TiO$_2$ Coatings Formed by Atomic Layer Deposition for Enhanced Corrosion Performance of Mg-biomaterials

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1. Introduction

Magnesium (Mg) alloys have experienced increased attention in the area of biomaterials due to Mg being considered a resorbable biomaterial. Mg alloy implants can potentially be designed to degrade in the body, thus an implant would not remain in the body for longer than is needed to perform its task. Mg and many of its alloys, are considered to be biocompatible and non-toxic in the body; however, due to the high rate at which Mg degrades a negative host response is expected. A novel approach to inhibit corrosion rate using thin film coatings on a Mg alloy (AZ31B) via atomic layer deposition (ALD) is proposed. TiO$_2$ is grown in an atomic layer-by-layer fashion during ALD allowing sub-nanometer thickness control of growth, with excellent coating uniformity and step coverage. TiO$_2$ coatings and their impact on the corrosion resistance of AZ31B were characterized using atomic force microscopy, scanning electron microscopy, electrochemical impedance spectroscopy, and linear polarization measurements.

2. Atomic Layer Deposition on AZ31B

Sample Prep –
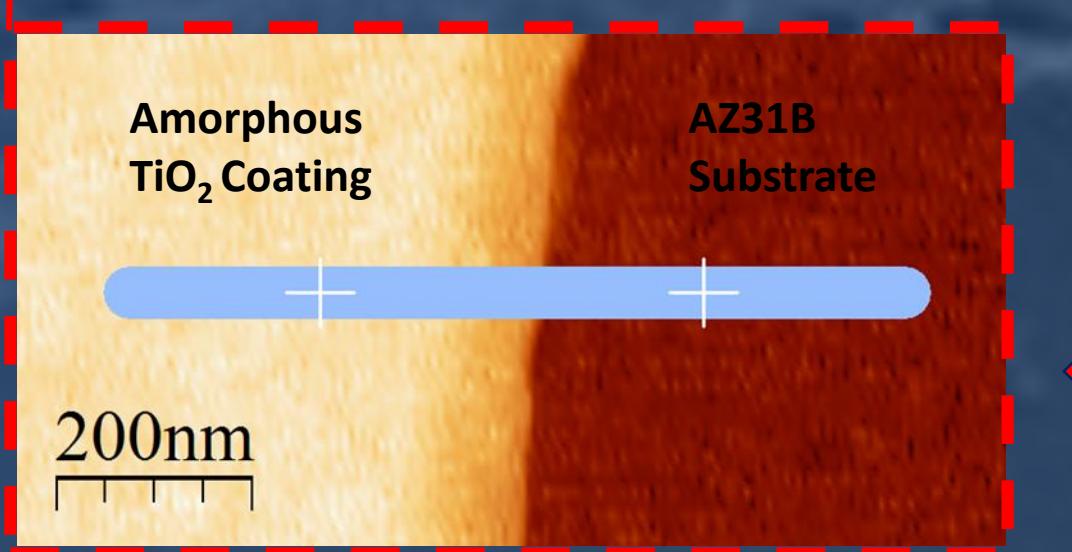AZ31B Sample size ~20 x 20 mm. Prior to ALD process all samples surface's where prepared as follows:

- 600 grit SiC paper
- 800 grit SiC paper
- 1200 grit SiC paper
- 3 µm Alumina Slurry
- 1 µm Alumina Slurry
- 0.05 µm Alumina Slurry
- Photoresist on corner

ALD –
Following sample prep, GemStar™ Benchtop ALD was used to apply TiO$_2$ to AZ31B substrate.
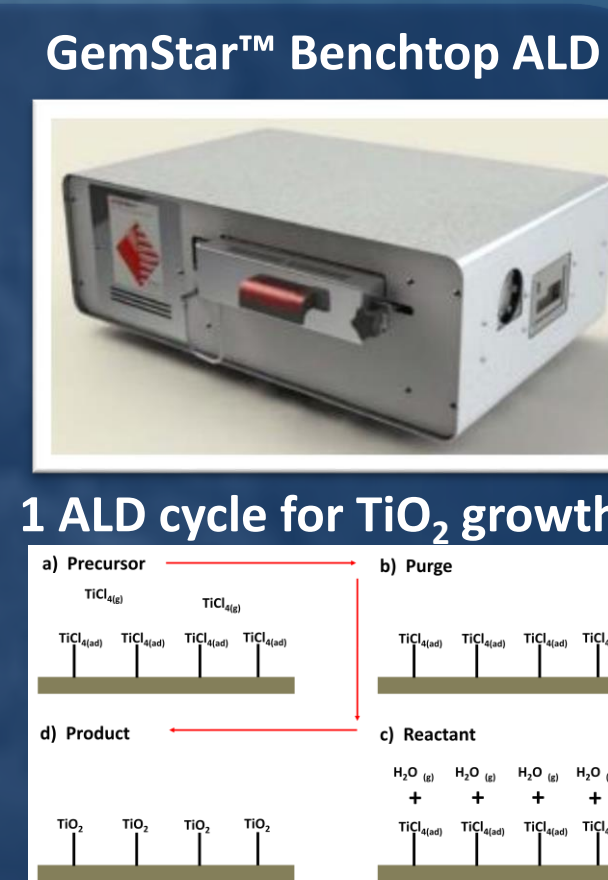
Run Parameters:
- TiCl$_4$ - Ar Purge - H$_2$O - Ar Purge (1 cycle)
- 100 °C maintained during ALD process
- Estimated 0.052 nm / cycle

GemStar™ Benchtop ALD

1 ALD cycle for TiO$_2$ growth

Verification of Coating Thickness –
AFM image of area between photoresist and growth of Amorphous TiO$_2$ layer.

Amorphous TiO$_2$ Coating / AZ31B Substrate
200nm

AFM height image and profile across the edge of a 100 nm thick TiO$_2$ coating. The height profile confirms the coating thickness.

Atomic Force Microscopy (AFM) –
AFM was used to confirm coating thickness on samples.

A probe with tip radius of ~5-10nm connected to a cantilever is brought within nanometers of the samples surface. Tip-surface interactions exert a force on the tip that can be detected via laser beam and photodetector.
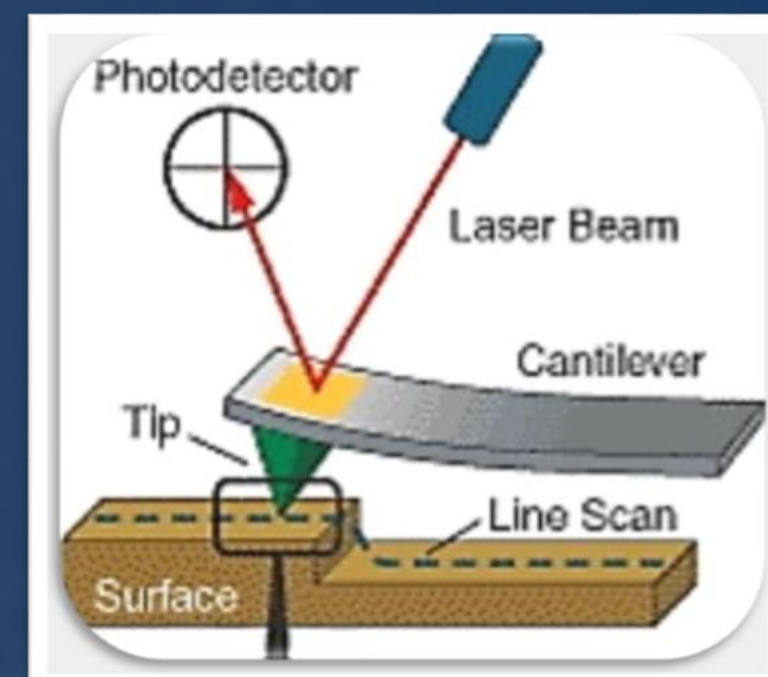
Information about the samples surfaced topography is gained as the tip is rastered across the sample.

Atomic Force Microscopy - What is it? By Keysight Technologies http://www.keysight.com/main/editorial.jspx?ckey=1774141&id=1774141&nid=-33986.0&lc=spa&cc=vE

3. Potentiostat

Potentiostat –
A three electrode system with solution can be modeled as a circuit. Each component in a electrochemical cell can be modeled with circuit elements. This is the basis of collecting and analyzing data with the Potentiostat which applies either AC or DC current to the electrochemical cell.
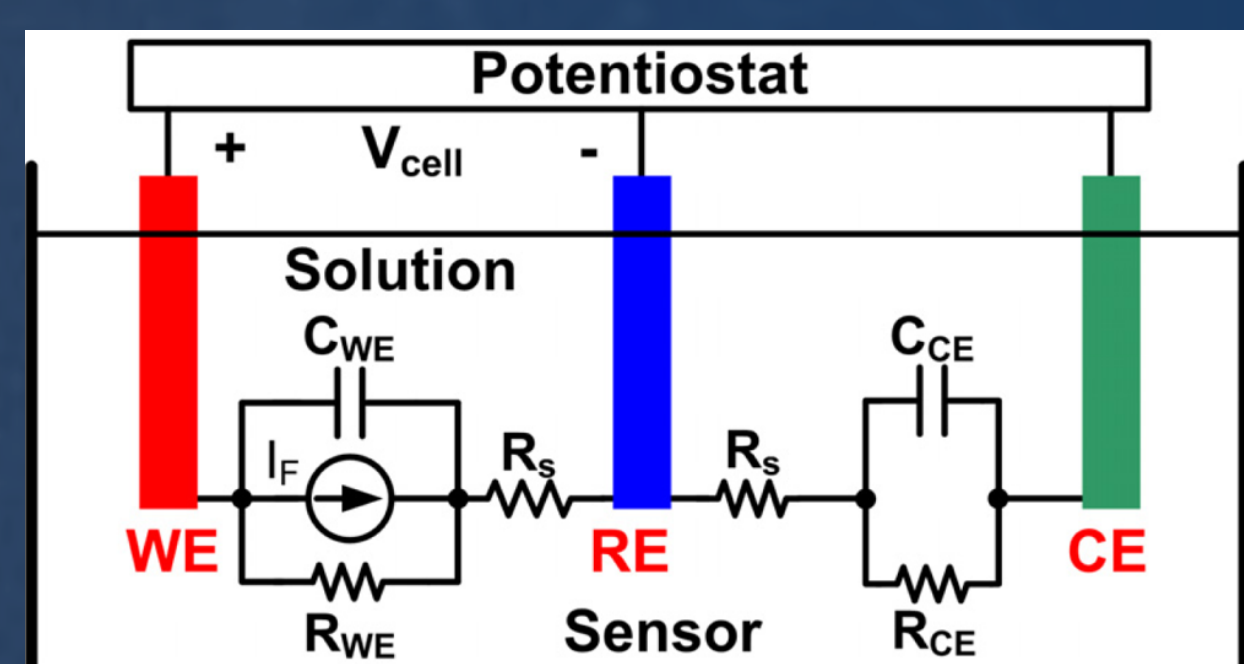
Real-Time Telemetry System for Amperometric and Potentiometric Electrochemical Sensors (Wei-Song Wang) http://www.mdpi.com/1424-8220/11/9/8593/htm

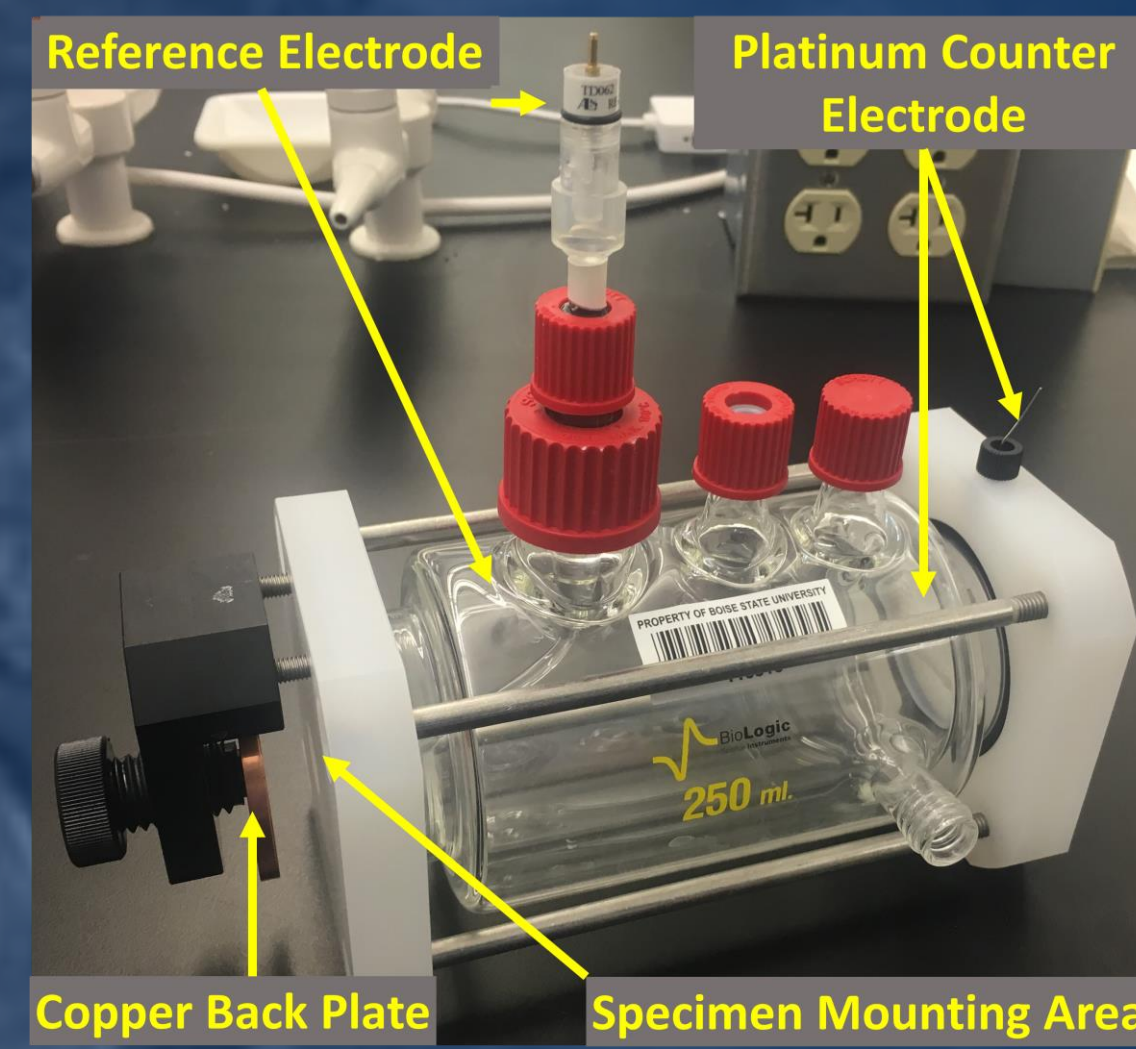## 4. Electrochemical Cell

Working Electrode –
Electrode where the potential is controlled and where the current is measured. In corrosion testing, the working electrode is a sample of the corroding metal.

Reference Electrode –
Electrode whose potential is constant, therefore can be taken as standard against which the potentials of other electrodes can be measured. Saturated Calomel Electrode (SCE) is based on the reaction between elemental mercury and mercury chloride (Hg$_2$Cl$_2$) . The aqueous phase in contact with Hg$_2$Cl$_2$ is a saturated solution of potassium chloride in water.
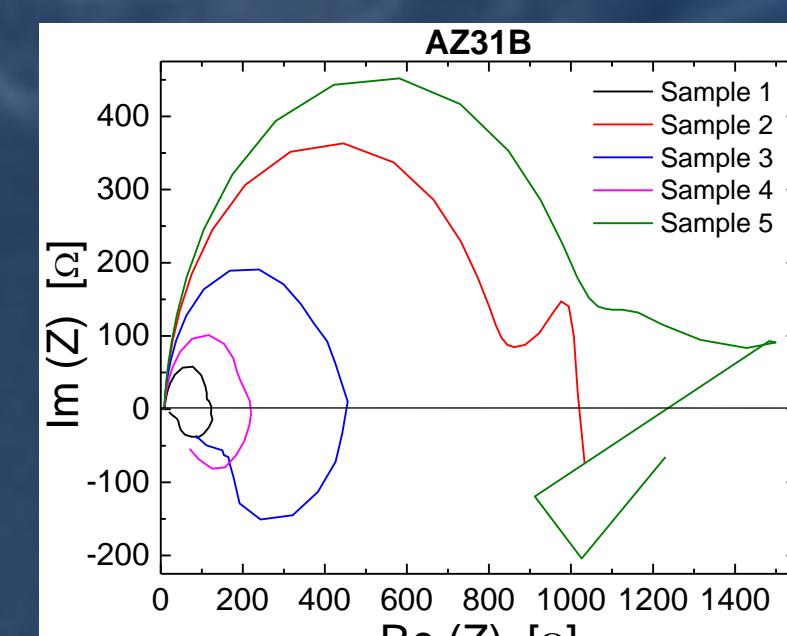
Counter Electrode –
The main function of the counter electrode is to provide the location of the second electron transfer reaction. A platinum mesh counter electrode was used the electrochemical cell.

Reference Electrode / Platinum Counter Electrode
Copper Back Plate / Specimen Mounting Area

5. Electrochemical Impedance Spectroscopy and Anodic Polarization

Electrochemical Impedance Spectroscopy (EIS) –
EIS measures the impedance of a complex system using AC current over a range of frequencies. A Nyquist plot is a typical way to represent data collected during EIS testing. Ohm's Law (V=IR) is used to derive the model for the Nyquist plot.

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

Where:
ω = angular frequency
$V(t) = V_0 \sin(\omega t)$
$I(t) = I_0 \sin(\omega t + \theta)$
θ = phase angle between $V(t)$ and $I(t)$

$$Z(\omega) = Z'(\omega) + Z''(\omega)$$

Where: Z''= real component Z''= imaginary component

Using EC-lab software with the Potentiostat, EIS data can be modeled with an equivalent circuit for the electrochemical cell.
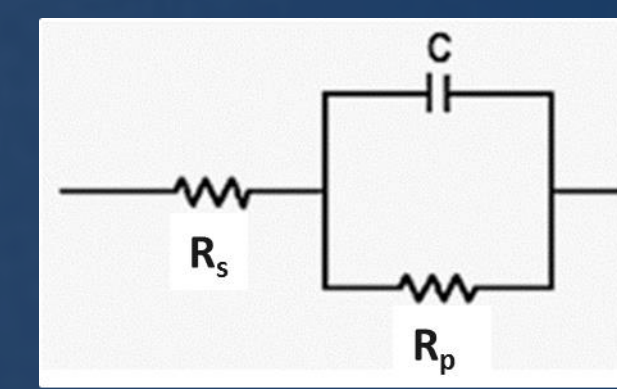
With equivalent circuit, fitting functions within software calculates values for polarization resistance (R$_p$) and solution resistance (R$_s$) .
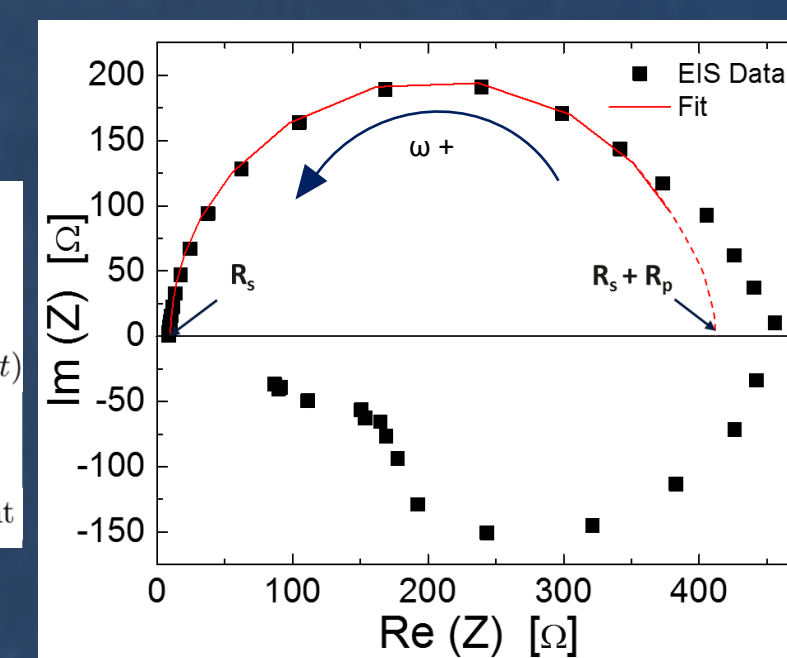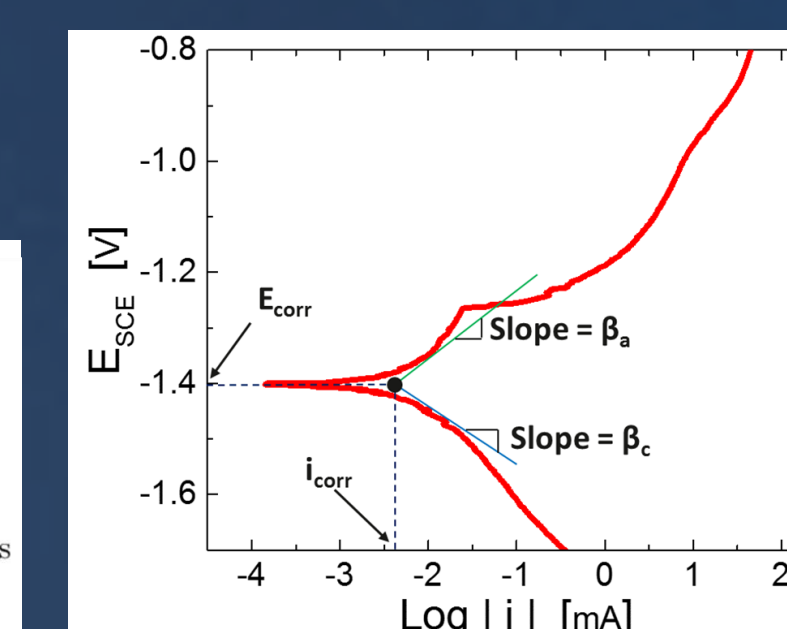
Anodic Polarization (AP) –
A change of the working electrode's potential is caused by current (DC) flowing across an electrode-to-electrolyte interface. A Tafel Plot, in which potential is plotted vs applied current, is used to extrapolate Tafel constants. From Tafel constants (β$_{a,c}$) corrosion potential (E$_{corr}$) and corrosion rate (i$_{corr}$) are obtained by the following model.

$$\beta_a = \frac{\eta_a}{\log\left(\frac{i_a}{i_0}\right)}$$

$$\beta_c = \frac{\eta_c}{\log\left(\frac{i_c}{i_0}\right)}$$

Where:
β$_{a,c}$ = Anodic and cathodic tafel constants
η$_{a,c}$ = Overpotential in Anodic and Cathodic regions
i$_{a,c}$ = Anodic and Cathodic current densities
i$_0$ = equilibrium current density
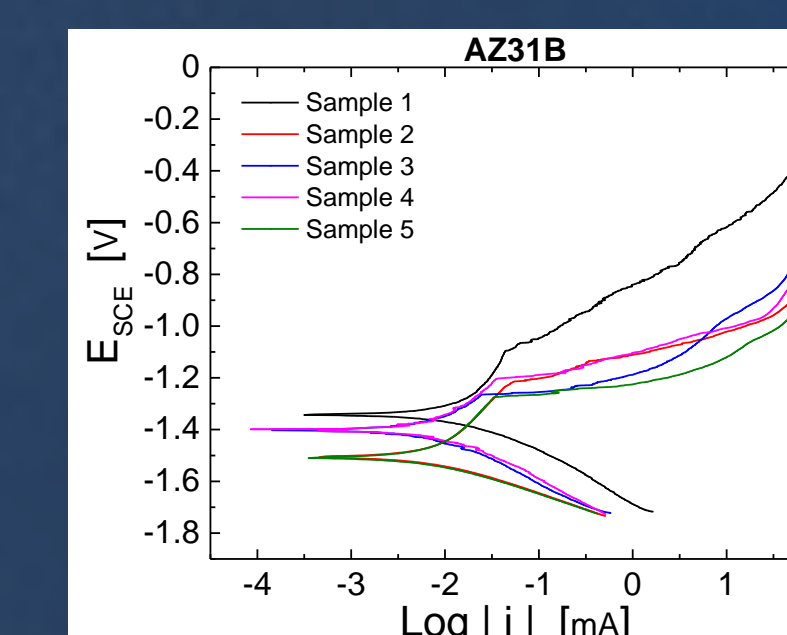
Using EC-lab software with the Potentiostat, a linear regression is used to fit tangent lines to anodic and cathodic Tafel regions. The slope of these tangent lines are the Tafel constants.

At the intersection of these tangent lines, values for E$_{corr}$ and i$_{corr}$ can be obtained.

Slope = β$_a$
Slope = β$_c$

6. Analysis of Data

EIS Data –
EIS testing was conducted with the following parameters:
- Starting frequency (f$_i$) 1MHz
- Ending frequency (f$_f$) 10mHz
- 51 points sampled from f$_i$ to f$_f$
- Amplitude of 10mV

Data from EIS testing was fitted and polarization resistance (R$_p$) was calculated for each sample. From the following model it can be shown that $\frac{1}{R_p} \propto i_{corr}$.

$$i_{corr} = \frac{\beta_a\beta_c}{2.3(R_p)(\beta_a + \beta_c)}$$
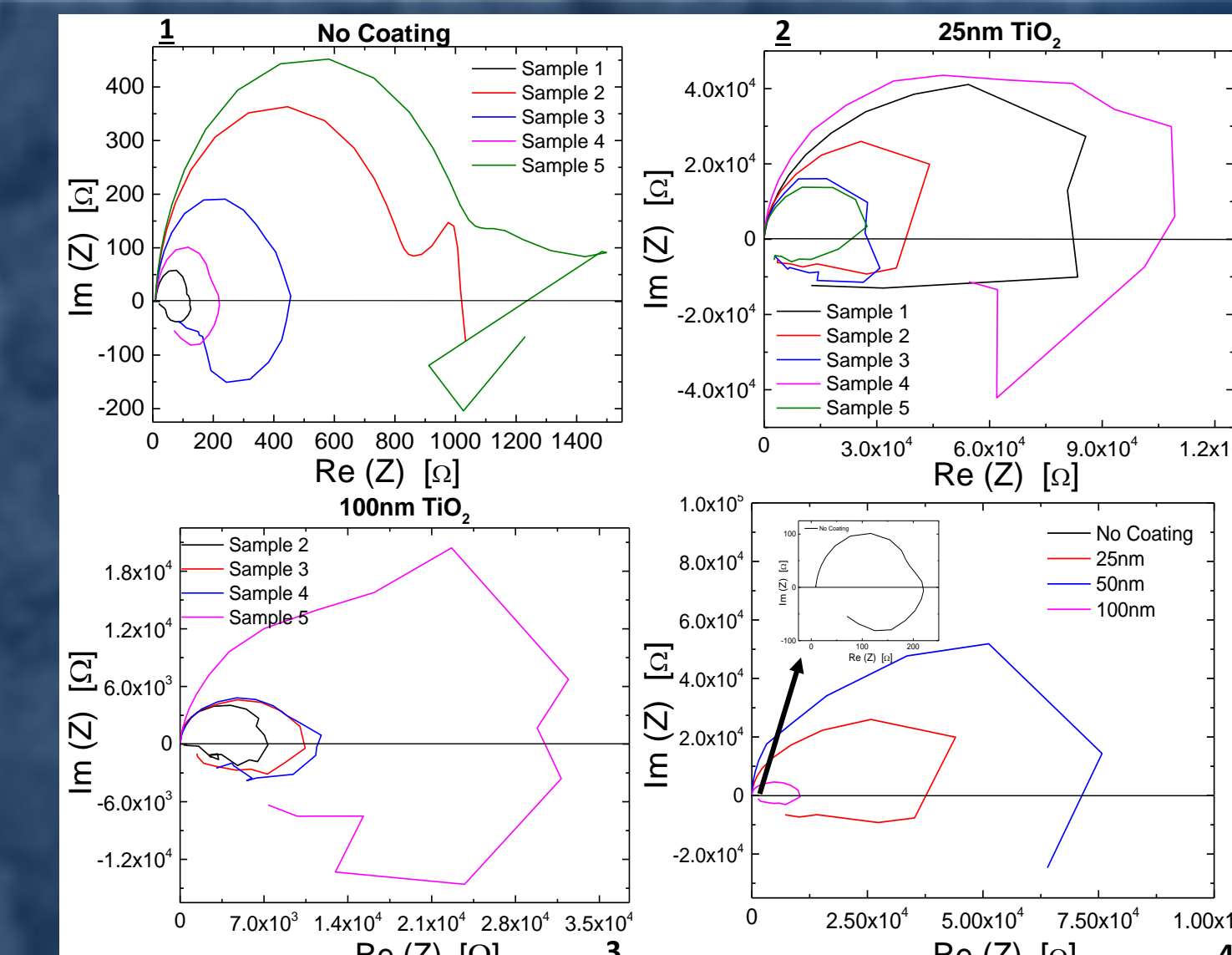
Nyquist plots for No Coating (1), 25nm (2), 100nm (3) and a comparison plot using data sets closest to calculated average values (4).

From comparison plot (4), it can be seen that with the application of a thin film TiO$_2$ coating the R$_p$ value increases by several orders of magnitude. Thus lowering the corrosion rate i$_{corr}$.
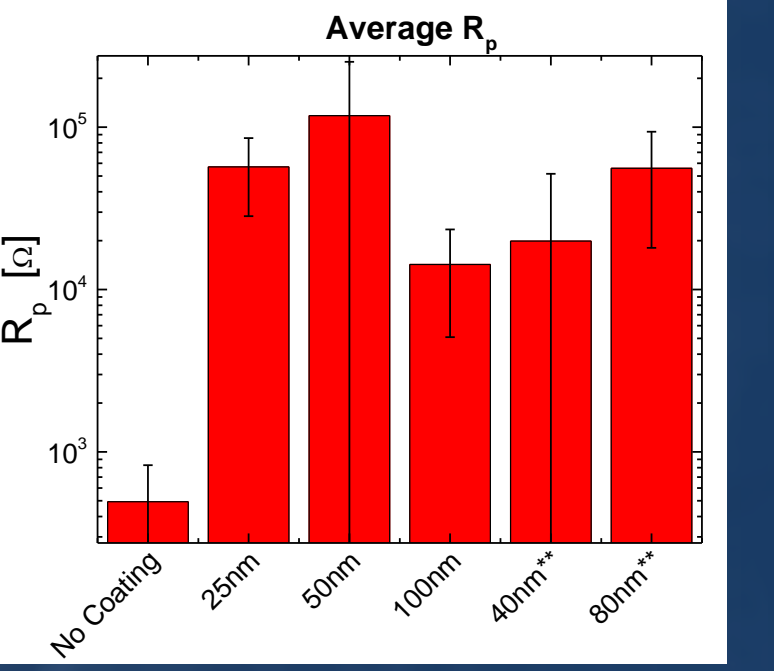
Average R$_p$ values for all samples coated. (** indicate samples in which the coating was confirmed to be non-uniform.)

AP Data –
AP testing was conducted with the following parameters:
- Energy range -2.5V – 2.5V
- Starting energy range (E$_i$) -0.15mV from open circuit potential (E$_{OC}$)
- Ending energy range (E$_f$) -0.15mV from open circuit potential (E$_{OC}$)
- Data recorded every 0.1 seconds

AP testing gives another method to calculate i$_{corr}$ by extrapolating Tafel constants β$_{a,c}$.
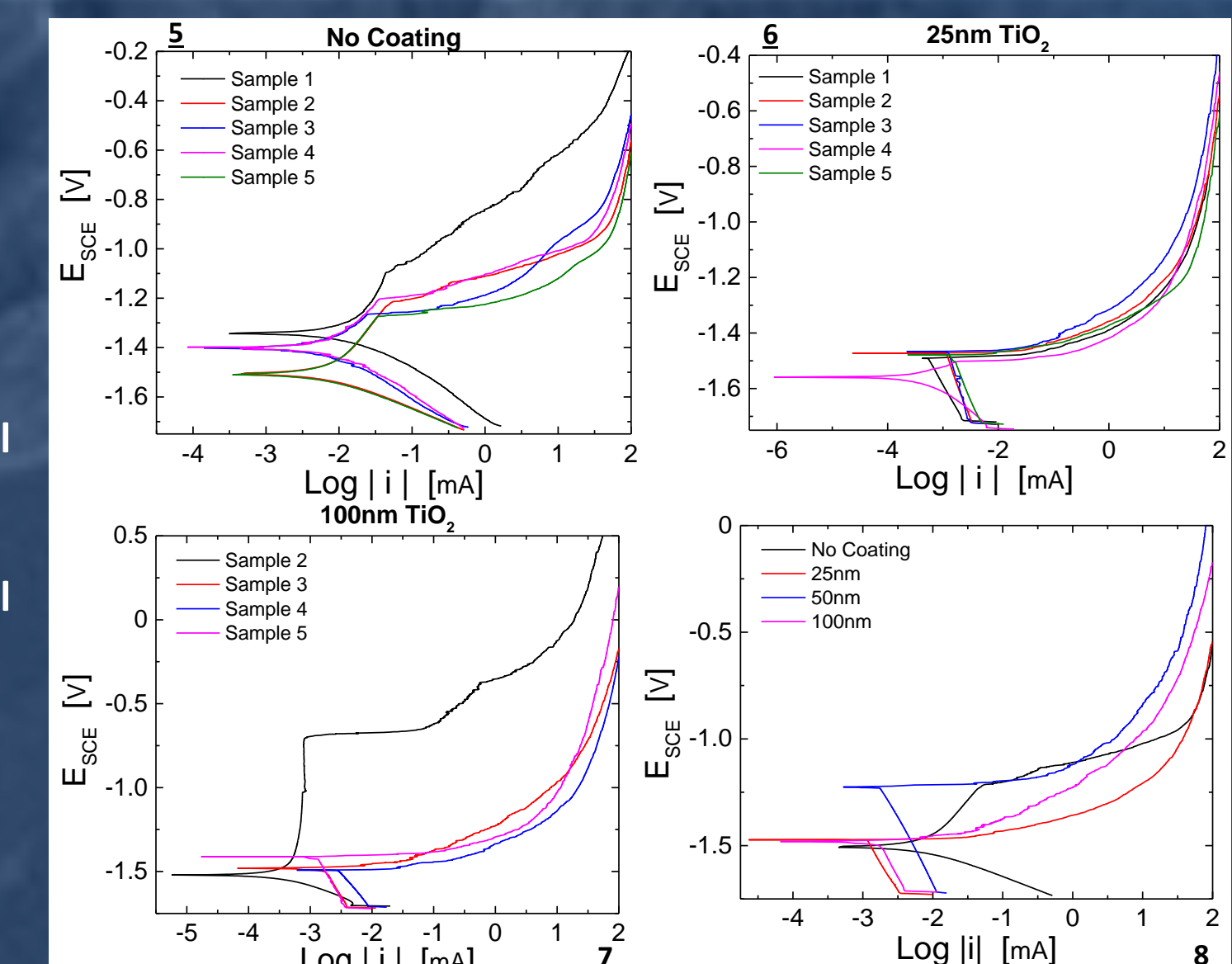
Tafel plots for No Coating (5), 25nm (6), 100nm (7) and a comparison plot using data sets closest to calculated average values (8).

Data suggests atypical Tafel behavior for samples with coatings applied (linearity of plotted data near E$_{corr}$), giving inconsistent values for β$_{a,c}$ and therefor i$_{corr}$.
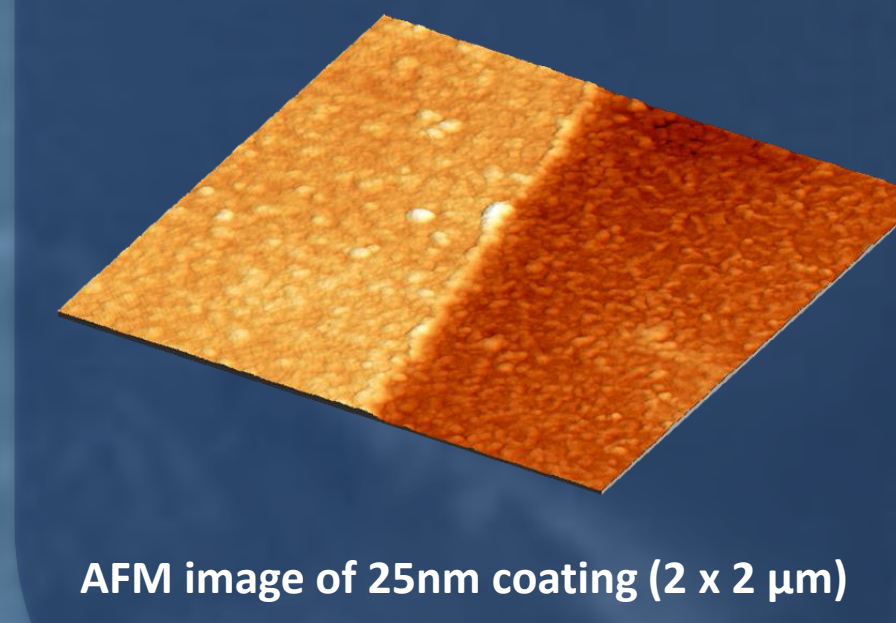
Average i$_{corr}$ (Tafel)
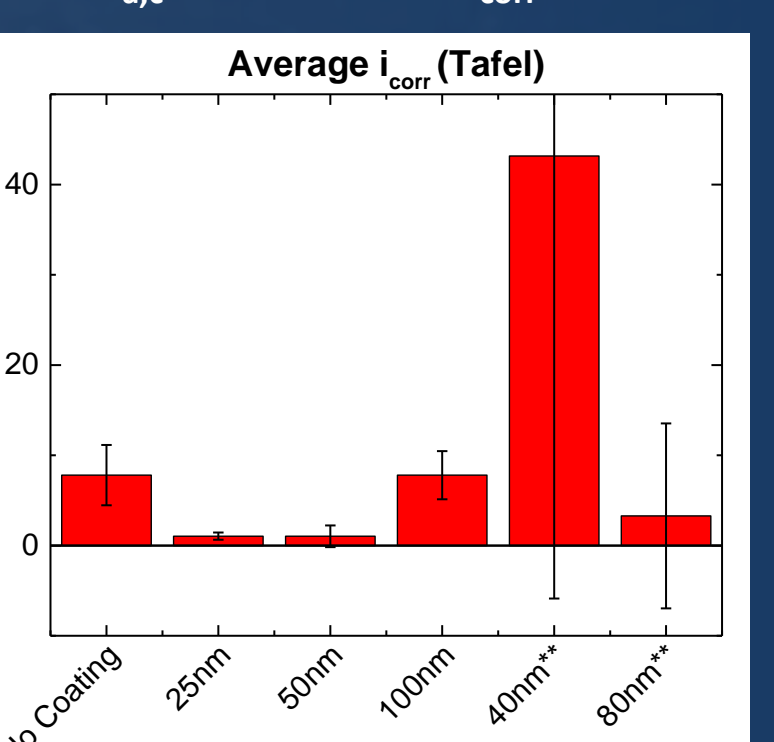
(** indicate samples in which the coating was confirmed to be non-uniform.)
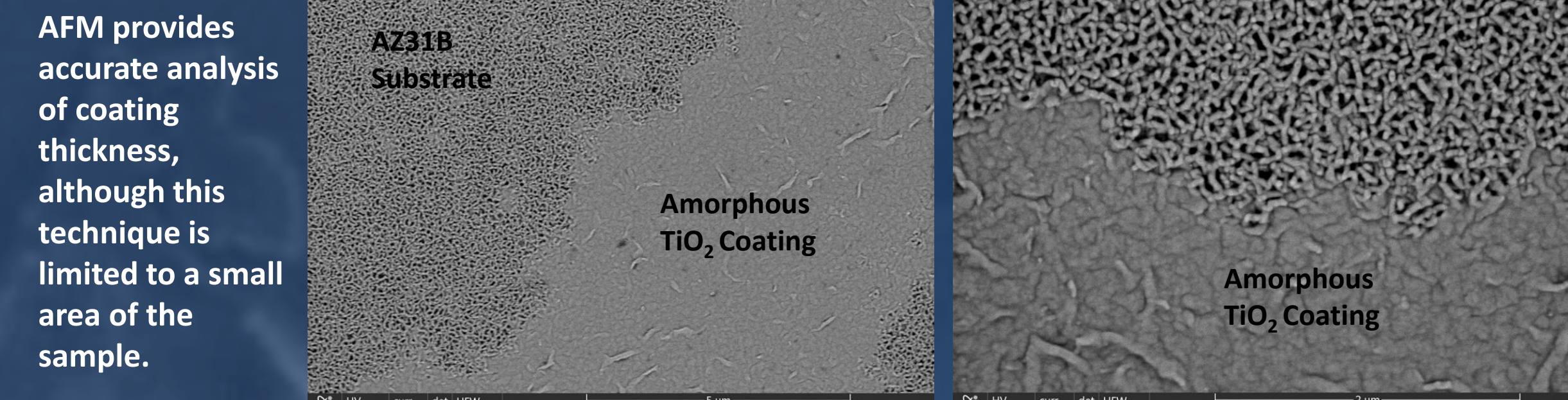
Microscopy of Tested Samples
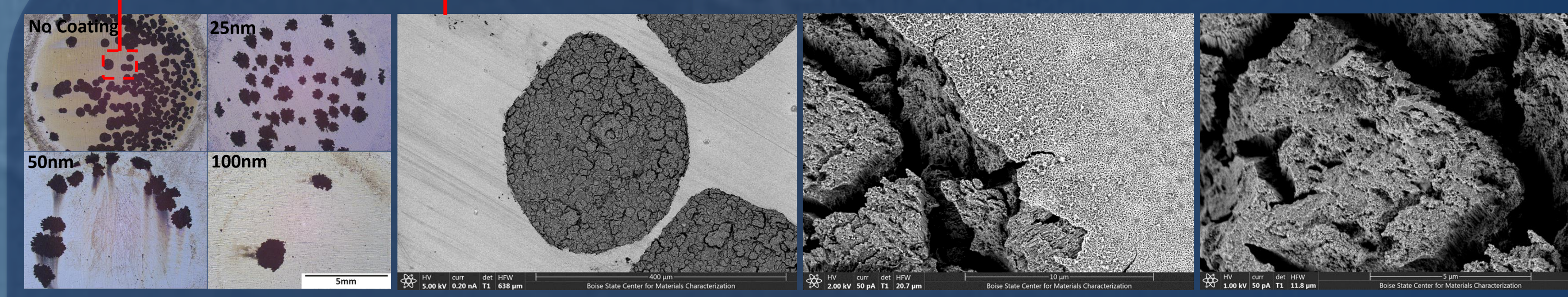
No Coating / 25nm / 50nm / 100nm
Optical Microscopy of corroded samples.

High resolution SEM images of corroded area.

AFM image of 25nm coating (2 x 2 µm)

AFM provides accurate analysis of coating thickness, although this technique is limited to a small area of the sample.

AZ31B Substrate / Amorphous TiO$_2$ Coating

Back Scatter SEM images showing non-uniform coatings on 40nm** sample (post corrosion outside of corroded area).

7. Future Work

Further research will be conducted with different precursor molecules during the ALD process and analysis of any contaminates that may be left on the samples. Modification of electrochemical testing procedure including, monitoring hydrogen evolution, using different solutions (synthetic physiological buffers), as well as conducting electrochemical testing at elevated temperatures.

8. Acknowledgments