# Correlation Between Electrochemical Behavior and Neutral Salt Fog Corrosion on TCP Coated AA2024

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# Outline



- Experimental purpose
- Aluminum alloy 2024-T3
- Background of preventing corrosion on aluminum
- Background of salt fog and electrochemical measurements
- Salt fog and electrochemical results
- Summary and conclusions

# Purpose



## Neutral salt fog corrosion test

link

- Current standard to test performance = ASTM B117
  - Poor correlation with actual field performance, but good process control check
  - Testing to failure requires up to 1,000 hours (more than one month)
  - Difficult to thoroughly and quantitatively compare processes

## Electrochemical analysis

- New method to test performance
  - Good correlation with field performance on other metals[1,2]
  - Good correlation with salt fog when flaws introduced to coatings on aluminum[3]
  - Fast (hours to days)
  - Easily and comprehensively compare and rank processes, different coatings, different base metals
  - Has mainly been tested/linked with field tests with primed/painted panels with or without scribes


1) J. Bundy, K & Bricka, M. (2019). AN ELECTROCHEMICAL APPROACH FOR INVESTIGATING CORROSION OF SMALL ARMS MUNITIONS IN FIRING RANGES.
2) Lins, Vanessa, Gomes, Edelize Angelica, Costa, Cíntia Gonçalves, Castro, Maria das Mercês Reis, & Carneiro, Rogerio Augusto. (2018). Corrosion behavior of experimental nickel-bearing carbon steels evaluated using field and electrochemical tests. *REM - International Engineering Journal*, *71* (4), 613-620.
3) S. R. Taylor, Francesco Contu, C. N. Hunter, and L. Fenzy **The Prediction of Long-term Coating Performance from Short-term Electrochemical Data, Part I. Inhibited Aerospace Coating Systems - Comparison to Salt Spray Data,** Electrochemical Society Transactions 2010 24: 185-196.


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# Purpose: New Process Control Check



- Link electrochemical analysis to neutral salt fog testing for coated but undamaged metals
- Optimize new pretreatment processes more quickly and efficiently with electrochemical analysis
- Future uses in new product development and in new pretreatment process development
  - Save time and money on extensive salt fog testing or developing new products/processes that do not perform well in field testing

# Aluminum Alloy 2024-T6

# Difficulties with 2000 Series Alloys



- High copper content alloyed with the base aluminum
  - Forms large copper sites on surface which tend to coat unevenly
  - Forms galvanic cell between Cu and Al, promoting Al degradation
- High levels of corrosion compared to other aluminum alloys
- More difficult to coat uniformly and homogeneously
- **Requires more careful surface preparation and coating formation than any other aluminum alloy to produce the best, most corrosion resistant conversion coatings**

# Catastrophic Aluminum Failures

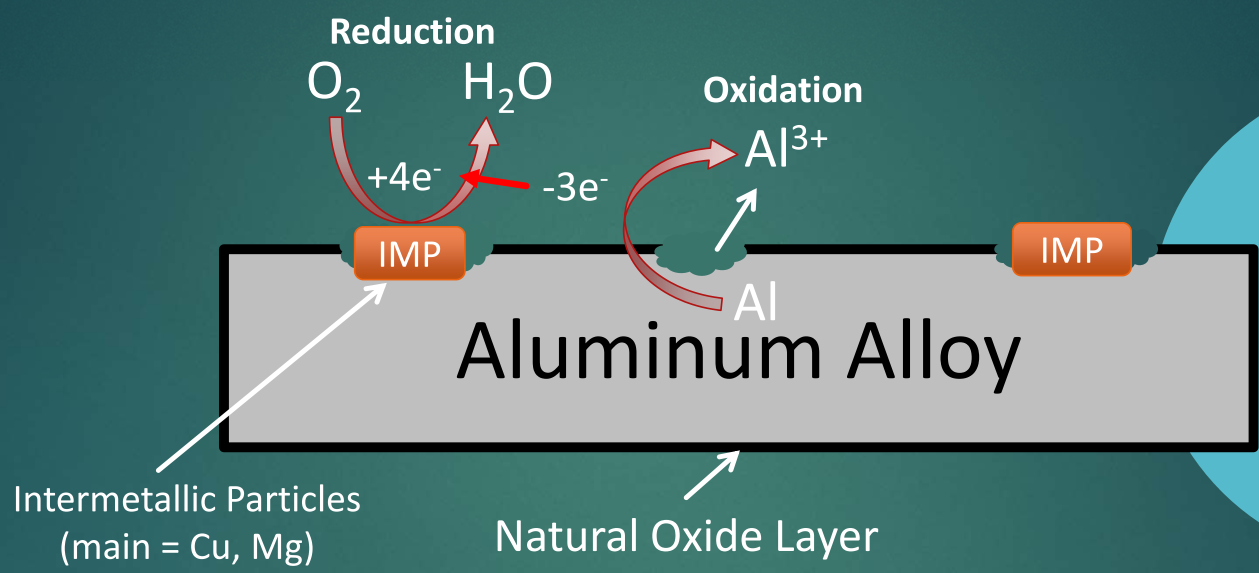


- Corrosion of aluminum on vehicles tends to be cosmetic rather than catastrophic like steel corrosion was in the past
  - Early implementation of Al hoods on Fords had galvanic corrosion/paint delamination due to direct connection with steel brackets
- More catastrophic failures seen with aerospace applications of aluminum
  - Crash in 1992 due to corrosion pitting and fatigue at engine fuse pins connecting strut to wing
  - Crash in 1999 due to fuselage skin panels disbonding and fatigue cracking at lap joints
  - Crash in 2005 due to losing a wing from corrosion causing fatigue cracks on the wing/fuselage junction brackets

1) https://web.archive.org/web/20111019164744/
2) http://www.ntsb.gov/news/2005/051222a.htm
3) https://corrosion-doctors.org/Aircraft/Aloha.htm

# Background- Preventing Corrosion on Aluminum Alloys

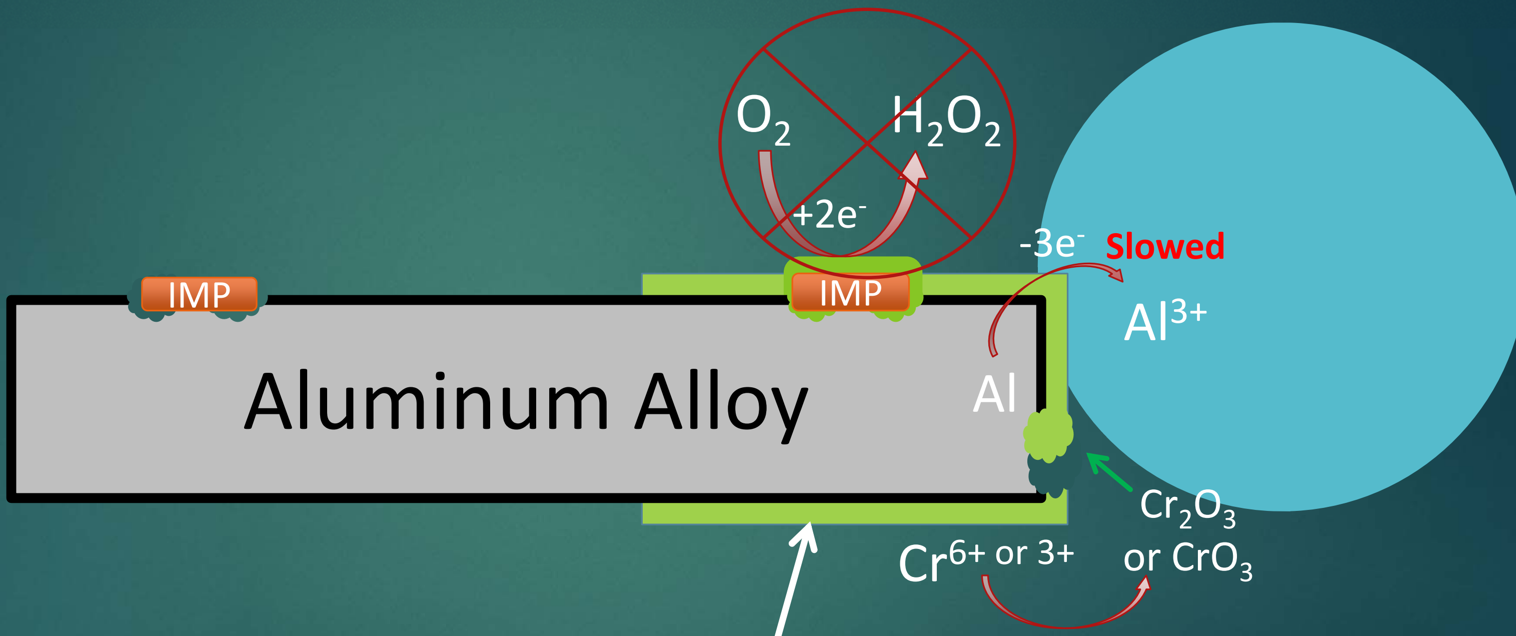
# Aluminum Alloy Corrosion




| Element (Weight %) | Cu | Fe | Mg | Mn | Si | Zn | Ti | Cr | Al |
|---|---|---|---|---|---|---|---|---|---|
| 2024-T3 | 3.8-4.9 | 0.5 | 1.2-1.8 | 0.3-0.9 | 0.5 | 0.25 | 0.15 | 0.1 | 90.9-93.7 |

# Aluminum Alloy Corrosion






~~Chromate conversion coating: Cr(VI)~~

Trivalent chromium process (TCP) coating: Cr(III)

# European Union Directives (27 EU Nations)



- Registration, Evaluation, Authorization, and restriction of Chemicals (REACh) ban on hexavalent chromium in European Union
  - Prohibition and regulation of use due to toxicity and human health risks
  - Three major governing EU bodies - European Parliament, the Council of the European Union, and the Commission of the European Community
  - **Effective 9/21/2017**

- End of Life Vehicle (ELV)
  - Four heavy metals - hexavalent chromium (~ 70%), cadmium, lead and mercury.
  - **Effective 7/1/2007**
- Restriction of Hazardous Substance (RoHS)
  - Hexavalent chromium, cadmium, lead, mercury, PBB (polybrominated biphenyls) and PBDE (polybrominated diphenyl ether)
  - Effective 7/1/2006
- Waste Electrical & Electronic Equipment (WEEE)
  - **Effective 12/31/2006**

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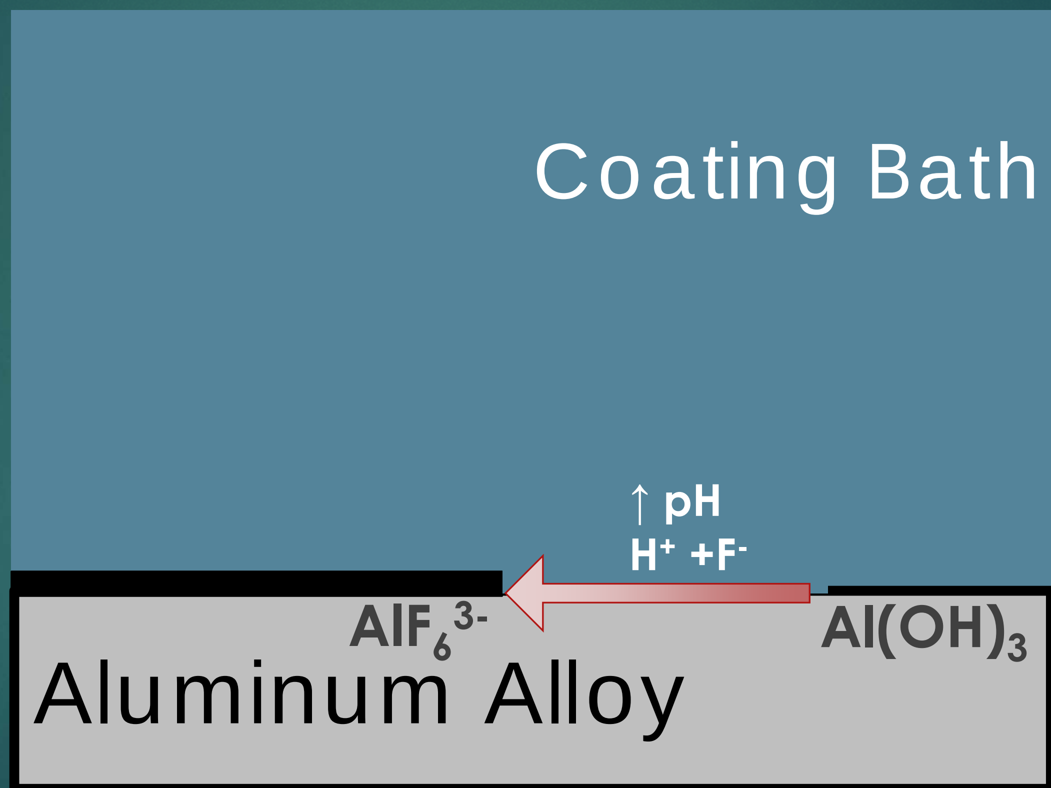
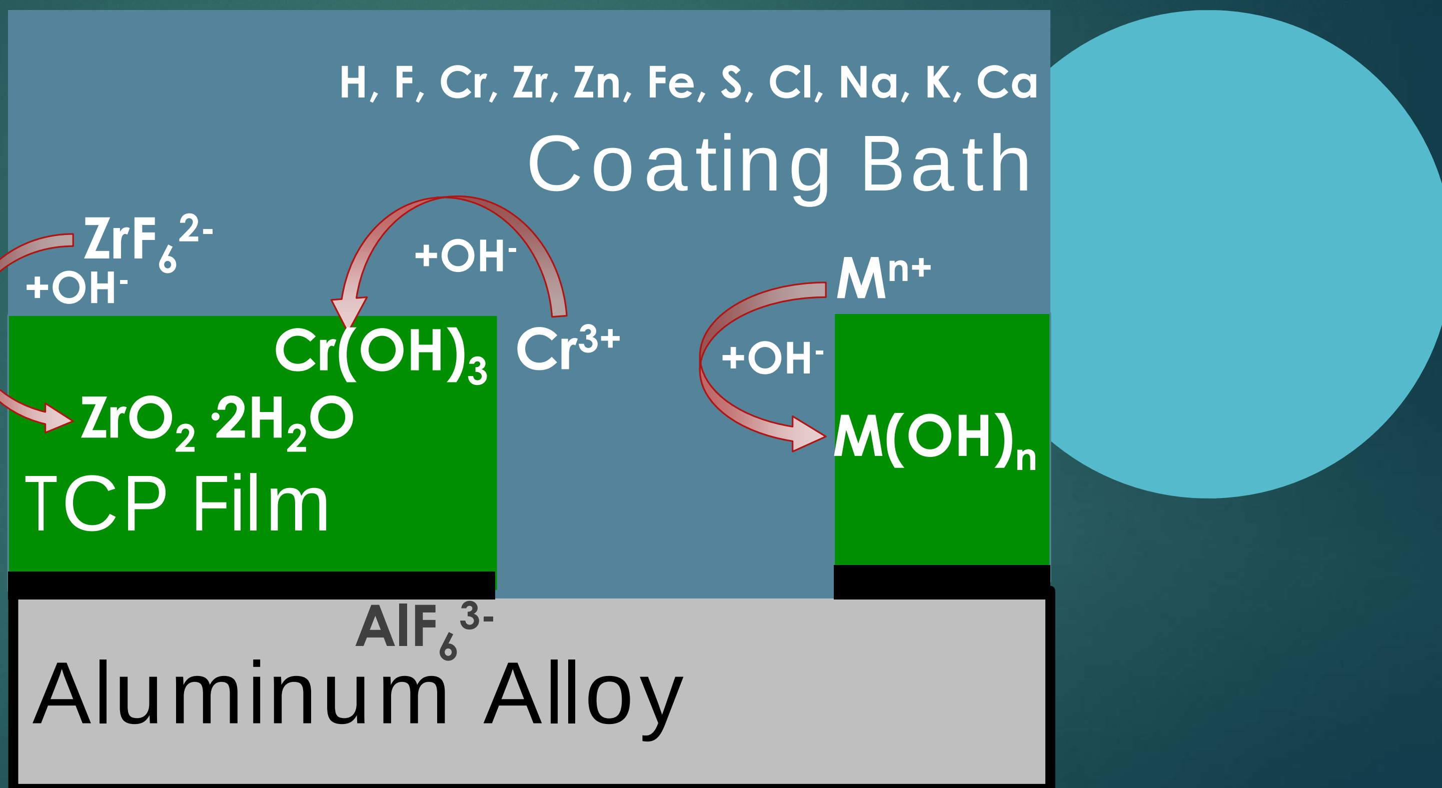
# TCP Film Composition and Corrosion Protection



# TCP Film Composition and Corrosion Protection





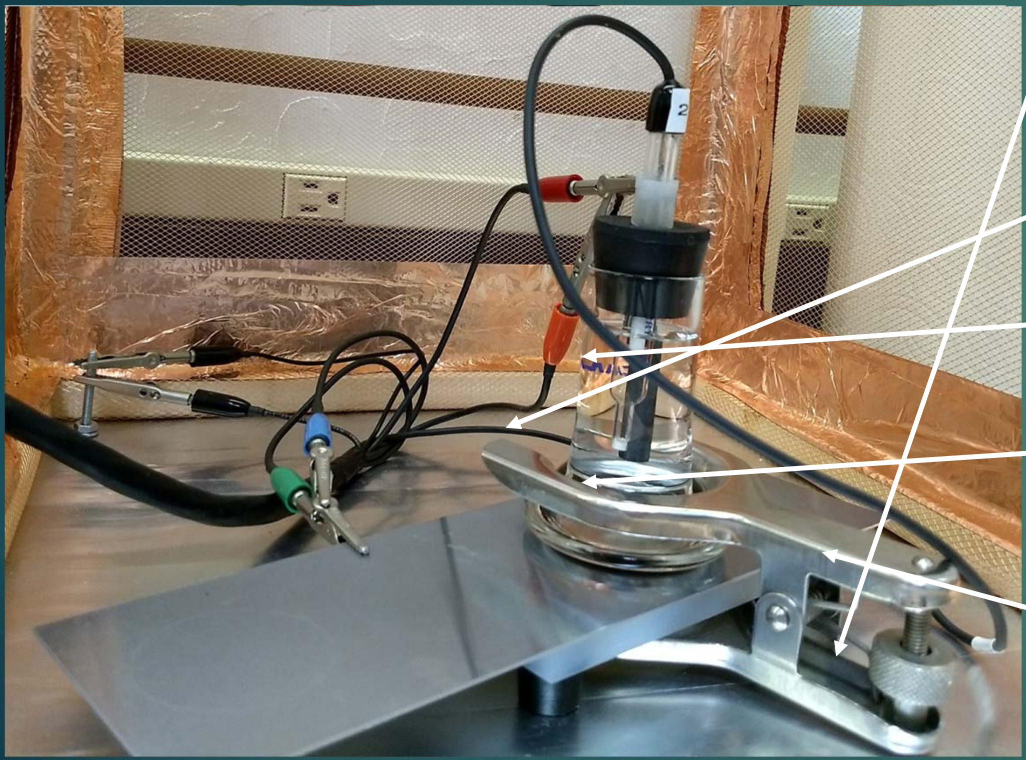
# Background- Salt Fog and Electrochemical Measurements

# Salt Fog Setup


- Following ASTM B-117, MIL-DTL-5541, and MIL-DTL-81706
  - 5 ± 1% by mass NaCl fog at pH 6.85 ± .35
  - 35 ± 2°C inside the chamber, dispersing fog at 1.5 ± 0.5 mL/hour
  - Chamber performance checked daily (minus weekends/holidays) with chamber open for < 1 hour
  - Panels set up in chamber at 6° from vertical, no salt spray directly impinging the panels
  - Time in salt fog and number of pits recorded upon failure (one panel with >5 pits or >15 pits over all 5 panels exposed)

# Electrochemical Analysis Setup





- Working electrode= aluminum alloy 2024-T3 coated with TCP-HF processed with iron based deoxidizer
- Counter electrode = carbon rod
- Reference electrode = saturated calomel
- Electrolyte = 1 M NaCl **or** 10% v/v Harrison's solution (3.5% ammonium sulfate + 0.5% NaCl)
- Run inside Faraday cage to prevent noise interference
- Using Gamry potentiostat and fitting software

# Experimental Plan



- More aggressive pretreatments cause poor coating formation and performance
- Full comparison of best and worst practices with an aggressive pretreatment condition
  - Iron-based deoxidizer: more aggressive pretreatment than recommended

- Best process = shortest salt fog time to failure with the least pits
- Worst process = longest salt fog time to failure with the most pits

- Want to link the best and worst performing processes (via salt fog testing) to the electrochemical behavior
  - Should show the same trends and rankings

# Panel Processing



Cleaner → Overflow Rinse Cycle → Deoxidizer/ Activation → Overflow Rinse Cycle → Trivalent Conversion Coating → Overflow DI Rinse

- Alkaline cleaner
- Double water rinse
- Iron-based deoxidizer
- Double water rinse
- Trivalent chromium conversion coating
- Short DI water rinse

- 24 hour cure time (ambient temperature away from coating line) before salt fog or electrochemical testing

# Salt Fog and Electrochemical Results

# Salt Fog Results



Failure – >5 pits on one panel or >15 pits over all 5 panels

| Panel name | Salt Spray Time to Failure (hours) | Pits at 336 hours, passing MIL-DTL-81706 requirements? | Pits per panel (total pits) |
|---|---|---|---|
| T1 | 336 | 7, failed | 5+, 1, 1, 0, 0 (7) |
| T2 | 840 | 0, passed | 5+, 5+, 0, 0, 0 (16) |
| T3 | 336 | 25+, failed | 5+, 5+, 5+, 5+, (25+) |
| T4 | 336 | 5+, failed | 5+, 0, 0, 0, 0 (10+) |

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# Open Circuit Potential Measurements

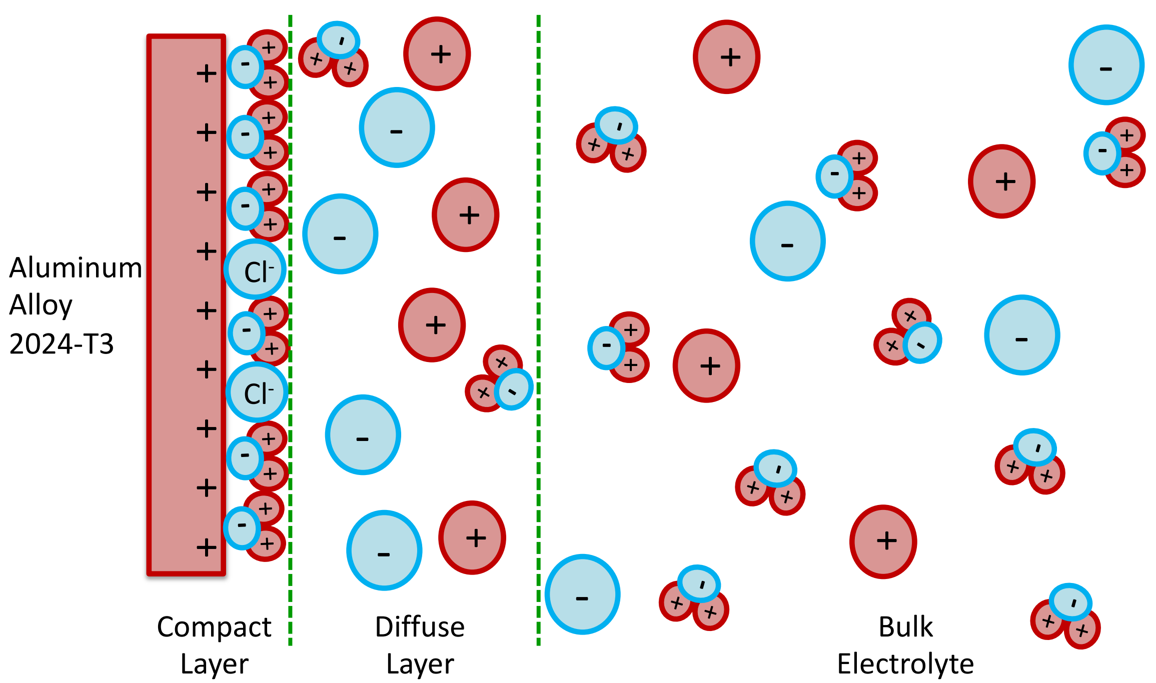


- Measure voltage between reference electrode and working electrode (coated aluminum panel) due to formation of double layer at the working electrode surface
  - Potential due to rearrangement of water molecules and salt ions at the coated metal surface because of the naturally occurring charge
- Less negative potential indicates better corrosion resistance and a lower initial charge on the coated metal surface

# Aqueous Electrolyte-Electrode Interface: Gouy-Chapman-Stern Model

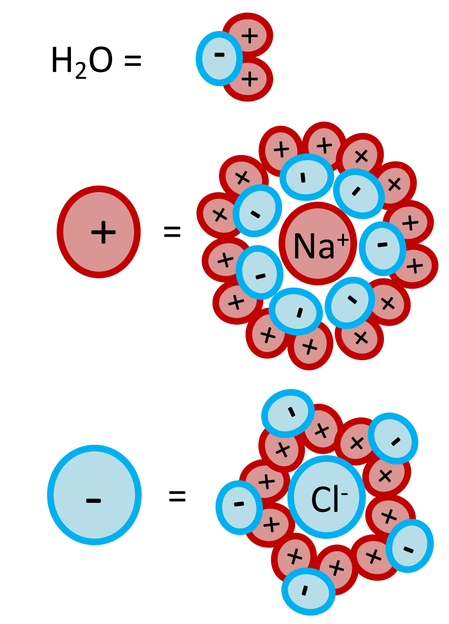


**Aqueous Electrolyte-Electrode Interface: Gouy-Chapman-Stern Model**




***Electrode interface: only electrostatic attraction***

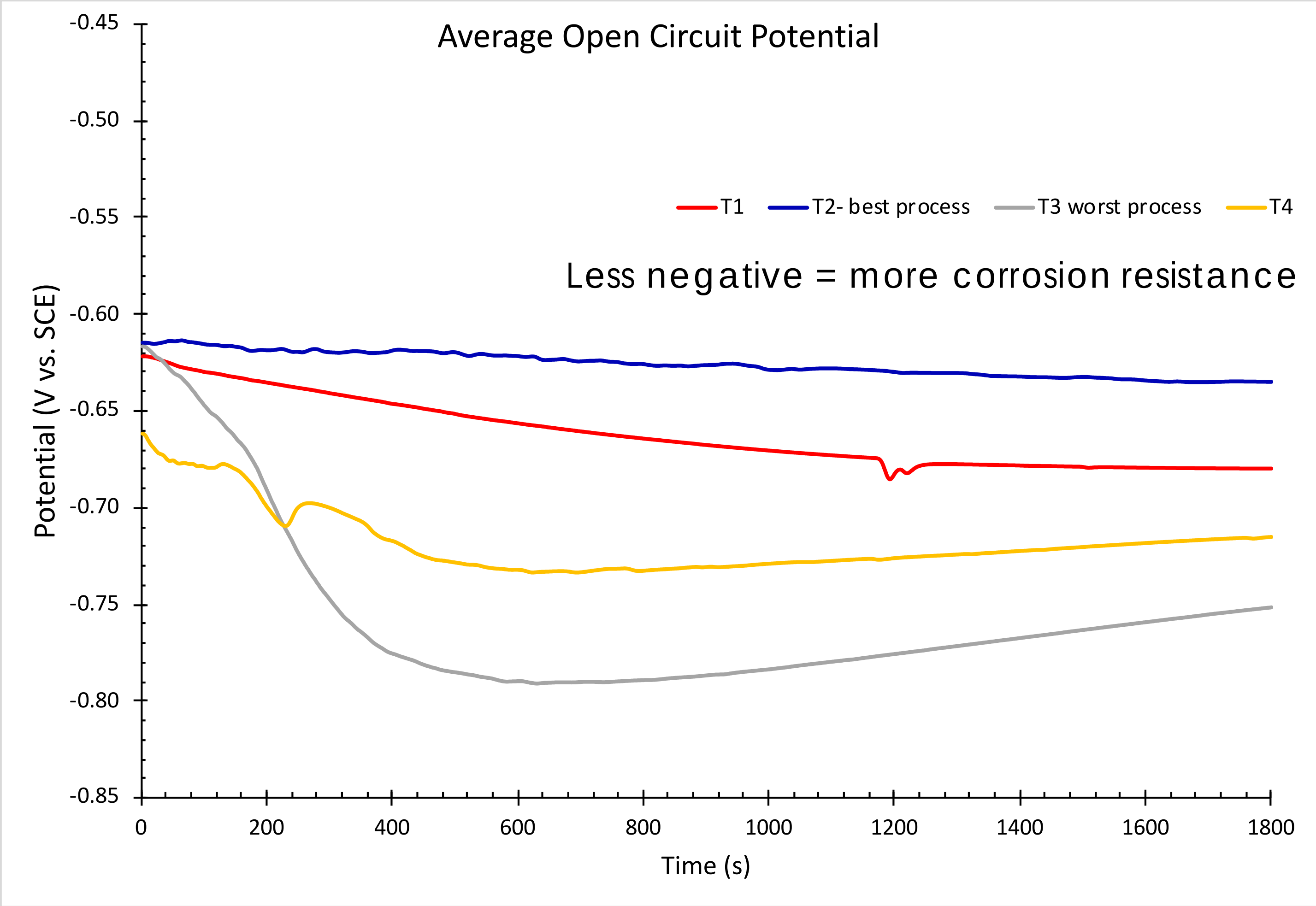
Legend




Bard, A. J.; et. al. Electrochemical Methods: Fundamentals and Applications, 2nd ed.; John Wiley and Sons, Inc.: New York, 2001, pp 226-260.

# Electrochemistry- Open Circuit Potential in 1 M NaCl



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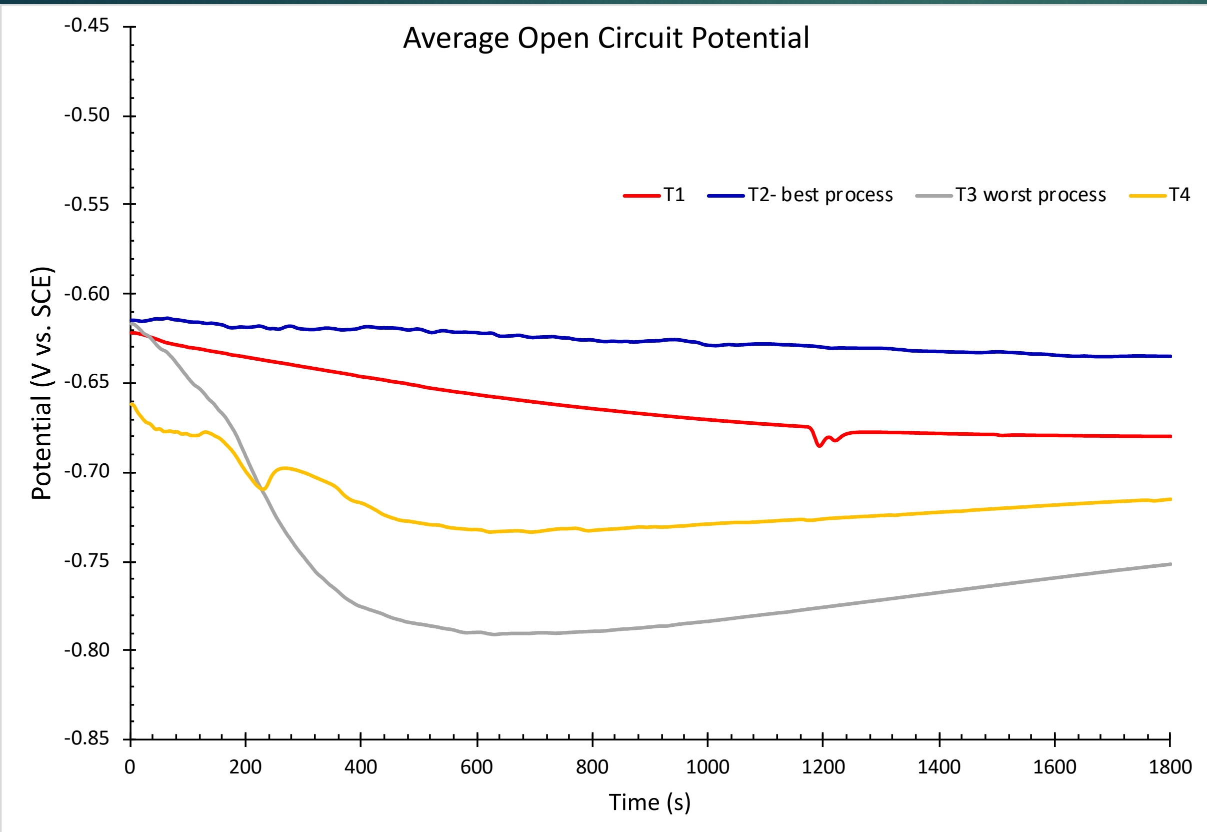
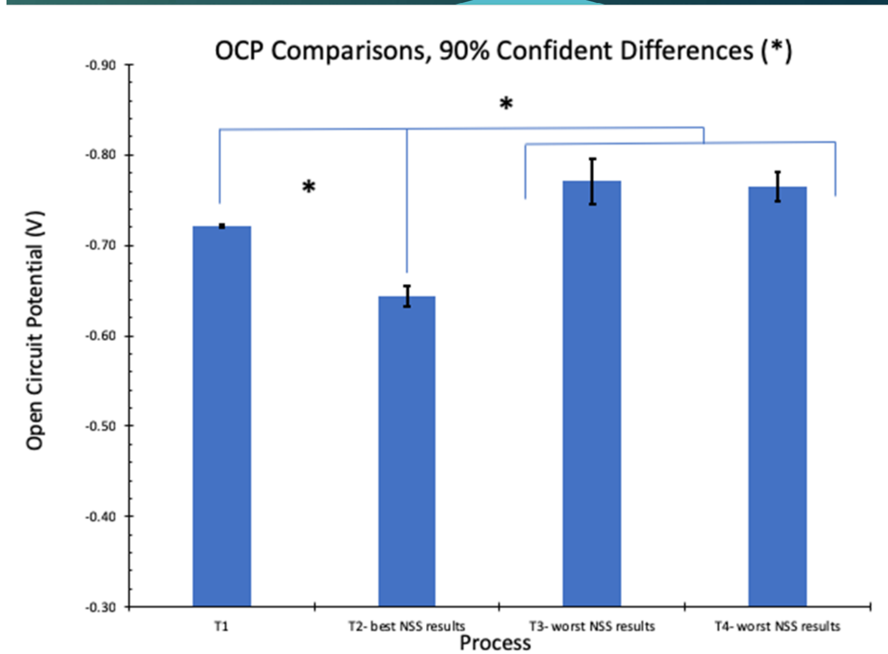
# Electrochemistry- Open Circuit Potential in 1 M NaCl





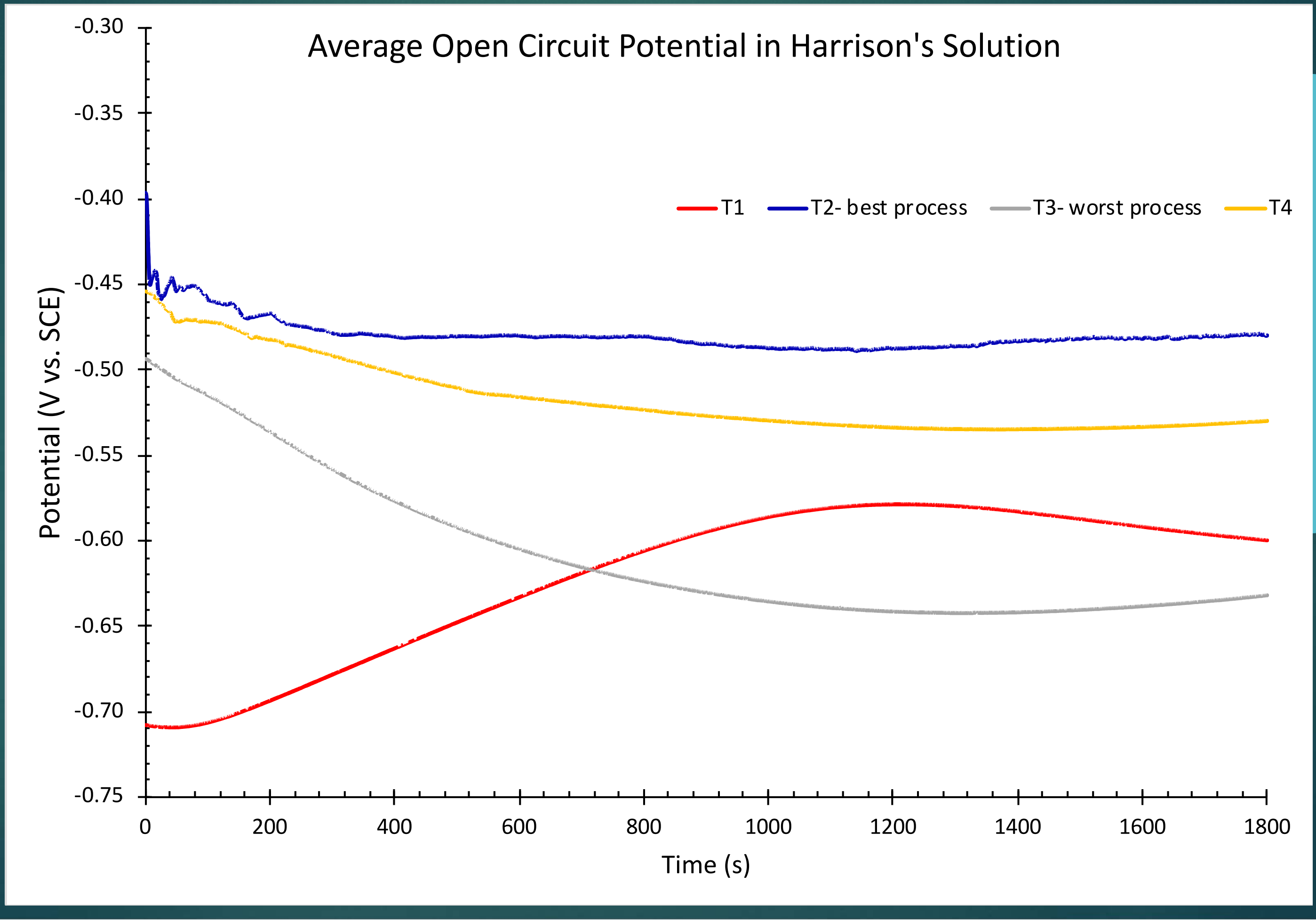




n = 3, presented as average ± standard error of the mean

Less negative = more corrosion resistance

# Electrochemistry- Open Circuit Potential in Harrison’s Solution





# Electrochemical Impedance Spectroscopy Measurements



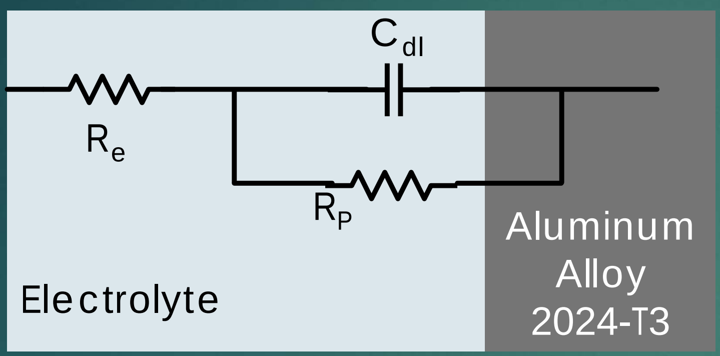
- Current due to applied sine wave potential measured and converted to a resistance with a frequency component called *impedance*
  - Fit to a representative circuit descriptive of the electrode/electrolyte interface

- Resistance to current flow (polarization resistance) indicates the resistance to corrosion
  - Higher resistance = less corrosion

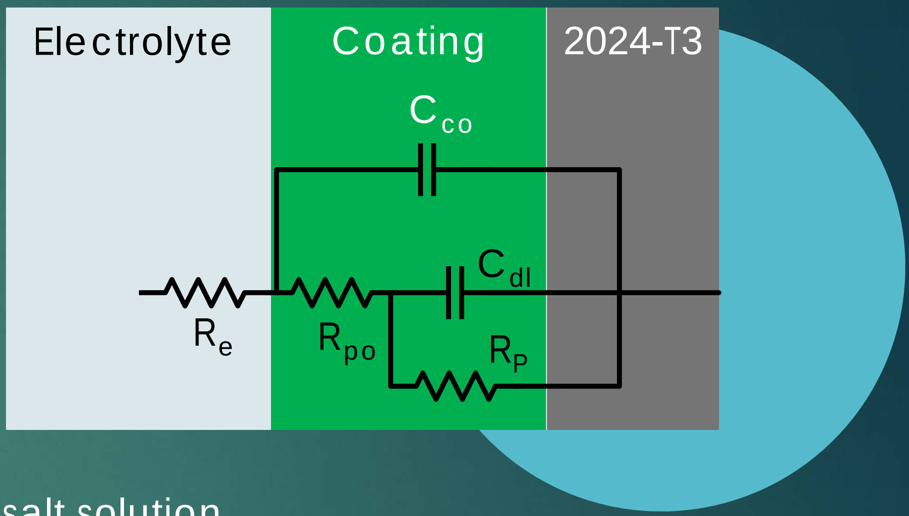
# Fitting Nyquist Plots to Equivalent Circuits



**Uncoated**




**Coated**

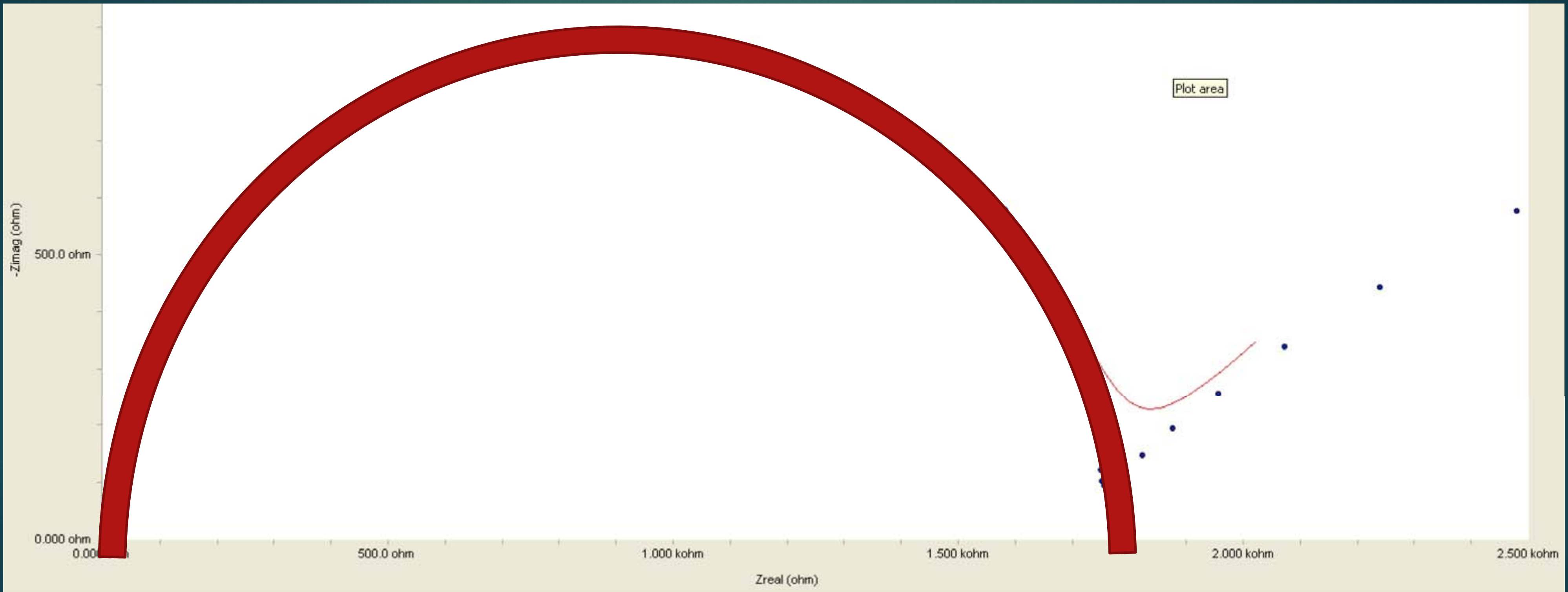



$R_e$ = electrolyte resistance = $e^-$ flow resistance through salt solution
$C_{dl}$ = double layer capacitance = charge held in double layer interface
$R_P$ = polarization resistance = $e^-$ flow resistance through double layer *(or double layer and coating)*

$R_{po}$ = pore resistance = $e^-$ flow resistance through pores in coating
$C_{co}$ = coating capacitance = charge held in coating

# Fitting Nyquist Plots to Equivalent Circuits

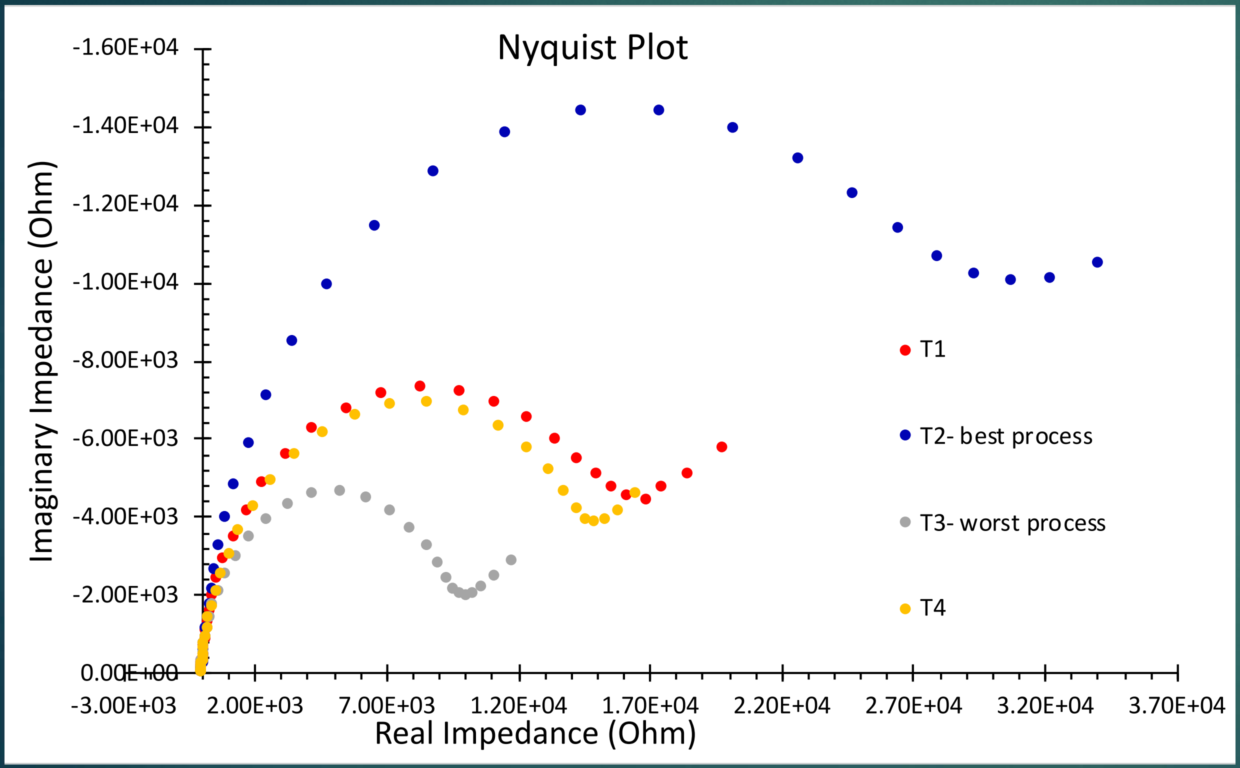


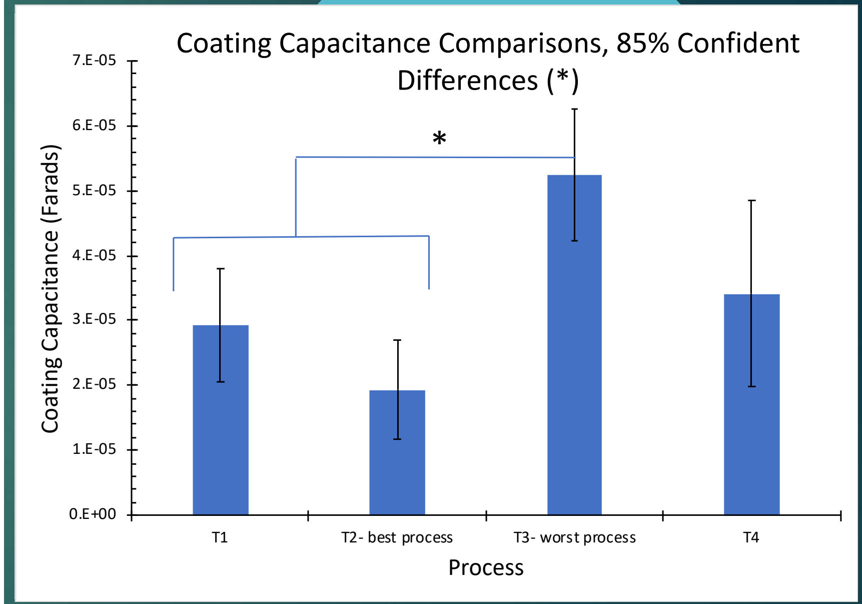



$R_P$ = polarization resistance = diameter of semi-circle

# Electrochemistry- Nyquist Plots and Equivalent Circuit Fitting in 1 M NaCl





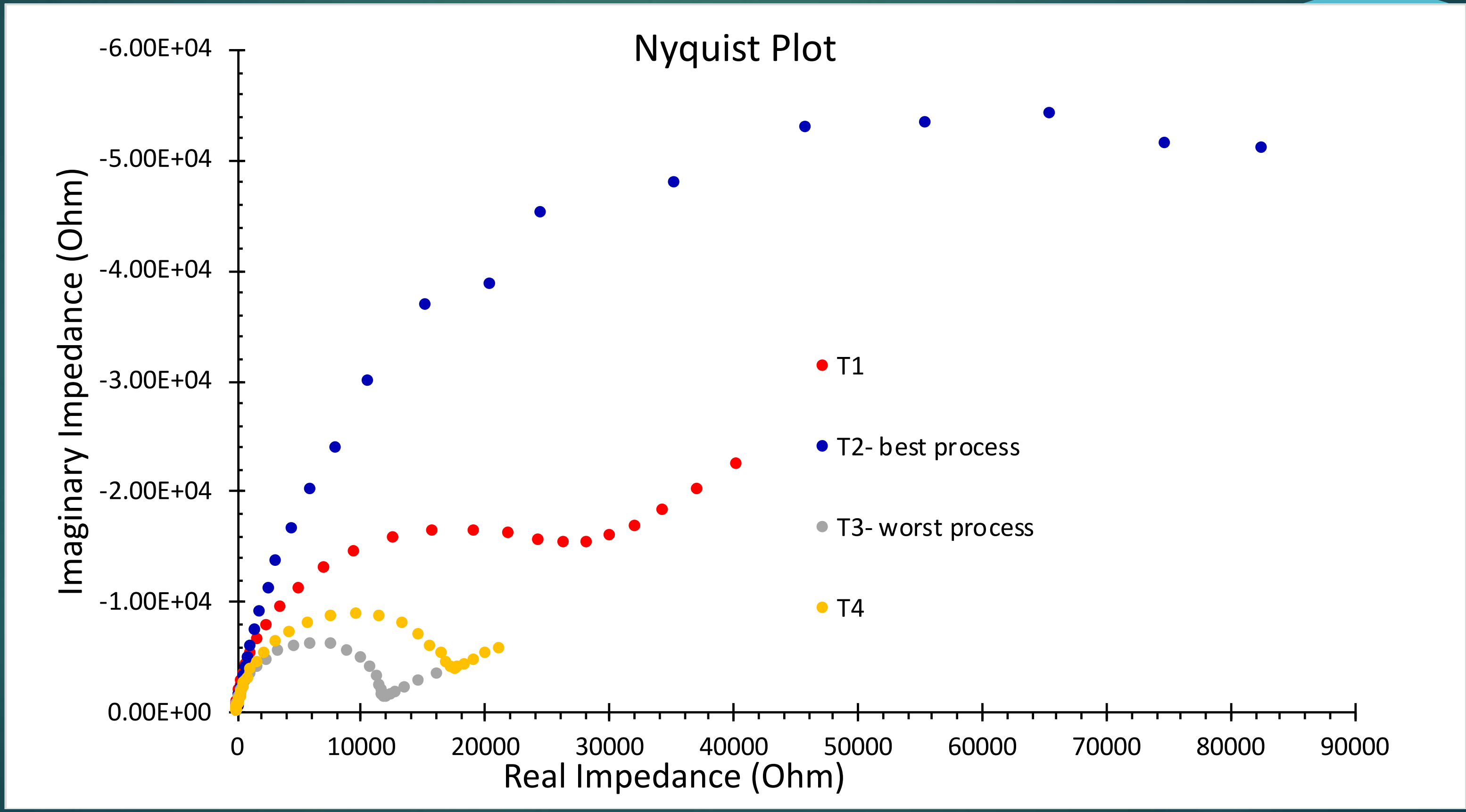




n = 3, presented as average ± standard error of the mean

Larger semicircle = more corrosion resistance

# Electrochemistry- Nyquist Plots and Equivalent Circuit Fitting- Harrison's Solution





# Tafel Measurements

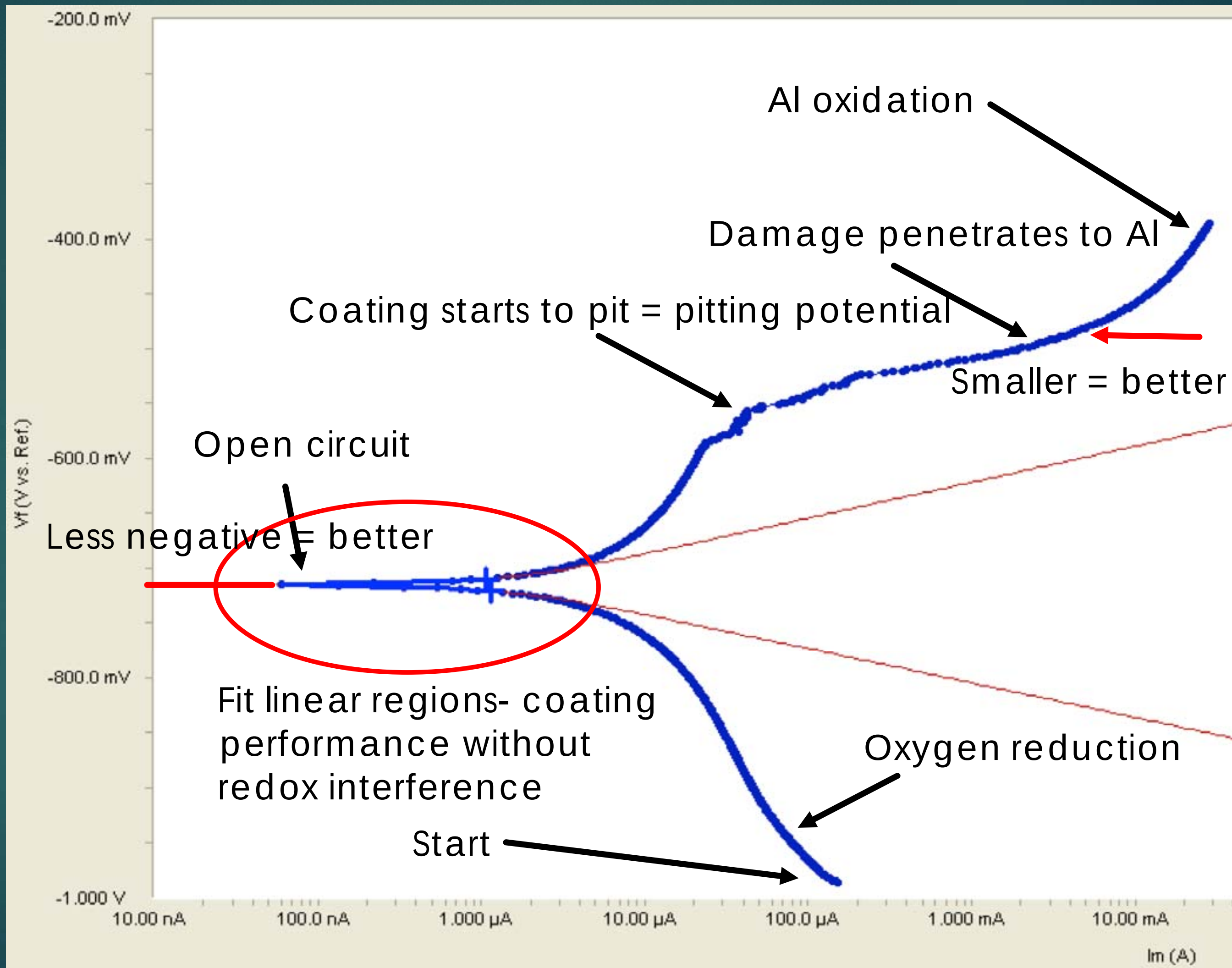


- Applied potential slowly ramped, going from a point more negative than the open circuit potential to a point more positive than the open circuit potential to induce corrosion
  - More negative potentials = oxygen reduction
  - More positive potentials = aluminum oxidation

- Differences in the current flow indicate the performance of the coated metal working electrode
  - Lower current = less corrosion

# Fitting Tafel Data with Butler-Volmer Equation






Blue = raw data
Red = fitting

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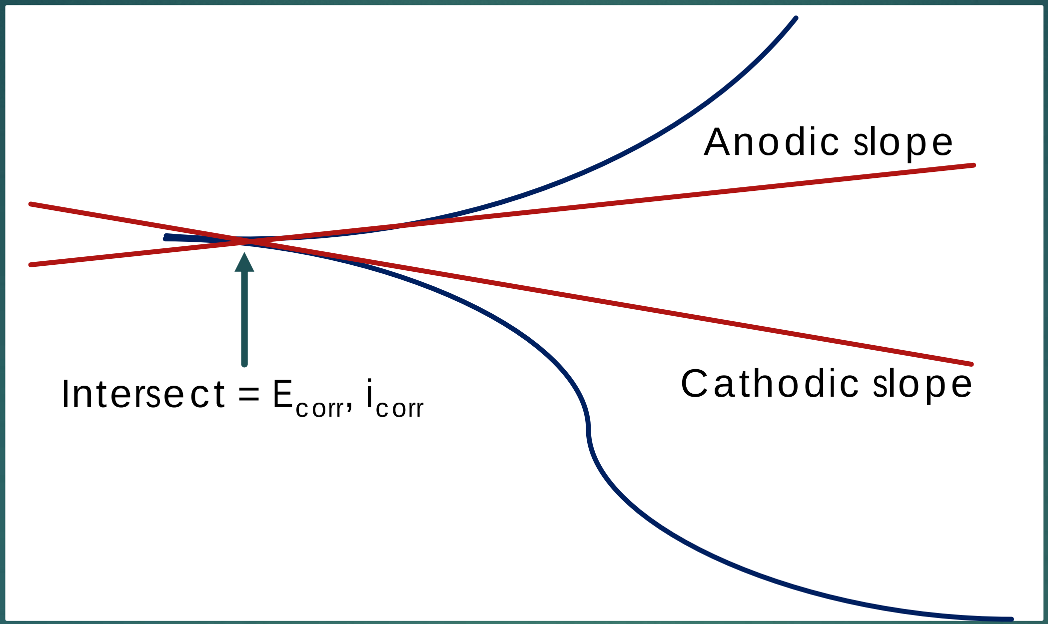
# Fitting Tafel Data with Butler-Volmer Equation






$$I = i_{corr}\left(e^{\frac{2.303(E-E_{corr})}{b_a}} - e^{\frac{-2.303(E-E_{corr})}{b_c}}\right)$$

I = measured current
E = applied potential
$E_{corr}$ = corrosion potential
$i_{corr}$ = corrosion current
$b_a$ = anodic Tafel slope
$b_c$ = cathodic Tafel slope

https://www.palmsenscorrosion.com/knowledgebase/polarization-curves/

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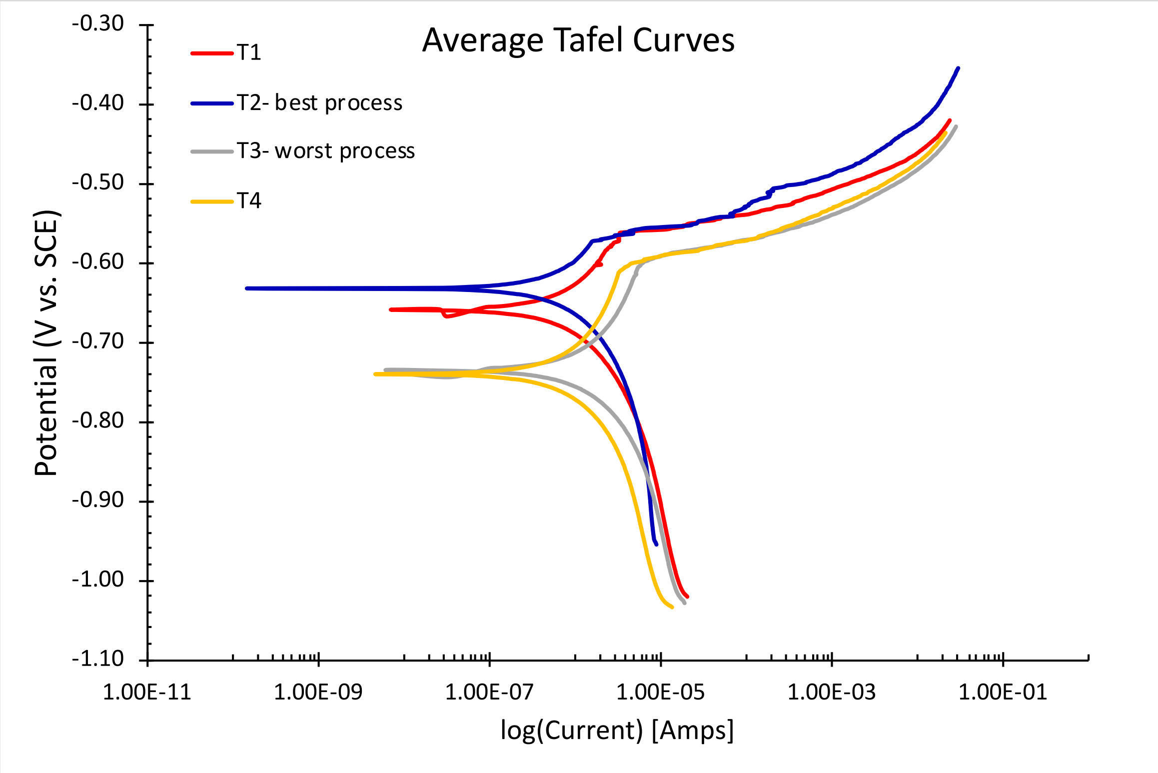
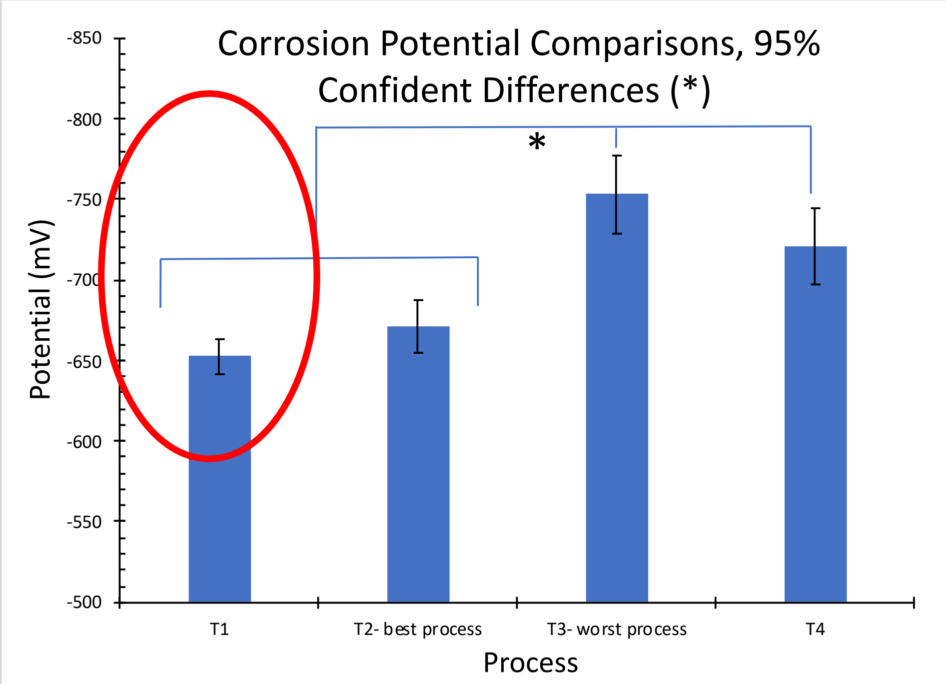
# Electrochemistry- Tafel Plots with Butler-Volmer Fitting in 1 M NaCl






n = 3, presented as average ± standard error of the mean

Lower current flow, more positive plateau = more corrosion resistance

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# Salt Fog Results Compared to Electrochemistry- 1M NaCl



| Panel name | Salt Spray Time (# pits) | Open Circuit Potential (V) | Polarization Resistance (kΩ) | Coating Capacitance (Farads) | Corrosion Current (μA) | Corrosion Potential (V) |
|---|---|---|---|---|---|---|
| T1 | 336 hr (7) | -0.7210(11) | 15(5) | 2.9(8)E-5 | 3(1) | -0.652(11) |
| T2 | 840 (0 at 336, 16 at failure) | -0.644(11) | 28(5) | 1.9(8)E-5 | 0.97(10) | -0.671(16) |
| T3 | 336 (20+) | -0.771(25) | 9(1) | 5(1)E-5 | 2.2(5) | -0.753(24) |
| T4 | 336 (5+ on one panel) | -0.765(16) | 14(4) | 3(1)E-5 | 0.9(3) | -0.720(23) |

mean(standard error in the last digits)

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# Summary and Conclusions

# Electrochemical Analysis Vs Salt Fog for Establishing Best Operating Parameters



## Salt Fog

- Indicated process T2 performed the best, with the longest salt spray time before failure
- Indicated process T3 performed the worst, with the shortest salt spray time and the largest amount of pits in that time
  - Processes T1 and T4 showed the same short salt spray time with fewer pits

## Electrochemistry

- All measurements line up well with salt spray performance
  - Open circuit
    - Most positive for the best process and most negative for the worst
  - EIS: polarization resistance
    - Highest for the best process and lowest for the worst
  - EIS: coating capacitance
    - Lowest for the best process and highest for the worst
  - Tafel: corrosion current
    - Lowest for the best process and high for the worst
  - Tafel: corrosion potential
    - Most positive for the best process and most negative for the worst

# Conclusions



## Salt Fog

- Ranked process for time in salt spray and pit numbers
  - T2 > T1 > T4 > T3

## Electrochemistry

- Ranked processes for various electrochemical parameters:
  - T2 > T1 > T4 > T3

**Excellent correlation → can use electrochemistry as a predictor of salt fog performance**

# Future Electrochemical Testing



- Determine best conversion coating processes on different types of aluminum alloys (5052, 6061, 7075) and different light metals (Mg, Zn/Ni)
- Product reliability control for new products
- Link exact time in salt spray to electrochemical performance for global cutoffs on coating performance
- Different pretreatments to determine best performing full process rather than just optimizing one step of the pretreatment

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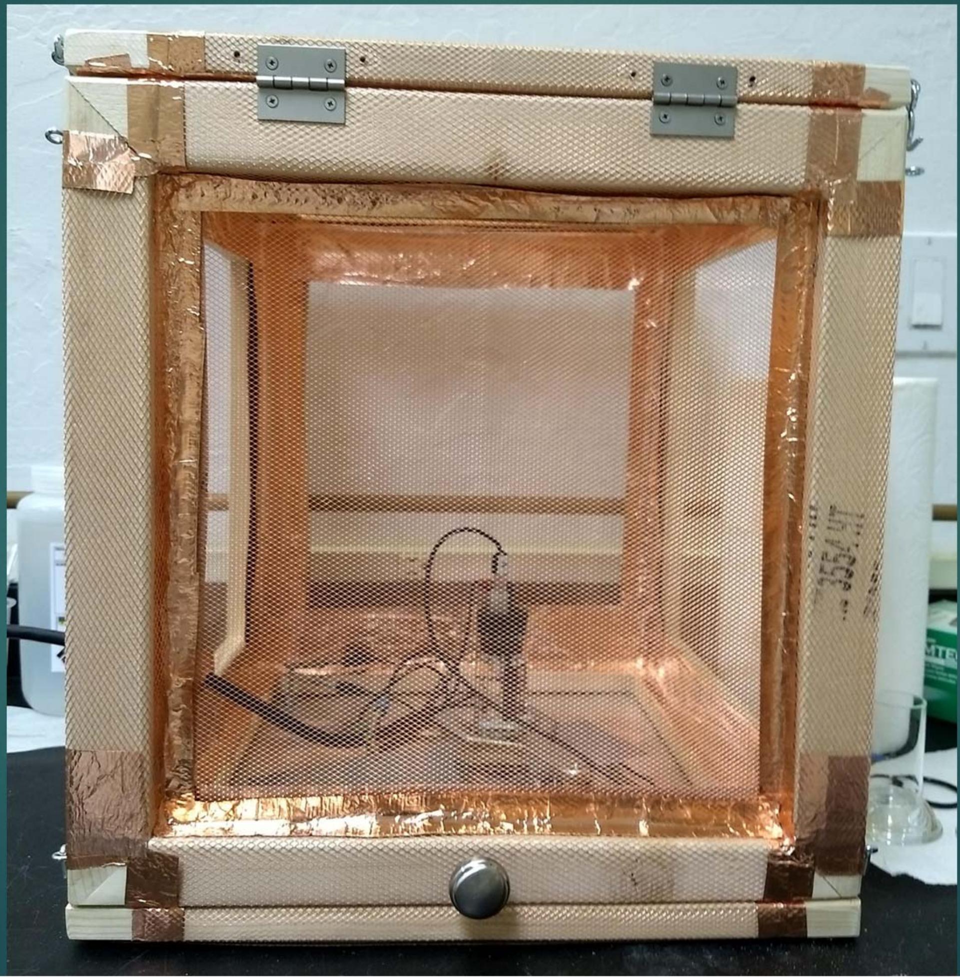
# Questions?

See us at Booth 1118

# Supplemental Slides

# Full Faraday Cage with Electrochemical Cell Setup





# Fitting with Gamry software- Levenberg-Marquardt algorithm

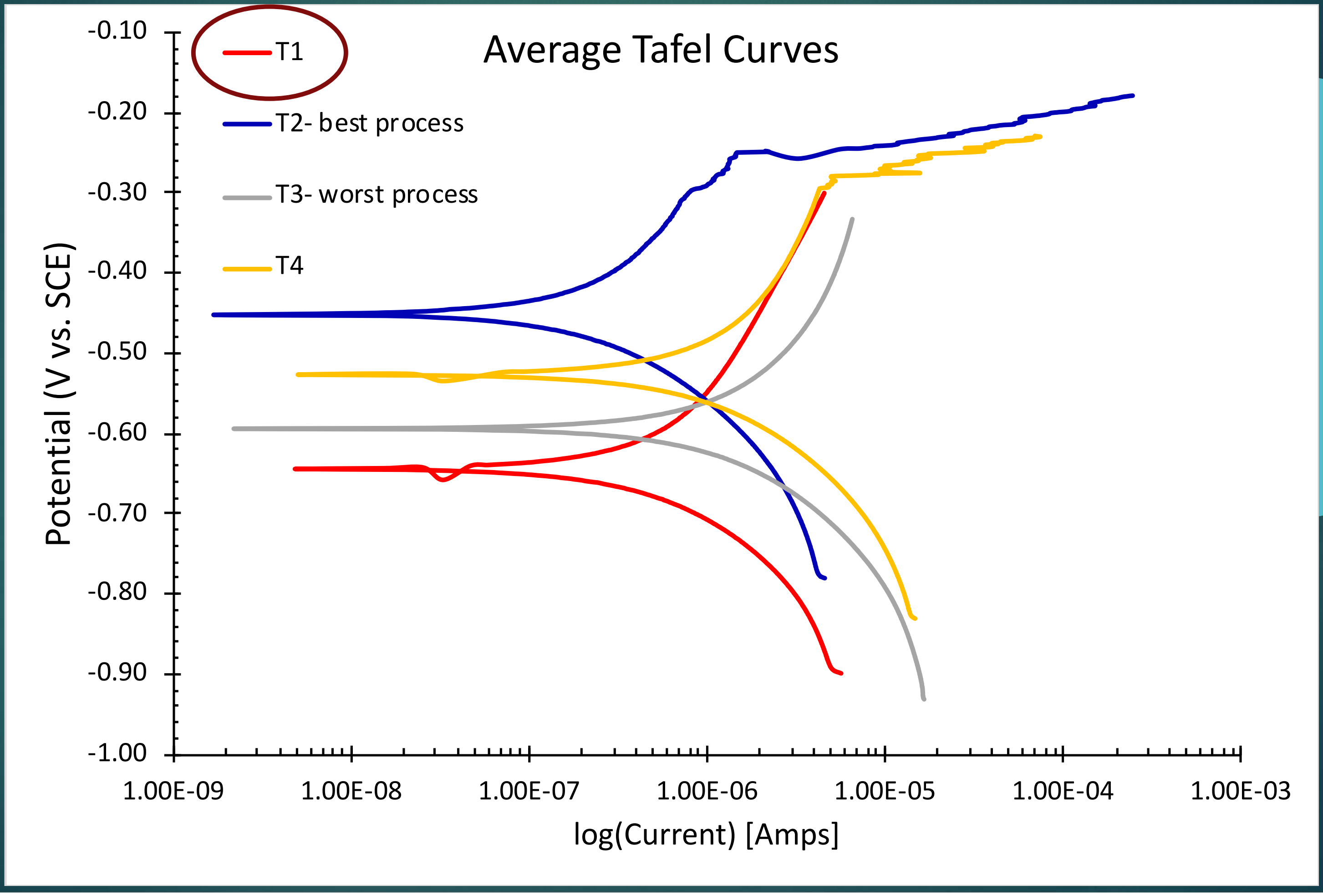


- Damped least -squares method
  - Set of data pairs, fit to a curve model where the sum of the squares of the deviations from actual data are minimized
  - Iterative process, with an initial guess provided then algorithm converges on the minimum deviation
  - Damping factor adjusted at each iteration to slowly approach the actual minimum
- Interpolates between Gauss-Newton algorithm and gradient descent
  - More robust than Gauss-Newton, but slower to fit

Levenberg, Kenneth (1944). "A Method for the Solution of Certain Non-Linear Problems in Least Squares". Quarterly of Applied Mathematics. 2 (2): 164–168.

# Electrochemistry- Tafel Plots with Butler-Volmer Fitting in Harrison's Solution





# Salt Fog Results Compared to Electrochemistry- 10% v/v Harrison's Solution



| Panel name | Salt Spray Time (# pits) | Open Circuit Potential (V) | Polarization Resistance (Ω) | Coating Capacitance (Farads) | Corrosion Rate (mpy) | Corrosion Potential (V) |
|---|---|---|---|---|---|---|
| T1 | 336 hr (7) | -0.6000 | 24,280 | 2.81E-5 | 0.16 | -0.6450 |
| T2 | 840 (6, 10) | -0.4800 | 98,640 | 0.38E-5 | 0.03 | -0.4520 |
| T3 | 336 (four panels with 5+) | -0.6320 | 11,300 | 0.31E-5 | 0.24 | -0.5940 |
| T4 | 336 (one panel with 5+, three others starting to pit) | -0.5300 | 15,500 | 0.23E-5 | 0.51 | -0.5260 |

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