densities had further increased, as compared with Figure 15(b). In addition, the cathodic region corresponding to the site of copper addition had increased in area due to diffusion of copper with increasing time. The corresponding vector overlay that was created using the SVET software is shown in Figure 16(b). In the video image, which was captured immediately after the scan, the coated panel containing the CuCl$_2$-filled scribe is visible. The length of each vector is determined by the magnitude of current density. The vector tail represents the origin of the current source. Vectors that point upward represent anodic current density while vectors that point downward represent cathodic current density. Comparison of the 2-D scan after 112 hours with the corresponding vector overlay verified that the copper-containing region was cathodic while the adjacent area was anodic.

![Current density map and vector overlay](image)

**Figure 16:** Panel with 10% Harrison’s solution drop under coating after 112 hours total electrolyte exposure, (a) current density map, and (b) corresponding vector overlay.
Because the sample with a 10% Harrison’s solution drop below the coating revealed no underlying corrosion after 85 hours electrolyte immersion without additional means of damage, a more aggressive solution of 0.2% CuCl₂ in Harrison’s solution was prepared. As before, a drop of this solution was placed on a bare Al 2024-T3 panel and allowed to dry. The sample was then coated with a clear, water-based epoxy. Unlike the previous sample, the salt drop was visible under the coating, so the panel was masked and positioned on the SVET sample holder such that the salt drop was located in the approximate center of the scanned region. The current density map after 107 minutes electrolyte exposure for the panel with the drop of 0.2% CuCl₂ in Harrison’s solution is shown in Figure 17. The region in the center of the scan corresponding to the salt drop appeared predominantly cathodic while the surrounding area was anodic. This behavior is similar to that of the previous sample where CuCl₂ powder was placed in the scribe. Once aluminum forms a Galvanic couple with copper, aluminum corrodes preferentially because copper is the more noble metal.
**Figure 17:** Current density map of a panel with drop of 0.2% CuCl$_2$ in Harrison’s solution under coating after 107 minutes total electrolyte exposure.

The two-dimensional current density map of the previous sample after 7 hours total electrolyte exposure is shown in Figure 18(a). The cathodic region in the center corresponding to the salt drop increased in area, as compared with Figure 17. In addition, the magnitude of both the anodic and the cathodic current densities increased, indicating corrosion activity. The corresponding vector overlay diagram is shown in Figure 18(b). In the video image, which was captured immediately after the scan, the dark circular region in the approximate center of the scanned region represents the 0.2% CuCl$_2$ drop. Comparison of the 2-D mapping after 7 hours exposure with the corresponding vector overlay verified that the copper-containing region was cathodic while the adjacent area was anodic.
Figure 18: Panel with drop of 0.2% CuCl$_2$ in Harrison’s solution under coating after seven hours exposure, (a) current density map, and (b) corresponding vector overlay diagram.

The current density map after 22 hours total electrolyte exposure is shown in Figure 19. The magnitudes of anodic and cathodic current densities changed very little as compared with Figure 18(a). Cathodic current in the center of the scan corresponding to the CuCl$_2$ drop was still present, although the area of cathodic activity was much smaller as compared to Figure 18(a). It is possible that the copper deposits left behind after the aluminum corroded dissolved in solution and exposed underlying aluminum that was free to corrode, leading to the increase in area corresponding to anodic activity.$^{22}$
Figure 19: Current density map of panel with drop of 0.2% CuCl₂ in Harrison’s solution under coating after 22 hours total electrolyte exposure.

Very little change was observed in the current density maps obtained after 22 hours of total electrolyte exposure. Therefore, an external potential was applied after 25 hours of total electrolyte exposure to accelerate the electrochemical activity at the substrate. The resulting 3-D current density map is shown in Figure 20. The inverted cone-like shape corresponds to the salt drop region. The magnitude of the anodic current density increased significantly from 50 μA/cm² to approximately 8000 μA/cm². On continued application of the potential, the coating “broke”, and violent bubbling occurred at the drop site. Because imposing potential resulted in extensive corrosion damage in a very short period of time, it was determined to be the preferred method of creating artificial corrosion damage.
Figure 20: Current density map of panel with drop of 0.2% CuCl$_2$ in Harrison’s solution under coating after 25 hours total electrolyte exposure and potential applied during scan.

From this study, corrosion initiation and progression under a coating was successfully investigated using SVET. Creating artificial damage allowed results in a reasonable amount of time. The sample with the drop of 10% Harrison’s solution under the coating showed no significant corrosion damage after 85 hours of electrolyte exposure, so additional means of damage were utilized. Scribing the sample resulted in an initial increase in current, but the metal eventually passivated. Adding CuCl$_2$ to the scribe increased corrosion activity due to galvanic action. Likewise, placing a drop of 0.2% CuCl$_2$ in Harrison’s solution under the coating accelerated corrosion activity because of galvanic action. Finally, since imposing a potential resulted in extensive and immediate corrosion damage, this method proved to be the most promising way to initiate corrosion.
4.3 POLARIZATION CONDITIONS AND COATING CURE STUDY

After examining several methods to accelerate corrosion damage, imposing an external potential to the panel as discussed in Section 4.2 proved to be the most promising way to achieve corrosion initiation in a short period of time. However, the coating on the sample subjected to polarization shown in Figure 20 broke immediately after applying a +250 mV potential over open circuit. Violent bubbling and excessive buildup of corrosion product resulted. The mechanism of corrosion could be better understood if corrosion were initiated slowly, allowing detection of the early stage of initiation and the subsequent observation of corrosion progression with time. To this end, samples were prepared to allow the investigation of optimum polarization conditions while simultaneously studying coating cure. In practice, aircraft are normally painted and placed in hostile environments before complete coating cure. Therefore, it was decided to study the correlation between cure time and polarization conditions.

Three aluminum panels were coated on the same day. Approximately twenty-four hours after coating, the samples were masked with waterproof tape, leaving a 25-mm² area exposed for testing. A sample cell was glued to the panel immediately after masking. The samples were subjected to the test schedule listed in Table 2.
Table 2: Cure time between coating application and SVET testing.

<table>
<thead>
<tr>
<th>Panel Number</th>
<th>Days between coating application and beginning of test</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
</tr>
</tbody>
</table>

The general speculation was that Panel 1, with only 4 days of cure, would provide less corrosion protection than Panel 3, which cured for 18 days prior to electrolyte exposure and SVET testing.
4.3.1 Coating Cure of Four Days: First Experiment

Panel 1 was immersed in electrolyte four days after coating, and testing began immediately after immersion. Following 24 hours of open circuit measurements, the potential of the sample was measured using the EG&G potentiostat. The open circuit potential was found to be $-180 \text{ mV}$. An external potential was applied to the sample for the remainder of the week. The immersion times and corresponding polarization values are shown in Table 3. The sample was initially polarized to $-155 \text{ mV}$, a step of only 25 mV above open circuit, to slowly initiate corrosion.

Table 3: Immersion times and corresponding polarization values for Panel 1.

<table>
<thead>
<tr>
<th>Immersion times</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 24 hours</td>
<td>Open circuit</td>
</tr>
<tr>
<td>25 - 50 hours</td>
<td>-155</td>
</tr>
<tr>
<td>51 - 93 hours</td>
<td>-105</td>
</tr>
<tr>
<td>94 - 95 hours</td>
<td>-75</td>
</tr>
<tr>
<td>96 - 97 hours</td>
<td>-50</td>
</tr>
<tr>
<td>98 - 99 hours</td>
<td>-25</td>
</tr>
<tr>
<td>100 - 101 hours</td>
<td>25</td>
</tr>
</tbody>
</table>

After 24 hours of electrolyte immersion at open circuit, no visible damage was detected. The current density maps for the first 24 hours revealed a mixture of anodic and cathodic sites. The maximum anodic current density was very small, only 10 $\mu \text{A/cm}^2$, supporting the lack of corrosion activity.
The first visible damage site occurred out of range of the scan parameters along the lower edge (near the tape) after 54 hours of total electrolyte exposure. After 62 hours of total electrolyte exposure, the corrosion damage spread sufficiently to be included in the scanned region. Initially, the damage site was anodic with current density equal to 400 \( \mu \text{A/cm}^2 \), as seen along the lower edge (coordinates 934.2, -1841.2) in Figure 21(a). According to the corresponding vector overlay diagram shown in Figure 21(b), the largest anodic current density vector was located in the center of the damage site, and the area surrounding the damage was also anodic.

![Figure 21](image_url)

**Figure 21:** Sample with four days of coating cure and 62 hours total electrolyte exposure, polarized to -105 mV, (a) current density map, and (b) corresponding vector overlay diagram.

After 64 hours of total electrolyte exposure, the site corresponding to the visible damage (coordinates 727.9, -1841.2) switched from anodic to cathodic current density of -1000 \( \mu \text{A/cm}^2 \). Regions to the right and left of the corrosion site were anodic with a magnitude of 1000 \( \mu \text{A/cm}^2 \), as seen in Figure 22(a). A possible
explanation for the change from anodic to cathodic activity is that the aluminum at
the damage site corroded, leaving behind copper deposits that acted as cathodes. The
current density map after 66 hours of total electrolyte exposure is shown in Figure
22(b). The cathodic region corresponding to the damage increased in area as well as
in magnitude. The maximum cathodic current density magnitude in the damaged area
was −1200 μA/cm². The area surrounding the damage was anodic with a maximum
current density of 600 μA/cm². A possible explanation for the increase in cathodic
current density magnitude and area is that the aluminum in the anodic region of
Figure 22(a) (coordinates 934.2, -1648.6) dissolved during the corrosion process and
left behind copper precipitates that acted as cathodes. These copper cathodes were
responsible for the cathodic activity (coordinates 934.2, -1648.6) in Figure 22(b).

Figure 22: Current density maps of sample with four days of coating cure after, (a)
64 hours electrolyte exposure, polarized to −105 mV, and (b) 66 hours electrolyte
exposure, polarized to −105 mV.
At total electrolyte exposure times of 70 hours and beyond, the current density in the area of the corrosion damage once again switched from cathodic to anodic activity. The current density map after 75 hours total electrolyte exposure is shown in Figure 23(a). Anodic current density with a maximum magnitude of 200 μA/cm² was present at the damage site. The corresponding vector overlay in Figure 23(b) confirmed that current density in and around the corrosion damage was anodic. A possible explanation for the switch from cathodic to anodic current density in the damaged region is that the copper left behind after aluminum dissolution went into solution since it was no longer anchored to the matrix. Once the copper dissolved, the underlying aluminum was exposed and began to corrode.

**Figure 23:** Sample with four days of coating cure and 75 hours electrolyte exposure, polarized to −105 mV, (a) current density map, and (b) corresponding vector overlay diagram.
4.3.2 Coating Cure of Eleven Days

Panel 2 was immersed in electrolyte solution eleven days after coating, and testing began immediately after immersion. The potential of the sample was measured and found to be $-645$ mV after approximately 24 hours of exposure at open circuit. An external potential was applied to the sample for the remainder of the week. The immersion times and corresponding polarization values are shown in Table 4. The sample was initially polarized to $-155$ mV, a step of $490$ mV above open circuit, to match the polarization conditions applied to Panel 1.

Table 4: Immersion times and corresponding polarization values for Panel 2.

<table>
<thead>
<tr>
<th>Immersion times</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 24 hours</td>
<td>Open circuit</td>
</tr>
<tr>
<td>25 – 51 hours</td>
<td>-155</td>
</tr>
<tr>
<td>52 – 96 hours</td>
<td>-105</td>
</tr>
</tbody>
</table>

Visible damage was first detected along the top right edge of the sample after 24 hours total electrolyte exposure at open circuit. The 2-D current density map after 26 hours electrolyte exposure is shown in Figure 24(a). A small region of anodic current density of magnitude $300 \mu$A/cm$^2$ along the top right edge (coordinates 1302.6, 1829) corresponded to the corrosion damage. The vector overlay in Figure 24(b) confirmed that the damage site and surrounding area was anodic.
Figure 24: Sample with eleven days of coating cure and 26 hours electrolyte exposure, polarized to $-155$ mV, (a) current density map, and (b) corresponding vector overlay diagram.

The current density map and corresponding vector overlay diagram after 50 hours of total electrolyte exposure is shown in Figures 25(a) and 25(b). The center of the damage site along the top edge appeared as a cathodic semicircle (coordinates 1306.6, 1835.1) with current density magnitude of $-200 \ \mu\text{A/cm}^2$. The surrounding region of corrosion that radiated outward from the original damage site was anodic, with the maximum current density of $300 \ \mu\text{A/cm}^2$ located at the boundary between damaged and undamaged substrate. The best explanation as to why the center of the damage was cathodic while the spreading region of damage was anodic is that corrosion initiated at the center cathodic region. As a result, corrosion activity was going on at this site for a longer period of time, allowing the aluminum to dissolve and leave cathodic copper deposits. The growing region of damage did not corrode.
long enough to dissolve aluminum and expose copper. A second region of damage was observed along the left edge (center located at coordinates -2146.6, 1063.7) in Figure 25(b). The current density that corresponded to this site was anodic, with the maximum current density of 250 $\mu$A/cm$^2$ located in the center of the damage site.

![Figure 25](image_url)

**Figure 25:** Sample with eleven days of coating cure and 50 hours electrolyte exposure, polarized to $-155$ mV, (a) current density map, and (b) corresponding vector overlay diagram.

The current density map and corresponding vector overlay after 64 hours of total electrolyte exposure are shown in Figures 26(a) and 26(b). Two additional damage sites—both along the bottom edge (coordinates 655.1, -1636.2) and (coordinates 1948.2, -1636.2) were observed. The current density at all four damage sites was anodic with an average magnitude equal to 300 $\mu$A/cm$^2$, a slight increase in current density as compared with Figure 25(a). The activity at the damage site along
the top edge switched from cathodic to anodic activity. A possible explanation for this reversal, a familiar trend seen in maps in Section 4.3.1, is that copper, left behind after aluminum dissolution, went into solution and exposed underlying aluminum that began to corrode.

Figure 26: Sample with eleven days of coating cure and 64 hours electrolyte exposure, polarized to -105 mV, (a) current density map, and (b) corresponding vector overlay diagram.

The results for Panel 2 (coating cure for eleven days) were unexpected. The corrosion resistance of Panel 2 was worse than the corrosion resistance of Panel 1 (coating cure for four days). Four total corrosion sites initiated during the week of testing, with the first site appearing after only 24 hours of exposure at open circuit. Recall that only one damage site initiated on Panel 1 after 54 hours of total electrolyte exposure (24 hours open circuit + 30 hours polarization).
4.3.3 Coating Cure of Eighteen Days

Panel 3 was immersed in electrolyte solution eighteen days after coating, and testing began immediately after immersion. The potential of the sample was measured and found to be -600 mV after approximately 24 hours of open circuit measurements. An external potential was applied to the sample for the remainder of the week. The immersion times and corresponding polarization values are shown in Table 5. Because corrosion damage first appeared after only 16 hours of electrolyte exposure at open circuit, the sample was initially polarized to -550 mV, a step of 50 mV above open circuit.

Table 5: Immersion times and corresponding polarization values for Panel 3.

<table>
<thead>
<tr>
<th>Immersion times</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 25 hours</td>
<td>Open circuit</td>
</tr>
<tr>
<td>26 - 47 hours</td>
<td>-550</td>
</tr>
<tr>
<td>48 - 72 hours</td>
<td>-500</td>
</tr>
<tr>
<td>73 - 96 hours</td>
<td>-450</td>
</tr>
<tr>
<td>97 - 103 hours</td>
<td>-400</td>
</tr>
</tbody>
</table>

The vector overlay diagram after 28 hours total electrolyte exposure is shown in Figure 27. Activity in and surrounding the damage site located along the top right edge was initially anodic with a maximum current density of 200 μA/cm².
**Figure 27:** Vector overlay diagram for sample with eighteen days of coating cure and 28 hours electrolyte exposure, polarized to −550 mV.

The current density map after 55 hours of total electrolyte exposure is shown in Figure 28(a). Anodic current density of magnitude 400 μA/cm² corresponding to the damage site (coordinates 1081.2, 1823) was present along the top edge. A small cathodic site (coordinates 1298, 1630.8) was located to the right of the anodic activity. The presence of this cathodic site may be due to the presence of copper deposits left behind after aluminum dissolution. The current density map after 76 hours total electrolyte exposure is shown in Figure 28(b). The current density along the top right edge was a mixture of anodic and cathodic activity, with maximum current density magnitudes of 400 μA/cm² and −400 μA/cm², respectively. While the magnitude of anodic current density did not increase, as compared with Figure 28(a), the cathodic region corresponding to coordinates (1298, 1630.8) increased in
magnitude as well as area, possibly due to the dissolution of aluminum in the anodic region surrounding the cathodic site in Figure 28(a).

![Current density maps (a) and (b) for sample with coating cure and electrolyte exposure](image)

**Figure 28:** Current density maps of sample with eighteen days of coating cure, (a) 55 hours electrolyte exposure, polarized to −500 mV, and (b) 76 hours electrolyte exposure, polarized to −450 mV.

After 97 hours total electrolyte exposure, the center of the damage site, where corrosion initiated, was completely cathodic with a maximum current density magnitude of −2000 μA/cm², as seen in Figure 29(a). The surrounding ring of damage was primarily anodic with current density equal to 300 μA/cm². The region of damage that was anodic in Figure 28(b) (coordinates 1081.2, 1642.3) switched to cathodic activity, most likely due to the presence of copper left behind after aluminum dissolution. Current density in the spreading ring of damage was anodic, probably because the corrosion at this location was more recently initiated than the damage in the center, giving the aluminum less time to corrode and expose copper deposits. After 98 hours total electrolyte exposure, the activity in the center of the
damage switched from cathodic activity to primarily anodic activity, as seen in Figure 29(b). The anodic current density in this region was 1400 \mu A/cm^2. The border between damaged and undamaged substrate, located at coordinates (214.3, 1449.4), (647.8, 1063.7), and (1514.7, 870.9), was primarily cathodic with a current density magnitude of -200 \mu A/cm^2. A possible reason for the change from cathodic to anodic activity in the center of the damage site is that copper deposits present at the cathodic site (coordinates 1298, 1642.3) in Figure 29(a) dissolved into solution. Underlying aluminum was then exposed and corroded, accounting for the anodic current density in the center of the damage. The cathodic sites along the border between the damaged and undamaged substrates may be due to the copper redepositing.

![Current density maps of sample with eighteen days of coating cure after, (a) 97 hours electrolyte exposure, polarized to -400 mV, and (b) 98 hours electrolyte exposure, polarized to -400 mV.](image)

**Figure 29:** Current density maps of sample with eighteen days of coating cure after, (a) 97 hours electrolyte exposure, polarized to -400 mV, and (b) 98 hours electrolyte exposure, polarized to -400 mV.
The coating cure study produced unexpected results. Panel 1, with only 4 days of coating cure, demonstrated the best corrosion resistance. Open circuit potential after 24 hours electrolyte exposure was $-180 \text{ mV}$. Only one corrosion site initiated during the week of testing. This site appeared after 54 hours of total electrolyte exposure (24 hours open circuit testing, 25 hours polarization to $-155 \text{ mV}$, and 5 hours polarization to $-105 \text{ mV}$).

Four corrosion sites initiated on Panel 2, the sample with 11 days of coating cure. Open circuit potential after 24 hours of electrolyte exposure was $-645 \text{ mV}$. The first visible damage site occurred after only 24 hours of electrolyte exposure at open circuit. The second, third, and fourth sites appeared after approximately 36 hours, 56 hours, and 65 hours of exposure, respectively.

Although only one corrosion site initiated on Panel 3, this sample with 18 days of coating cure exhibited the worst corrosion resistance. Open circuit potential after 24 hours of electrolyte exposure was $-600 \text{ mV}$. The first damage site appeared after only 16 hours electrolyte exposure at open circuit. It is also important to note that this sample was initially polarized to $-550 \text{ mV}$, a step of only 50 mV from open circuit while Panel 2 was initially polarized to $-155 \text{ mV}$, a step of 490 mV from open circuit. In addition, the magnitudes of current density for Panel 3 were the highest among all three panels.

There is no clear explanation as to why the panel with the shortest coating cure exhibited the best corrosion resistance. It is possible that shortly after coating application, the primer is most pliable, providing good adhesion and barrier properties, but with increasing time, amines from the coating curing agent cause the
coating to become brittle. A brittle coating easily cracks and is susceptible to corrosion\textsuperscript{23}.

All three panels did, however, display a similar corrosion mechanism. In each instance, the damage site initiates as an anodic site. With increasing time, the anodic activity at the damage site switches to cathodic activity. One possible explanation for this behavior is that aluminum dissolution at the damage site leaves behind copper deposits that act as cathodes. As time progresses further, activity at the damage site switches once again from cathodic back to anodic activity. It is possible that the copper deposits left behind after corrosion of aluminum are no longer anchored to the matrix and, as a result, dissolve into solution. Underlying aluminum is exposed and begins to corrode. A better understanding of the corrosion mechanisms is important because the information can be utilized by coating formulation experts to aid in the development of corrosion resistant coatings.

In addition, all damage sites on Panels 1, 2, and 3 initiated at the tape edges. A possible explanation for this behavior is that corrosion activity is accelerated by the presence of crevices formed by the tape. Another possible cause is that reaction of the coating with methacrylates from the adhesive tape diminishes the corrosion resistance properties of the coating.
4.3.4 Coating Cure of Four Days: Second Experiment

To investigate reproducibility of the results, a fourth panel was prepared in the same manner as Panels 1, 2, and 3. Panel 4 was immersed in electrolyte solution four days after coating, and testing began immediately after immersion. After approximately 24 hours of open circuit measurements, the potential of the sample was measured and found to be $-755 \text{ mV}$. Recall that the open circuit potential of Panel 1 in the first experiment was $-180 \text{ mV}$ after 24 hours of open circuit exposure. The more negative potential of Panel 4 indicates that the coating on Panel 4 is not as good a barrier as the coating on Panel 1. An external potential was applied to the sample for the remainder of the week. The immersion times and corresponding polarization values are shown in Table 6. The sample was initially polarized to $-155 \text{ mV}$ to match the polarization conditions applied to Panel 1. Corrosion damage first appeared in the lower left corner after 23 hours of electrolyte exposure at open circuit.

<table>
<thead>
<tr>
<th>Immersion times</th>
<th>Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 23 hours</td>
<td>Open circuit</td>
</tr>
<tr>
<td>24 - 96 hours</td>
<td>$-155$</td>
</tr>
</tbody>
</table>

The current density map and corresponding vector overlay diagram after 23 hours total electrolyte exposure at open circuit are shown in Figures 30(a) and 30(b).
For easier identification, a box was placed around the small corrosion site that initiated along the left lower edge in Figure 30(b). The current density closest to this site was anodic with a maximum magnitude of 40 μA/cm².

Figure 30: Sample with four days of coating cure and 23 hours electrolyte exposure, open circuit testing, (a) current density map, and (b) corresponding vector overlay diagram.

After 30 hours total electrolyte exposure, the damage site spread considerably, and the current density in the region of damage switched to cathodic activity. The current density map in Figure 31(a) revealed a semicircle of cathodic current density at coordinates (-2065, -1298.1) corresponding to the damage in the lower left corner. The maximum current density magnitude in this region was -2500 μA/cm². The damage site contained cathodic current density probably because the aluminum corroded and left copper precipitates that acted as cathodic sites. It can be seen in Figure 31(b) that, barring two small anodic vectors at the bubble edges, the damage
site and surrounding region was cathodic. The two anodic vectors may have been the result of the probe physically touching the bubble.

Figure 31: Sample with four days of coating cure and 30 hours electrolyte exposure, polarization to $-155$ mV, (a) current density map, and (b) corresponding vector overlay diagram.

After 44 hours of total electrolyte exposure, the region of damage contained both anodic and cathodic current density of increased magnitude as compared with Figure 31(a). From Figure 32(a), the center of damage where corrosion initiated remained cathodic (current density magnitude of $-4000 \ \mu\text{A/cm}^2$), possibly because corrosion activity at the center was going on for a longer period of time, allowing the aluminum to dissolve and leave cathodic copper deposits. The border between damaged and undamaged substrate was anodic with a current density of 4000 $\mu\text{A/cm}^2$. This growing region of damage was anodic, possibly because it did not corrode long enough to dissolve aluminum and expose copper. This region of anodic
current density at the edge of the damage site also increased in area as compared with Figure 31(a). One explanation for this increase in anodic area might be that the growing region of delamination at the border of the damage exposed new aluminum that began to corrode. The current density mapping after 46 hours total electrolyte exposure is shown in Figure 32(b). The damage site was entirely anodic except for a small sliver of cathodic activity along the edge at coordinates (-2065, -720.6). The maximum anodic current density remained at 4000 µA/cm², the same value as in Figure 32(a). The increase in anodic activity was probably the result of copper deposits, which are no longer attached to the aluminum matrix, dissolving in solution. Once the copper was gone, underlying aluminum was exposed and began to corrode.

Figure 32: Current density maps of sample with four days of coating cure after, (a) 44 hours electrolyte exposure, polarized to –155 mV, (b) 46 hours electrolyte exposure, polarized to –155 mV.
After 48 hours of electrolyte exposure, it was noted that the damage site was blistered and raised. To avoid contact with the raised blister, the probe was raised 150 μm above the blister. The current density map after 49 hours of total electrolyte exposure is shown in Figure 33(a). The damage site at coordinates (-2070.8, -1410.4) was still anodic, but the maximum current density was only 400 μA/cm². The decrease in current density is thought to be due to a fifty-minute break in polarization while the probe was repositioned above the blister. Again, the new probe position was 150 μm above the blister, and the current was significantly dissipated in solution. The current density map after 66 hours of total electrolyte exposure is shown in Figure 33(b). The current density in the damaged region was still anodic but had increased in magnitude to 900 μA/cm², supporting the theory that the decrease in current after the probe was raised was caused by the break in polarization and increase in probe height.
Figure 33: Current density maps of sample with four days of coating cure after, (a) 49 hours electrolyte exposure, polarized to $-155$ mV, and (b) 66 hours electrolyte exposure, polarized to $-155$ mV.

After 85 hours of total electrolyte exposure, the activity in the damage site started to switch from anodic to cathodic current density, as seen in Figure 34(a). Cathodic sites appeared at (-1648.3, -1404.3) and (-1014.7, -1016.7). The anodic current density increased to 3000 $\mu$A/cm$^2$ while the cathodic current density magnitude was $-1200$ $\mu$A/cm$^2$. Two hours later, the cathodic region increased in area although there was no increase in cathodic current density, as shown in Figure 34(b). A possible explanation is that dissolution of aluminum in the matrix left copper behind. The copper sites acted as cathodes, contributing to the increase in cathodic current density. The vector overlay corresponding to 87 hours of total electrolyte exposure is shown in Figure 34(c) for comparison. Three additional corrosion sites
can be seen in Figure 34(c). These sites were located at the edges of the scan parameters and appeared as anodic sites in Figure 34(b).

**Figure 34**: Current density maps and vector overlay of sample with four days of coating cure after, (a) 85 hours electrolyte exposure, polarized to \(-155\) mV, (b) 87 hours electrolyte exposure, polarized to \(-155\) mV, and (c) 87 hours electrolyte exposure, polarized to \(-155\) mV.
The results from the second experiment with four days of coating cure do not correlate with the results from the first experiment. There are several plausible reasons for the lack of reproducibility, including variations in the aluminum alloy microstructure, sample cleaning and preparation, coating application, and coating thickness. More tests should be conducted with multiple samples to statistically account for variations.

Although the corrosion resistance of Panel 4 in the second experiment was significantly worse than the corrosion resistance of Panel 1 in the first experiment, the corrosion mechanism observed in the three previous samples (Panels 1, 2, and 3) was also noted in Panel 4. The damage site initiated as an anodic site. As time progressed, the damage site switched from anodic to cathodic and back to anodic current density.
CHAPTER 5

SUMMARY

Initial electrochemical experiments were performed on a partially delaminated coated Al 2024-T3 panel. Large differences in impedance properties of the delaminated and intact coating regions were detected using EIS. Corrosion currents in the both regions were then measured using the SVET. Anodic current was detected only in the delaminated coating region, indicating the presence of conductive pathways.

SVET was also used to detect corrosion on panels with intact coatings. However, little or no corrosion damage was measured in panels with high-resistance barrier coatings after weeks and even months of continuous electrolyte exposure.

Methods of creating artificial corrosion damage were then investigated to initiate corrosion and obtain reasonable results in a short period of time.

Drops of 10% Harrison’s solution and 0.2% CuCl₂ in Harrison’s solution were placed on the bare metal prior to coating to chemically accelerate corrosion. No corrosion was detected on the panel containing the drop of 10% Harrison’s solution after 85 hours of electrolyte exposure. The sample was scribed to mechanically induce corrosion. Immediately upon scribing, anodic current in the region of the scribe increased. However, the metal soon passivated, and the current density
significantly decreased with time. Cupric chloride was then placed in the scribe. The resulting current density increased due to galvanic action of copper with the Al 2024-T3 panel. Likewise, increased anodic current density was observed on the panel with the drop of 0.2% CuCl₂ in Harrison’s solution because of galvanic action of copper with the Al 2024-T3 panel. Finally, imposing an external potential was investigated as a means of electrochemically accelerating corrosion damage. Extensive action leading to coating breakdown, excessive bubbling, and buildup of corrosion product resulted from the application of anodic potential to the coated sample. The quick and measurable damage resulting from imposed potential proved to be the most promising way to achieve corrosion initiation in a short period of time.

Samples were prepared to examine optimum polarization conditions and coating cure. Interesting results were obtained from the coating cure study. The panel with the shortest coating cure demonstrated the best corrosion resistance, while the panel with the longest coating cure showed the worst performance. More tests need to be conducted before concrete conclusions can be drawn. All four panels did, however, display similar corrosion behavior. The damage site always initiated at an anodic site. With increasing time, the anodic activity at the damage site switched to cathodic activity, possibly because aluminum dissolution made the site copper-rich resulting in cathodic current. With increasing time, corrosion activity at the damage site switched once again from cathodic back to anodic. Again, the copper deposits left behind after corrosion of aluminum dissolved into solution because they were no longer anchored to the matrix. Underlying aluminum was exposed and began to dissolve.
5.1 FUTURE WORK

Several recommendations for future work are presented. The coating cure study should be repeated with multiple panels to statistically account for variations in panel preparation, coating application, etc. Another suggestion would be to initiate the coating cure study complete system including primer and topcoat. Non-Destructive Evaluation (NDE) techniques such as ultrasonics should also be used to investigate physical changes, such as pore size, in the coating with cure time.

In addition, coated panels should be tested in parallel for examination of corrosion damage using SVET as well as NDE techniques such as acoustics, thermography, and eddy currents. The data from all techniques could then be correlated to develop a model to predict the useful life of a coating.

All the above recommendations can be easily implemented in the ongoing NDE-MURI effort.


13. Applicable Electronics, Inc., 22 Buckingham Drive, Sandwich, MA 02563.


17. Micro Probe, Inc., 11715 Tifton Drive, Potomoc, MD 20854.


23. Pacinda, G. Personal communication.