

Electrochemical Corrosion Tests for Tank 241-AY-101 Core 325, Segments 16R1 and 16R2

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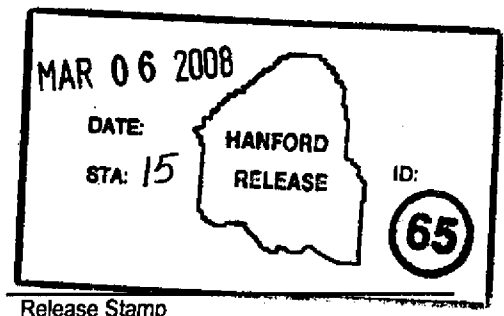
Abstract: The interstitial liquid in the double-shell tank 241-AY-101 settled solids layer is below the hydroxide chemistry control limit required by HNF-SD-WM-TSR-006, Tank Farms Technical Safety Requirements, Administrative Control 5.16, "Corrosion Mitigation Controls." Operating tanks outside of the specification may increase the propensity corrosion of the carbon steel wall. This report is concerned with generalized electrochemical corrosion mechanism that may occur at specific loci. All cyclic potentiodynamic polarization scans exhibited a negative hysteresis, scan reversing at lower current density, indicating that there was no pitting propensity. The general electrochemical corrosion rates ranged from $4.4E-02$ to $1.5E-03$ mpy with the first round of coupons, while the second round yielded corrosion rates of $2.5E-03$ to $2.9E-02$ mpy.

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List of Terms

Abbreviations

AC	Administrative Control
AN-107	tank 241-AN-107
ASTM	American Society for Testing and Materials
CPP	cyclic potentiodynamic polarization
DST	double shell tank
OCP	open circuit potential
TGA	thermogravimetric analysis

Units

°F	degrees Fahrenheit
mA/cm ²	milliamperes per square centimeter
<u>M</u>	molar or moles per liter
mV	millivolts

1. INTRODUCTION

The interstitial liquid in the double-shell tank (DST) 241-AY-101 (AY-101) settled solids layer is below the hydroxide chemistry control limit required by HNF-SD-WM-TSR-006, *Tank Farms Technical Safety Requirements*, Administrative Control (AC) 5.16, "Corrosion Mitigation Controls." The AC 5.16 limits for the AY-101 solids layer interstitial liquid are presented in Table 1.

From the March 2007 Core 325 sampling event, the interstitial liquid hydroxide (OH⁻) concentration was at pH 11.1, or 0.0013 M, near the tank bottom. The AC 5.16 lower hydroxide concentration limit for the tank waste interstitial liquid is 0.01 M, equivalent to pH 12. The bottom sludge region is out of compliance with the lower hydroxide concentration limit, CH2M-0701373, "Request for Approval of Recovery Plan to Restore Chemistry Control in Tank 241-AY-101."

Table 1. Chemistry Control Limits Applicable to Tank 241-AY-101 Interstitial Liquid.

Variable	Limits
OH ⁻	0.010 <u>M</u> < [OH ⁻] ≤ 8.0 <u>M</u>
NO ₂ ⁻	0.011 <u>M</u> ≤ [NO ₂ ⁻] ≤ 5.5 <u>M</u>
[NO ₃ ⁻]/([OH ⁻] + [NO ₂ ⁻])	<2.5

Notes:

1. The brackets [] denote concentration in M (molarity or moles/L).
2. These limits apply to waste with a NO₃⁻ concentration ≤ 1.0 M and a waste temperature less than 167 °F.

Table 2 gives the waste composition from the March 2007 sampling campaign, RPP-RPT-33858, *Final Report for Tank 241-AY-101, Cores 324 and 325 in Support of the Corrosion Mitigation and Criticality Safety Programs*. The Table 1 limits apply to all the samples except supernatant sample Segment 2A. Because the Segment 2A nitrate (NO₃⁻) concentration is greater than 1 M, different limits than those in Table 1 apply to this sample. These limits require the hydroxide concentration to be greater than or equal to 0.13 M and the sum of hydroxide and nitrite (NO₂⁻) concentrations to be greater than or equal to 0.53 M. Therefore, with the exception of the bottom segment of the sludge, AY-101 is within chemistry compliance.

The AC 5.16 limits were established to control corrosion on the inside of the primary tank wall of the DST (Table 1). Operating tanks outside of the specification may increase the propensity for corrosion of the carbon steel wall. However, since aggressive ion NO₃⁻ and chloride (Cl⁻) concentrations are low (0.06 M and 0.01 M, respectively) in the interstitial liquid in the bottom region of the sludge and corrosion inhibitor chemical NO₂⁻ and carbonate (CO₃⁻²) concentrations are dominant (0.88 M and 2.3 M respectively); the tank wall and knuckle would be less susceptible to stress corrosion cracking, which is the major corrosion mechanism of concern.

Table 2. Tank 241-AY-101 Waste Composition from March 2007 Sample Results.

Sample Location (Corresponding Segment of Core 325)	OH ⁻ (M)	NO ₂ ⁻ (M)	NO ₃ ⁻ (M)
Supernatant- top layer (Segment 1A)	0.43	0.12	0.82
Supernate - top layer (Segment 2A)	0.71	0.21	1.33
Supernate – bottom (Segment 14)	0.67	0.60	0.11
Sludge - top (Segment 15)	0.05	0.83	0.06
Sludge – bottom (Segment 16)	0.0013*	0.88	0.06

*Sludge OH⁻ concentration based on pH measurement.

This report is concerned with the generalized electrochemical corrosion mechanism that may occur at specific loci on a carbon steel coupon, fabricated from the same type of steel as used in construction of the AY-101 primary tank wall, and immersed in the out-of-specification sludge. Information reported will focus on generalized corrosion as determined by mathematical analysis of the Tafel region, the breakdown potential, the repassivation potential, and pitting propensity. In addition, the results of long-term open circuit potential (OCP) measurements will be presented.

To determine the pitting potential, cyclic potentiodynamic polarization (CPP) scans were carried out. The CPP scan consists of a forward scan from approximately -100 mV versus OCP to a reverse point of up to 5 mA/cm² [American Society for Testing and Materials (ASTM) G61-86, *Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys*]. In this study, the reversal coincided with the work being carried out at CC Technologies^{®1} using Hanford tank waste simulant materials.

The OCP and CPP testing used a composite of portions of Core 325 Segments 16R1 and 16R2. The portions of the two segments used for the composite were selected and carefully recovered following the segment extrusions in the hot cell to minimize cross contamination with hydrostatic head fluid present in the top end of the segment samplers. After the electrochemical scans were completed, the composite 16R1 and 16R2 was centrifuged and submitted for analysis. Table 3 shows the results for hydroxide, nitrite, and nitrate.

Table 3. Core 325 Segments 16R1 and 16R2 Composite Analysis

Sample	OH ⁻ (M)	NO ₂ ⁻ (M)	NO ₃ ⁻ (M)
16R1/16R2 composite liquid	0.0005*	0.71	0.07
16R1/16R2 composite solid	Not determined	0.68	0.07

* 16R1 liquid OH⁻ concentration based on pH measurement.

¹ CC Technologies[®] is a registered trade mark of Cortest Columbus Technologies, Inc., Dublin, Ohio.

This report describes data obtained under the execution of RPP-PLAN-34691, *Electrochemical Corrosion Tests for Tank 241-AY-101 Core 325, Segments 16R1 and 16R2*. The work was carried out under ATL-MP-1011, *ATL Quality Assurance Project Plan for 222-S Laboratory*, and ATS-MP-1032, *222-S Laboratory Quality Assurance Plan*.

2. MATERIALS AND METHODS

The coupons used in this study were obtained from Metal Samples^{®2} and were A537 Class 1 EL410 (right cylinder configuration) with an area of approximately 5.64 cm². All coupons were prepared by a surface treatment of 600-grit wet sandpaper followed by sonication in acetone for 2 minutes and then fixing the coupon to a type 316 stainless steel electrode rod.

As an instrument check, a scan using the ASTM G5-94, *Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements*, was carried out in a 500- mL I-CHEM^{®3} jar used as the electrochemical cell before and after the AY-101 scans.

The potentiostat used is a PARSTAT^{®4} 2263 with data collection and analyses software, PARSTAT[®] PowerSuite, Advanced Electrochemistry Software, Version 2.33. The potentiostat has a 20-V compliance voltage and a maximum current of up to ±200 mA.

After surface preparations, the coupons were allowed to equilibrate for 18 to 24 hours before a CPP scan was initiated.

3. RESULTS

The sample from AY-101 was dilatant in its rheological behavior and proved significantly more difficult to work with than any previous DST sludge and saltcake samples. During the testing period, a number of plant shutdowns occurred interrupting the progress of the testing. Therefore, two rounds of CPP tests were performed. Results from both rounds of tests are presented.

Figure 1 shows the electrochemical cell response to the ASTM G5-94 method. The cell response agrees well with the standard results demonstrating proper performance of the equipment and cell configuration.

After surface preparations, the coupons were allowed to equilibrate in AY-101 sludge sample for 18 to 24 hours before a CPP scan was initiated. The CPP scans from the first and second rounds are presented in Appendix A and B, respectively. The OCP traces are presented in Appendix C (first round) and Appendix D (second round).

Table 4 shows the results from the CPP scans for the first round of testing. The OCP given in the table is taken from the CPP scans (Appendix A). Originally, there were to be three coupons

² Metal Samples[®] is a division of Alabama Specialty Products, Inc., Munford, Alabama.

³ I-CHEM[®] is a subsidiary of Nalge Nunc International Corporation, Rochester, New York.

⁴ PARSTAT[®] PowerSuite is a registered trademark of Princeton Applied Research, Oak Ridge, Tennessee.

scanned in different regions of the saltcake, followed by a long-term (7 day) coupon equilibration test. The 7-day equilibration coupon was to have OCP measured at the end of the period. The first coupon was equilibrated for 18 hours and then a CPP scan was performed. During the plant shutdown, the second coupon of the first round equilibrated in the sludge for 8 days (the length of the plant shutdown) instead of the planned 18 to 24 hours prior to performing the CPP scan. A third coupon was equilibrated for 18 hours and then a CPP scan was performed. Note the more positive OCP for the second coupon, which equilibrated in the AY-101 sludge a factor of 10 longer than the first and third coupons. This change in OCP can also be seen in the first round OCP scans shown in Appendix C. The OCP measurements made after the initial 18-hour equilibration period (but before the CPP scans) for the first and second coupons are nearly identical. However, the OCP of the second coupon measured a second time 8 days later after the plant shutdown period ended gave a substantially more positive OCP value.

Figure 1. Electrochemical Cell Response to High and Low ASTM Reported Values.

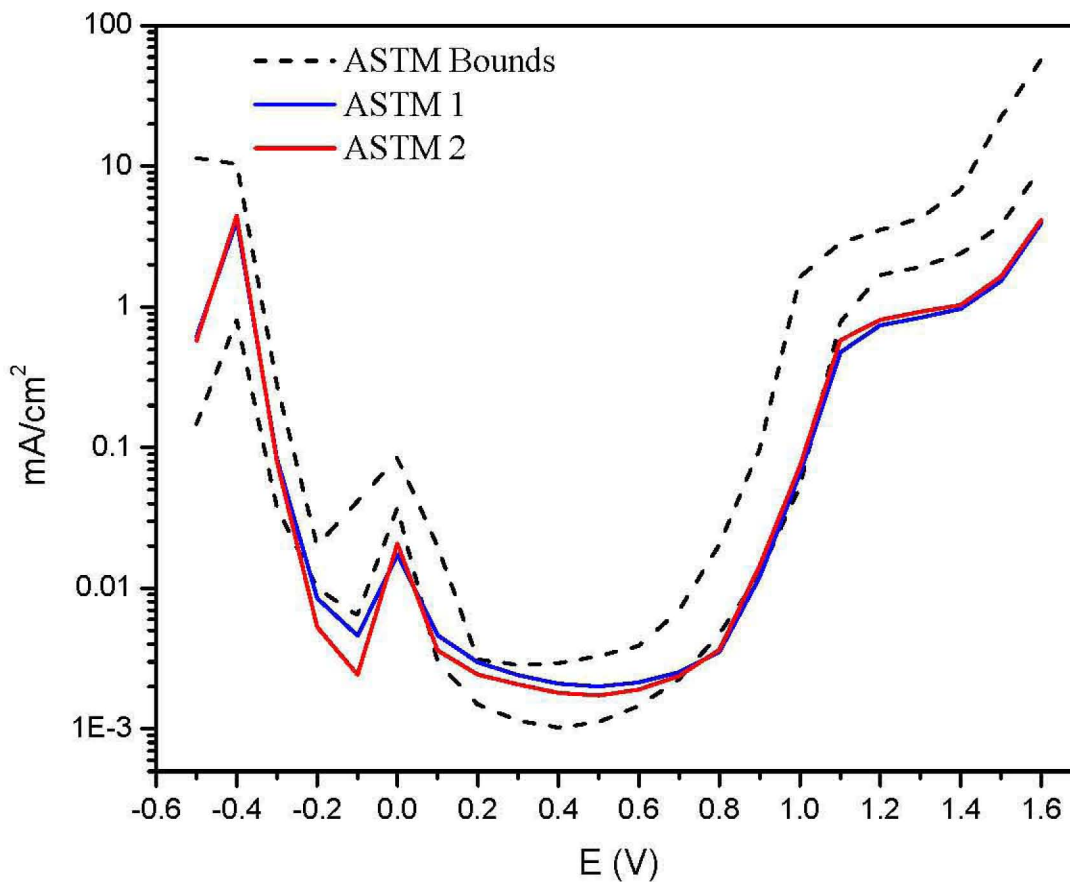


Table 4. Cyclic Potentiodynamic Polarization Results, First Round.

Date	OCP (mV)	Corrosion Rate (mpy)	Chi-Square
9/18/07	-0.128	1.5E-03	88.12
9/27/07*	-0.052	1.9E-03	55.0
9/28/07	-0.124	4.4E-02	72.6

* Coupon pre-equilibrated in sample 8 days instead of nominal 18 hours due to plant shutdown.

Because of the interruption in testing caused by the plant shutdown, a second round of testing, which incorporated three coupons equilibrating for 18 hours, then scanned, and followed by a long-term (7 day) equilibration and scan, was initiated. Table 5 shows the results for the CPP scans obtained during the second round. The OCPs given in the table are taken from the CPP scans (Appendix B). Note the OCP dependence on equilibration time for the second testing round (Table 4 and Appendix D) similar to the behavior discussed for the first testing round.

Table 5. Cyclic Potentiodynamic Polarization Results, Second Round.

Date	OCP (mV)	Corrosion Rate (mpy)	Chi-Square
10/09/07	-0.089	4.1E-03	31.6
10/11/07	-0.075	2.0E-02	29.48
10/13/07	-0.094	2.9E-02	49.1
10/24/07*	-0.044	2.5E-03	56.1

* Coupon pre-equilibrated in sample 7 days.

4. DISCUSSION

All CPP scans exhibited a negative hysteresis, scan reversing at lower current density, indicating that there was no pitting propensity. The general electrochemical corrosion rates ranged from 1.5E-03 to 4.4E-02 mpy with the first round of coupons, while the second round yielded corrosion rates of 2.5E-03 to 2.9E-02 mpy. Open circuit potentials range from approximately 100 mV to 125 mV for coupon equilibration times of 18 hours up to approximately 40 mV for coupon equilibration times of 7 to 8 days.

5. REFERENCES

- ASTM G5-94, 1994 (Reapproved 1999), *Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements*, American Society for Testing and Materials, West Conshohocken, Pennsylvania.
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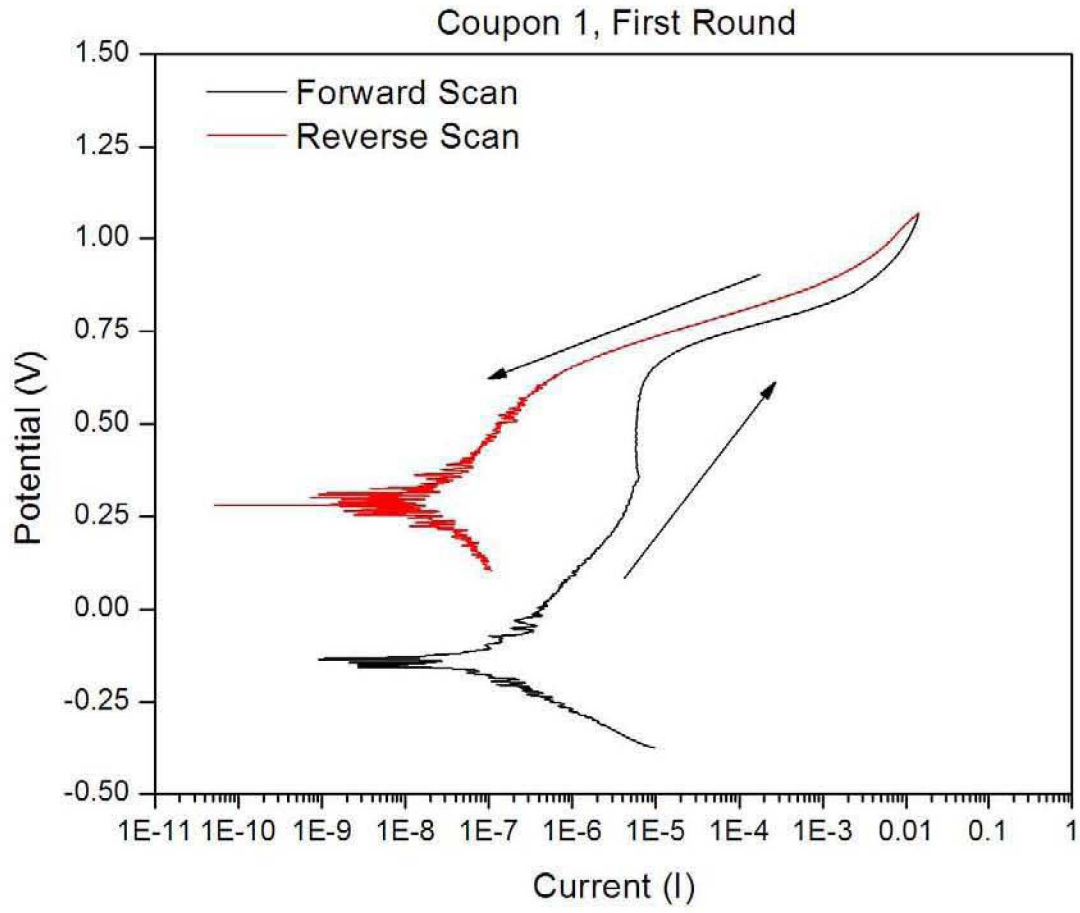
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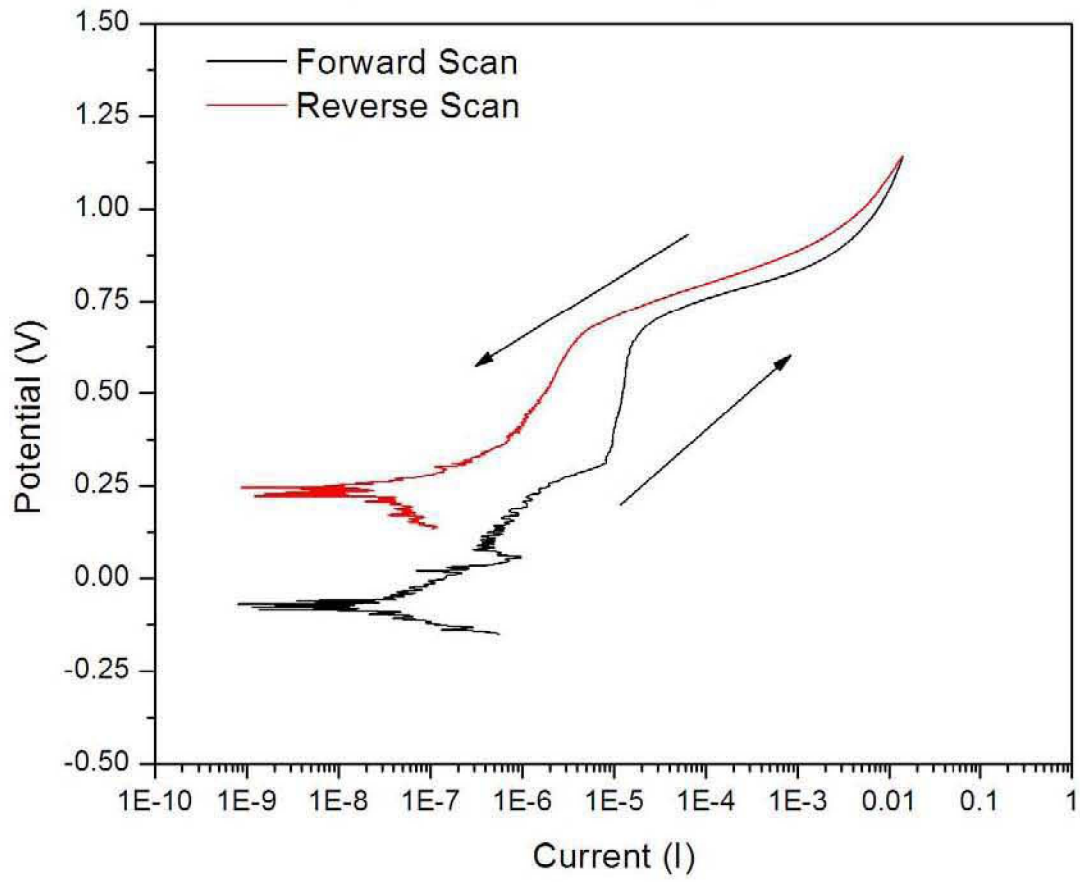
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Appendix A

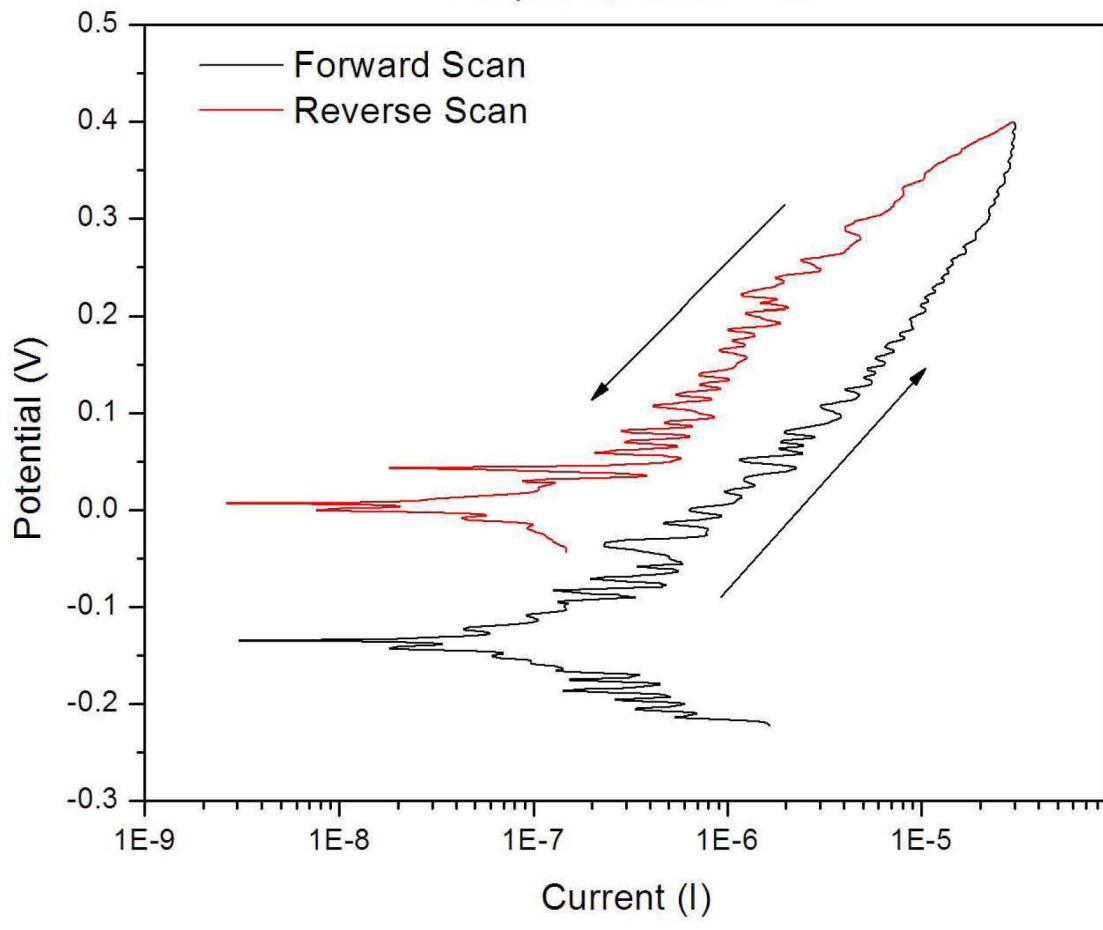
Cyclic Potentiodynamic Polarization Scans, First Round



Coupon 2, First Round Equilibrated 8 Days

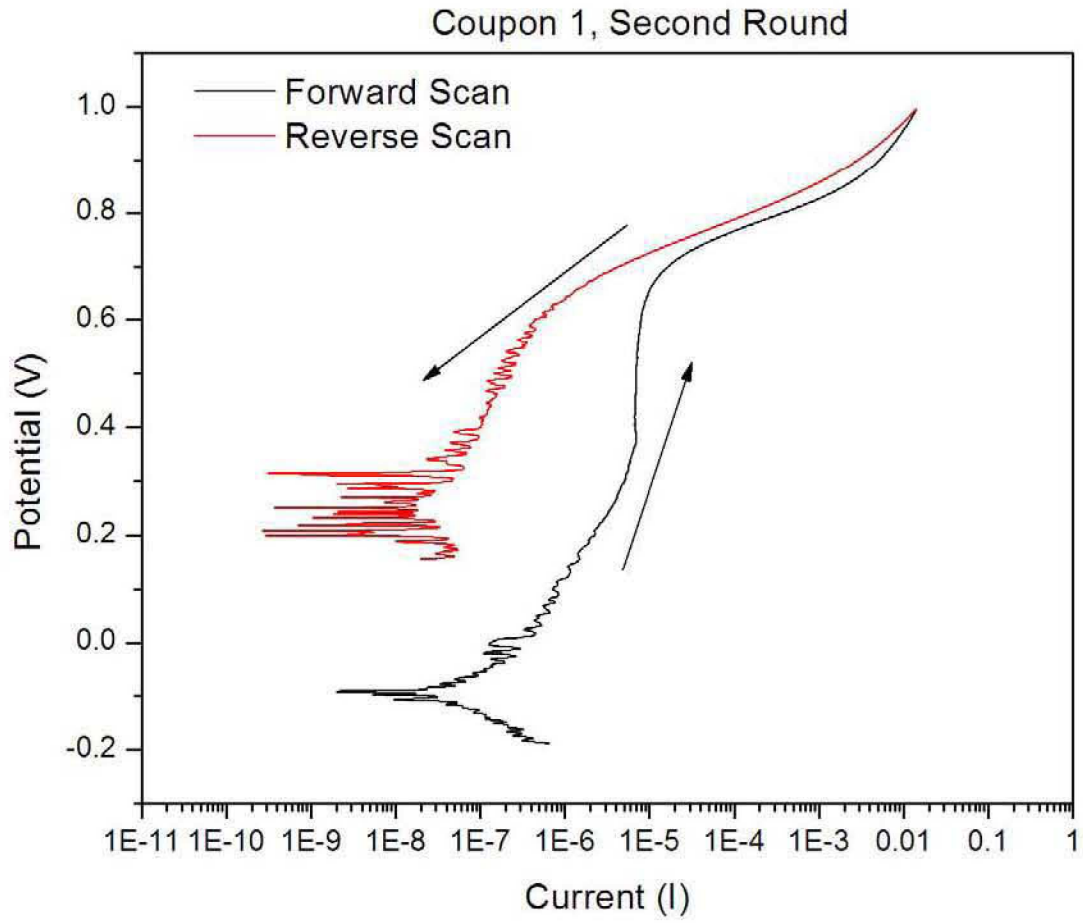


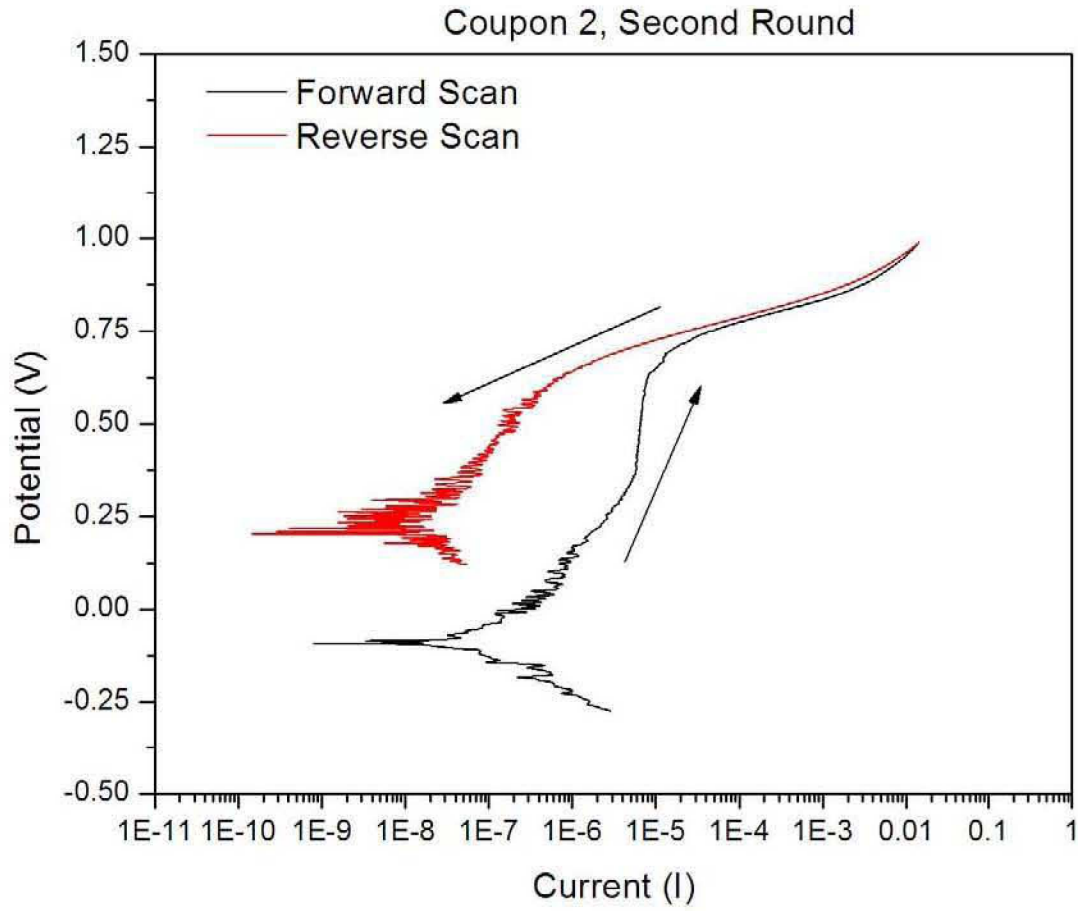
Coupon 3, First Round

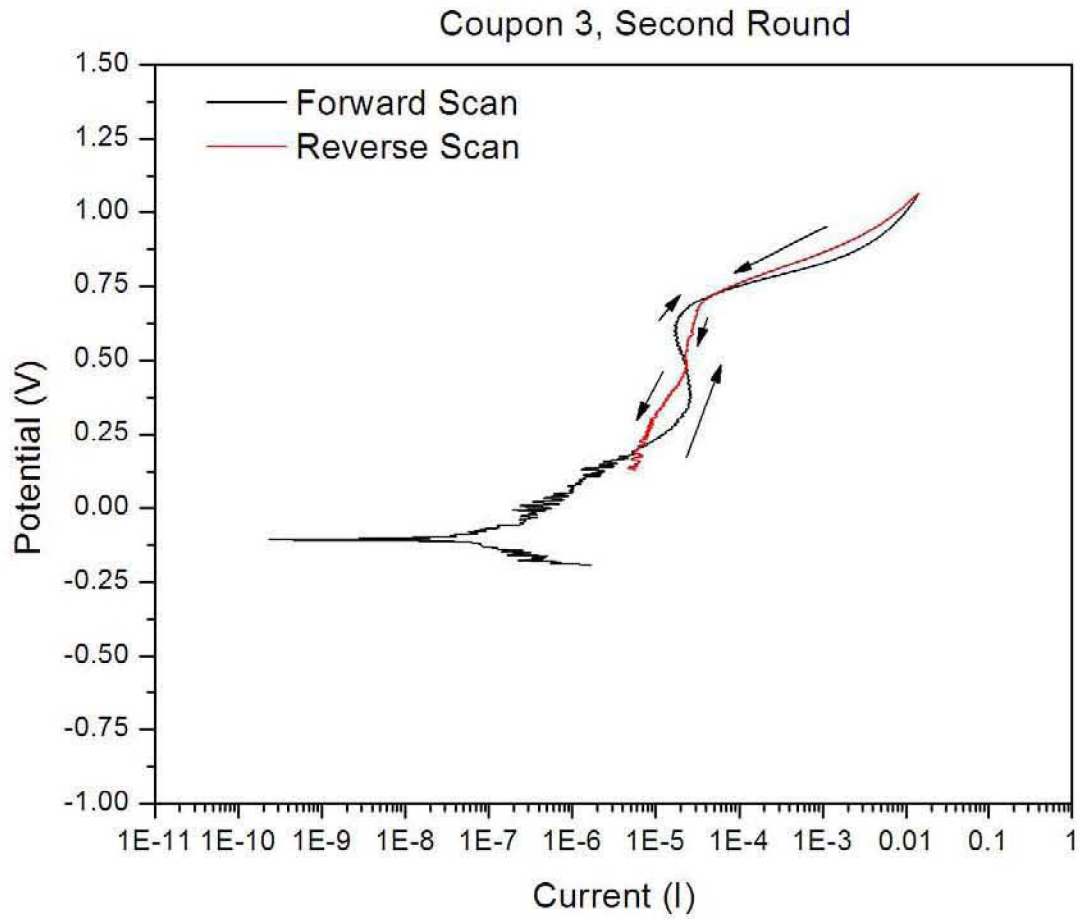


Appendix B

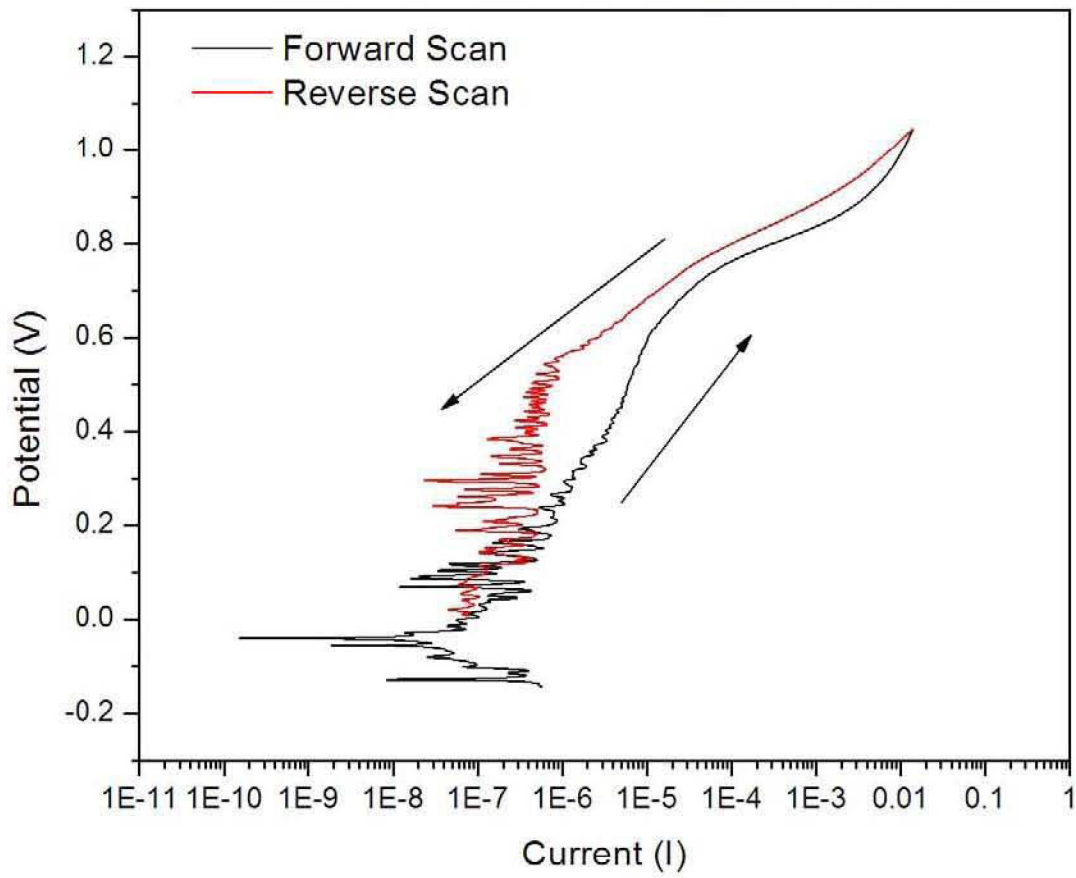
Cyclic Potentiodynamic Polarization Scans, Second Round





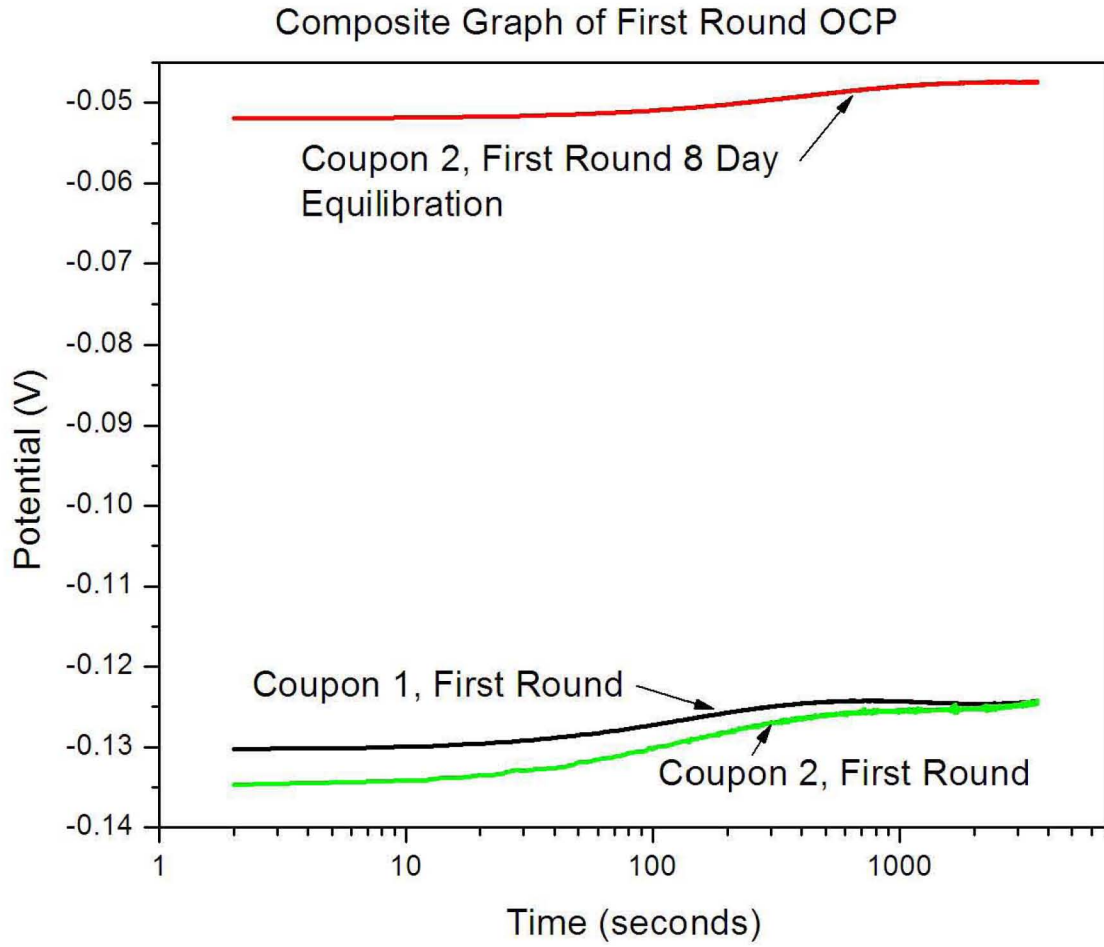


Coupon 4, Second Round Equilibrated 7 Days



Appendix C

Composite Open Circuit Traces, First Round



Appendix D

Composite Open Circuit Traces, Second Round

