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Modeling Galvanic Corrosion in Cadmium and Zinc-Nickel Plating Systems using Mixed Potential Theory

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Outline

- Introduction
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  - Problem Statement
- Technical Approach & Modeling Methods
- Case Study: Zn-Ni Electroplating
  - Motivation for Research
  - Model Assumptions
- Results
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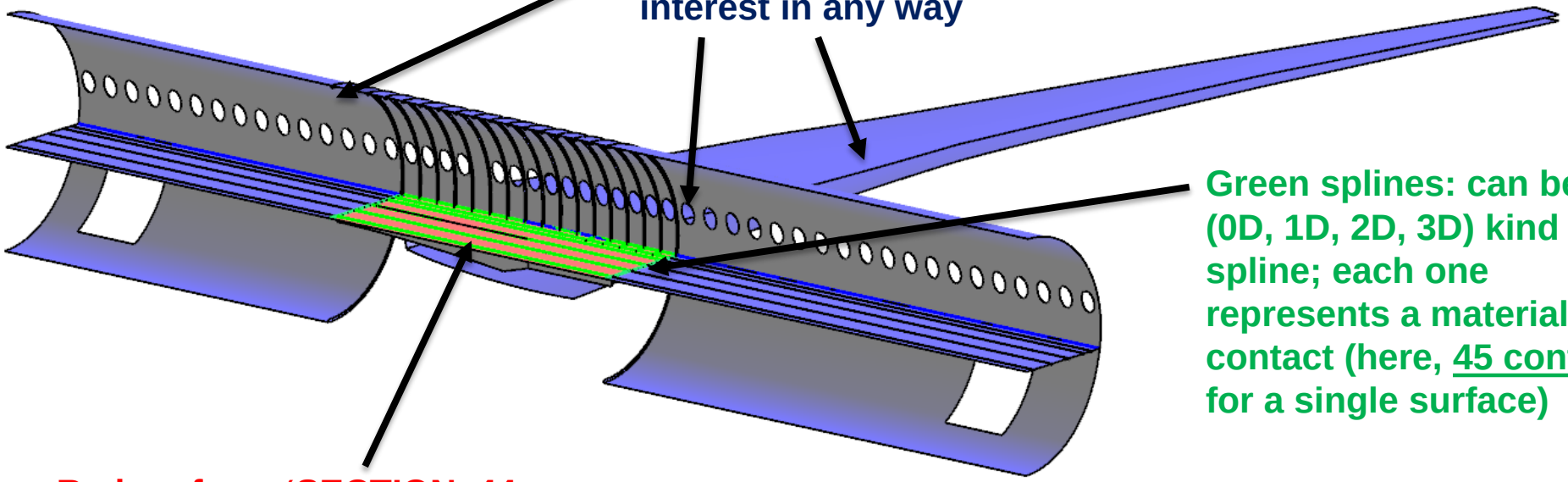
  - Steel Coupled to Plating: Cd and Zn-Ni
  - Atmospheric Corrosion Test Results
- Conclusions
- Future Work / Needs
- Acknowledgments

Introduction
Galvanic Corrosion Risks in Aircraft

Example: Identifying material contacts for a single surface (Section 44 passenger floor)



Blue surfaces: all surfaces of differing material contacting the surface of interest in any way

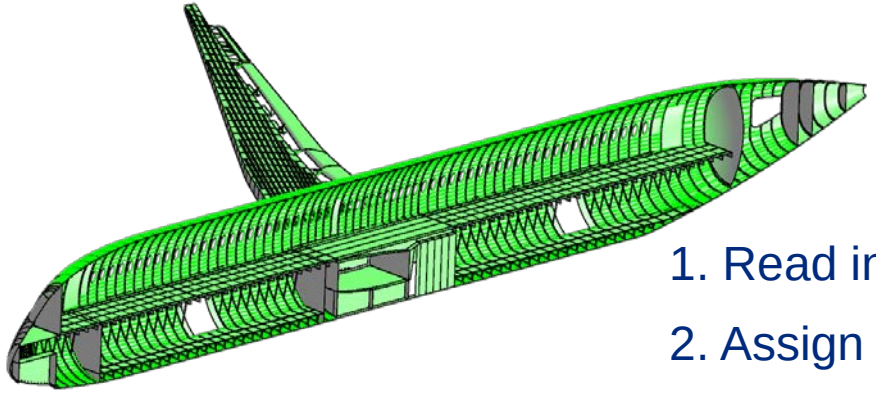
Green splines: can be any (0D, 1D, 2D, 3D) kind of spline; each one represents a material contact (here, 45 contacts for a single surface)

Red surface: 'SECTION_44--passenger_floor' (surface of interest)

Note: Aircraft model is notional and does not correspond to a formal engineering drawing.

Galvanic Corrosion Risk – *Greater than the sum of the parts*

Example: Notional geometric model of commercial aircraft. Random assignment of materials.



1. Read in aircraft geometry
2. Assign materials to geometry
3. Build material contact list
4. Build corrosion lookup table
5. Calculate corrosion rates on material contacts
6. Aggregate surface risks
7. Create visualization plots

```
*******************************************************************************
RACE B787-900 EXAMPLE CORROSION DEMONSTRATION CODE: CONCEPT #1
    Joel Thompson
    Applied Mathematician
    richard.j.thompson3@boeing.com
    256-464-7681
*******************************************************************************
Reading RACE B787-900 aircraft geometry...
    ...found 3076 aircraft parts
Randomizing material assignments to the 787 aircraft manifest...
Building 787 connectivity mapping...
    ...building bounding box information around aircraft parts...
    ...built 3076 bounding boxes
Building 787 material contact list...
    ...built 73380 material contacts.
Building corrosion property lookup table...
    ...built 2209 table elements
Calculating corrosion properties...
    ...pinging 73380 requests to the corrosion tool...
    (took 319.00ms to calculate corrosion properties...)
Calculating aggregate corrosion risks on aircraft parts...
    (took 2.50m to aggregate corrosion risks...)
Rendering aggregate risk color plot...
total program execution time: 6.15m
```

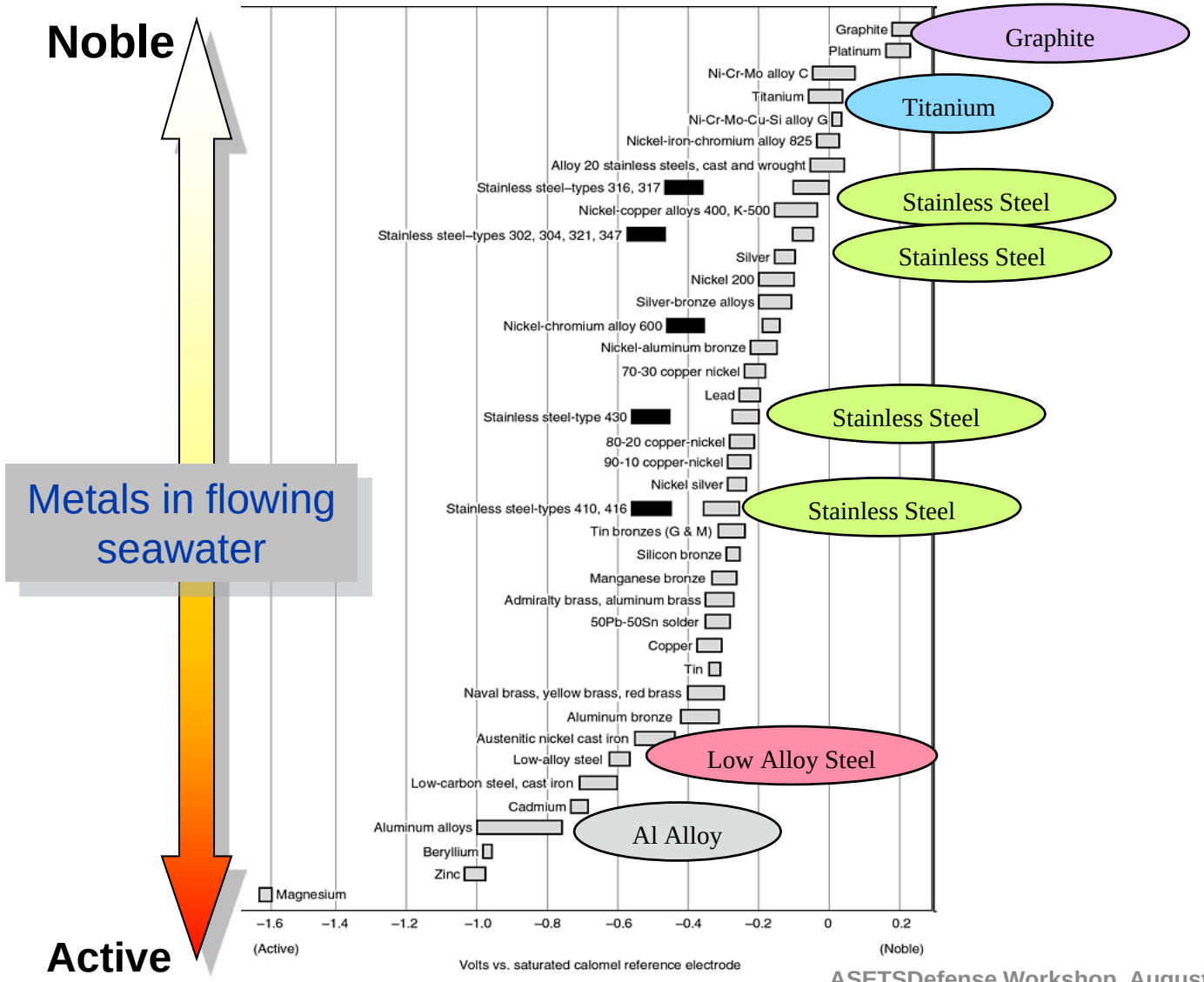
3076 parts

73380 material contacts!

Note: Aircraft model is notional and does not correspond to a formal engineering drawing.

Thompson, R.J., et al. U.S. Patent Application No. 15,213,116 (2016)

Problem Statement – *Insufficient Design Tool*



What's the corrosion rate?

Where's Zn-Ni?

This isn't an atmospheric environment.

Which is the cathode?

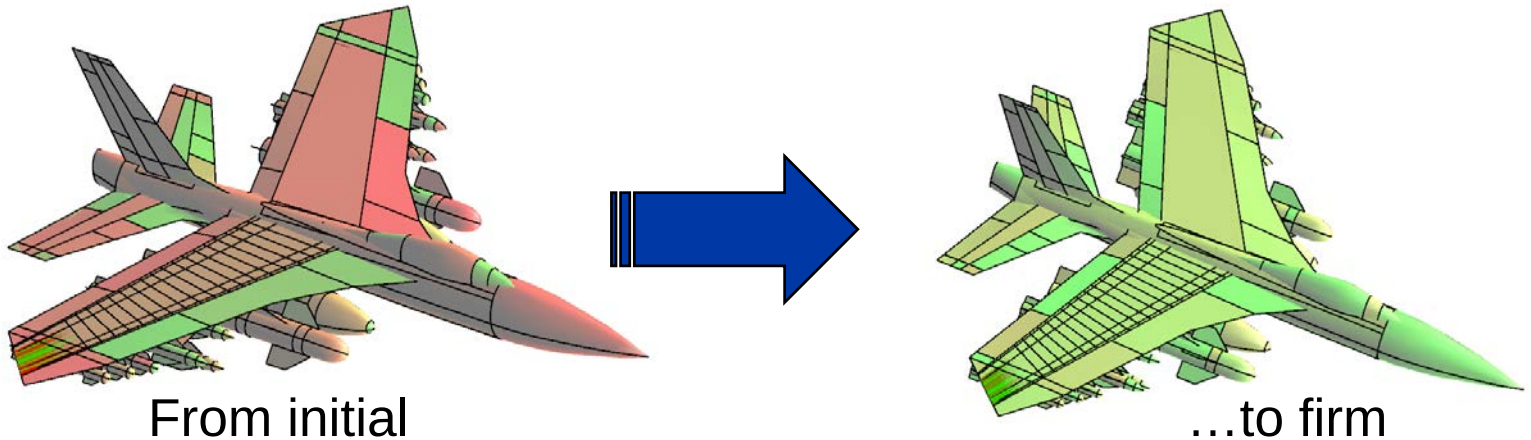
Is there a difference between 2024 and 7075?

Does temper affect position?

Corrosion severity and susceptibility not quantified by the traditional galvanic series (MIL-STD-889).

Technical Objective

- Use modeling to generate *quantitative information* about relative risks of galvanic corrosion.
  - Kinetic understanding – corrosion rate vs. potential.
  - Mechanistic understanding – informed material selection.
  - Improve materials selection on new designs.
  - Determine corrosion inspection or reliability frequencies.
  - Predict corrosion performance and costs during retrofit.



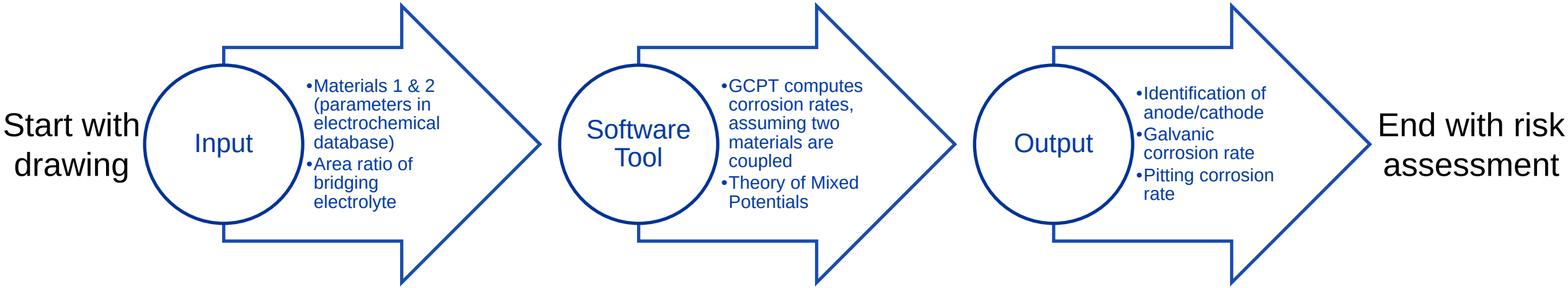
From initial design…

…to firm configuration.

Note: Aircraft model is notional and does not correspond to a formal engineering drawing.

Technical Approach

- Use Galvanic Corrosion Predictor Tool (GCPT) that quantitatively predicts galvanic corrosion rates between dissimilar materials.
- Develop software tool that aides corrosion risk assessments.



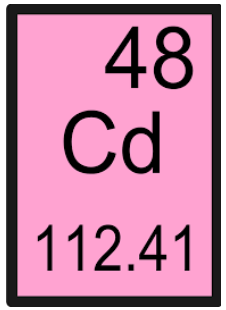
Case Study
Galvanic Corrosion of Electroplated Steel

- Modeling to evaluate Zn-Ni plating as a sacrificial coating for 4130.
- GCPT and polarization database used to calculate corrosion rates for both steel substrate (cathode) and plating (anode).
- Calculations repeated for Cd plating to compare the performance of Zn-Ni versus Cd.

- But… why?

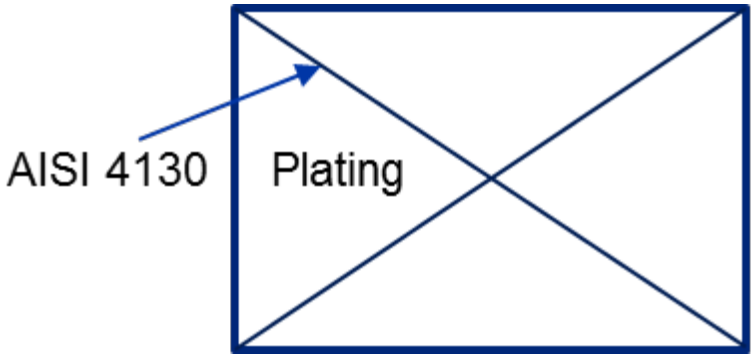
EHS
Regulations
Sustainability
Supply Chain

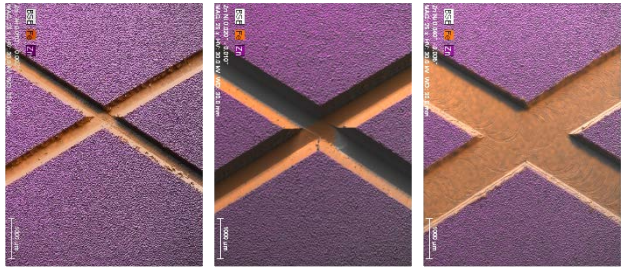
Aerospace
Requirements



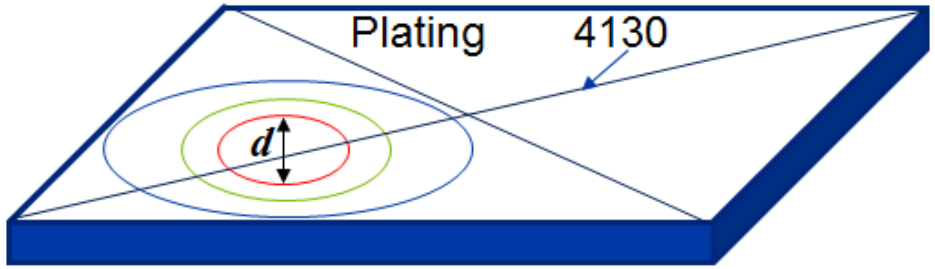
OSHA®

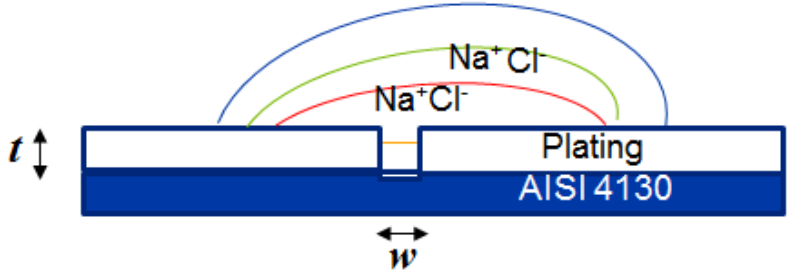
Model Geometry & Assumptions



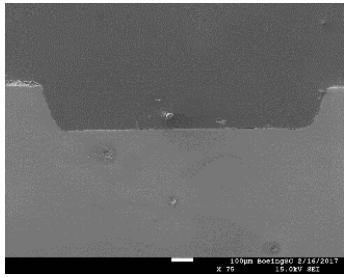


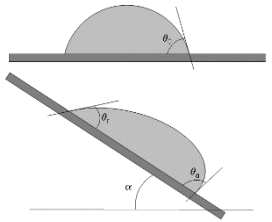
254 µm 508 µm 1016 µm

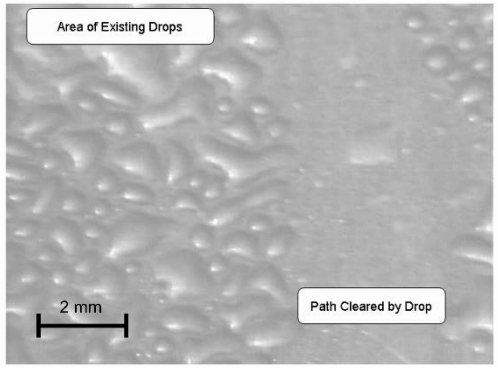




- 4” x 6” (10.16 cm x 15.24 cm) test panel with x-scribe.
- X-scribes have varying widths.
- X-scribe penetrates through coating, into 4130 substrate.
- Atmospheric conditions cause variations in electrolyte film thickness & droplet diameter.
- Substrate/plating interface galvanically coupled through thin film 3.5% NaCl solution.
- Corrosion rate of plating depends on anode:cathode ratio.







Chen, F.F., et al. Prog Org Coatings (2017), vol. 111

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Model Parameters

Parameters that impact anode:cathode ratio:

- Plating thickness
- Electrolyte film thickness & droplet diameter
  - Diameters assumed to be 0.10-2.5 mm
- Scribe width
- Scribe depth into the substrate

Parameter	Unit	Model Values
Plating thickness, t	µm	12.7, 15.24, 17.78, 20.32
Electrolyte film thickness; represented by droplet diameter, d	mm	0.1016, 1.016, 2.54
Scribe width, w	µm	508, 1524
Scribe depth into the substrate, D	µm	254

Cathode Area

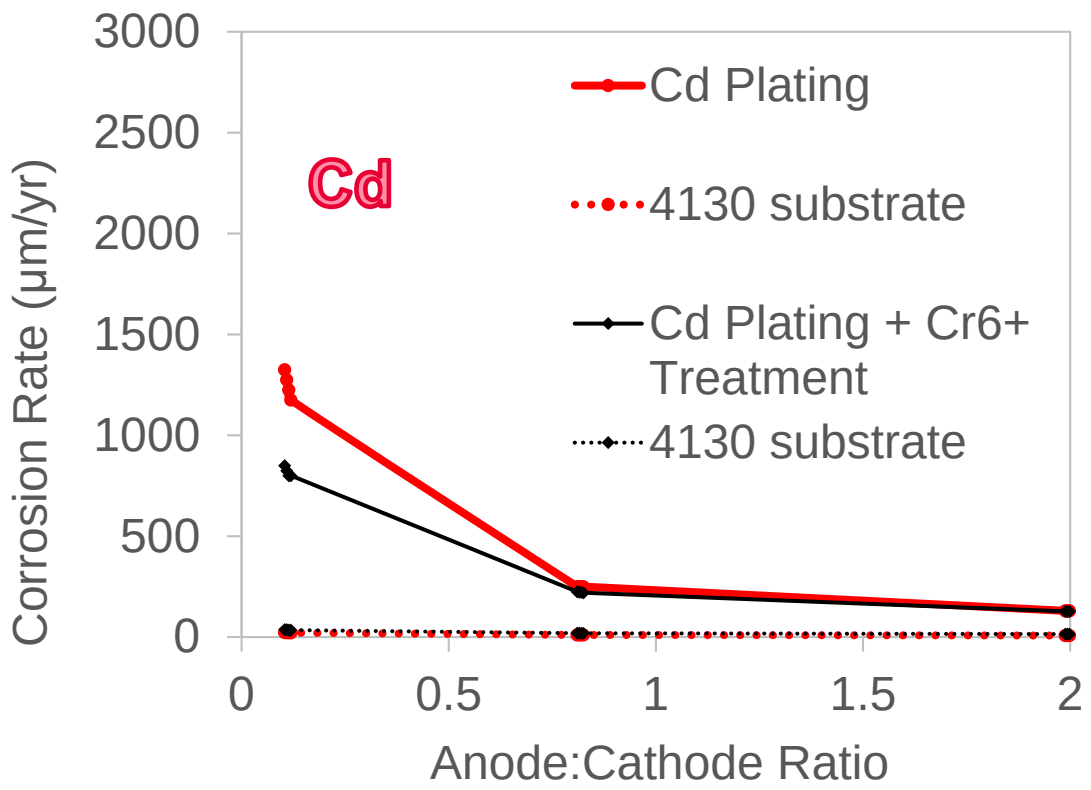
- $A_C = dw + 2dD$

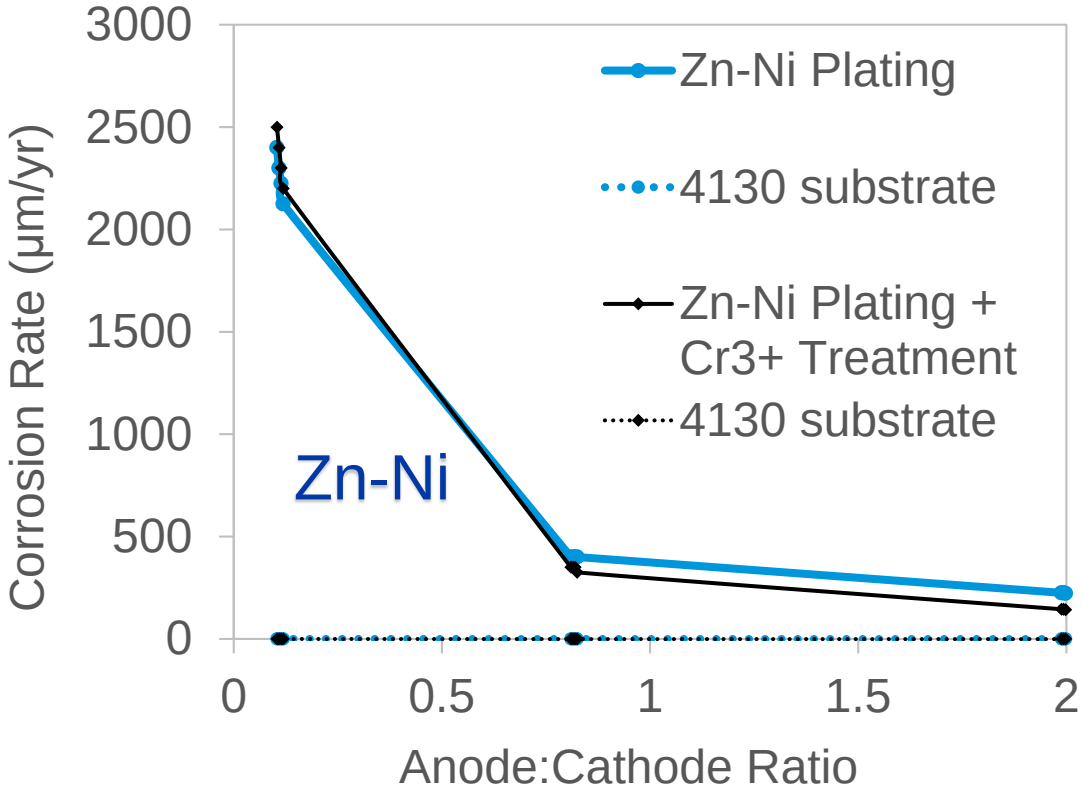
Anode Area

- $A_A = \pi(d/2)^2 + 2dt$

$$A_A/A_C = [\pi(d/2)^2 + 2dt]/[dw + 2dD]$$

Results – *Cd vs. Zn-Ni Plating*



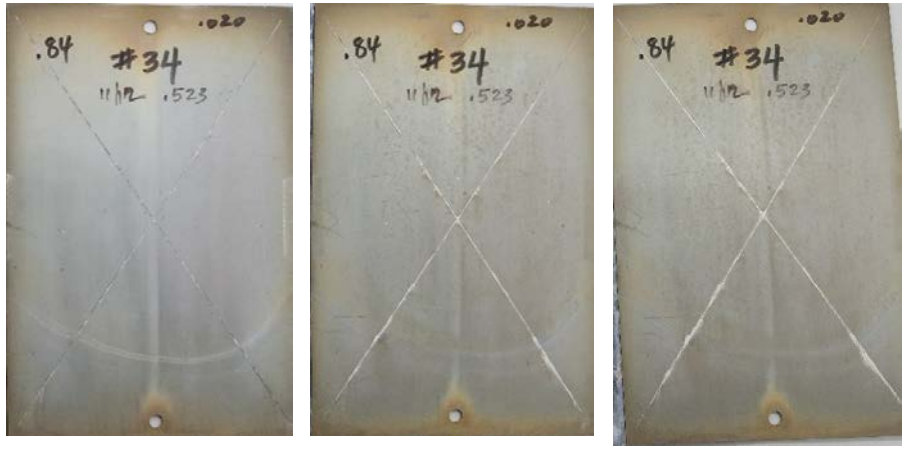


- Sight decrease in steel corrosion rate when 4130 is coupled with Zn-Ni versus Cd.
- Predicted *increase in corrosion rate* of Zn-Ni plating for wide scribes.
- Zn-Ni plated layer will deplete more rapidly than Cd for anode:cathode ratios <1.
- Faster depletion of plating will cause increased rust formation at longer testing times.

Results
Atmospheric Corrosion Testing

Cd — 508 µm

96 hours | 336 hours | 500 hours

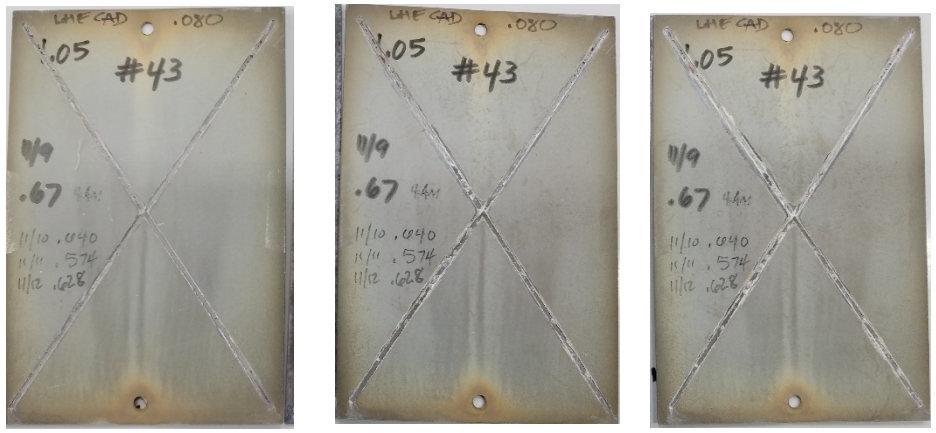


Zn-Ni — 508 µm

No Image

Cd — 2032 µm

96 hours | 336 hours | 500 hours



Zn-Ni — 2032 µm

Results

Appearance after 500 hours of salt spray exposure

508 µm

1524 µm

1016 µm

2032 µm

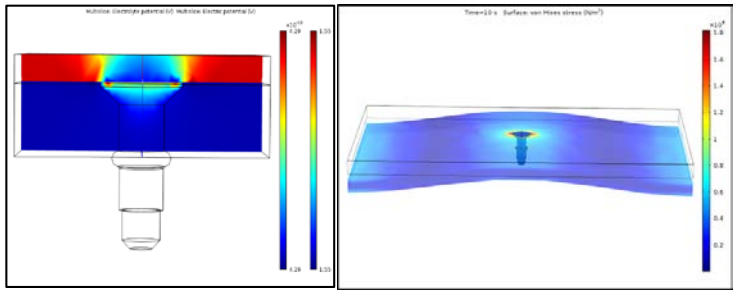
Cd-Ti Zn-Ni Cd Cd-Ti Zn-Ni Cd

Conclusions

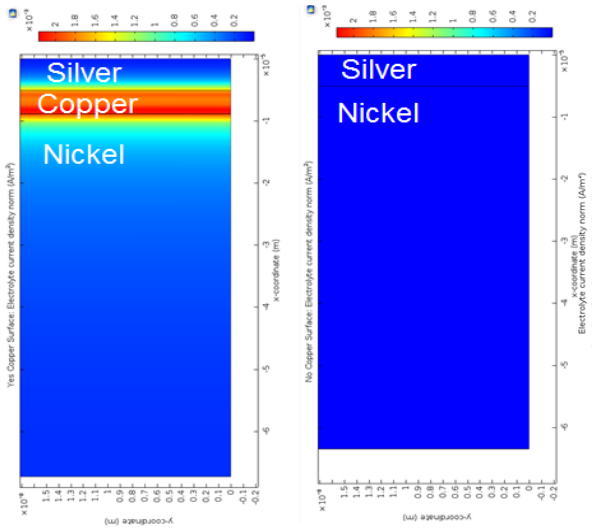
- GCPT used to assess the performance of Zn-Ni plating as a sacrificial coating for high strength steel.
  - Model assumes plating couples with 4130 bare steel via electrolyte in the scribe line.
  - For scribed test panels with width 508 µm, predicted corrosion rate for Zn-Ni plating is significantly greater (~ 2 times) compared to Cd plating.
  - Corrosion rate for Zn-Ni plating is even greater (~ 2.3 times) compared to Cd plating when scribe is wider (1524 µm).
  - Model predicts Zn-Ni plated layer will deplete much more rapidly than Cd, when testing with wide scribes.
  - Addition of post-plating chromate treatment does not influence corrosion rates of Zn-Ni and has a small effect on Cd-plating, when coupled to bare steel.
  - Model predictions consistent with observations in neutral salt spray testing.
  - Implications for testing Zn-Ni or other developmental plating materials.

Future Work / Needs

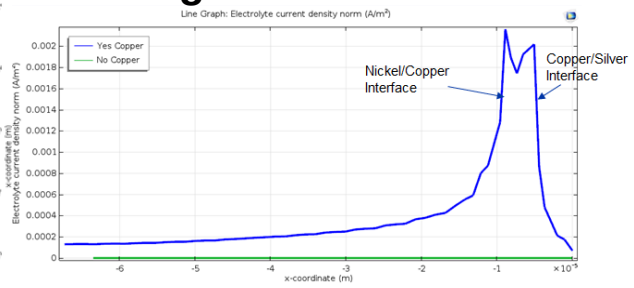
- Repeating calculations for Cd-Ti plating.
- On-going validation and verification of the tool.
- Expanding to 2D/3D multiphysics calculations.
- Risk mapping & optimization for design.
- Incorporation of other environments that impact corrosion of aerospace material systems.
  - e.g., thin film electrolytes, atmospheric conditions.
  - e.g., wet/dry cycling events that occur in service.
- Dynamic simulations with both environmental and mechanical inputs.



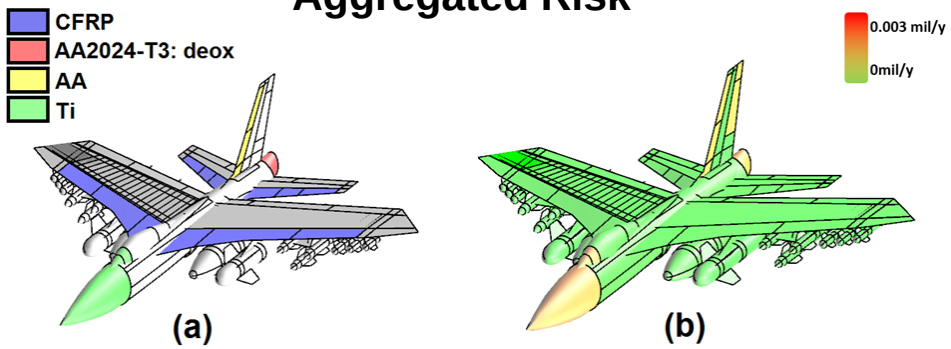
Lab Validation of Dynamic Simulations



Interactions at Coating Interfaces



Combinatorial Optimization to Minimize Aggregated Risk



Acknowledgments

- Special thanks to Eric Steele, Elizabeth Malczewski-Killelea, and Michael Lawton.
- Initial development of GCPT
  - Funded by Office of Naval Research, through ONR project, “Galvanic Corrosion Prediction Tool with Next Generation Galvanic Series for Metals and Finishes.”
  - Project supported Sea-Based Aviation National Naval Responsibility (SBA-NNR), Airframe Structures and Materials Program, managed by Bill C. Nickerson.
  - Original project lead, Dennis Dull, and other early contributors: Glen Rasmussen, Andrew Booker, and Shan Luh.

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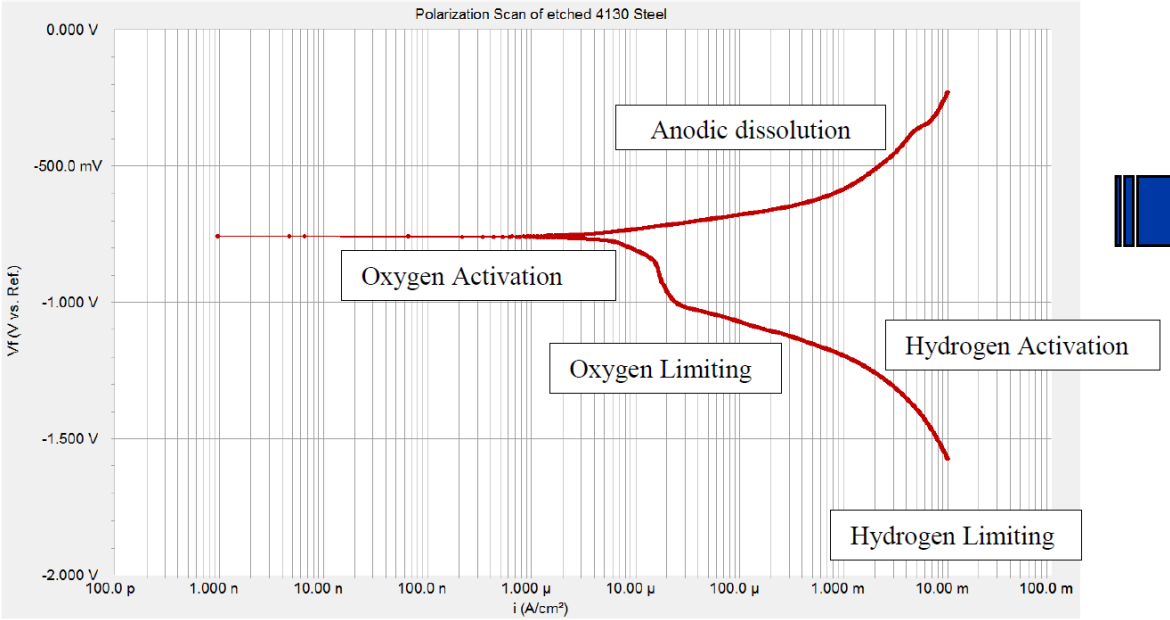
Backup Slides

- Modeling methodology developed for assessing galvanic corrosion risk in aerospace material systems, sub-components, and assemblies.
- Method is based upon quantitative corrosion rate data.
- Interactive galvanic corrosion predictor tool (GCPT) predicts galvanic corrosion rates between dissimilar materials in 3.5% NaCl solution.
- Galvanic interactions modeled using curve-crossing algorithm based on Theory of Mixed Potentials.
- Geometric model of 4” x 6” test panel showed that anode:cathode ratio depends on film thickness and width of X-scribe.
  - Much smaller than 1 for scribe width of 508 µm.
  - Even smaller for wider scribes of 1524 µm.
- Corrosion rate of anode (plating) increases exponentially when anode:cathode ratios are smaller than 1.

Modeling Methods



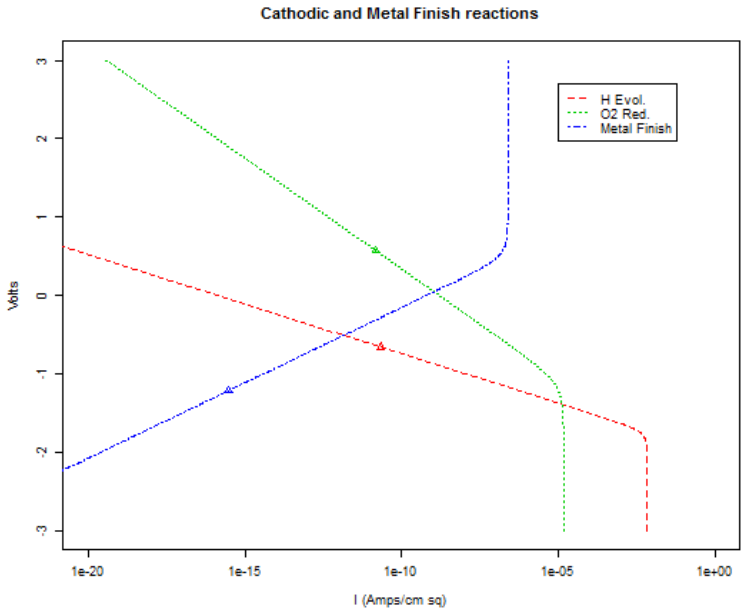
Experimental Polarization Curve of Etched 4130

$$i_{metal\ (anodic)} = i_0^{metal} e^{\frac{2.3(E-E_{eq-metal})}{b_a}}$$

$$i_{pit} = i_0^{pit} exp^{\frac{2.3(E-E_{pit})}{b_{pit}}}$$

$$i_{O_2(cathodic)} = \lambda_{O_2}(E)\ i_0^{O_2} exp^{\frac{-2.3(E-E_{O_2})}{b_{cO_2}}}$$

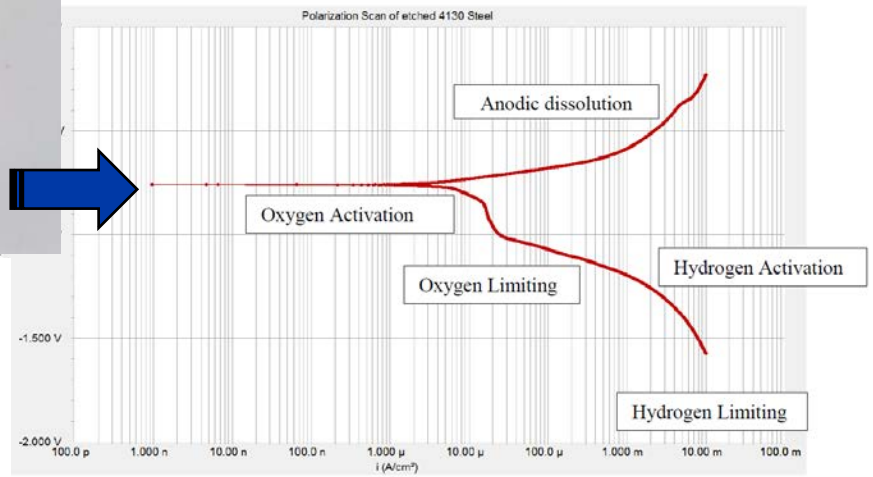
$$i_{H_2(cathodic)} = \lambda_{H_2}(E)\ i_0^{H_2} exp^{\frac{-2.3(E-E_{H_2})}{b_{cH_2}}}$$



- Galvanic interactions between dissimilar materials modeled using a curve-crossing algorithm.
- Based on the Theory of Mixed Potentials.
- Algorithm first de-convolutes potentiodynamic polarization data using Tafel equations.
- Uses set of rate equations for four independent reactions.

Experimental Methods

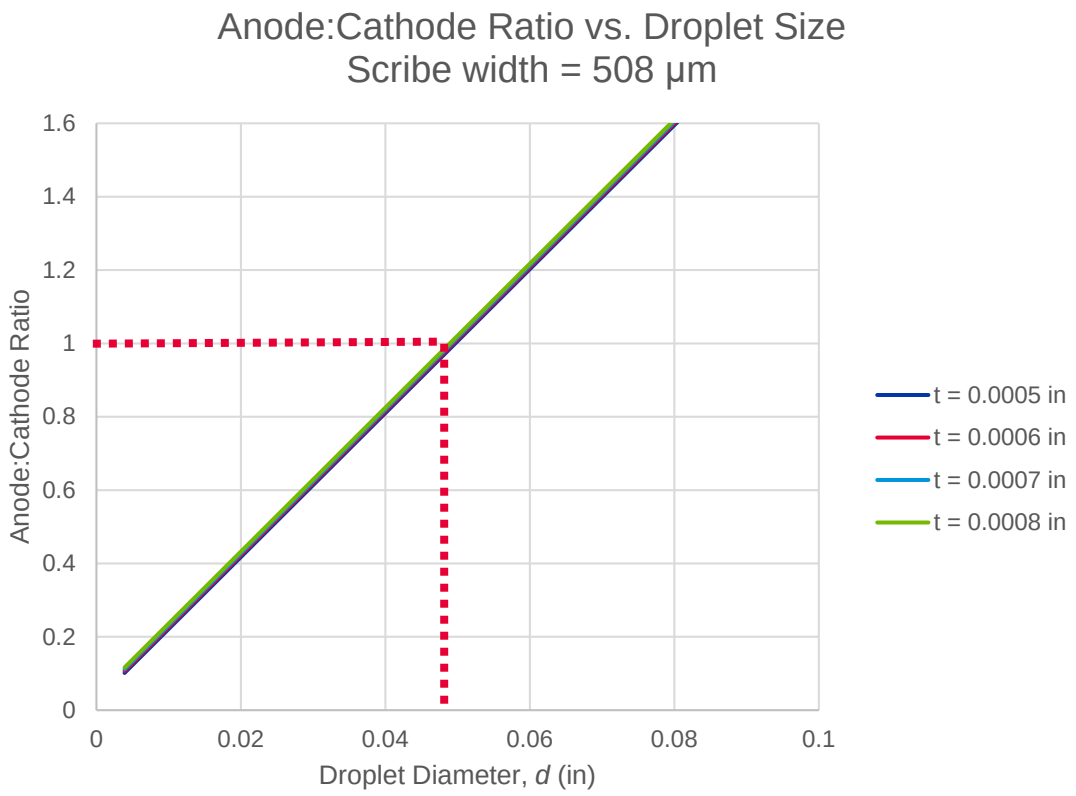
- Each polarization scan conducted at a scan rate of 0.05 mV/sec (180 mV/hour).
- Anodic/cathodic scans begin at open circuit potential (OCP).
- Potentials referenced versus a saturated calomel electrode (SCE).
- Potential scanned from -1700 mV to +1200 mV vs. SCE (unless a maximum current density of 10 mA/cm² was exceeded).
- Experiments conducted in 3.5% NaCl solution in deionized water at stagnant conditions.
- Used flat cell with 10 cm² test area and platinum mesh counter electrode.
- Flat cell enclosed in an aluminum Faraday cage.
- Test specimens cleaned with isopropyl alcohol (IPA) prior to experimentation.

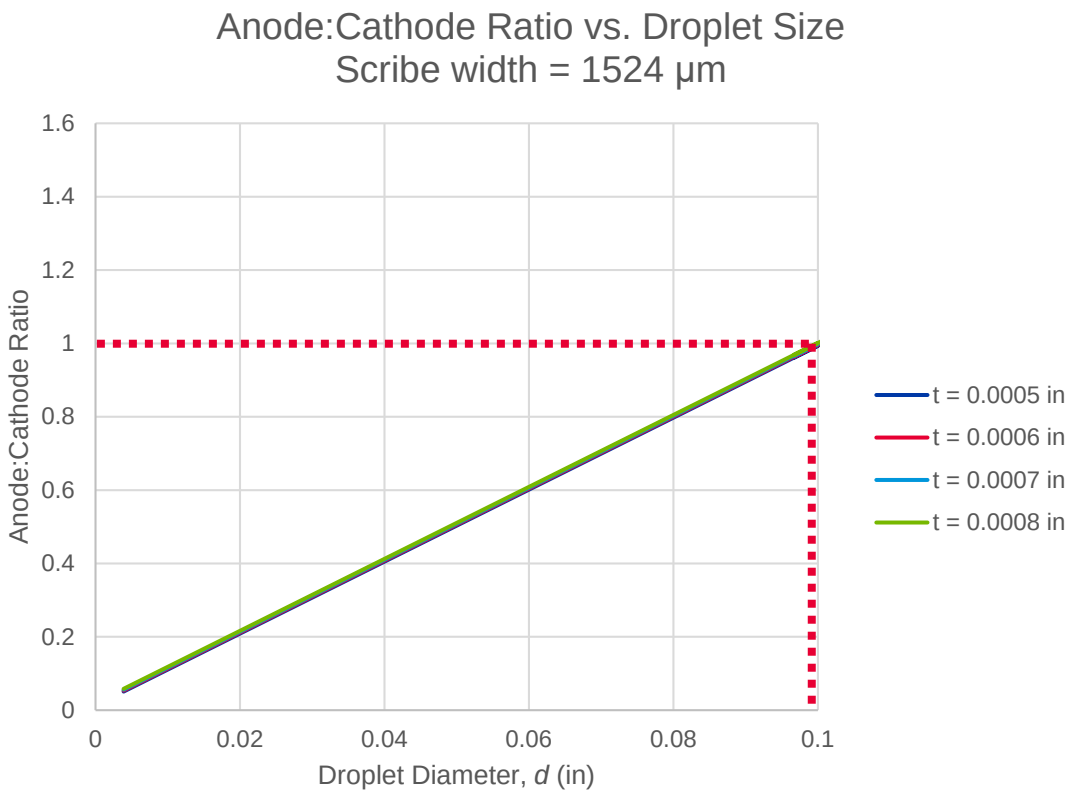


Gamry Reference 600

Results

$$A_A/A_C = [\pi(d/2)^2 + 2dt]/[dw + 2dD]$$





- For X-scribed panel, anode:cathode ratio is linear function of droplet diameter.
- Corrosion rate of anode (plating) increases when ratios are smaller than 1.
- Wider scribes (steel cathode) increase corrosion rate of plating.