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CORROSION OF DIFFERENT MATERIALS CONNECTED
TO CARBON FIBER

BY

JORDAN ANGEL ORTIZ

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

MECHANICAL ENGINEERING

UNIVERSITY OF RHODE ISLAND

2018

MASTER OF SCIENCE THESIS
OF
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UNIVERSITY OF RHODE ISLAND
2018

ABSTRACT

In this study, Impedance Spectroscopy (EIS), was performed. The corrosion resistance versus time of exposure of both carbon fiber and metal alloys were thoroughly examined and compared for just over a 200-day period. Collecting this data revealed drastic changes in impedance values for several of the 11-examined fastener/carbon fiber interconnections immersed in 3.5% sodium chloride (NaCl) solution, from day one of exposure to day sixty specifically. The range of impedance values directed the pre-selection of one stainless-steel and titanium fastener for further assessment, with the goal of recognizing that EIS could detect trends of corrosion and degradation of material.

Equivalent R/C Circuit modeling was created and conducted from the impedance data obtained via potentiostat for selected stainless steel and titanium fasteners. This was done to determine how many interfaces the interconnected model contained. After trials of 1RC, 2RC, 3RC and 4RC imbedded circuit analysis, the identification of three overall interfaces was suggested. This meant the interconnected system contained three interfaces that were reacting with seawater within the replicated galvanic system. After EIS and equivalent R/C circuit analysis was complete, the identification of interactions between the interfaces and what type of surface changes had taken place was completed by a well-known electron microscopy process.

Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) was conducted on both selected fasteners and carbon fiber coupons. The primary focus was on the metal fasteners, the carbon fiber was to be studied in the future. The enhanced photos revealed corrosion of the stainless-steel fastener. Specifically, there was signs

of crevice corrosion on the outer threads in between two interfaces. There was also the identification of chlorine atoms on the surface of stainless steel fasteners, recognizing the cause of corrosion was by chemical reaction and not mechanical failure.

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CHAPTER 1

INTRODUCTION

PURPOSE OF EXPERIMENT

The main focus and goal of this research was to determine what metals would work best with carbon fiber when immersed in seawater environments. Specifically, the idea was to fasten the metal to the carbon fiber and re-create a steady state sea condition of a possible vessel, offshore drilling vessel or offshore wind farm. The U.S. Coast Guard and Maritime Industry also have thousands of small passenger vessels that are built with composite materials and fastened with various metal alloys. The fasteners are used for the structure, vital systems and through hull penetrations which are directly exposed to the seawater environment, ultimately corroding after time and exposure. Therefore, by utilizing modern day electro-chemistry, corrosion and analysis techniques, a display of what could happen with metal selection would be investigated and proven.

There were three main investigations of carbon fiber to metal galvanic interactions in this study, by applying electron impedance spectroscopy (EIS), equivalent R/C modeling and lastly scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). These investigative techniques were selected due to having a history of use and proven to be extremely accurate within the world of corrosion evaluation. The materials used were chosen for their known properties and also their ranking on the galvanic series. [1, 2] The carbon fiber was sourced from the

Department of Defense and its overall lay-up and properties are proprietary information that was not disclosed for the study. However, carbon itself was designated for multiple reasons, one due to the fact that it serves as a conductor and is very noble on the galvanic series. [1, 2] When connected to some metal alloys this creates an anodic reaction for the metal and a cathodic reaction for the composite, leading to corrosion of the metal, along with de-lamination, fracture and blistering of composite vessel hulls. For this study, stainless-steel and titanium metal alloys were the metals chosen for the anode of a galvanic system. Each metal alloy was in the form of fasteners to be connected to the carbon fiber via tap and threading. Titanium was utilized due to its inherently strong resistance to corrosion and high nobility. In comparison, stainless-steel is much lower on the Galvanic Series and is less noble. The idea was to select metals that were far apart on the Galvanic Series and also factually have been subjected to corrosion in all engineering fields.

This type of situation in terms of corrosion is prevalent during internal structure and dry-dock examinations conducted by owners, operators and Coast Guard Marine Inspectors. There has been an extensive amount of research completed in the field of electrochemical corrosion for materials which include; graphite-polymer composites, graphite-epoxy composites and fasteners immersed in seawater. [1-9] This research qualitatively indicated that metals can be induced to corrode by connection to carbon fiber composite in a marine environment and at the same time the composites are damaged by blistering or cracking of polymer over fibers. However, importantly, there is no quantitative electrochemical information and no time dependent data or models directly related to carbon fiber galvanically connected to metal alloys which

would assist in early detection of damage processes and determination of electrochemical behavior.

Further research is needed in order to improve decision making for materials used during new construction of vessels and engineering applications. A substantial amount of principal will be saved on the behalf of the maritime industry. The prevention of catastrophic failure would be significantly decreased, saving the lives of thousands of passengers and licensed mariners. With that stated, the objective of the overall research was to investigate metal alloy behavior when connected to carbon fiber and immersed in seawater to determine if they would corrode and degrade. This would then give a direction to the engineering and maritime industry as to what to expect in the future and assist with material selection.

CHAPTER 2

REVIEW OF LITERATURE

THEORETICAL BACKGROUND – ELECTROCHEMICAL PROCESS

In this study an electrochemical process was the main operating process to cause damage. This process occurs when there is a known transfer of electrons between atoms and molecules, which either go to or from them. This results in the change of oxidation state. This process transpires when a voltage is applied directly to a metal alloy for example a difference in potentials between materials. With this reaction there comes the depletion or degradation of the materials involved in the process. This progression is normal in the marine environments, especially in seawater. The ocean water is approximately 3.5% NaCl and is an extremely good environment for corrosion to take place. [2] There are two main factors that cause this corrosion specifically to occur, one being conductivity and the other oxygen solubility. Metal alloys react differently in this environment due to their variable compositions resulting in nobility and individualistic properties. With that said, it is important that the control of corrosion is to be consistently studied and prevented.

THEORETICAL BACKGROUND – CORROSION

There are several types of corrosion that occur on the surface of different metal alloys. Each type of corrosion is dependent on several factors. For the purpose of metals in a seawater environment the following corrosion cases can occur; crevice,

pitting, stray current and galvanic corrosion. Corrosion is initiated by having four necessary elements. The interaction of these elements directly leads to corrosion. First is an anode, which is the electrode where oxidation reactions generate electrons and positive metallic ions are formed from atoms. Normally the anode is deemed the “sacrificial anode”, which is the metal that in fact corrodes. The second element of this cell is a cathode, which is the electrode that is on the receiving end of the electrons produced by the anode. In the marine environment, negative hydroxyl ions will be produced at the cathode. The cathode is usually totally protected from corrosion. However, in the case of carbon fiber composites, these hydroxyl ions can cause damage in the form of blisters or cracking as they combine with positive sodium ions and form sodium hydroxide on the carbon fiber surface. Sodium hydroxide forms an osmotic cell which increases pressure inside the composite, resulting in blisters or cracking of polymer. The third element is an electrolyte, which would be seawater. This liquid will serve as the main conductor to which current can flow and be carried. Lastly, the fourth element is a return current path, meaning a conductive pathway is needed to connect the anode to the cathode, which in this case is direct contact between the metals and carbon fibers in the thread region. If one of these elements is not present then it is fair to say that corrosion will not occur. When corrosion does occur on the surface of metal, it is affected in the forms of pits, crevices and overall material loss.

THEORETICAL BACKGROUND – EIS

Electrochemical Impedance Spectroscopy (EIS) has been utilized for several years to detect and monitor corrosion rates of materials over a period of time. What the process completes, is the measurement of a metals impedance to current flow, which is also directly related to the corrosion current. The impedance of a material is defined as the difference of frequency-dependent potential divided by the frequency-dependent current. A potentiostat delivers a small voltage perturbation, between a reference electrode and a working electrode within an electrochemical cell. Then the potentiostat measures the current response between the working electrode and a counter electrode and associated control software computes the impedance. The overall test time varies for each metal or material being studied. However, utilizing recent software and programs, it can take as long as just a few minutes to gather the data. The impedance values are then plotted in the form of impedance versus frequency curves, which can later be analyzed.

THEORETICAL BACKGROUND – R/C EQUIVALENT MODELING

Electrochemical cells can be modeled as an equivalent electrical circuit for the purpose of further analyzing impedance data. The circuit is created similarly to that of a normal closed loop circuit in the field of electrical engineering, using a resistor and capacitor in parallel to represent an electrochemical interface such as a metal to solution interface. Historically in electrochemistry, the simplest circuit to represent an electrochemical interface is known as the single Randles circuit, Figure 1. [2] Depending on how many interfaces the metal-based system being measured contains,

the number of parallel RC elements in the model to be applied will be increased to represent each interface. The EIS response of an equivalent circuit can therefore be calculated and compared to the actual EIS response to an electrochemical cell. This means that the measured impedance can be compared to theoretical models and the individual circuit elements values can be computed to provide the theoretical data. These elements can be compared in order to prove how many interfaces from a combination of resistors and capacitances of the material being measured is interacting within the cell. An example of a double interface could be paint on the surface of metal. The paint and solution represent one interface and the metal and solution represent a second interface.

THEORETICAL BACKGROUND – SEM-EDS

Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) is commonly used in several engineering applications. Its purpose is to obtain detailed high-resolution examination of surfaces of a material being studied, to determine if any surface dependent processes have occurred that changes the appearance and provides information towards the mechanism for the changes. This technique depends on an electron beam interacting with the surface of interest. A primary electron beam is directed onto a material surface, then electrons will be emitted from that surface, which include backscattered electrons, secondary electrons and in addition x-rays. These secondary electrons are collected by a detector within the system and from the magnitude of the collected signal as a function of spatial position on the materials surface, an image is produced. Backscattered electron images differentiate areas by

atomic number, meaning it allows the identification of heavy or light elements that are present on the surface of the material being studied. If the x-rays emitted from the surface are collected they can be analyzed by their energy, which is unique for each element, permitting detection of elements on the surface being inspected.

CHAPTER 3

METHODOLOGY

ELECTROCHEMICAL TESTING

Electrochemical Impedance Spectroscopy (EIS) is a non-destructive process used to determine the corrosion resistance of materials with extended time periods. [1, 2, 3, 8, 10] The term impedance refers to the frequency dependent resistance to current flow of a circuit element (resistor, capacitor, inductor, etc.) This technique measures a periodic small-amplitude alternating current (AC) signal resulting from application of an AC voltage signal, which is conducted for several pre-determined sinusoidal frequencies (cycles/s) to investigate the working electrode (WE).

In this study metal fasteners will serve as a WE. The application of small sinusoidal potential of a fixed frequency induces a current with the WE then the impedance, the voltage divided by the resulting current is computed at each frequency. By using small amplitude, it does not disturb the properties of the material being evaluated, essentially making EIS a non-destructive test (NDT). This directly correlates to what is happening on a samples surface in terms of corrosion rate. A common three electrode electrochemical cell is utilized for the entire cycle of the experiment conducted on the carbon fiber and metal samples. The EIS set-up is detailed in Figure 1. [11] The carbon fiber sample is detailed in Figure 2, reconstructed using a 3D modeling program.

EXPERIMENTAL TECHNIQUES

Carbon fiber test coupons were machined to be an approximate cross section of 1.25 inches by 1.0 inches; each were fastened with one of the two types of alloy (stainless steel and titanium) to be evaluated. The carbon fiber samples were drilled and tapped using ANSI standard, 8-32 tap for the stainless steel and 10-24 for the titanium fasteners. The exact taps used for the purpose of the experiment are detailed in Figure 3. The layup of the carbon fiber was 0/90 unidirectional ply laminates, each ply was approximately 12 microns thick. The volume ratio of fibers to polymer was approximately 70 to 30. The samples were obtained from a 0.1-inch-thick sample with dimensions of 6.0 inches by 1.0 inches, Figure 4. The drill and tap were directly centered on the sample in order to capture maximum surface area during the experiment, presented in Figure 5. The area of the carbon fiber sample that was exposed to the electrolyte solution was 0.7 inches in diameter of the surface layer for all samples along with the fastener fixed at the center, in the upright direction, Figure 2. The pipes utilized were 4.0 inches in length, the inner diameter was 0.7 inches and outer diameter was 1.0 inches. A sealant was used, 3M FM-5200 fast cure industrial grade adhesive, which provided a bond between the sectioned PVC tubing, carbon fiber and fastener which in turn prevented leaks from occurring throughout the overall experiment. The long-term samples were set up on 04/29/17 and the short-term samples were set up on 10/16/2017.

After the initial set-up of the sample was complete and the adhesive had time to cure, then the 3.5 % NaCl solution was added. A period of 24 hours was given to every sample in order for the seawater solution to stabilize. At that point EIS was

performed over a time period of exposure. This exposure time started at days 1, 3, 5 then continued to day 30, 60 and ultimately ending just over 200 for all the samples. There were long-term (LT) and short-term (ST) samples created for this experiment. Time dependent impedance data was recorded.

In terms of the experimental set-up, the electrodes utilized were the counter electrode (CE), reference electrode (RE) and the sample, which was the working electrode (WE). The CE used was platinum, this electrode was used due to its stability [1, 2], the WE were the actual carbon fiber/fastener interconnection and the RE was a saturated calomel electrode, Figure 6. The electrochemical impedance $|Z|$ of each sample was measured at intervals to collect time dependent data. All the electrodes were electrically connected to a PC via cell cables in order to acquire proper readings. The system was calibrated each time readings were taken in advanced to ensure accuracy using a “Dummy Cell”, Figure 7. A pre-test was performed on other steel and aluminum metal alloys in order to validate the system was taking accurate readings, this delivered precise analyses for each sample connected. Respectively, each cell cable was color coordinated in order to guarantee correct experimental set-up, Table 1.

After initial set-up the EIS was performed, recording data, which commenced at day 1 and continued to day 30 and ultimately until just over 200 days. The overall testing schedule for recording purposes was days 1, 3, 5, 10 then every three days until over 200 days was achieved. Time dependent impedance data $|Z|$ in ohms (Ω) was recorded along with the solution resistance (R_s) in ohms (Ω), frequency (F) in Hertz (Hz) and phase angle (PA) in degrees. [Appendices] Impedance curves ($|Z|$ -Curves)

were generated for all 11 samples, determining if any increase or decrease in data gave indications of possible corrosion or degradation of material. The increase or decrease in values were recorded in order to identify future trends or stability of the material being evaluated. The potentiostat was fixed with initial parameters detailed in Figure 8, which remained consistent for entire study.

Calculations of impedance data versus area of fastener exposed inside the three-electrode electrochemical cell were derived using a dial caliper, Table 5. This determined if the amount of area exposed (fastener) associated with the impedance values obtained via potentiostat, Table 2. The main focus after obtaining the impedance data was to somehow correlate or compare the data to the amount of metal surface area exposed to the seawater solution. This would determine if the higher or lower $|Z|$ values were surface area dependent. This would indicate that the higher the value of impedance obtained was due to the surface area exposed for each metallic alloy.

Subsequently, when the surface areas were obtained the next phase was to attempt to identify which samples were showing the most significant changes in impedance over the time exposed. This would recognize any developments of increase or decrease in values and be used as a secondary proof, isolating which metals needed to be studied further. Graphs were produced to represent at frequency of 0.01 Hz and 60 days of exposure, detailing how stable or unstable the samples actually were and if values were similar or different, Figures 10, 11, 12, 13. Also a bar graph was generated to represent all the stainless steel (SS) and titanium (Ti) impedance readings from day 1 and over day 200, Figure 9. This information was

specifically utilized to isolate which samples were to be chosen for supplementary analysis.

DISCUSSION OF EXPERIMENTAL TECHNIQUES

In general, both these materials, stainless steel and titanium alloys obtain their corrosion protection by forming passivating surface layers during exposure. Titanium alloys are thought to be stronger passivators than stainless steel. This is mainly due to the stainless steels relying on chromium for passivation, which is usually only 18% by weight of the material, while titanium is usually around 90% by weight in alloys. The greater amount of passivators in the titanium alloy would suggest a better passivating system, especially as Pourbaix diagrams indicate that titanium has a much more stable passive layer over a wide pH range. Indeed, data from US Navy test on crevice corrosion indicates 304 and 316 stainless steels were not particularly resistant to crevice corrosion, and this is also supported by experimental data. On the other hand, titanium alloys are strongly resistant to crevice corrosion in a marine environment from both empirical and experimental data. One interpretation of the data would then follow along the lines that the continual decrease in long term data, along with some scatter would be indicative of an unstable passive film for stainless steel, while a very stable impedance value after a slight decrease would be indicative of a stable surface condition for the titanium.

For stainless steels, the presence of the chloride ion in solution is a destabilizing ion for the passive film that is formed. As it is present in the sodium chloride solution, then crevice corrosion would be expected. In addition, the cathodic carbon fibers would polarize the steel into its anodic region and tend to induce crevice

corrosion. For titanium alloys the chloride ion at neutral pH ranges is not a destabilizing ion and crevice corrosion would not be expected.

After all the EIS data was collected and analyzed, the next phase was to determine how many actual interfaces were required to model the experimental data to provide an indication of the processes occurring. The way this was to be accomplished was by performing equivalent R/C circuit modeling. This process has been completed in the past and in previous studies for composite materials and metals containing surface layers, for example paint on the surface of a steel vessel hull. [6, 7] The idea is to represent the physical sample in an analog circuit. Bode plots will be generated from analyzing the single circuit and the curves will be compared with the EIS data $|Z|$ curve. Both curves will be evaluated to determine if they match. The notion is if they match and are a “true fit”, then the exact number of interfaces will be confirmed. This modeling will be described in the next chapter.

Figure 1: EIS experimental set-up diagram & Simple Randles Equivalent Single Circuit

Figure 2: Solid-works 3D Model - Sample set-up

Figure 3: SAE Standard Taps (ANSI Left/8-32 and Right/10-24)

Figure 4: Original Carbon Fiber Sample

Figure 5: Drill and Tap set-up (Centered and aligned using bench vise)

Figure 6: Experimental set-up

Figure 7: Universal Dummy Cell for calibration of EIS system

Potentiostatic EIS

Default Save Restore OK Cancel

Estat ☒ PCI4300-35026

Test Identifier Potentiostatic EIS

Output File SS4_091517_Jortiz

Notes... SS4 Short Term Sample Testing, Jortiz
Third Testing Day

Initial Freq. (Hz) 100000

Final Freq. (Hz) 0.1

Points/decade 10

AC Voltage (mV rms) 10

DC Voltage (V) 0 ☐ vs Eref ☒ vs Eoc

Area (cm²) 1

Conditioning ☐ Off Time(s) 15 E(V) 0

Init. Delay ☒ On Time(s) 30 Stab.(mV/s) 0

Estimated Z (ohms) 100

Optimize for: ☐ Fast ☒ Normal ☐ Low Noise

Figure 8: EIS input values for potentiostatic system

Figure 9: Impedance Vs Time Bar Graph Day 1 and Day 60 (11 Samples) at 0.1 Hz

Figure 10: Impedance $|Z|$ Data of Ti2 over time of exposure

Figure 11: Impedance $|Z|$ Data of Ti2 over time of exposure (unstable area to be evaluated)

Figure 12: Impedance $|Z|$ Data of SS2 over time of exposure

Figure 13: Impedance $|Z|$ Data of SS2 over time of exposure (unstable area to be evaluated)

Color	Type	Name	Normal Connection
Blue	Banana Plug	Working Sense	Connected to metal sample #1
Green	Banana Plug	Working Electrode	Connected to metal sample #1
White	Pin Jack	Reference Electrode	Connected to reference electrode
Red	Banana Plug	Counter Electrode	Connected to metal sample #2
Orange	Banana Plug	Counter Sense	Connected to metal sample #3
Long Black	Banana Plug	Floating Ground	Leave open or connected to a Faraday shield
Short Black	Banana Plug	Chassis Ground	Connect to Faraday Shield to reduce EMI

Table 1: Cell Cable Connections for EIS program set-up

Samples	Day 1 Z (Ω)	Last Data Point (Ω)	Difference in Z (Ω)
SS1 (L.T.)	1.91E+04	1.46E+03	17603
SS2 (L.T.)	9.91E+03	1.98E+03	7932
SS3 (L.T.)	5.58E+03	1.74E+03	3841
SS4 (S.T.)	5.88E+03	4.63E+03	1246
SS5 (S.T.)	3.93E+03	4.87E+03	-947
SS6 (S.T.)	2.46E+03	5.32E+03	-2854
Ti1 (L.T.)	8.03E+03	2.68E+03	5351
Ti2 (L.T.)	4.95E+03	2.75E+03	2203
Ti3 (L.T.)	5.54E+03	2.64E+03	2907
Ti4 (S.T.)	6.96E+03	6.70E+03	266
Ti5 (S.T.)	7.22E+03	5.94E+03	1280

Table 2: Impedance Vs Time Data Day 1 and last data point (11 Samples)

Long Term Samples - Titanium				
Sample ID	Date		Day #	Impedance (Ω)
Ti2	4/28/2017	42853	0	4.95E+03
Ti2	5/27/2017	42882	29	2.67E+03
Ti2	6/16/2017	42902	49	2.63E+03
Ti2	9/13/2017	42991	138	2.60E+03
Ti2	9/15/2017	42993	140	2.53E+03
Ti2	9/18/2017	42996	143	2.61E+03
Ti2	9/20/2017	42998	145	2.65E+03
Ti2	9/27/2017	43005	152	2.62E+03
Ti2	9/29/2017	43007	154	2.65E+03
Ti2	10/2/2017	43010	157	2.71E+03
Ti2	10/4/2017	43012	159	2.69E+03
Ti2	10/6/2017	43014	161	2.60E+03
Ti2	10/11/2017	43019	166	2.64E+03
Ti2	10/16/2017	43024	171	2.69E+03
Ti2	10/18/2017	43026	173	2.74E+03
Ti2	10/21/2017	43029	176	2.67E+03
Ti2	10/23/2017	43031	178	2.42E+03
Ti2	10/30/2017	43038	185	2.71E+03
Ti2	11/6/2017	43045	192	2.70E+03
Ti2	11/17/2017	43056	203	2.78E+03
Ti2	11/29/2017	43068	215	2.75E+03

Table 3: Long Term Titanium Impedance Values (Day 1-215) at 0.1 Hz

Long Term Samples - Stainless Steel				
Sample ID	Date	Day #	Impedance (Ω)	
SS2	4/28/2017	42853	0	9.91E+03
SS2	5/27/2017	42882	29	3.66E+03
SS2	6/16/2017	42902	49	3.80E+03
SS2	9/13/2017	42991	138	3.64E+03
SS2	9/15/2017	42993	140	1.74E+03
SS2	9/18/2017	42996	143	1.79E+03
SS2	9/20/2017	42998	145	3.71E+03
SS2	9/27/2017	43005	152	1.91E+03
SS2	10/2/2017	43010	157	2.06E+03
SS2	10/4/2017	43012	159	1.90E+03
SS2	10/6/2017	43014	161	1.98E+03
SS2	10/11/2017	43019	166	2.09E+03
SS2	10/16/2017	43024	171	1.89E+03
SS2	10/18/2017	43026	173	2.08E+03
SS2	10/21/2017	43029	176	2.21E+03
SS2	10/30/2017	43038	185	2.18E+03
SS2	11/1/2017	43040	187	1.99E+03
SS2	11/15/2017	43054	201	2.08E+03
SS2	11/20/2017	43059	206	1.98E+03

Table 4: Long Term Stainless Steel Impedance Values (Day 1-206)

SS2 Measurement (in)	Ti2 Measurement (in)	LOA SS2 (in)	LOA Ti2 (in)	CF Thickness (in) SS2	CF Thickness (in) Ti2
0.775	1.09	0.975	1.45	0.148	0.1475
0.754	1.09	0.976	1.448	0.1475	0.148
0.759	1.11	0.975	1.451	0.1455	0.148
0.762666667	1.096666667	0.975333333	1.449666667	0.147	0.147833333
Total Fastener Exposed (in)	Ti2	SS 2			
	0.353	0.212666667			

Table 5: Total length of fastener and carbon fiber exposed to seawater for SS2 and Ti2 samples

EQUIVALENT CIRCUIT MODELING - TECHNIQUES

Modeling is a very important factor in the process of electrochemical impedance spectroscopy (EIS). It serves as a tool to determine the corrosion resistance of a material. This process works in various ways in terms of set-up and overall techniques. However, an equivalent model begins with a simple “Randles Circuit” which can be viewed in Figures 1 and 26. The circuit has one resistor representing the solution or electrolyte resistance, R_s , and one resistor, R_{ct} representing the charge transfer resistance and one capacitor, representing the double layer capacitance, in parallel representing the metal interface.

For this experiment, the relationship between impedance experimental data and the number of electrochemical interfaces representing the galvanic system of a metal fastener in a carbon fiber composite in a marine environment was investigated. The electrochemical interface was represented by a combination of a resistor and capacitance or a constant phase element indicating a non-perfect capacitor. This number of interfaces was unknown at the start of EIS testing and so was a new development in corrosion studies. Theoretically the overall electrochemical model could have at least three interfaces as suggested by the schematic diagram of a fastener in the composite, Figure 22. With that said 2, 3 and 4 R/C interface circuits were investigated to determine which correctly simulated the experimental data. Each can be viewed separately in Figures 23, 24 and 25 respectively. The objective was to run a given model to fit data for stainless-steel and titanium fasteners previously identified, SS2 and Ti2. After the model is created and run, it then produces a curve showing the model data compared to the experimental data.

To determine which circuit would work best and give the most accurate analog display of the interconnected model, trial and error was employed. The R/C circuits also had to be created similarly to that of what is known to be done with a close looped circuit that is in series. This way if a 2R/C circuit did not operate and did not show a good “fit” in comparison to the impedance curve selected, then a 3R/C circuit would be attempted. However, the circuits would need to be imbedded within each other to remain a closed loop. With the EIS data obtained over all 11 samples, random test dates were selected. Then, each model was running to determine what equivalent R/C circuit created was best fit. A rank order was completed for the selected dates, from 1-3, and if a tie took place it was noted between R/C circuits. The goal was to be as exact as possible in determining which R/C circuit represented the number of interfaces that were actually present.

EQUIVALENT CIRCUIT MODELING - DISCUSSION

Before analysis could be completed the SS2 and Ti2 Impedance $|Z|$ data over time of exposure needed to be evaluated at the unstable areas, Figures 11, 13. Meaning, the erratic increases and decreases of a specific day was selected to be modeled between 2RC, 3RC and 4RC fashioned circuits. For the Ti2 data there was a total of five points selected for circuit analysis and nine for SS2. Each R/C model would create a corresponding Y2- Fit Z Curve. Each of these fit curves were then produced on a Bode Plot to be analyzed for the best match along with the original Z-Curve from the EIS data collected. Figures 14 through 21 show each R/C circuit modeled, from 2 to 4 R/C, for SS2 and Ti2. Their respective resistance values are captured in the “Goodness of Fit” figures.

Figure 14: Bode Plot of SS2 Day 1 (2RC, 3RC, 4RC)

Figure 15: SS2 Day 1 2RC Model Data & Goodness of Fit Value

Figure 16: SS2 Day 1 3RC Model Data & Goodness of Fit Value

Figure 17: SS2 Day 1 4RC Model Data & Goodness of Fit Value

Figure 18: Bode Plot of Ti2 Day 1 (2RC, 3RC, 4RC)

Figure 19: Ti2 Day 1 2RC Model Data & Goodness of Fit Value

Figure 20: Ti2 Day 1 3RC Model Data & Goodness of Fit Value

Figure 21: Ti2 Day 1 4RC Model Data & Goodness of Fit Value

Figure 22: Interfaces reacting within sample

Figure 23: 2 RC Equivalent Model

Figure 24: 3 RC Equivalent Model

Figure 25: 4 RC Equivalent Model

R_s = Solution Resistance

R_{ct} = Resistance to charge transfer across metal/electrolyte interfaces

C_{dl} – Double layer capacitance from charging of the double layer

Figure 26: Simple Randles Equivalent Circuit

R_s = Solution Resistance

C_{dl} – Double layer capacitance from charging of the metal solution double layer

R_{po} – Paint Resistance between paint and solution

R_{ct} – Charge transfer resistance between metal and solution

C_c – Coating Capacitance

Figure 27: Single Paint Coating Equivalent Circuit

Sample ID		SS2			SS2			SS2			SS2			SS2		
Data Date		4/28/2017			5/27/2017			6/16/2017			9/13/2017					
Model Used		2 RC	3 RC	4 RC	2 RC	3 RC	4 RC	2 RC	3 RC	4 RC	2 RC	3 RC	4 RC	2 RC	3 RC	4 RC
Goodness of Fit Value		1.69E-04	1.81E-04	8.14E-05	2.63E-03	7.10E-04	9.02E-04	4.56E-03	2.15E-03	1.66E-03	6.00E-03	6.08E-03	1.93E-03			
Curve Fitment Ranking (1-3)		2	3	1	3	1	2	3	2	1	2	3	1			
R1	ohm Solution Resistance	7.677	7.727	7.681	16.45	16.57	16.87	12.11	12.15	12.16	3.958	3.948	4.379			
R2	ohm Resistance Interface #1	3.65E+03	3.06E+03	1.74E+03	2.15E+03	6.16E+02	7.70E-05	7.94E+02	1.82E+02	1.66E+02	7.21E+02	7.20E+02	1.68E+02			
R3	ohm Resistance Interface #2	9.46E+04	9.02E+04	389.7	7.69E+09	2.48E+03	166.1	1.36E+07	6.38E+02	8.15E+01	1.23E+09	1.48E+06	8.57E+01			
R8	ohm Resistance Interface #3		2.47E+03	8.15E+04		1.87E+06	1.78E+03		3.60E+06	5.66E+02		2.91E-04	5.22E+02			
R11	ohm Resistance Interface #4			55.04			1.77E+06			1.00E+06			6.21E+05			
Yo4	S*s'a Interface #1	1.17E-04	1.13E-04	1.01E-04	2.43E-04	1.83E-04	1.01E-04	2.03E-04	1.19E-04	7.73E-05	2.06E-04	2.06E-04	6.58E-05			
a5	Interface #1	6.75E-01	6.78E-01	6.87E-01	5.94E-01	6.22E-01	6.80E-01	6.25E-01	6.71E-01	7.06E-01	6.12E-01	6.11E-01	7.15E-01			
Yo6	S*s'a Interface #2	1.97E-05	2.33E-05	1.50E-06	1.39E-04	6.82E-05	9.15E-07	1.88E-04	6.69E-05	1.02E-05	2.03E-04	2.03E-04	2.37E-03			
a7	Interface #2	9.38E-01	8.95E-01	9.81E-01	9.57E-01	8.24E-01	6.38E-01	1	7.88E-01	9.63E-01	1	1	8.65E-01			
Yo9	S*s'a Interface #3		8.13E-04	3.39E-05		1.52E-04	1.13E-04		2.08E-04	9.64E-05		5.57E-02	1.00E-04			
a10	Interface #3		1.13E-04	8.28E-01		9.98E-01	6.71E-01		9.62E-01	8.27E-01		5.31E-02	8.20E-01			
Yo12	S*s'a Interface #4			2.90E-02			1.84E-04			2.14E-04			2.26E-04			
a13	Interface #4			1.00E+00			8.89E-01			1.66E-03			9.26E-01			

	SS2			SS2			SS2			SS2			SS2		
	9/15/2017			9/20/2017			9/27/2017			10/16/2017			11/20/2017		
	2 RC	3 RC	4 RC	2 RC	3 RC	4 RC	2 RC	3 RC	4 RC	2 RC	3 RC	4 RC	2 RC	3 RC	4 RC
5.08E-04	1.67E-04	1.55E-04		2.81E-03	6.20E-04	2.95E-04	2.24E-04	2.22E-04	2.16E-04	5.58E-04	1.59E-04	1.33E-04	6.85E-04	1.64E-04	1.66E-04
3	2	1		3	2	1	3	2	1	3	2	1	3	1	2
6.63	6.966	7.197		6.51	6.819	7.139	12.32	12.89	12.74	12.86	13.1	12.67	13.06	13.47	13.45
7.24E+02	2.24E+02	1.43E+02		8.58E+02	239.4	307.5	1.77E+03	1.41E-03	2.20E+03	1.30E+03	654.73	3.35E+02	1.35E+03	5.81E+02	1.11E+03
9.13E+08	1.08E+03	7.40E+01		3.36E+06	746.2	34.96	8.90E+08	2.67E+03	6.35E-04	2.01E+09	905.4	7.43E+00	1.06E+09	1.19E+03	612.9
	1.39E+06	770			2.22E+05	772.3		5.00E+05	47.2		1.09E+06	1.07E+03		1.33E+06	9.61E+03
		3.46E+05				4.60E+05			3.73E+05			2.96E+05			4.46E+05
3.62E-04	2.35E-04	1.27E-04		2.47E-04	1.47E-04	3.75E-05	4.28E-04	4.24E-05	5.46E-05	4.76E-04	3.92E-04	1.43E-04	3.98E-04	2.99E-04	3.04E-04
5.67E-01	6.12E-01	6.69E-01		5.97E-01	6.47E-01	7.66E-01	5.41E-01	6.93E-01	6.62E-01	5.36E-01	5.57E-01	6.04E-01	5.50E-01	5.83E-01	5.81E-01
4.70E-04	3.02E-04	3.54E-05		1.68E-04	7.87E-05	1.03E-04	3.32E-04	4.71E-04	4.24E-04	2.71E-04	1.15E-04	1.43E-04	3.23E-04	1.51E-04	1.36E-04
7.13E-01	5.55E-01	7.91E-01		1	8.14E-01	6.65E-01	8.77E-01	4.82E-01	4.94E-01	9.61E-01	9.00E-01	5.94E-01	8.66E-01	8.02E-01	8.40E-01
	3.04E-04	3.13E-04			1.81E-04	1.02E-04		2.11E-04	1.95E-04		2.62E-04	2.13E-04		3.16E-04	3.28E-04
	8.50E-01	6.10E-01			1	8.60E-01		9.98E-01	1		9.67E-01	6.94E-01		9.25E-01	9.21E-01
		4.03E-04				1.68E-04			6.26E-05			2.82E-04			2.27E-09
		7.65E-01				1			7.83E-01			9.55E-01			5.71E-01

Table 6: SS2 R/C Modeling Data (Nine Selected Erratic Points)

Sample ID			Ti2			Ti2		
Data Date			4/28/2017			5/27/2017		
Model Used			2 RC	3 RC	4 RC	2 RC	3 RC	4 RC
Goodness of Fit Value			9.51E-03	2.35E-04	2.42E-04	9.18E-03	2.51E-03	2.50E-03
Curve Fitment Ranking (1-3)			3	1	2	3	2	1
R1	ohm	Solution Resistance	16.52	14.1	14.27	11.82	11.74	11.69
R2	ohm	Resistance Interface #1	2.37E+04	6.893	280.2	39.39	31.61	1.25E+03
R3	ohm	Resistance Interface #2	1.21E+08	299.4	6.037	2.75E+09	1.08E+03	31.69
R8	ohm	Resistance Interface #3		8.18E+04	7.19E+04		8.66E+05	8.70E+05
R11	ohm	Resistance Interface #4			52.88			2.781
Yo4	S*s^a	Interface #1	3.07E-04	5.19E-05	1.74E-05	1.49E-04	1.08E-04	1.09E-04
a5		Interface #1	7.11E-01	7.28E-01	8.27E-01	6.80E-01	7.03E-01	7.01E-01
Yo6	S*s^a	Interface #2	3.21E-09	1.91E-04	2.19E-04	3.71E-04	2.49E-04	2.58E-04
a7		Interface #2	7.36E-01	7.30E-01	7.24E-01	7.02E-01	7.59E-01	7.54E-01
Yo9	S*s^a	Interface #3		4.12E-05	4.79E-05		1.85E-04	1.76E-04
a10		Interface #3		9.35E-01	9.07E-01		9.68E-01	9.93E-01
Yo12	S*s^a	Interface #4			1.92E-05			1.03E-03
a13		Interface #4			6.57E-01			6.44E-01

Ti2			Ti2			Ti2			Ti2		
6/16/2017			9/13/2017			10/21/2017			11/29/2017		
2 RC	3 RC	4 RC	2 RC	3 RC	4 RC	2 RC	3 RC	4 RC	2 RC	3 RC	4 RC
7.10E-03	7.10E-03	2.58E-03	9.00E-03	3.01E-03	7.08E-04	5.51E-03	6.25E-03	2.23E-04	7.92E-03	2.39E-03	1.28E-03
2 (tie)	2 (tie)	1	3	2	1	2	3	1	3	2	1
11.78	11.31	11.22	6.487	5.682	5.725	6.521	6.582	5.928	7.732	7.269	7.195
79.33	33.47	584.7	389.7	10.47	91.09	543.5	406.6	141.6	424.2	21.66	173.9
3.04E+09	534.1	34.84	6.15E+06	340.4	5.933	1.02E+06	1.06E+06	7.66	1.18E+08	385.8	18.41
	9.27E+05	7.33E+05		1.68E+05	475.2		8.84E-04	572.7		1.07E+06	408.1
		51.58			2.42E+05			2.40E+05			2.77E+05
2.07E-04	1.13E-04	1.25E-04	3.49E-04	1.01E-04	2.18E-05	4.13E-04	3.82E-04	5.44E-05	4.00E-04	1.25E-04	1.15E-04
6.84E-01	7.13E-01	7.01E-01	6.70E-01	7.16E-01	8.35E-01	6.37E-01	6.46E-01	7.60E-01	6.34E-01	7.06E-01	7.08E-01
3.51E-04	2.16E-04	2.13E-04	2.37E-04	1.75E-04	1.15E-04	1.79E-04	2.15E-04	1.34E-04	1.84E-04	1.83E-04	1.03E-04
7.68E-01	7.87E-01	7.88E-01	1	7.39E-01	7.94E-01	1	8.99E-01	7.53E-01	1	7.23E-01	7.85E-01
	2.34E-04	2.27E-04		3.02E-04	2.06E-04		1.61E-06	1.70E-04		2.47E-04	1.16E-04
	9.77E-01	1		9.52E-01	8.01E-01		1.35E-01	8.29E-01		9.62E-01	9.51E-01
		1.386			2.40E-04			2.05E-04			2.19E-04
		1.02E-01			1			1			9.67E-04

Table 7: Ti2 R/C Modeling Data (Five Selected Erratic Points)

SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE SPECTROSCOPY (SEM-EDS)

The main purpose of SEM-EDS is to provide visual proof of what is occurring on the surface at an extremely high resolution in the form of an image. The primary electron beam scanned across a materials surface, it then causes secondary electrons to be emitted. Then a detector analyzes the secondary electrons and an image is formed for review and analysis. [2] In this research, there was a great significance of utilizing this well-known engineering process. With the culmination of using the non-destructive test of; electrochemical impedance spectroscopy and equivalent circuit R/C circuit analysis, SEM-EDS surface examination was the final step in verifying exactly what was happening chemically or mechanically to both the fastener and carbon fiber coupon. The main subject for analysis under high-resolution were the SS2 and Ti2 galvanic samples.

Energy dispersive X-ray Spectroscopy was a tool for the chemical identification of individual elements during this research utilized in conjunction with SEM. [2, 15] The method would aid in determining what elements were present at the surface of either the metal or carbon fiber at high special resolution. This would assist in determination of whether corrosion or degradation of material present was caused by a chemical reaction or from another possible source. The SEM-EDS testing machine used was the JEOL JSM-5900 low vacuum SEM that was modified to acquire and display the video signal through an X-Stream imaging system. The SEM came with an 8" chamber, 5 axis motorized stage, Oxford EDS, and chamber-view system, which is detailed in Figures 32 and 33.

SEM-EDS – EXPERIMENTAL TECHNIQUES

There were several conditions and techniques that were required to obtain the samples for high-resolution images. After SS2 and Ti2 were selected for examination these galvanic samples were then emptied of the electrolyte solution immediately and the solution collected into vials for potential future study. Then each emptied sample was placed into individual packages to preserve the samples and not allow any risk of contamination. After this took place, methods to remove the fasteners from the carbon fiber without any damage needed to be considered. This consideration was due to the fact that the fasteners were threaded very carefully into the carbon fiber samples by hand and sealed with a marine grade adhesive, possibly posing difficulty for detachment. Fortunately, the fasteners were able to be extracted manually due to the adhesive not being epoxy/resin based. A small amount of heat was applied to the adhesive and the fasteners were removed accordingly. At this point both the SS2 and Ti2 fasteners were placed in separate packages, to be later cleaned and surface prepared for evaluation.

The carbon fiber test coupons were similarly removed by hand from the plastic tubes with minimal heat applied and placed in a separate container and dated accordingly. The next phase was to determine how to clean the surface area on the fasteners that retained adhesive outside of the area either in the carbon fiber or in the salt water, without causing any mechanical damage or remove valuable information. It was critical to preserve any surface coatings that were created due to the fasteners being immersed in the electrolyte for the extended period of time. A low power rotary tool was utilized, along with a rotary brass cleaning brush bit. This cleaned the area

which retained adhesive, Figure 28. After the fasteners were stripped, they were then prepared by placing a piece of copper tape to delineate the exposed area of carbon fiber and salt water contact and ready for SEM analysis, Figure 30. This was extremely important for the SEM-EDS progression, and the ability to distinguish the exact area that was exposed to the electrolyte solution as well as the carbon fiber/fastener interface. The specific distances were already determined previously, which can be identified in Table 5 of Chapter II.

Once the removal and surface preparation were completed then the fasteners and carbon fiber coupons were ready for SEM-EDS evaluation. The examination was conducted with the University of Rhode Island Environmental SEM Laboratory (ESEM). The Ti2 and SS2 fasteners along with the carbon fiber coupons they were adhered to, were then placed into the SEM-EDS chamber, as shown in Figure 32. At that point after the items were placed inside the chamber they were then analyzed at several selected points in real time. First, the SS2 fastener was examined following the Ti2 fastener then their respective carbon fiber coupons. The detailed high-resolution images that were taken and are detailed in Figures 36-45.

Once the SEM portion of the process was completed, then the EDS was accomplished for both fasteners and carbon fiber coupons. The ESEM Laboratory processed individualistic spectrum reports, which provided critical information for the fasteners and carbon fiber coupons. Certain points on each fastener and carbon fiber coupon were investigated for elements that may be present on the surface, which would indeed aid in confirming that corrosion was present on an atomic element level. These reports are provided in Figures 46-57 respectively.

Figure 28: SS2 and Ti2 Fasteners removed from inter-connection post 365 days.

Figure 29: SS2 and Ti2 Fasteners stripped for SEM-EDS

Figure 30: SS2 and Ti2 Fasteners prepped for SEM-EDS with copper sheathing detailing area exposed.

Figure 31: JEOL JSM-5900 Low Vacuum SEM-EDS System

Figure 32: SEM-EDS Sample set-up plate for insertion in to chamber

Figure 33: Carbon Fiber Sample with tapped hole not exposed to 3.5% NaCl for SEM

Figure 34: Carbon fiber sample detached from SS2 fastener and PVC

Figure 35: Carbon fiber sample detached from Ti2 fastener and PVC

Figure 36: Crevice Corrosion on SS2 fastener X400 resolution

Figure 37: Start of Crevice Corrosion on SS2 fastener X400 resolution and formation of Chloride ions.

Figure 38: Crevice Corrosion at outer thread of SS2 fastener X 200 resolution.

Figure 39: Chloride ion formation at thread region of SS2 fastener X 190 resolution.

Figure 40: Carbon Fiber threaded region X40 resolution – SS2

Figure 41: Carbon Fiber threaded region X40 resolution with delamination due to Fe
ion formation (rust) – SS2

Figure 42: Carbon Fiber delamination X100 resolution – SS2

Figure 43: Carbon Fiber threaded region with adhesive present X40 resolution – SS2

Figure 44: Ti2 fastener at exposed area to NaCl X100 resolution

Figure 45: Carbon Fiber threaded region X40 resolution – Ti2

Figure 46: EDS report, SS2 fastener at 300X resolution (1st area)

Figure 47: EDS report, SS2 fastener at 400X resolution (2nd area)

Figure 48: EDS report, SS2 fastener at 400X resolution (area of flaking of surface metal)

Figure 49: EDS report, Ti2 fastener at 100X resolution (exposed area)

Figure 50: EDS report, SS2 Carbon Fiber Sample at 40X resolution (1st area)

Figure 51: EDS report, SS2 Carbon Fiber Sample with tapped hole at 40X resolution
(2nd area)

Figure 52: EDS report, SS2 Carbon Fiber Sample with tapped hole at 40X resolution
(3rd area)

Figure 53: EDS report, SS2 Carbon Fiber Sample with tapped hole at 40X resolution
(4th area)

Figure 54: EDS report, SS2 Carbon Fiber Sample with tapped hole at 40X resolution
(5th area)

Figure 55: EDS report, SS2 Carbon Fiber Sample with tapped hole at 40X resolution
(6th area)

Figure 56: EDS report, Ti2 Carbon Fiber Sample with tapped hole at 40X resolution
(1st area)

Figure 57: EDS report, Carbon Fiber Sample with tapped hole only at 40X resolution
(1st area)

CHAPTER 4

RESULTS AND DISCUSSION

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

After completion of EIS, the figures were collected via potentiostat software and converted into excel with the main focus on impedance values over time. After close examination of the data, SS2 and Ti2 were chosen for further study, Table 2, Table 3 and Table 4. The selection process was directly gauged on their significant changes in values. The stainless steel (SS2) fastener, at day 1 of exposure displayed an impedance value of $9.91\text{E}+03 \Omega$. Then when readings were taken at day 206 of exposure, the impedance values drastically decreased to $1.98\text{E}+03 \Omega$. As for the titanium (Ti2) fastener, the impedance value began at $4.95\text{E}+03 \Omega$, then at day 215 is declined to $2.75\text{E}+03 \Omega$. This change indicated that the material being evaluated over time and exposure was experiencing possible corrosion or there was something happening to the material overall. However, the titanium samples inclusively remained consistent in terms of the impedance values after a certain period of time. After about the first 10 days of exposure to seawater solution the impedance remained in the range of $2.67\text{E}+03 \Omega$ to $2.78\text{E}+03 \Omega$. This was preliminarily expected to happen for the titanium sample, due to nobility and high ranking on the galvanic series [1, 2].

EQUIVALENT R/C MODELING

For the purposes of modeling, the potentiostat software contained pre-created models which were used initially to see how good a fit they were. There were two main equivalent circuit models used, a carbon fiber based and the other paint based. The paint-based R/C model can be viewed in Figure 27. These models were the starting point for developing an EIS model using electrical circuit elements. This led to correlating theoretically how many interfaces the inter-connected model created contained. Therefore, the model was analyzed first for possible interfaces within the galvanic system of a metal fastener in a carbon fiber composite. A detailed 3-D model was completed to represent the hypothetical interfaces that reacted with the electrolyte solution, 3.5% NaCl, Figure 22. After trial and error, the two pre-created models were not showing accurate results via Y2 Fit Z-Curves.

This then led to attempting to re-create circuits that would represent what physically is occurring in the cell on an analog scale. Initially a 2R/C circuit was created then a 3R/C and lastly a 4R/C, Figures 23, 24 and 25. After this was completed then circuit analysis took place, specifically for SS2 and Ti2. Each Y2 Fit Z-Curve was generated by the potentiostat software and each R/C model was ranked for goodness of fit from 1 to 3, best fit to worst, or a tie in between a respective two models, Tables 6 and 7.

After review of the erratic points that corresponded to certain dates when EIS was conducted, it was suggested that overall that the 3R/C circuit was the best and true fit. What this meant was that the SS2 and Ti2 fasteners contained the same number of interfaces, which are indicated to be three overall. These interfaces are as follows;

carbon fiber to fastener, fastener to electrolyte and lastly carbon fiber to electrolyte, as shown in Figure 22. This successful circuit analysis further indicated that the initial assumptions and theories at the initial set-up of the inter-connected model.

Previous research involving carbon fibers under an impressed voltage, from a potentiostat [9] modeled EIS data, and successfully used a 2R/C model. As shown here this model was not applicable when the voltage of the system was controlled by galvanic interactions. To understand this, further work should be considered as it is important to understand the exact process occurring.

SCANNING ELECTRON MICROSCOPY-ENERGY DISPERSIVE SPECTROSCOPY

After performing SEM-EDS the following results were identified for the galvanic samples. The SS2 fastener showed direct crevice corrosion in between two interfaces. These interfaces were the metal to electrolyte and the other being the carbon fiber to fastener. In Figure 36 and 38, there was clear crevice corrosion present at the exposed area of the fastener. Figure 37 and 39 identified the presence of a surface coating on the fasteners as well as cubic formation of sodium chloride. As for the carbon fiber coupons, there was signs of delamination of the woven fibers, detailed in Figures 41 and 42. EDS revealed that there was in fact iron elements present on the surface of the carbon fiber which is detailed in Figures 51 through 54. The spectroscopy also identified that the SS2 fastener had the key presence of chloride (Cl) and iron (Fe) peaks, which is evident in Figures 46, 47 and 49. The Ti2 sample presented no evidence of corrosion throughout the course of the entire experiment, as seen in Figure 44 and 49.

When the SEM-EDS was completed for SS2 and Ti2, there was visual support for corrosion at the crest of the stainless-steel fasteners that were immersed in seawater. The form of corrosion that formed on the stainless-steel fastener, SS2, was crevice corrosion. There are mechanisms for this type of corrosion, which is considered localized [1]. Crevice corrosion usually occurs on a metal that comes into contact with another mating surface. In this case, the mating surfaces are the carbon fiber composite and metal interface. The crevice actually can take place within a crack of the metal or under a surface deposit in a form of an acid solution. This reaction that takes place and causes a depletion of oxygen and is consumed. Usually crevice corrosion takes a long period of time, however when you have a case of extremely dissimilar or less noble metals, the process can be accelerated. Titanium is significantly more resistance to crevice corrosion than stainless steels for that very reason, its nobility is much greater.

The carbon fiber was not focus of this research, however future experiments should take place to determine the adverse effects that the material withstood, if any. It can be implied that by performing SEM-EDS after EIS data and equivalent circuit modeling, that the SEM-EDS information supported the suggestion that scatter and the large drop in the EIS data were indicative of corrosion, while a lower drop in EIS data with time and stable EIS data over a long period indicated no corrosion was occurring. It also indicated the mechanism of corrosion was in fact crevice corrosion. As crevice corrosion occurs at an interface, it is hidden from view. This is a then an interesting situation, as the threads of the fastener in the case of stainless steel are being removed, reducing the load bearing capability of the fastener. For the case of titanium, no

crevice corrosion was found and so the fastener and carbon fiber composite would be a much more stable load bearing situation. Further work on the reduction of load bearing capability by the crevice corrosion process would be interesting to continue further investigation.

CHAPTER 5

CONCLUSIONS

The experimental data proved by electron impedance spectroscopy (EIS), indicated several interesting features regarding the behavior of metal fasteners in contact with carbon fiber in a marine environment, facts were determined and proven to be accurate. The titanium samples remained consistent in terms of impedance values, showing no significant loss of material, nor did the data reveal a possibility of corrosion. The initial high values of impedance across all 11 samples did in fact correlate to the surface area and amount of metal expose to the seawater solution. The data collected for the stainless-steel samples unswervingly displayed rapid decrease in impedance values consistently. This suggested, that in fact there was a significant change occurring to the metal or carbon fiber. The EIS data also validated which samples to continue to analyze, and for this study SS2 and Ti2 where selected.

After performing equivalent R/C modeling a 3R/C EIS model was found to provide the best fit of EIS experimental data for a galvanic system, independent of metal alloy behavior. Then SEM-EDS process revealed that corrosion in fact took place on the stainless-steel fasteners. Although only one was identified for further investigation, it can be directly inferred that the other five fasteners exhibited similar behavior. To be exact crevice corrosion took place after the formation of sodium chloride atoms on the surface of the metal and having the other three elements needed for corrosion to exist. As for the titanium fasteners, it was originally theorized that the

metal would not exhibit much if any corrosion behavior. This was due to previous studies along with the material properties of the metal itself, being extremely noble. The carbon fiber did show signs of delamination; however, it couldn't be determined if it was caused by a chemical reaction or from mechanical failure from tapping the coupons.

Overall there is minimal or no research completed in terms of impedance within a "galvanic system". The outcome was not certain upon the start of the experimentation; however, it was proven that impedance values can be studied within a three-electrode connection. It has also been confirmed that the research has directly related corrosion to the instability and magnitude of the absolute drop of impedance. Lastly it was proven that corrosion occurred on the stainless-steel fasteners and the identification was directly attributed to the process of EIS and equivalent R/C modeling.

PROPOSED FUTURE STUDIES

MECHANICAL TESTING

The study of corrosion of metals and degradation of carbon fiber that is interconnected and immersed in seawater needs to be constant. It is vital to understand that this form of corrosion can be detrimental and ultimately lead to engineering failure at a large scale. There were certain items that were not accomplished in this research. Mechanical evaluation needed to be completed in the form of tensile (tension) and Barcol hardness tests. Meaning, the carbon fiber test coupon in its entirety, a coupon that was tapped then ultimately a coupon tapped and subjected to the seawater

environment. The tensile test of these three individual specimens would produce data relevant to the overall ultimate tensile and breaking strength along with significant elongation properties of the carbon fiber. The Barcol hardness test would be performed to gain an idea or a baseline of how the carbon fiber would react under loads and also how the fasteners when corroded were affected in terms of material properties and ability to remain whole.

FUTURE SCANNING ELECTRON MICROSCOPY EVALUATION

Although; due to the data and analysis completed by EIS and Modeling, which led to a significant corrosion evidence. There were also nine other fasteners that needed to be evaluated under SEM-EDS. Those specific fasteners were filled with epoxy resin, which can be seen in Figure 58. This was an original intended process; however due to time constraints, total cutting, surface preparation and polishing it was unable to be accomplished. The idea was to cut the samples in half creating a cross section that would then be slowly sanded down to the surface of the treaded region. Then the samples would be polished and placed into the SEM-EDS chamber for assessment. A burn out test also was unable to be completed, to determine the official lay-up and thickness of the carbon fiber. This specific test would also reveal how the material would withstand in extreme changes in temperature, hot/cold. Since the material was proprietary and distributed by the U.S. Government, the measurements taken for the purpose of research were done by hand. The determination of these unknowns, would aid in understanding the overall behavior of metals and materials subject to this environmental condition.

Figure 58: Epoxy/Resin filled sample for SEM continuation

APPENDIX A – RC MODELING GRAPHS

Figure 59: Bode Plot of SS2 Day 1 (2RC, 3RC, 4RC)

Figure 60: SS2 Day 1 2RC Model Data & Goodness of Fit Value

Figure 61: SS2 Day 1 3RC Model Data & Goodness of Fit Value

Figure 62: SS2 Day 1 4RC Model Data & Goodness of Fit Value

Figure 63: Bode Plot of SS2 Day 30 (2RC, 3RC, 4RC)

Figure 64: SS2 Day 30 2RC Model Data & Goodness of Fit Value

Figure 65: SS2 Day 30 3RC Model Data & Goodness of Fit Value

Figure 66: SS2 Day 30 4RC Model Data & Goodness of Fit Value

Figure 67: SS2 Bode Plot of SS2 Day 50 (2RC, 3RC, 4RC)

Figure 68: SS2 Day 50 2RC Model Data & Goodness of Fit Value

Figure 69: SS2 Day 50 3RC Model Data & Goodness of Fit Value

Figure 70: SS2 Day 50 4RC Model Data & Goodness of Fit Value

Figure 71: Bode Plot of SS2 Day 138 (2RC, 3RC, 4RC)

Figure 72: SS2 Day 138 2RC Model Data & Goodness of Fit Value

Figure 73: SS2 Day 138 3RC Model Data & Goodness of Fit Value

Figure 74: SS2 Day 138 4RC Model Data & Goodness of Fit Value

Figure 75: Bode Plot of SS2 Day 140 (2RC, 3RC, 4RC)

Figure 76: SS2 Day 140 2RC Model Data & Goodness of Fit Value

Figure 77: SS2 Day 140 3RC Model Data & Goodness of Fit Value

Figure 78: SS2 Day 140 4RC Model Data & Goodness of Fit Value

Figure 79: Bode Plot of SS2 Day 145 (2RC, 3RC, 4RC)

Figure 80: SS2 Day 145 2RC Model Data & Goodness of Fit Value

Figure 81: SS2 Day 145 3RC Model Data & Goodness of Fit Value

Figure 82: SS2 Day 145 4RC Model Data & Goodness of Fit Value

Figure 83: Bode Plot of SS2 Day 152 (2RC, 3RC, 4RC)

Figure 84: SS2 Day 152 2RC Model Data & Goodness of Fit Value

Figure 85: SS2 Day 152 3RC Model Data & Goodness of Fit Value

Figure 86: SS2 Day 152 4RC Model Data & Goodness of Fit Value

Figure 87: Bode Plot of SS2 Day 171 (2RC, 3RC, 4RC)

Figure 88: SS2 Day 171 2RC Model Data & Goodness of Fit Value

Figure 89: SS2 Day 171 3RC Model Data & Goodness of Fit Value

Figure 90: SS2 Day 171 4RC Model Data & Goodness of Fit Value

Figure 91: Bode Plot of SS2 Day 206 (2RC, 3RC, 4RC)

Figure 92: SS2 Day 206 2RC Model Data & Goodness of Fit Value

Figure 93: SS2 Day 206 3RC Model Data & Goodness of Fit Value

Figure 94: SS2 Day 206 4RC Model Data & Goodness of Fit Value

Figure 95: Bode Plot of Ti2 Day 1 (2RC, 3RC, 4RC)

Figure 96: Ti2 Day 1 2RC Model Data & Goodness of Fit Value

Figure 97: Ti2 Day 1 3RC Model Data & Goodness of Fit Value

Figure 98: Ti2 Day 1 4RC Model Data & Goodness of Fit Value

Figure 99: Bode Plot of Ti2 Day 30 (2RC, 3RC, 4RC)

Figure 100: Ti2 Day 30 2RC Model Data & Goodness of Fit Value

Figure 101: Ti2 Day 30 3RC Model Data & Goodness of Fit Value

Figure 102: Ti2 Day 30 4RC Model Data & Goodness of Fit Value

Figure 103: Bode Plot of Ti2 Day 49 (2RC, 3RC, 4RC)

Figure 104: Ti2 Day 49 2RC Model Data & Goodness of Fit Value

Figure 105: Ti2 Day 49 3RC Model Data & Goodness of Fit Value

Figure 106: Ti2 Day 49 4RC Model Data & Goodness of Fit Value

Figure 107: Bode Plot of Ti2 Day 138 (2RC, 3RC, 4RC)

Figure 108: Ti2 Day 138 2RC Model Data & Goodness of Fit Value

Figure 109: Ti2 Day 138 3RC Model Data & Goodness of Fit Value

Figure 110: Ti2 Day 138 4RC Model Data & Goodness of Fit Value

Figure 111: Bode Plot of Ti2 Day 176 (2RC, 3RC, 4RC)

Figure 112: Ti2 Day 176 2RC Model Data & Goodness of Fit Value

Figure 113: Ti2 Day 176 3RC Model Data & Goodness of Fit Value

Figure 114: Ti2 Day 176 4RC Model Data & Goodness of Fit Value

Figure 115: Bode Plot of Ti2 Day 215 (2RC, 3RC, 4RC)

Figure 116: Ti2 Day 215 2RC Model Data & Goodness of Fit Value

Figure 117: Ti2 Day 215 3RC Model Data & Goodness of Fit Value

Figure 118: Ti2 Day 215 4RC Model Data & Goodness of Fit Value

APPENDIX B - EIS DATA TABLES

	Date	F	RS (kΩ)	@_mHz	Z		PA (°)	@_mHz
SS1	9/15/2017	0.099994	1.922	100	1921.78	-44.0451	-44.05	100
	9/18/2017	0.099994	2.749	100	2749.42		-73.66	100
	9/20/2017	0.099994	2.859	100	2858.68	-71.8954	-71.9	100
	9/27/2017	0.099994	2.7	100	2699.61		-74.39	100
	9/29/2017	0.199461	1.271	199.5	1270.7	-70.4882	-70.49	199.5
	10/2/2017	0.099994	2.427	100	2426.52		-71.82	100
	10/4/2017	0.099994	1.822	100	1821.92	-57.9809	-57.98	100
	10/6/2017	0.099994	1.712	100	1712.05	-67.4606	-67.46	100
	10/11/2017	0.099994	1.944	100	1944.45		-79.09	100
	10/14/2017							
	10/16/2017	0.099994	1.9	100	1899.66		-71.31	100
	10/18/2017	0.099994	1.765	100	1765.41	-65.7273	-65.73	100
	10/21/2017	0.099994	1.932	100	1931.69	-69.9788	-69.98	100
	10/23/2017	0.099994	1.547	100	1547		-61.2	100
	10/25/2017							
	10/30/2017	0.099994	1.646	100	1645.61		-61.59	100
	11/1/2017	0.099994	1.704	100	1703.67	-62.1033	-62.1	100
	11/6/2017							
	11/15/2017	0.099994	1.115	100	1115.42		-53.48	100
	11/17/2017							

Table 8: SS1 EIS Experimental Data

SS2	9/15/2017	0.099994	1.736	100	1735.69	-53.4365	-53.44	100
	9/18/2017	0.099994	1.791	100	1791.47	-55.2323	-55.23	100
	9/20/2017	0.099994	3.71	100	3710.01	-73.8264	-73.83	100
	9/27/2017	0.099994	1.909	100	1908.64		-53.27	100
	9/29/2017	0.199461	1.336	199.5	1335.85	-50.7112	-50.71	199.5
	10/2/2017	0.099994	2.06	100	2060.29		-56.16	100
	10/4/2017	0.099994	1.903	100	1902.95	-56.475	-56.48	100
	10/6/2017	0.099994	1.984	100	1983.71	-56.7914	-56.79	100
	10/11/2017	0.099994	2.087	100	2086.83		-63.14	100
	10/14/2017							
	10/16/2017	0.099994	1.885	100	1884.83		-60.05	100
	10/18/2017	0.099994	2.083	100	2082.53	-59.7516	-59.75	100
	10/21/2017	0.099994	2.205	100	2205.15	-58.9306	-58.93	100
	10/23/2017	0.099994	2.207	100	2207.43		-50.07	100
	10/25/2017							
	10/30/2017	0.099994	2.175	100	2174.69		-59.69	100
	11/1/2017	0.099994	1.989	100	1988.53	-51.6262	-51.63	100
	11/6/2017							
	11/15/2017	0.099994	2.083	100	2082.84		-56.7	100
	11/17/2017							

Table 9: SS2 EIS Experimental Data

SS3	9/15/2017							
	9/18/2017							
	9/20/2017	0.099994	1.825	100	1824.67	-65.2929	-65.29	100
	9/27/2017	0.099994	1.882	100	1881.56		-67.76	100
	9/29/2017	0.199461	1.11	199.5	1109.51	-65.1161	-65.12	199.5
	10/2/2017	0.099994	1.884	100	1883.96		-67.99	100
	10/4/2017	0.099994	1.75	100	1749.88	-68.2985	-68.3	100
	10/6/2017	0.099994	1.865	100	1864.8	-70.3799	-70.38	100
	10/11/2017	0.099994	1.866	100	1865.8		-70.53	100
	10/14/2017							
	10/16/2017	0.099994	1.624	100	1624.31		-61.56	100
	10/18/2017	0.099994	1.644	100	1644.1	-67.8733	-67.87	100
	10/21/2017	0.099994	1.965	100	1964.89	-70.7076	-70.71	100
	10/23/2017	0.099994	1.784	100	1783.69		-61.07	100
	10/25/2017							
	10/30/2017	0.099994	1.941	100	1940.81		-70.54	100
	11/1/2017	0.099994	1.965	100	1964.54	-70.943	-70.94	100
	11/6/2017							
	11/15/2017							
	11/17/2017	0.099994	1.682	100	1682.07	-68.8187	-68.82	100

Table 10: SS3 EIS Experimental Data

SS4	9/15/2017	0.099994	6.361	100	6360.55	-67.5169	-67.52	100
	9/18/2017	0.099994	6.948	100	6948.25		-72.44	100
	9/20/2017	0.099994	7.21	100	7210.03	-73.7864	-73.79	100
	9/27/2017	0.099994	5.118	100	5118.31		-70.27	100
	9/29/2017	0.099994	5.209	100	5209.32	-70.8444	-70.84	100
	10/2/2017	0.099994	6.282	100	6282.1		-73.2	100
	10/4/2017	0.099994	6.044	100	6044.01	-72.836	-72.84	100
	10/6/2017	0.099994	7.099	100	7098.92	-75.4789	-75.48	100
	10/11/2017	0.099994	6.888	100	6887.92		-75	100
	10/14/2017	0.099994	4.691	100	4691.45		-70.55	100
	10/16/2017	0.099994	6.881	100	6881.49		-75.99	100
	10/18/2017	0.099994	5.588	100	5588.23	-72.2628	-72.26	100
	10/21/2017	0.099994	2.937	100	2936.87	-63.963	-63.96	100
	10/23/2017	0.099994	6.003	100	6002.92		-71.41	100
	10/25/2017	0.099994	4.815	100	4815.02	-68.3842	-68.38	100
	10/30/2017	0.099994	6.647	100	6647.17		-74.56	100
	11/1/2017	0.099994	5.714	100	5713.53	-71.9865	-71.99	100
	11/6/2017	0.099994	6.739	100	6739.85		-73.48	100
	11/15/2017							
	11/17/2017	0.099994	1.873	100	1872.66	-56.3755	-56.38	100

Table 11: SS4 EIS Experimental Data

SS5	9/15/2017	0.099994	5.857	100	5856.69	-65.2878	-65.29	100
	9/18/2017	0.099994	6.59	100	6590.3		-70.18	100
	9/20/2017	0.099994	5.524	100	5524.49	-68.315	-68.32	100
	9/27/2017	0.099994	5.405	100	5405.34		-68.33	100
	9/29/2017	0.099994	6.312	100			-71.64	100
	10/2/2017	0.099994	5.541	100	5541.22		-69.5	100
	10/4/2017	0.099994	6.222	100	6222.05	-71.4472	-71.45	100
	10/6/2017	0.099994	5.068	100	5067.53	-59.1617	-59.16	100
	10/11/2017	0.099994	7.281	100	7281.16		-75.75	100
	10/14/2017	0.099994	6.044	100	6043.6		-71.67	100
	10/16/2017	0.099994	6.998	100	6998.21		-74.16	100
	10/18/2017	0.099994	6.057	100	6056.74	-71.114	-71.11	100
	10/21/2017	0.099994	7.394	100	7393.66	-73.5202	-73.52	100
	10/23/2017	0.099994	3.043	100	3042.98		-64.31	100
	10/25/2017	0.099994	4.697	100	4697.1	-67.0945	-67.09	100
	10/30/2017	0.099994	4.031	100	4031.3		-51.23	100
	11/1/2017	0.099994	5.549	100	5549.05	-66.7834	-66.78	100
	11/6/2017	0.099994	4.381	100	4381.36		-61.75	100
	11/15/2017							
	11/17/2017	0.099994	5.295	100	5294.62	-70.887	-70.89	100

Table 12: SS5 EIS Experimental Data

SS6	9/15/2017	0.099994	3.036	100	3036.21	-60.4144	-60.41	100
	9/18/2017	0.099994	4.715	100	4714.6		-67.61	100
	9/20/2017	0.099994	5.063	100	5062.84	-69.8582	-69.86	100
	9/27/2017	0.099994	4.249	100	4248.74		-66.01	100
	9/29/2017	0.099994	5.264	100	5264.03	-53.8198	-53.82	100
	10/2/2017	0.099994	6.75	100	6750.22		-72.79	100
	10/4/2017	0.099994	6.715	100	6714.51	-72.0049	-72	100
	10/6/2017	0.099994	6.159	100	6159.04	-71.8153	-71.82	100
	10/11/2017	0.099994	4.568	100	4568.21		-67.38	100
	10/14/2017	0.099994	7.474	100	7474.26		-73.61	100
	10/16/2017	0.099994	5.843	100	5843.26		-70.48	100
	10/18/2017	0.099994	6.067	100	6066.64	-70.4407	-70.44	100
	10/21/2017	0.099994	7.332	100	7331.81	-72.3135	-72.31	100
	10/23/2017	0.099994	5.47	100	5469.81		-68	100
	10/25/2017	0.099994	5.636	100	5635.98	-68.5248	-68.52	100
	10/30/2017	0.099994	6.166	100	6165.75		-70.41	100
	11/1/2017	0.099994	6.281	100	6280.62	-70.7831	-70.78	100
	11/6/2017	0.099994	5.812	100	5811.94		-69.27	100
	11/15/2017							
	11/17/2017	0.099994	5.528	100	5528.45	-69.8467	-69.85	100

Table 13: SS6 EIS Experimental Data

Ti1	9/15/2017	0.099994	2.296	100	2296.02	-74.5769	-74.58	100
	9/18/2017	0.099994	2.586	100	2585.64		-76.56	100
	9/20/2017	0.099994	2.436	100	2436.47	-74.287	-74.29	100
	9/27/2017	0.099994	2.593	100	2592.71		-71.12	100
	9/29/2017	0.099994	2.585	100	2584.63	-77.2233	-77.22	100
	10/2/2017	0.099994	2.681	100	2681.03		-72.99	100
	10/4/2017	0.099994	2.676	100	2676.41	-77.7283	-77.73	100
	10/6/2017	0.099994	2.422	100	2421.85	-76.1566	-76.16	100
	10/11/2017	0.099994	2.619	100	2619.11	-77.8619	-77.86	100
	10/14/2017							
	10/16/2017	0.099994	2.665	100	2664.91		-77.98	100
	10/18/2017	0.099994	2.47	100	2470.29	-75.5436	-75.54	100
	10/21/2017	0.099994	2.723	100	2723.12	-77.448	-77.45	100
	10/23/2017	0.099994	2.693	100	2692.78		-76.93	100
	10/25/2017							
	10/30/2017	0.099994	2.666	100	2665.63		-76.65	100
	11/1/2017							
	11/6/2017	0.099994	2.634	100	2633.9		-76.8	100
	11/15/2017							
	11/17/2017	0.099994	2.68	100	2679.99	-77.331	-77.33	100

Table 14: Ti1 EIS Experimental Data

Ti2	9/15/2017	0.099994	2.533	100	2533.17	-76.0289	-76.03	100
	9/18/2017	0.099994	2.612	100	2611.8		-76.38	100
	9/20/2017	0.099994	2.65	100	2649.6		-76.83	100
	9/27/2017	0.099994	2.621	100	2621.3		-76.67	100
	9/29/2017	0.099994	2.65	100	2649.75	-77.2677	-77.27	100
	10/2/2017	0.099994	2.709	100	2708.9		-77.5	100
	10/4/2017	0.099994	2.689	199	2688.69	-77.5507	-77.55	100
	10/6/2017	0.099994	2.603	100	2603.47	-77.0013	-77	100
	10/11/2017	0.099994	2.64	100	2640.48	-77.5975	-77.6	100
	10/14/2017							
	10/16/2017	0.099994	2.686	100	2685.54		-77.73	100
	10/18/2017	0.099994	2.74	100	2740.44	-77.11	-77.11	100
	10/21/2017	0.099994	2.674	100	2674.07	-75.9291	-75.93	100
	10/23/2017	0.099994	2.419	100	2419		-73.72	100
	10/25/2017							
	10/30/2017	0.099994	2.709	100	2708.91		-76.52	100
	11/1/2017							
	11/6/2017	0.099994	2.969	100	2695.73		-76.95	100
	11/15/2017							
	11/17/2017	0.099994	2.777	100	2776.61	-77.5007	-77.5	100

Table 15: Ti2 EIS Experimental Data

Ti3	9/15/2017	0.099994	2.463	100	2463.37	-74.9667	-74.97	100
	9/18/2017	0.099994	2.546	100	2545.57		-75.35	100
	9/20/2017	0.099994	2.467	100	2467.26	-74.5787	-74.58	100
	9/27/2017	0.099994	2.538	100	2538.28		-75.62	100
	9/29/2017	0.099994	2.502	100	2502.19	-75.4295	-75.43	100
	10/2/2017	0.099994	2.632	100	2632.23		-76.4	100
	10/4/2017	0.099994	2.629	100	2628.97	-76.6625	-76.66	100
	10/6/2017	0.099994	2.562	100	2561.97	-76.3305	-76.33	100
	10/11/2017	0.099994	2.529	100	2529.33	-76.1565	-76.16	100
	10/14/2017							
	10/16/2017	0.099994	2.603	100	2603.05		-76.59	100
	10/18/2017	0.099994	2.649	100	2649.17	-76.9578	-76.96	100
	10/21/2017	0.099994	2.665	100	2665.08	-76.0522	-76.05	100
	10/23/2017	0.099994	2.6	100	2599.89		-74.78	100
	10/25/2017	0.099994	2.673	100	2632.67		-75.76	100
	10/30/2017							
	11/1/2017							
	11/6/2017	0.099994	2.614	100	2613.78		-75.87	100
	11/15/2017							
	11/17/2017	0.099994	2.685	100	2684.82	-76.1947	-76.19	100

Table 16: Ti3 EIS Experimental Data

Ti4	9/15/2017	0.099994	7.829	100	7829.03	-71.4532	-71.45	100
	9/18/2017	0.099994	8.294	100	8294.04		-72.72	100
	9/20/2017	0.099994	8.188	100	8166.06	-72.7379	-72.74	100
	9/27/2017	0.099994	6.795	100	6795.37		-75.55	100
	9/29/2017	0.099994	6.77	100	6769.68	-78.1014	-78.1	100
	10/2/2017	0.099994	6.871	100	6870.69		-78.32	100
	10/4/2017	0.099994	6.799	100	6798.79	-79.1468	-79.15	100
	10/6/2017	0.099994	5.711	100	5710.62	-76.5325	-76.53	100
	10/11/2017	0.099994	6.514	100	6513.72	-78.9881	-78.99	100
	10/14/2017	0.099994	6.527	100	6527.38		-78.68	100
	10/16/2017	0.099994	5.965	100	6687.17		-79.07	100
	10/18/2017	0.099994	6.73	100	6730.14	-79.0488	-79.05	100
	10/21/2017	0.099994	6.604	100	6604.31	-78.1159	-78.12	100
	10/23/2017	0.099994	6.713	100	6713.21		-78.51	100
	10/25/2017	0.099994	6.74	100	6740	-79.0917	-79.09	100
	10/30/2017							
	11/1/2017	0.099994	6.694	100	6693.74	-78.6972	-78.7	100
	11/6/2017							
	11/15/2017							
	11/17/2017	0.099994	6.812	100	6812.26	-78.8871	-78.89	100

Table 17: Ti4 EIS Experimental Data

Ti5	9/15/2017	0.099994	7.612	100	7612.32	-66.5606	-66.56	100
	9/18/2017	0.099994	6.679	100	6679.05		-70.21	100
	9/20/2017	0.099994	6.122	100	6122.48	-76.0723	-76.07	100
	9/27/2017	0.099994	5.841	100	5841.4		-75.63	100
	9/29/2017	0.099994	5.91	100	5909.77	-76.1447	-76.14	100
	10/2/2017	0.099994	5.997	100	5986.89		-75.8	100
	10/4/2017	0.099994	5.97	100	5970.1	-76.4932	-76.49	100
	10/6/2017	0.099994	5.858	100	5857.78	-76.1289	-76.13	100
	10/11/2017	0.099994	5.843	100	5843.36	-76.0128	-76.01	100
	10/14/2017	0.099994	5.924	100	5923.86		-76.65	100
	10/16/2017	0.099994	5.965	100	5964.77		-74.94	100
	10/18/2017	0.099994	6.008	100	6008.48	-76.0524	-76.05	100
	10/21/2017	0.099994	4.752	100	4752.13	-71.3943	-71.39	100
	10/23/2017	0.099994	5.952	100	5951.75		-73.7	100
	10/25/2017	0.099994	6.179	100	6179.12	-71.4389	-71.44	100
	10/30/2017							
	11/1/2017	0.099994	5.866	100	5866.18	-75.4118	-75.41	100
	11/6/2017							
	11/15/2017							
	11/17/2017	0.099994	5.942	100	5941.58	-74.8764	-74.88	100

Table 18: Ti5 EIS Experimental Data

APPENDIX C – CREVICE CORROSION CHEMICAL REACTION

Figure 119: Mechanism of Crevice Corrosion – Chemical Reaction

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