Anodic and Cathodic Limitations on Localized Corrosion and Stress Corrosion Cracking Propagation of Stainless Steel 304L in Atmospheric Environments

R. M. Katona[1,2]

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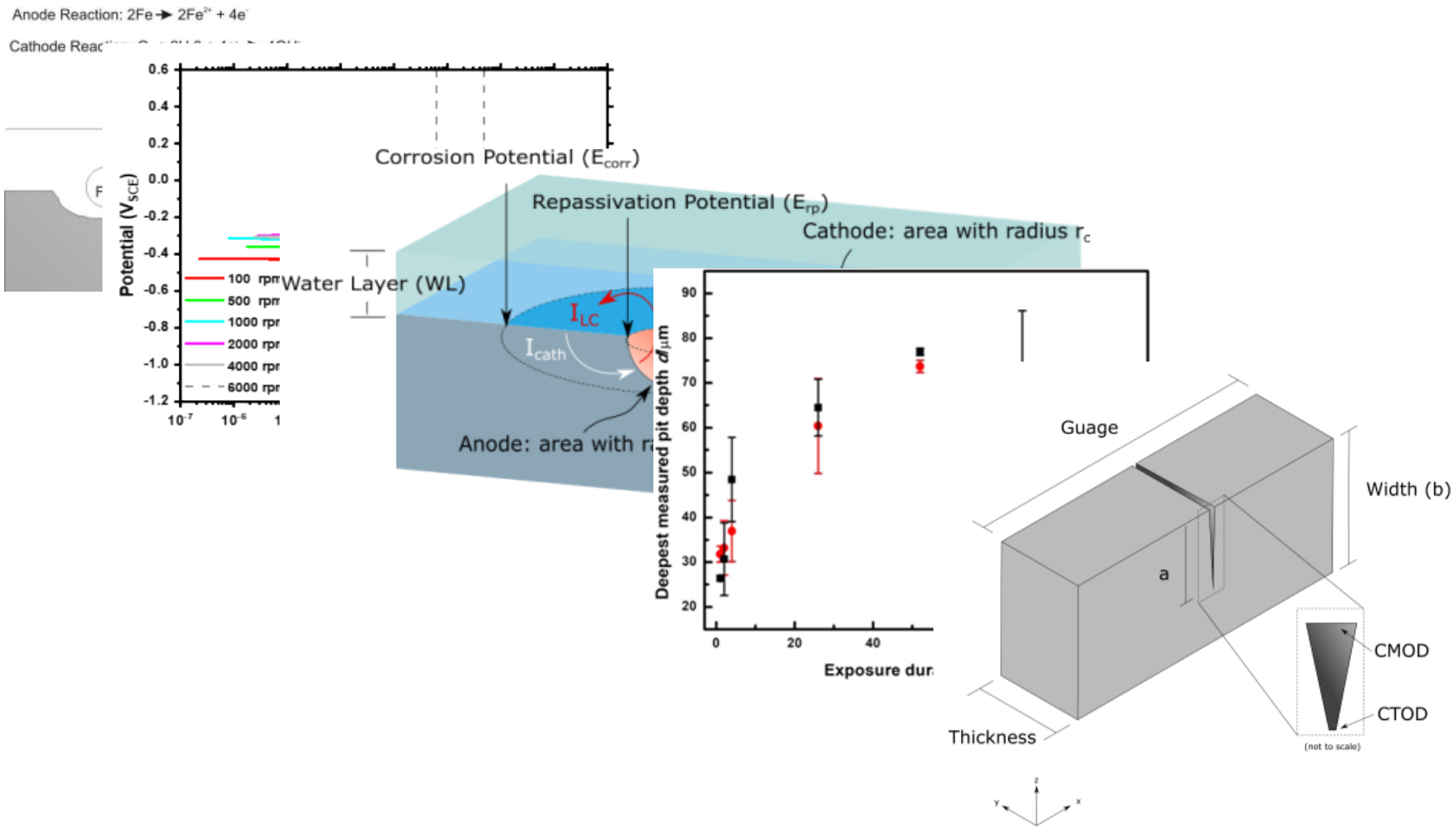
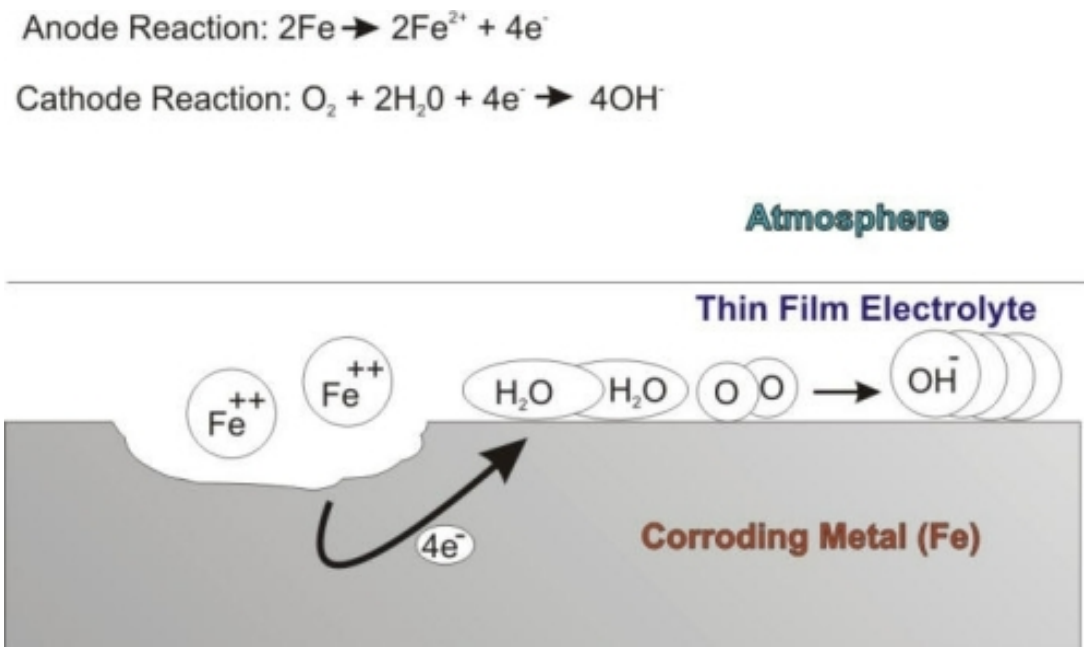
Overview


Anode Reaction: 2Fe → 2Fe2+ + 4e-
Potential (VSCE)
100 rpm
500 rpm
1000 rpm
2000 rpm
4000 rpm
6000 rpm
Corrosion Potential (Ecorr)
Repassivation Potential (Erp)
Cathode: area with radius rc
Water Layer (WL)
ILC
Icath
Anode: area with r
Deepest measured pit depth d µm
Exposure dur
Guage
Width (b)
a
CMOD
CTOD
Thickness
(not to scale)

Atmospheric corrosion

- Alloys are commonly exposed to atmospheric, marine environments
- Through salt enabled deliquescence or salt spray the creation of a water layer (WL) on the surface of an alloy allows for a corrosion cell to form
- Many factors will influence the corrosion
  - WL
  - Solution composition
  - Solution concentration
  - Temperature
  - Alloy
  - Reaction mechanisms



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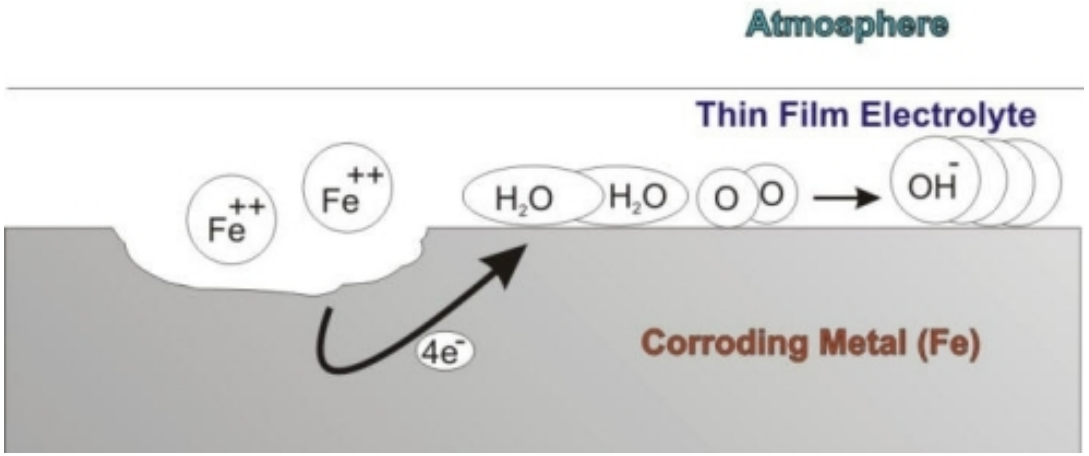
Anode Reaction: $2Fe \rightarrow 2Fe^{2+} + 4e^-$

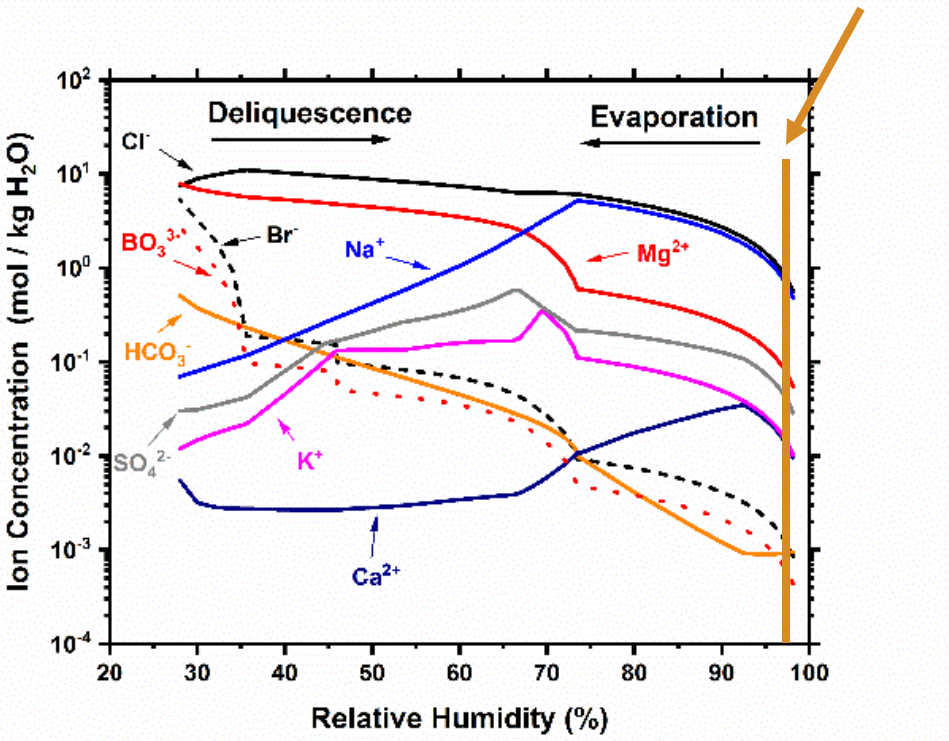
Cathode Reaction: $O_2 + 2H_20 + 4e^- \rightarrow 4OH^-$



Atmospheric Brines

- Dehydration of seawater brine shows wide variation in composition
- Important relative humidities:
  - Precipitation of NaCl ~ 75 % RH
  - Precipitation of $MgCl_2$ ~ 35 % RH

98 % RH ~ 0.6 M NaCl

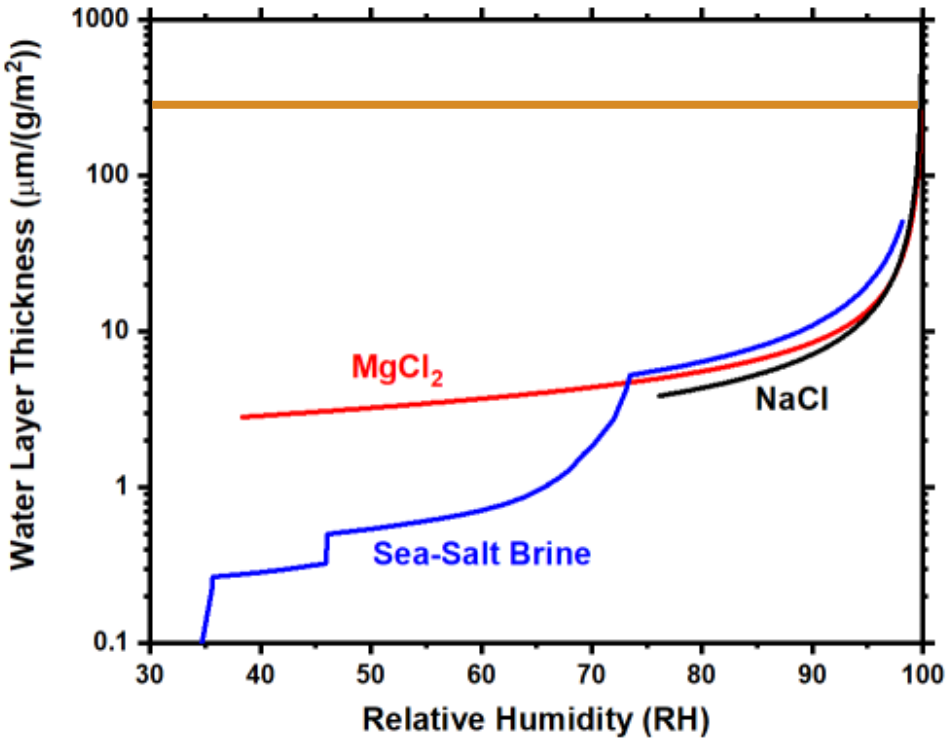


Thin Atmospheric Water Layers

- In atmospheric scenarios, salt enabled deliquescence is possible
- WL dependent upon:
  - Salt composition
  - Relative humidity
  - Temperature
  - Loading density

$$WL = \frac{LD * \rho_{sp}}{MW * C_{eq}}$$

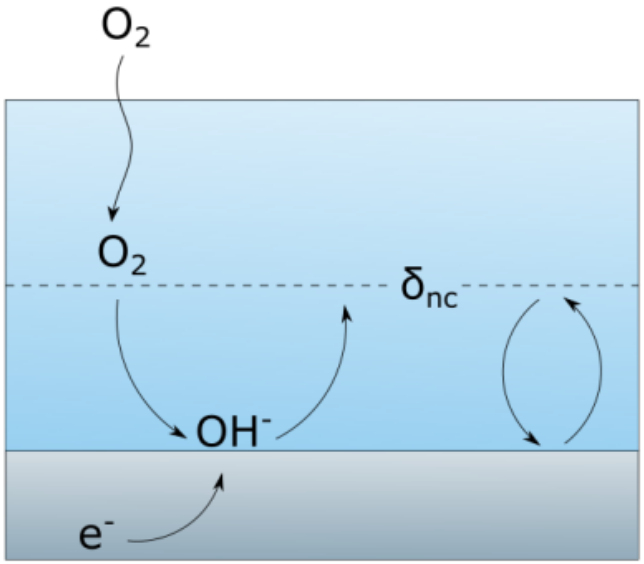
- $[Cl^-] \rightarrow WL$
- Under typical conditions a WL < 300 µm is expected

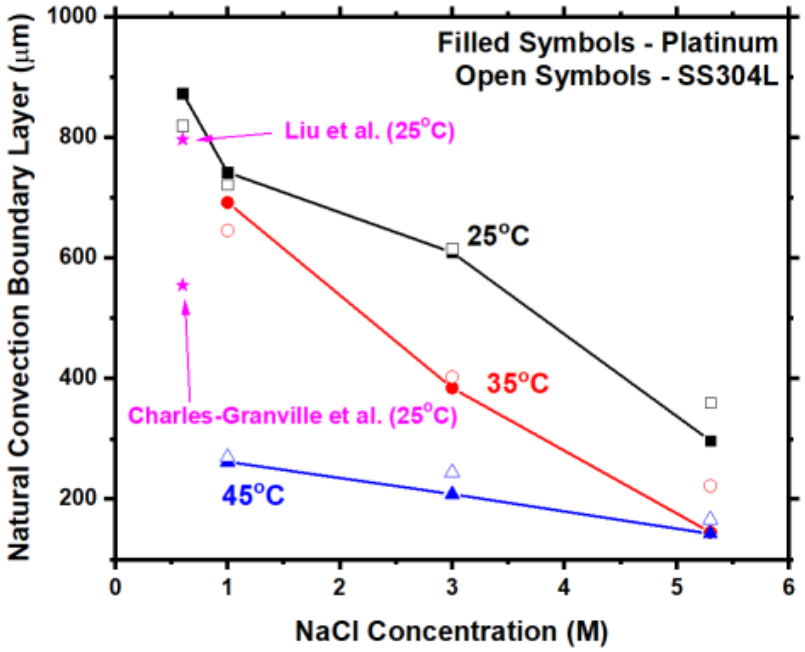


R.M. Katona, A.W. Knight, E.J. Schindelholz, C.R. Bryan, R.F. Schaller, R.G. Kelly. Electrocimicha Acta. Accepted. (2020).

What separates bulk from thin film conditions

- Natural convection separates bulk from thin film conditions





- Increasing chloride concentration and temperature decrease the natural convection boundary layer

Atmospheric corrosion

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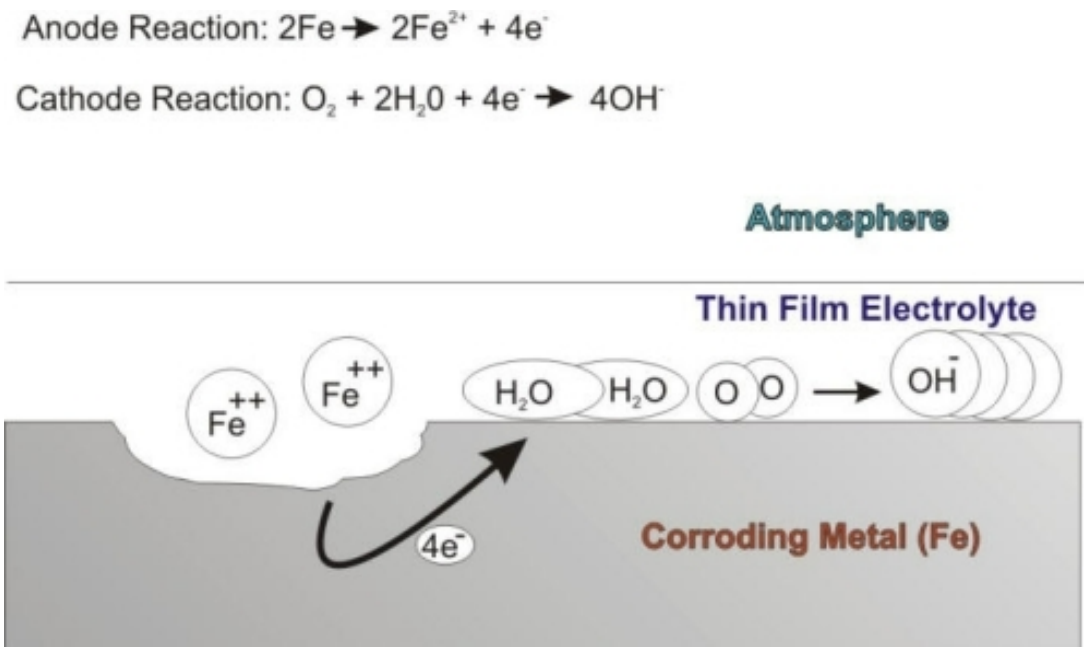
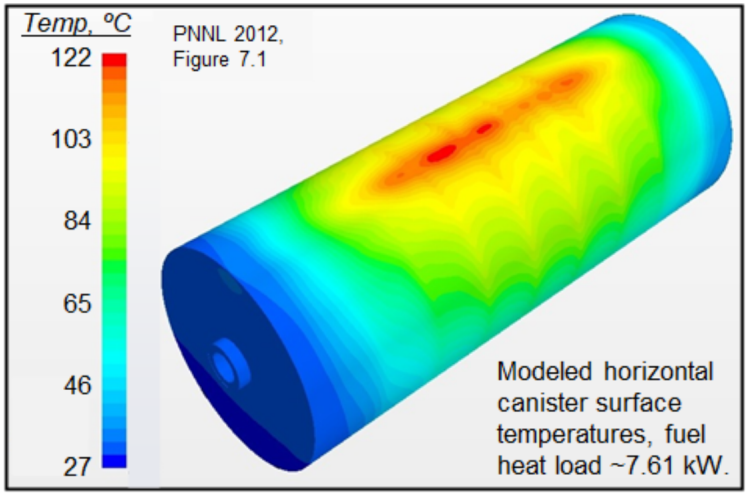
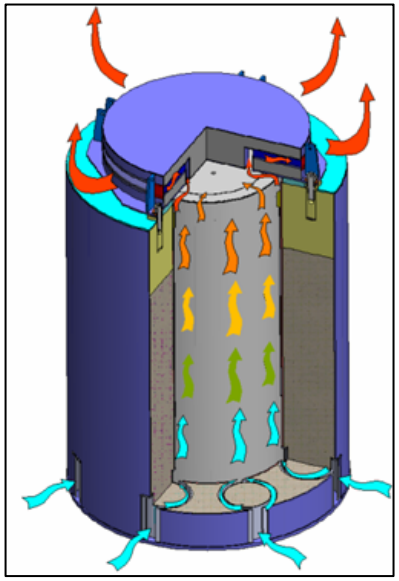
  - Solution composition
  - Solution concentration
  - ***Temperature***
  - Alloy
  - Reaction mechanisms



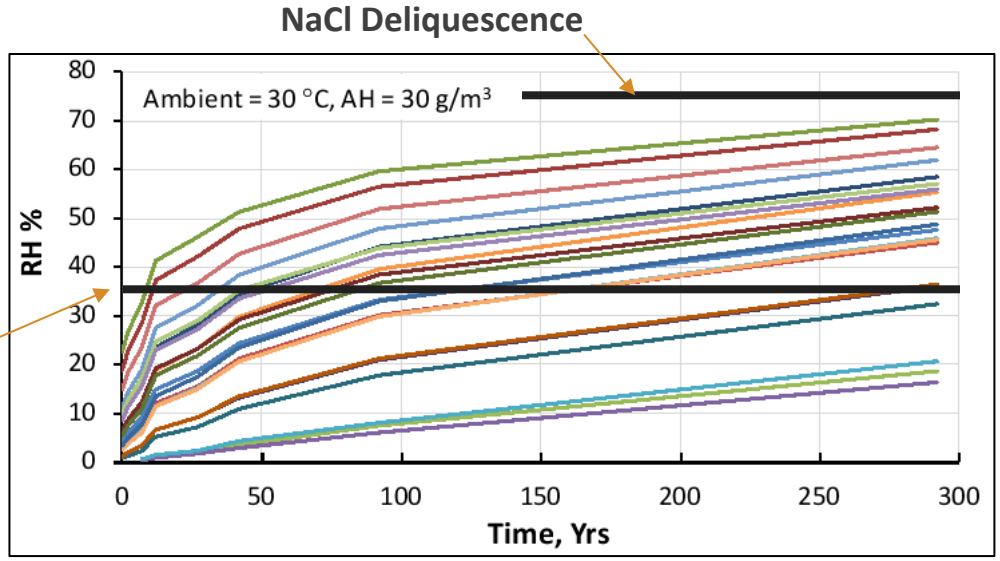
Temperatures

- Seasonal and diurnal fluctuations of temperature
- One specific application of work is for spent nuclear fuel storage
- Combination of ambient temperatures, ambient RH, and surface temperature





FCRD-UFD-2012-000114 Figure 7.3



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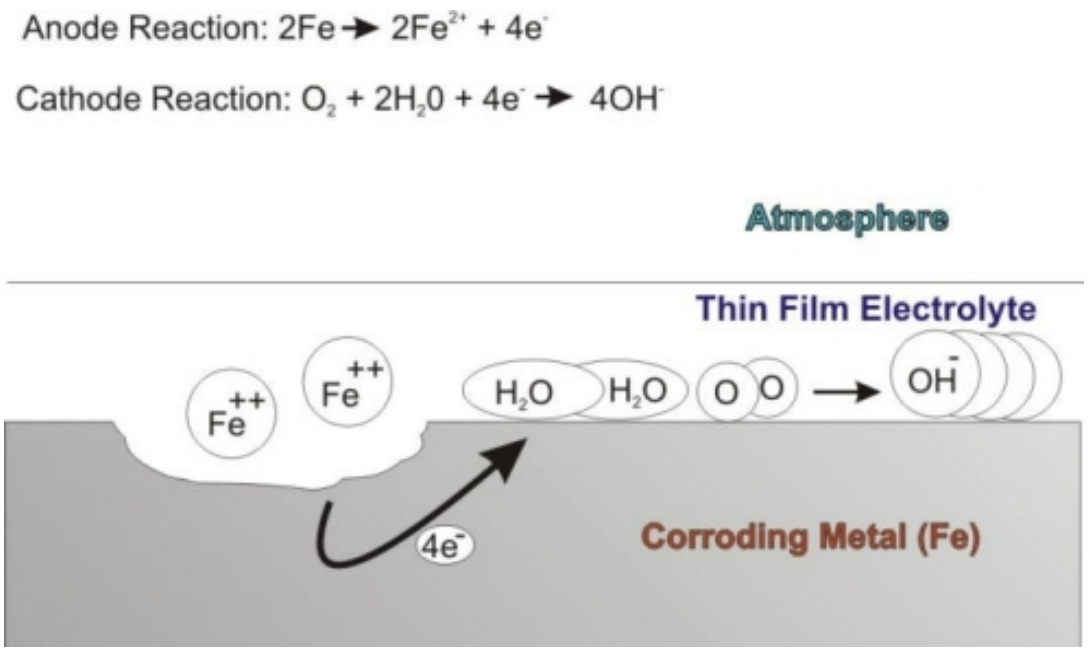
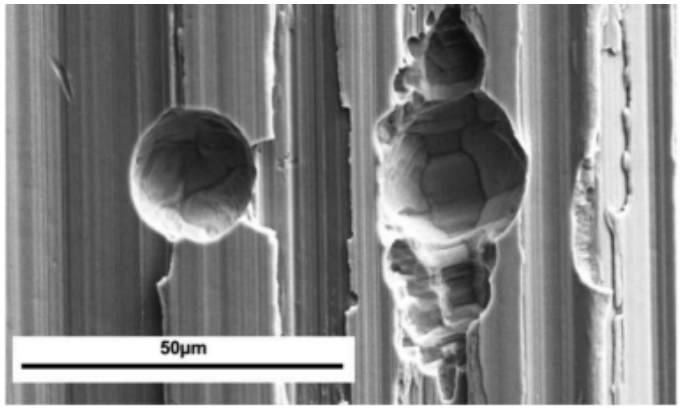
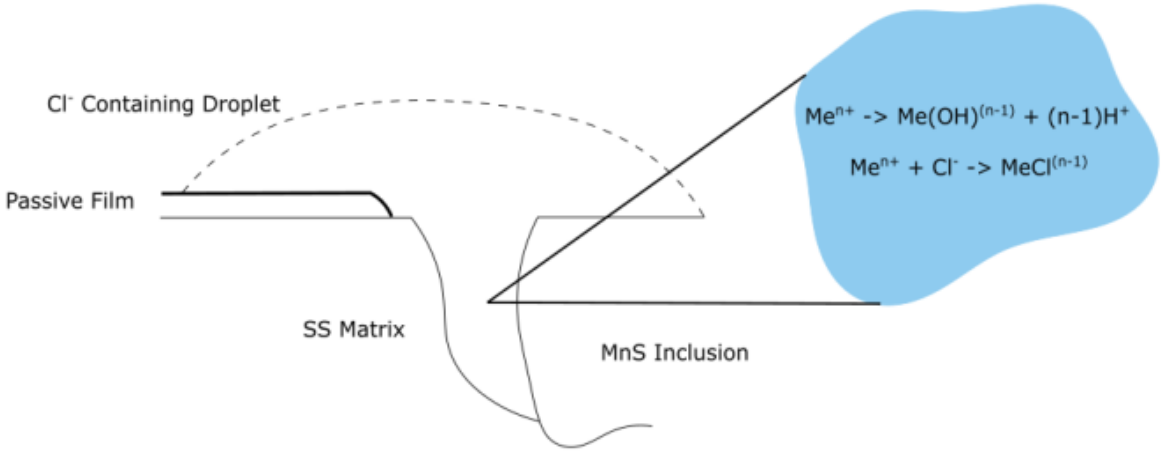
  - Temperature
  - ***Alloy***
  - ***Reaction mechanisms***



SS Susceptibility to Localized Corrosion

- Failure mechanisms for SS
  - Pitting corrosion, crevice corrosion, and stress corrosion cracking
- Pitting corrosion typically initiated at magnesium sulfide (MnS) inclusions
- Creation of an aggressive environment through metal ion hydrolysis





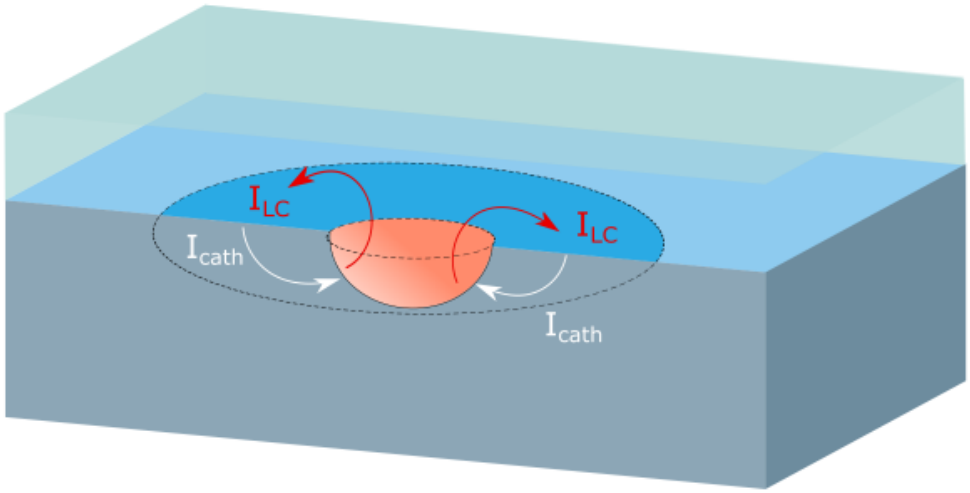
T.D. Weirich, et al., J. Electrochem. Soc. 166 (2019) C3477–C3487.

SS Reaction Mechanisms

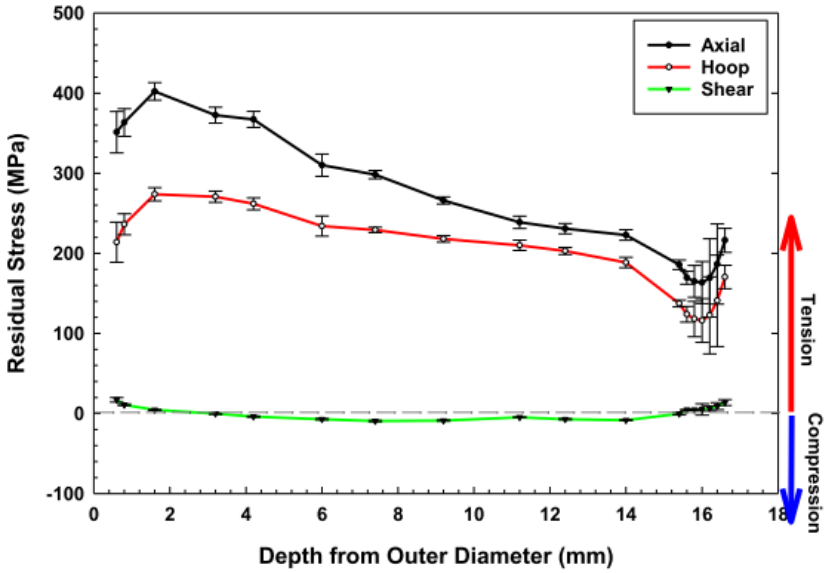
- There are various mechanisms for pit initiation, however always will have an aggressive environment in the pit
- Dissolution supported by cathodic reduction reaction
- In atmospheric scenarios typically thought to be oxygen reduction reaction

$$O_2 + 2H^+ + 4e^- \rightarrow 4OH^-$$

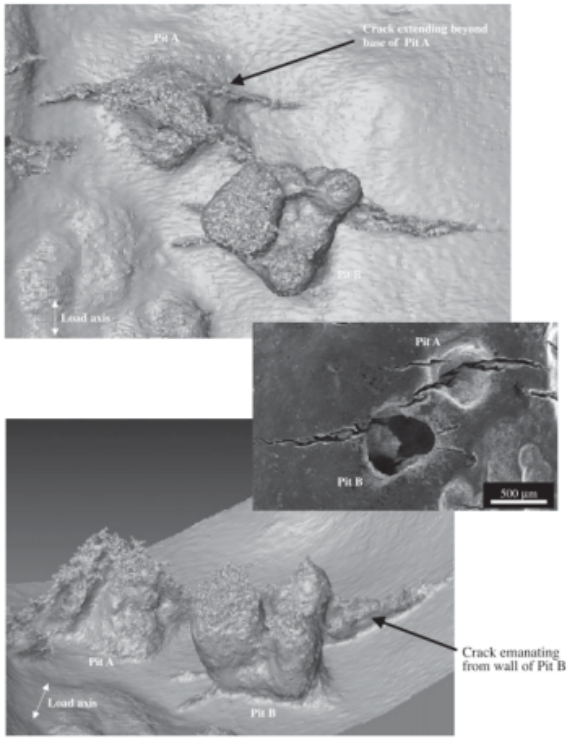
- Literature determined reaction mechanisms focus on dilute solutions typically at room temperature



Stress Corrosion Cracking



Residual stress in SS304L canister for SNF applications [1]



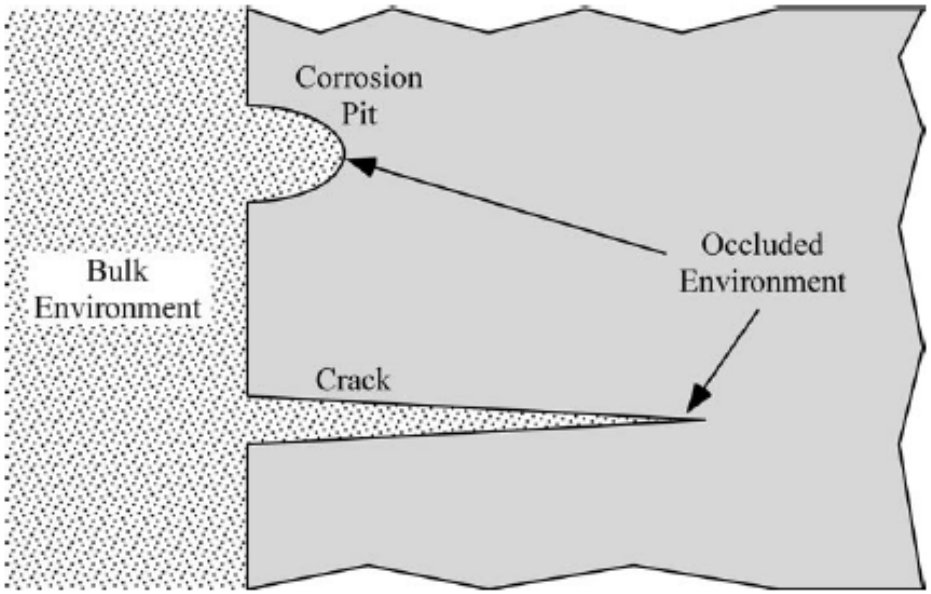
Cracks immerging from pitting corrosion damage [2]

- SCC is characterized by susceptible material in a susceptible environment undergoing cracking at a stress intensity below the fracture toughness of the material

[1] Bryan, C. R. and Enos, D. G., *Final Report: Characterization of Canister Mockup Weld Residual Stresses*, 2016

[2] Horner, D. A., et al., *Corrosion Science*, Vol. 53, 2011, p. 3466–3485

Stress Corrosion Cracking

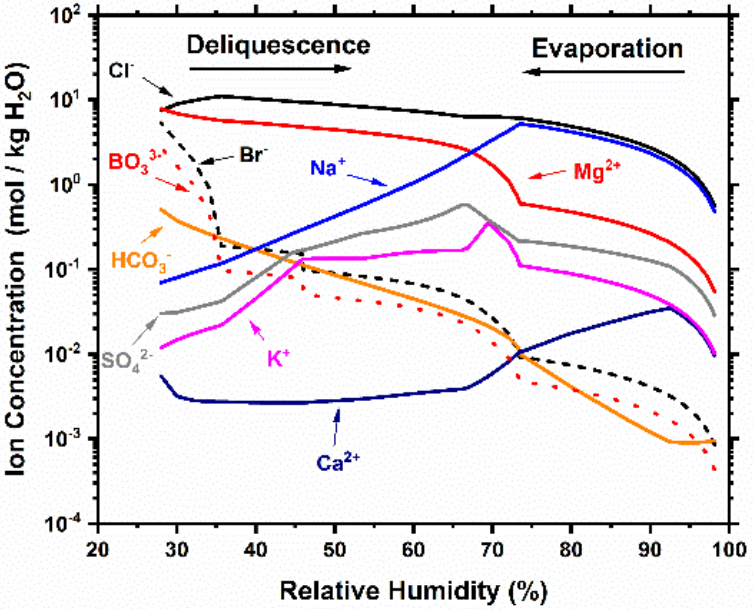


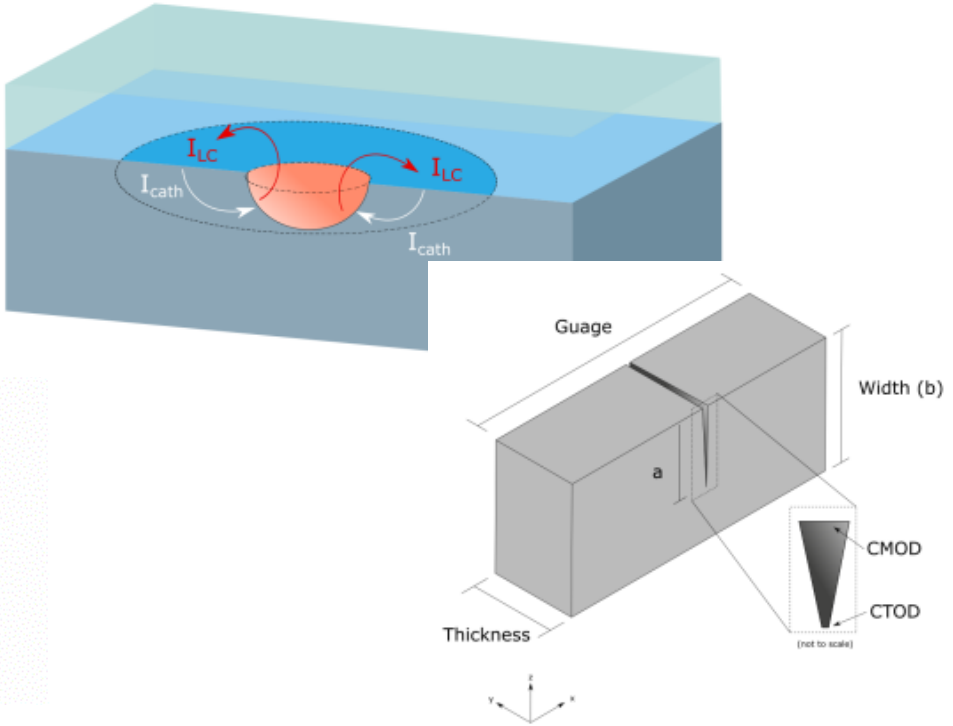
- Two things are generally accepted for SCC:
  - Bulk chemical and electrochemical conditions not maintained down the crack
  - Stress state and chemical/electrochemical conditions local to the crack tip control SCC
- Need to understand the occluded environment

[1] Anderson, T. L., *Fracture Mechanics - Fundamentals and Applications* T. L. Anderson, Editor, Third., 2005

What is missing in localized corrosion?

- Corrosion reaction mechanisms in high chloride containing solutions across a wide range of relative humidity and temperature





- Prediction and validation of localized corrosion in atmospheric environments containing various solution properties

Critical Dissertation Questions

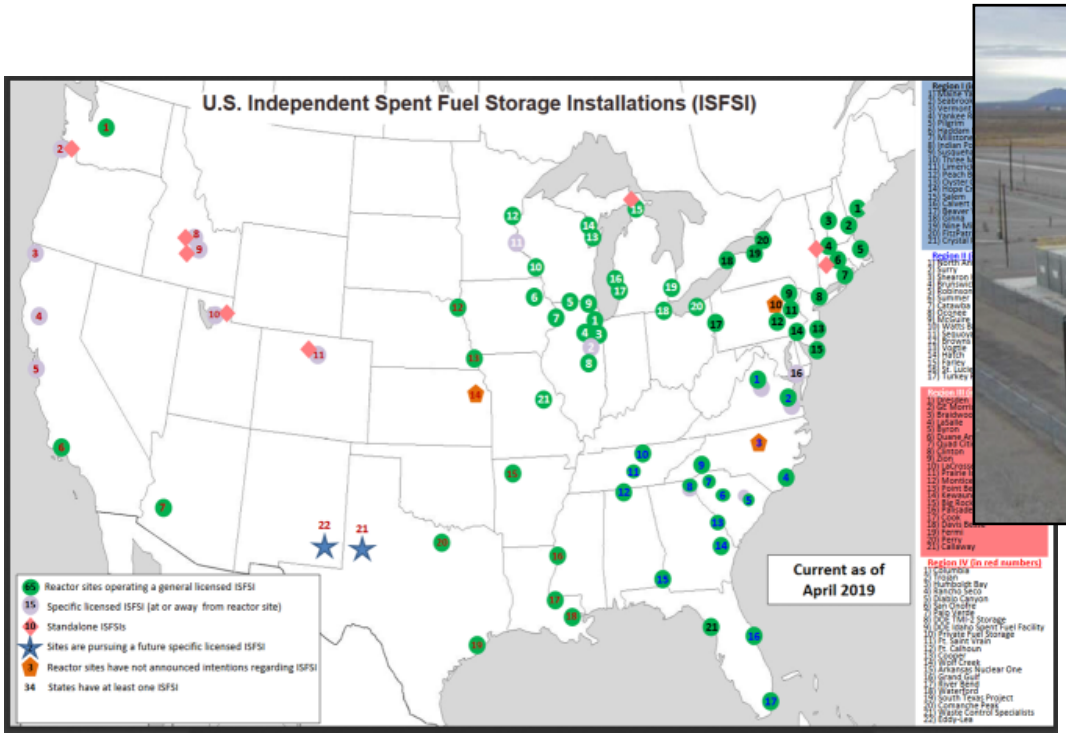
- What mechanisms control how external (solution composition, solution concentration, geometry, temperature) and internal (material) factors affect pitting and stress corrosion?
- To what extent can we predict damage from localized corrosion and stress corrosion cracking and what are the governing factors in these predictions?

Critical Dissertation Questions

- What ***mechanisms control*** how external (solution composition, solution concentration, geometry, temperature) and internal (material) factors affect ***pitting and stress corrosion?***
- To what extent can we ***predict damage from localized corrosion*** and stress corrosion cracking and what are ***the governing factors*** in these predictions?

General Dissertation Question

- Knowing pertinent weather and temperature related data, can we identify which regions/canisters that are potentially the worse for localized corrosion related scenarios?
- Can we understand effects of the environment on stress corrosion cracking?



Outline of Dissertation

- Chapter 2 – Cathodic Kinetics
- Chapter 3 – Water Layer
- Chapter 4 – Anodic Kinetics
- Chapter 5 – Modeling Corrosion
- Chapter 6 – Modeling SCC

- Environmental Factors
  - Temperature
  - Chloride concentration
  - Composition

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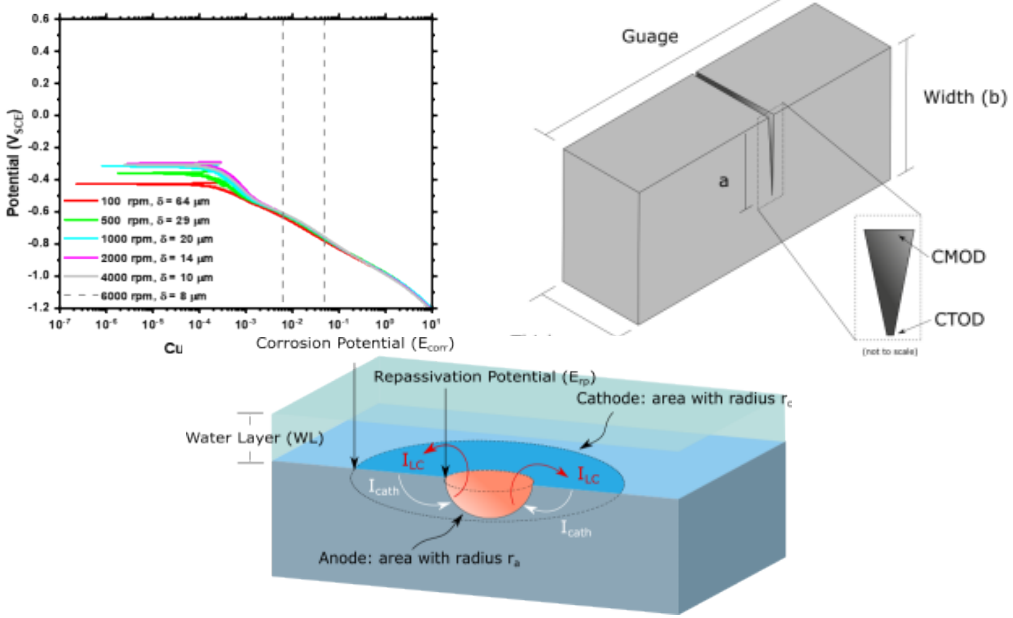

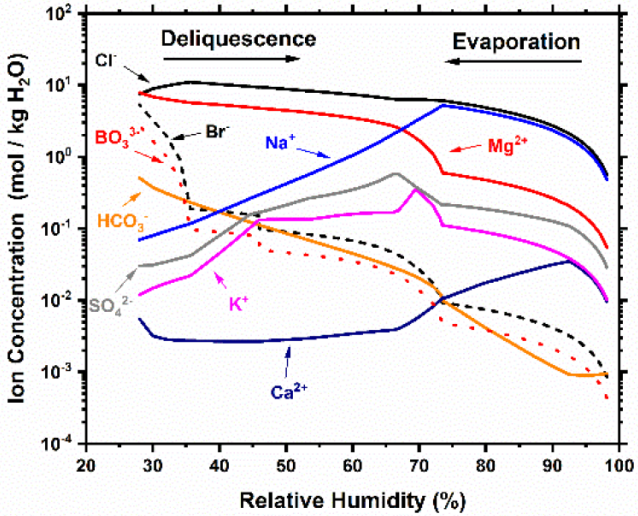

Overview

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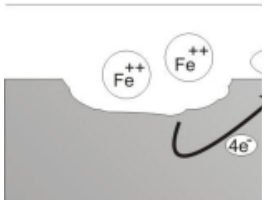
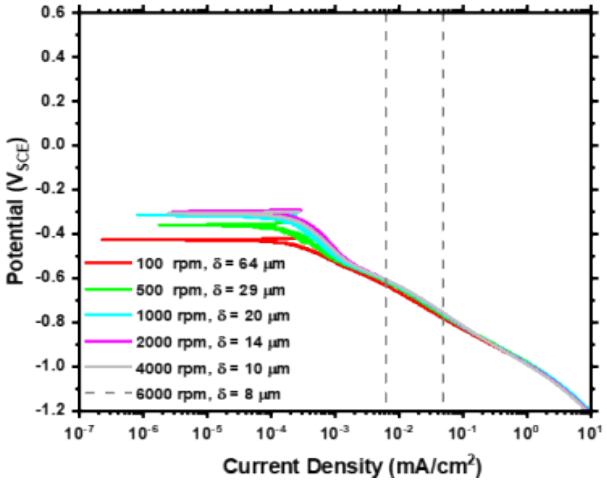
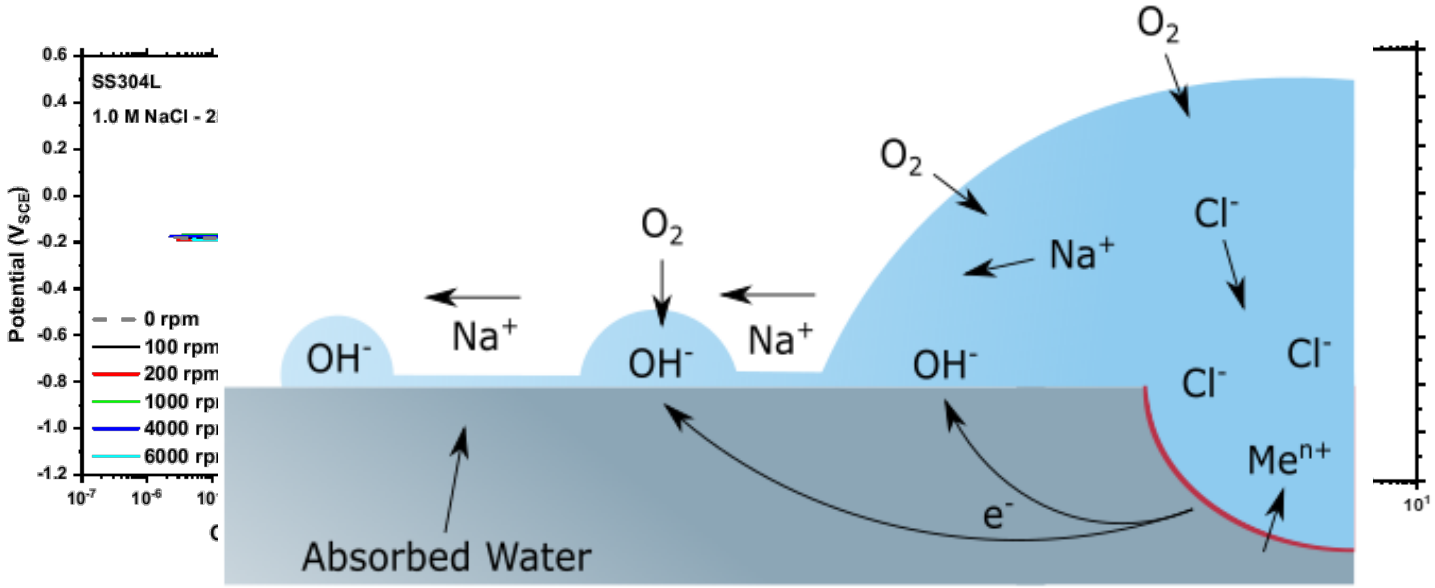




Cathodic Reaction Mechanisms

- For NaCl solutions (high RH), oxygen reduction (ORR) is dominant cathodic reduction reaction

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$



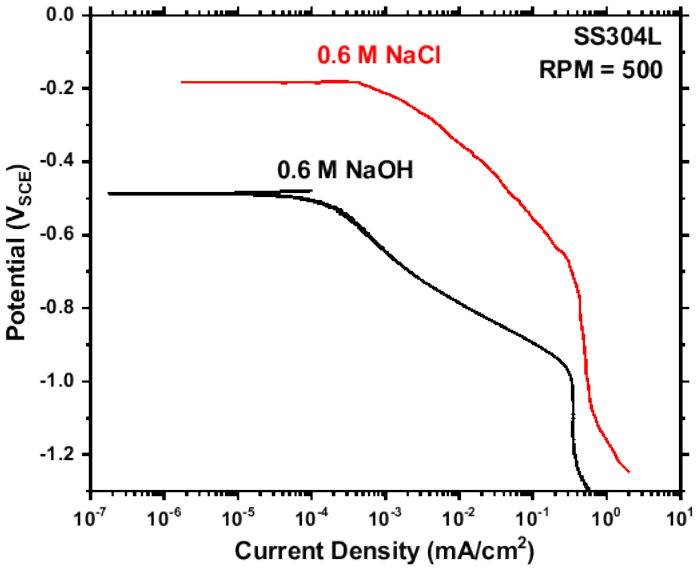
- Holds for all concentrations (0.6 – 5.3 M) and temperatures (25-45 ˚C) of NaCl explored

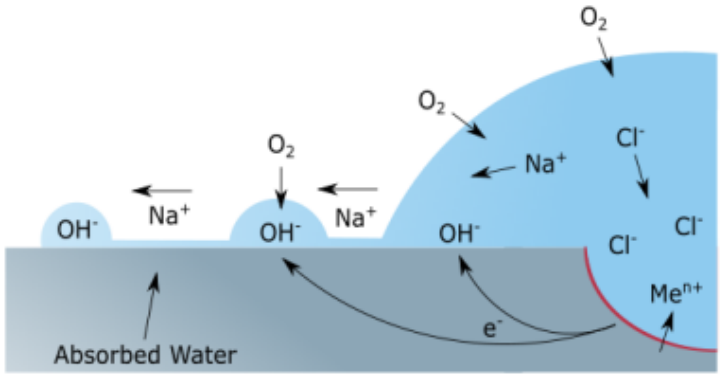
R.M. Katona et al., J. Electrochem. Soc. 168 (2021) 031512.

Cathodic Reaction Mechanisms

- NaOH solutions (evolved cathode of NaCl) exhibit one-electron transfer ORR as rate limiting step

$$O_2 + e^- \leftrightarrow O_2^-$$

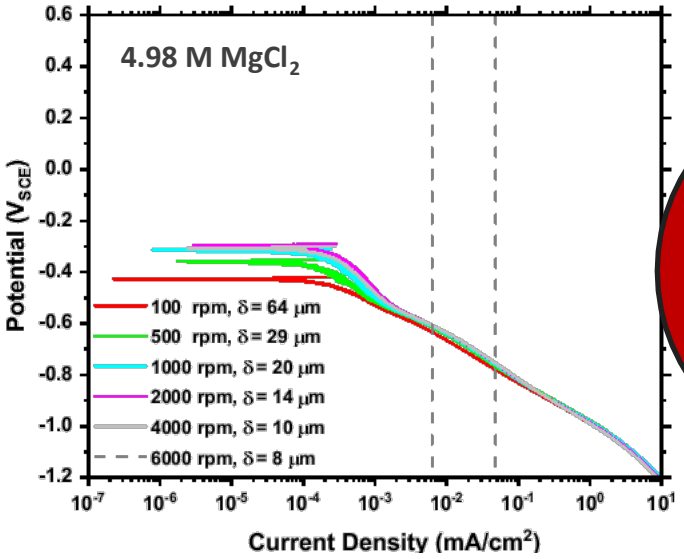


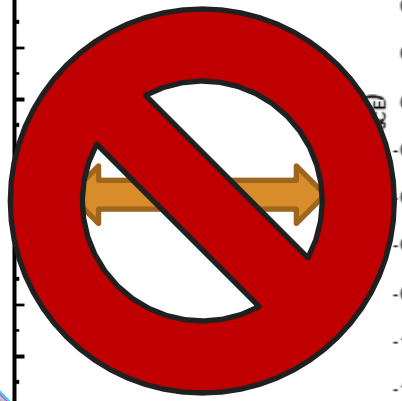


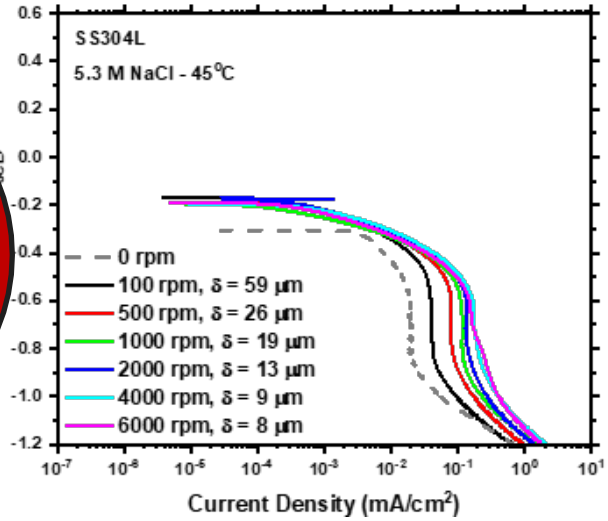
- ORR suppression in NaOH solutions
- Holds for high concentrations of NaOH
- Decrease in current density in NaOH solution in comparison to NaCl solutions

R.M. Katona, et al., Submitted to Journal of the Electrochemical Society (2021).

Cathodic Reaction Mechanisms



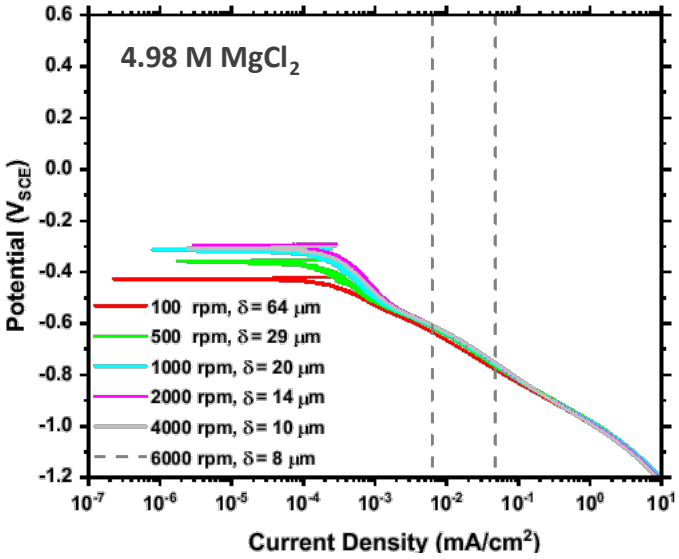


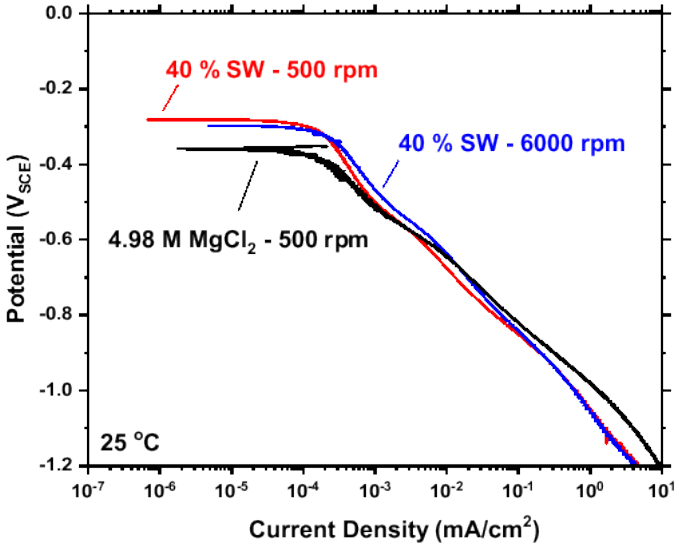


R.M. Katona, et al., Corros. Sci. 177 (2020) 108935.

Cathodic Reaction Mechanisms

- Hydrogen evolution (HER) dominant in $MgCl_2$ brines (low RH)
- Also present at elevated temperatures and for seawater solutions



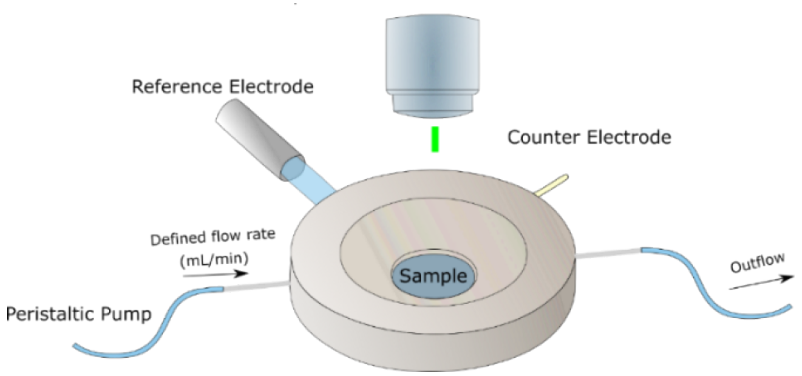


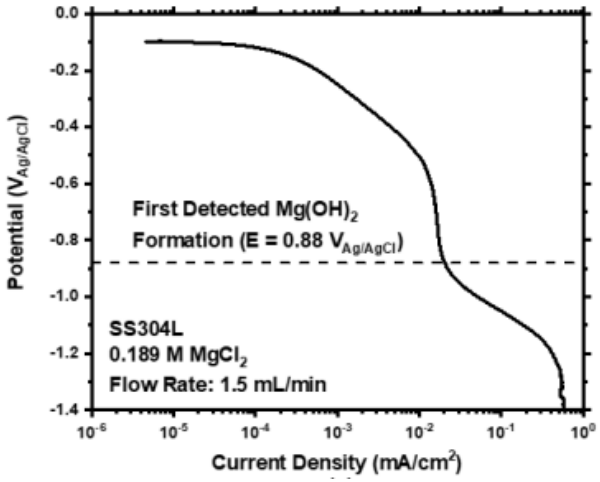
- Proposed HER due to ORR suppression due to precipitate formation in brine and localized corrosion

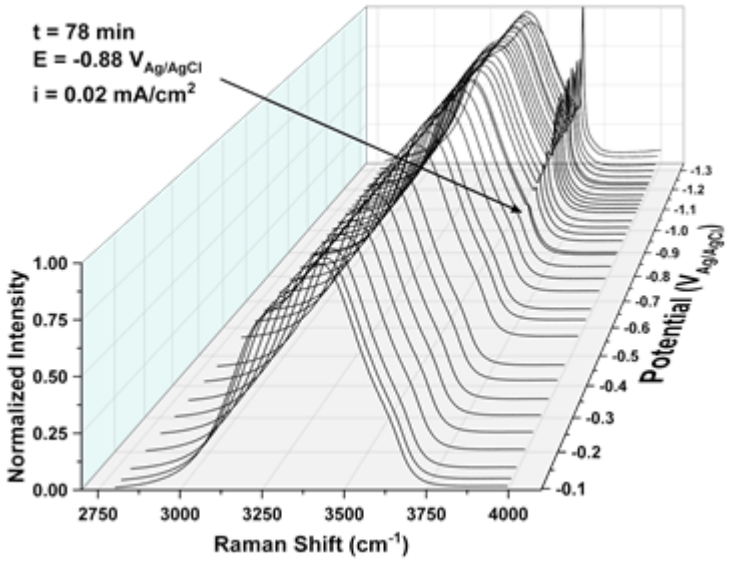
R.M. Katona, et al., Corros. Sci. 177 (2020) 108935.

In-situ Spectroelectrochemistry

- Visualization of precipitate formation in $MgCl_2$ solutions as a function of cathodic polarization





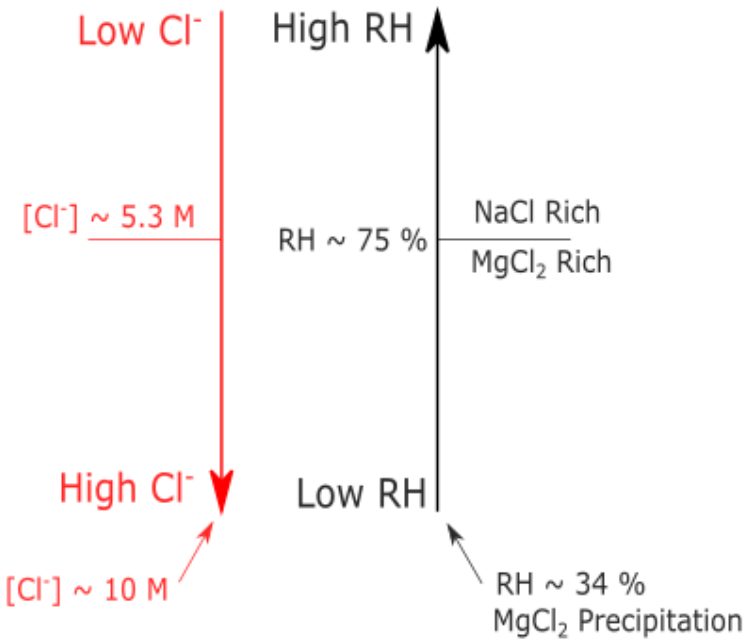


- $Mg(OH)_2$ identified
  - ORR suppression
  - $MgCO_3$ not kinetically stable
- Technique development to control boundary layer with flow rate

R.M. Katona, et al., Electrochem. Commun. 118 (2020) 106768.

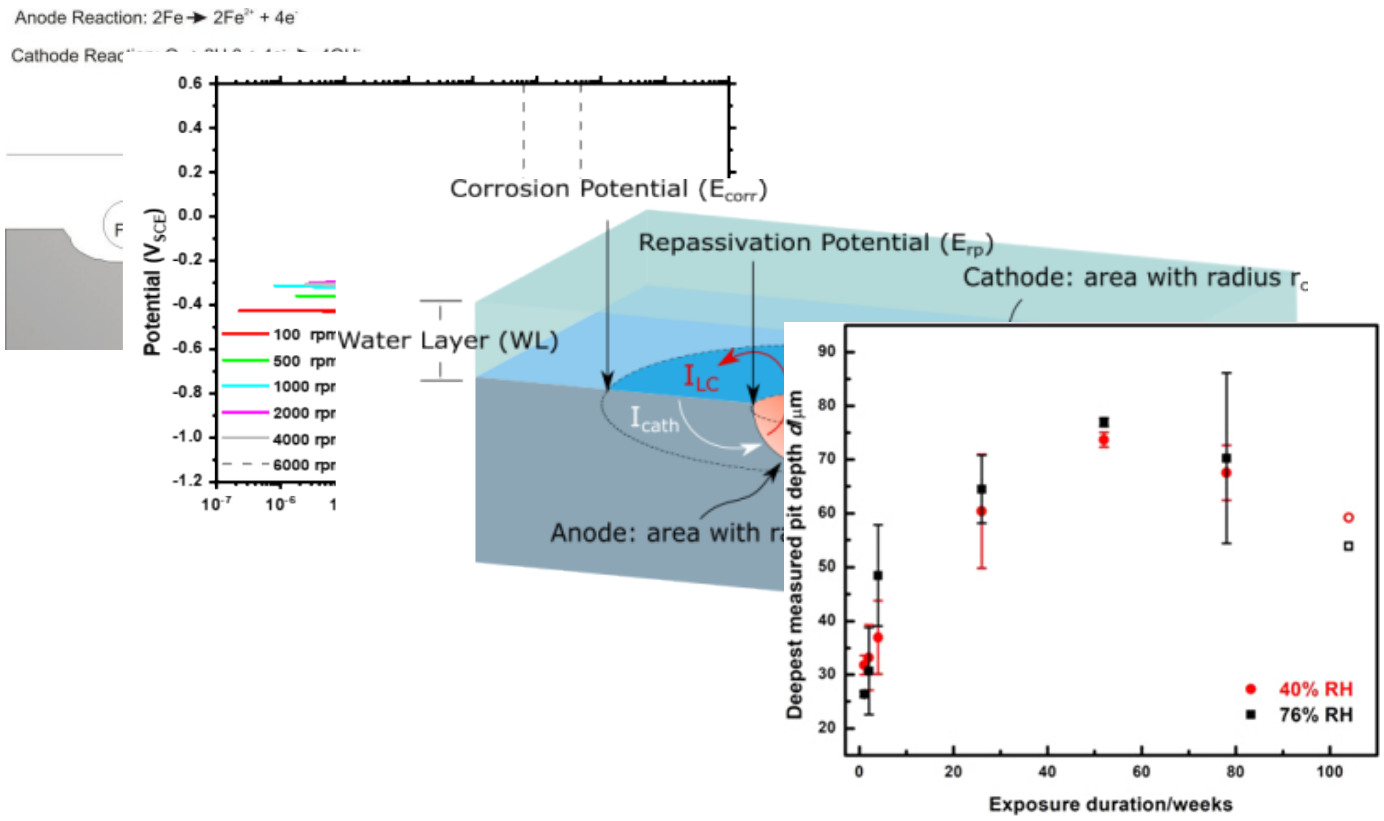
Cathodic Kinetics Summary

- Across wide range of solutions, various mechanisms are dominant



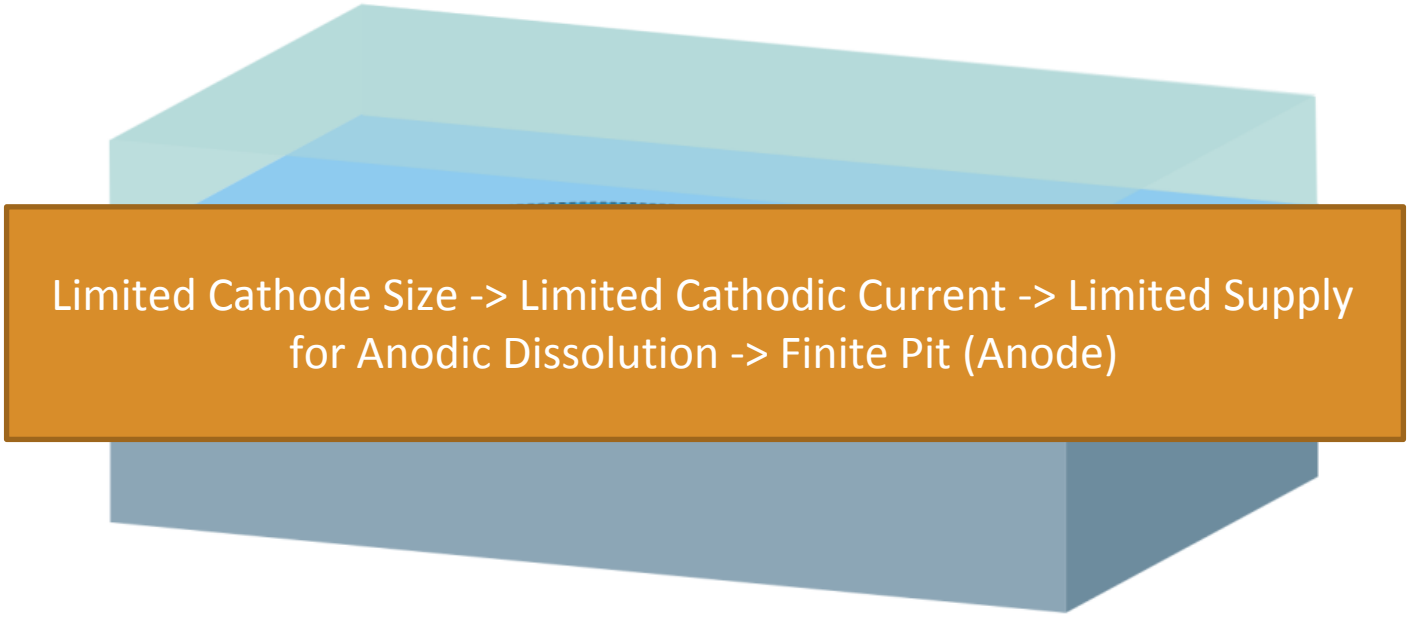
- Now that we know mechanisms, we can model corrosion scenarios

Overview


Anode Reaction: 2Fe → 2Fe2+ + 4e-
Cathode Reac
Potential (VSCE)
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
10-7
10-6
100 rpm
500 rpm
1000 rpm
2000 rpm
4000 rpm
6000 rpm
Corrosion Potential (Ecorr)
Repassivation Potential (Erp)
Cathode: area with radius rc
Water Layer (WL)
ILC
Icath
Anode: area with r
Deepest measured pit depth d/μm
90
80
70
60
50
40
30
20
0
20
40
60
80
100
Exposure duration/weeks
40% RH
76% RH

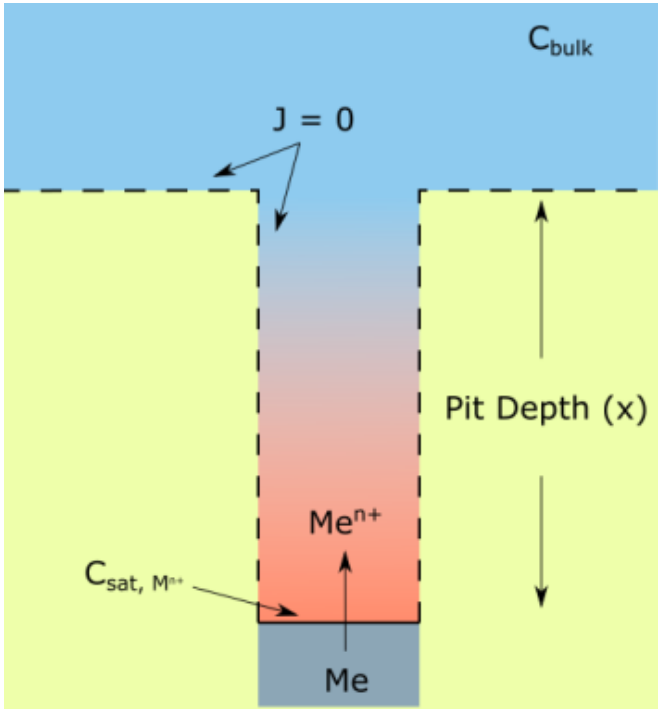
Modeling Localized Corrosion

- In chloride environments, pitting is highly probable, therefore worried about **maximum extent of corrosion**
- Pits (anode) are inherently coupled to the surrounding cathode



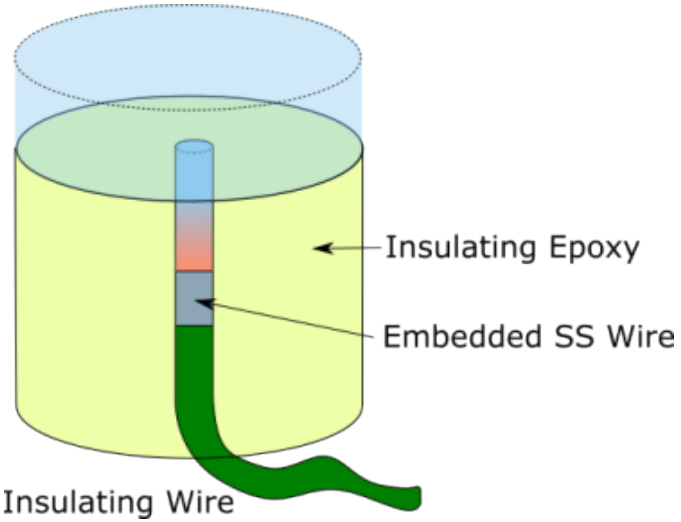
- Anode can only grow if sufficient supply from cathode
- Cathode current limited by reaction mechanism and physical geometry (water layer, sample size, etc.)

Modeling Localized Corrosion



Schematic of 1-D scenario with active alloy surrounded by no flux (J) boundary (J=0)

Studied through lead-in-pencil experiments under a salt film (full saturation) [1]

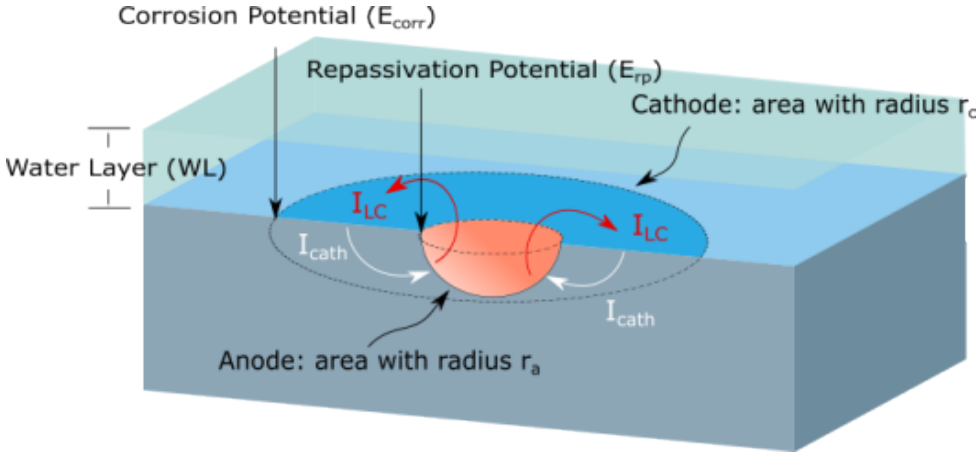


- Battle between outward ion diffusion and maintaining critical environment
- Galvele 1-Dimensional analysis yielded a pit stability product $(i \cdot x)$ [2]
  - Where i is current density and x is the pit depth

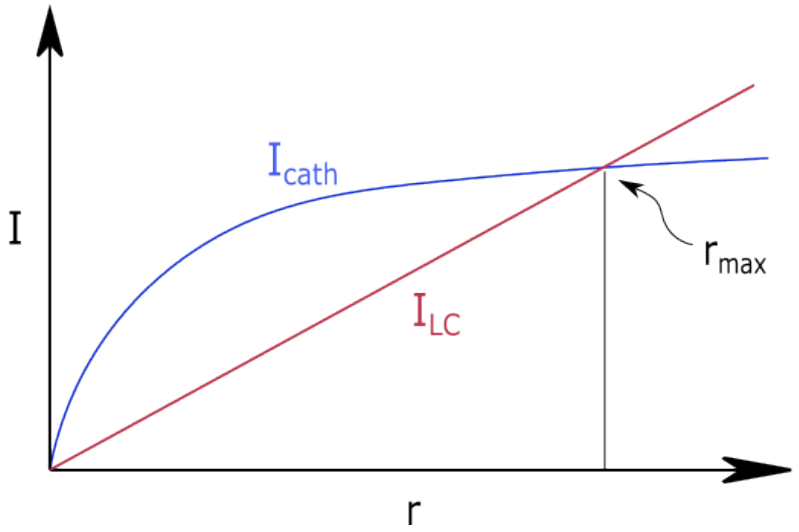
[1] Srinivasan, J. and Kelly, R. G., *Corrosion*, Vol. 73, 2017, p. 613–633
[2] Galvele, J. R.,, *Corrosion Science*, Vol. 21, 1981, p. 551–579

Modeling Localized Corrosion

- Finite cathodic current given by ohmic drop in thin electrolyte layers
- Anodic demand determined by ability to maintain aggressive environment



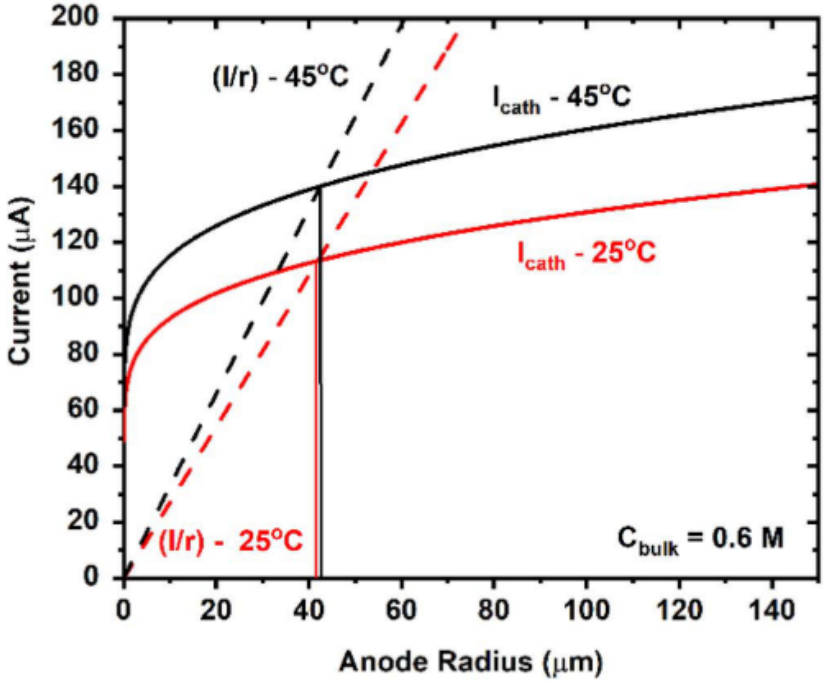
$$I_{c,max} \sim f(\kappa, WL, E_{OCP}, E_{RP}, r_a, i_{eq})$$

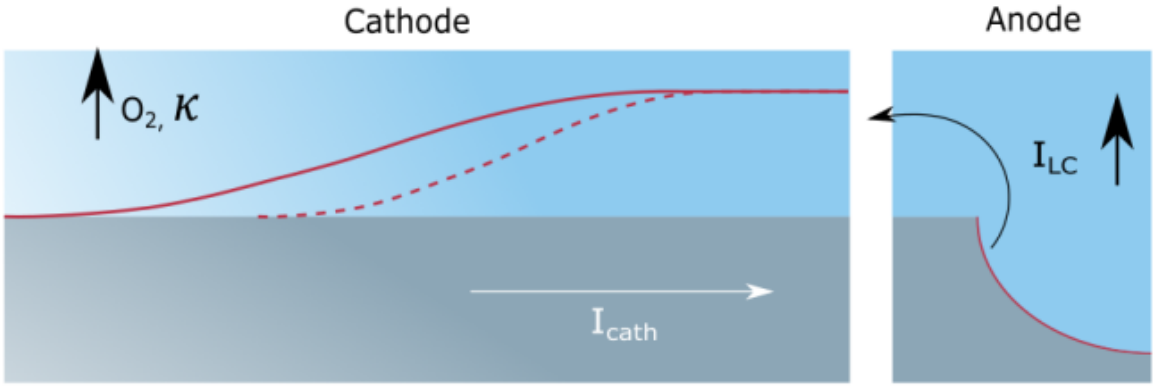


Anodic Demand = Cathodic Supply -> Max pit

Elevated Temperatures

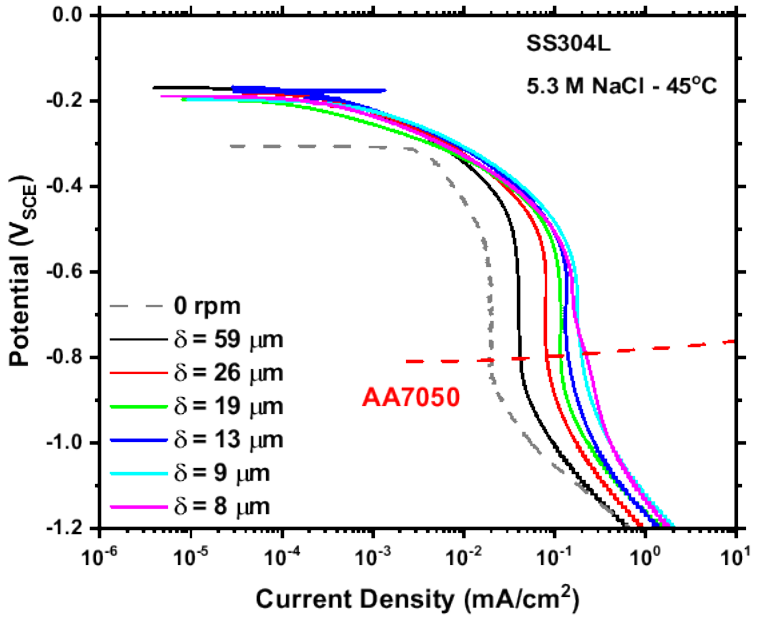
- Predicted maximum pit sizes relatively invariant to temperature fluctuations
- Competing phenomena between cathode supply and anodic demand
- Temperature variations may not be as important

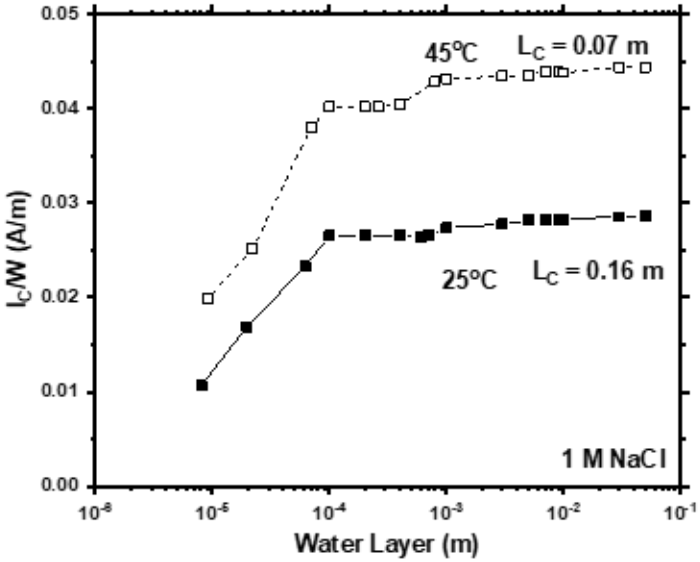




R.M. Katona, et al., J. Electrochem. Soc. 166 (2019) C3364–C3375.

Similar trends seen in Galvanic Modeling

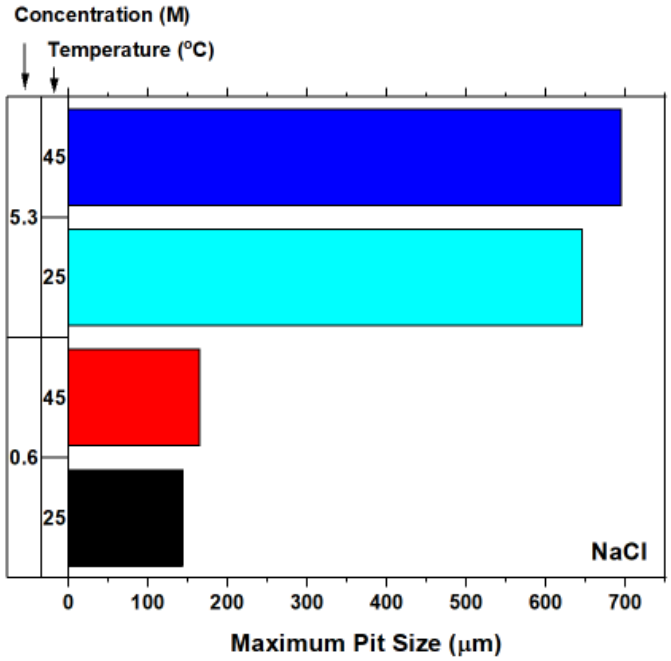


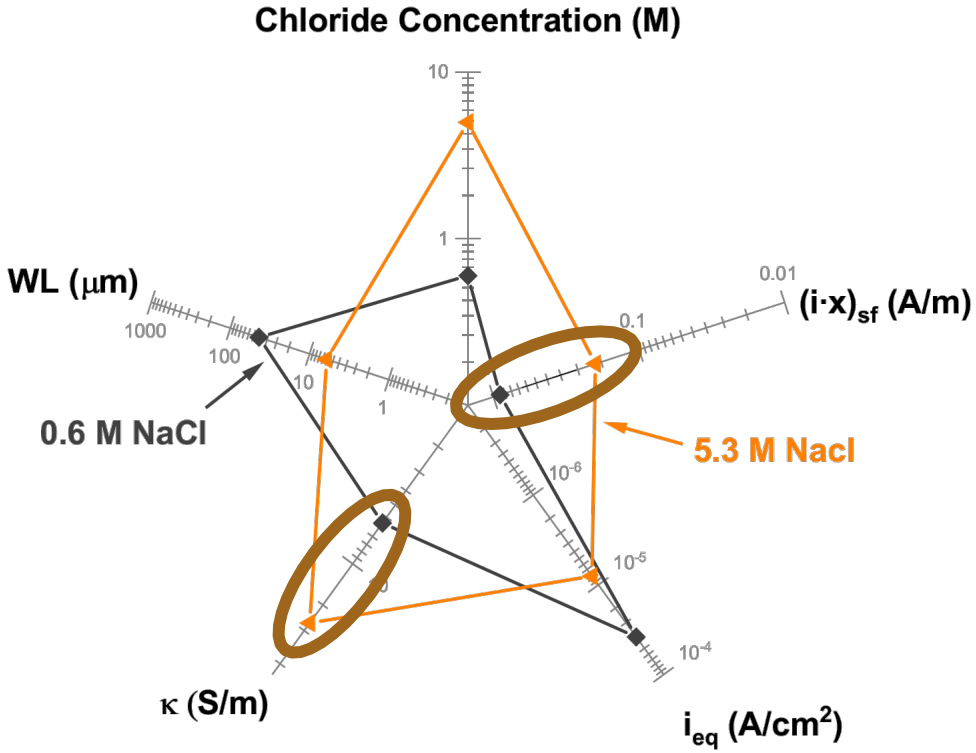


- Galvanic modeling between AA7050 and SS304L
- Increase in current per width with increase in temperature similar to max pit

Increasing Chloride Concentration

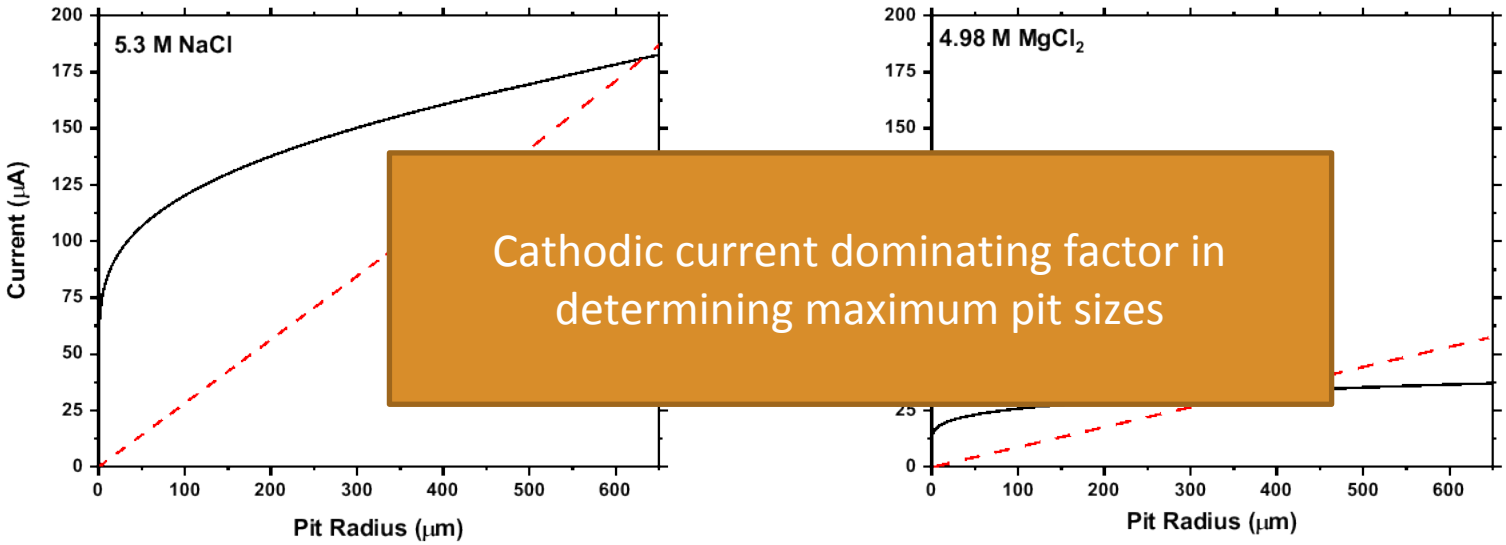
- Increasing chloride concentration increases maximum pit size





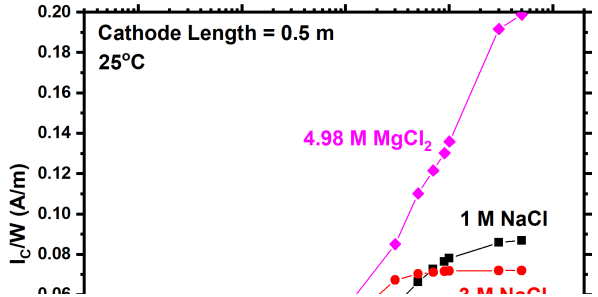
Change in Solution Composition

- Larger pit size in NaCl solutions despite nearly half the chloride concentration

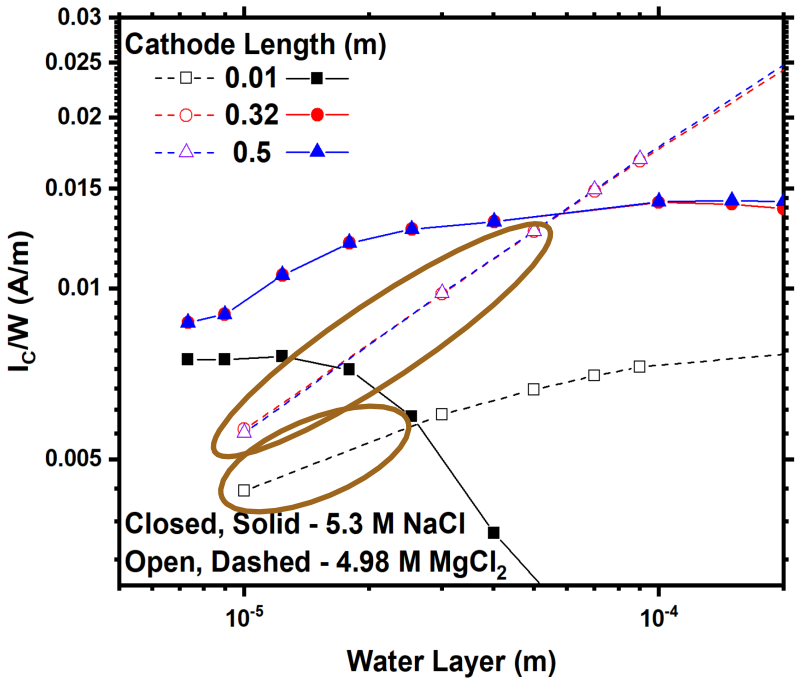


- $MgCl_2$ experiences ORR suppression and decreased conductivity

Similar trends seen in Galvanic Modeling



- $MgCl_2$ total cathodic per width suppressed at small WL thickness



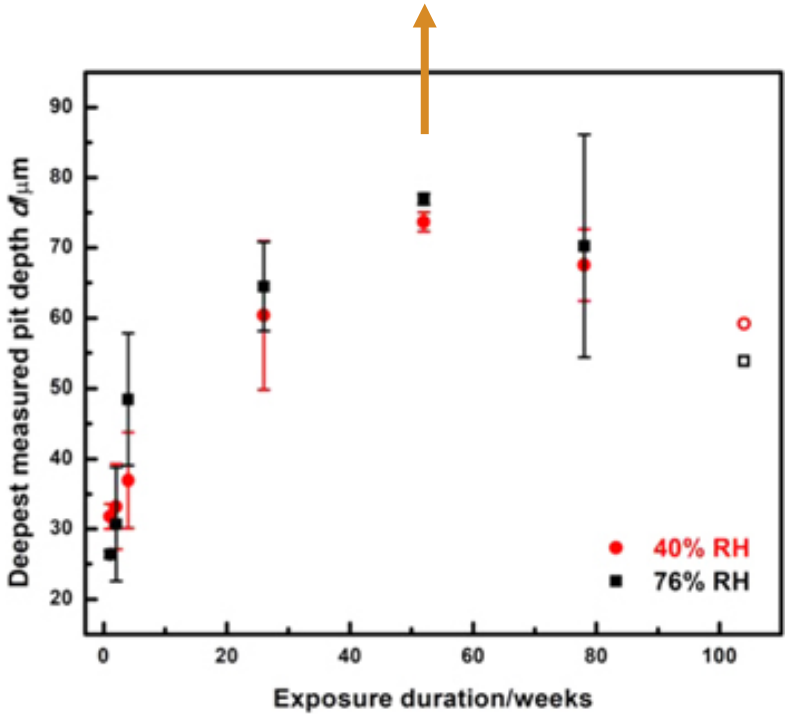
Comparison to Long Term Exposures

- 104-week exposures of SS304L to sea water solutions at 35 ˚C
  - 40 % sea salt brine ~ saturated $MgCl_2$ with thinner water layer
  - 76 % sea salt brine ~ saturated NaCl
- **Conservative estimates of the maximum pit**
  - Roughly 1.5 x larger estimate

Can we decrease the error in our predicted maximum pit sizes?

76 % Max Pit ~ 230 µm

40 % Max Pit ~ 110 µm

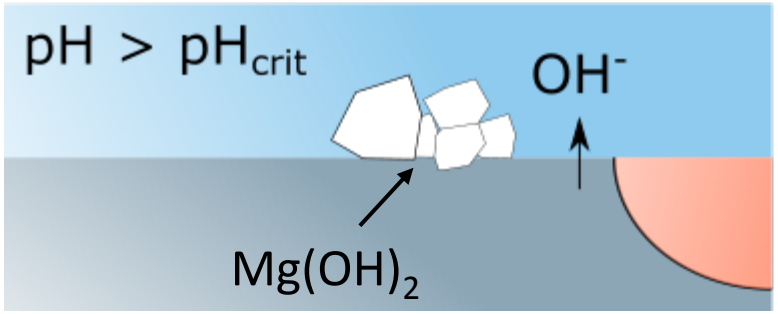


J. Srinivasan, et al. J. Electrochem. Soc. 168 (2021) 021501.

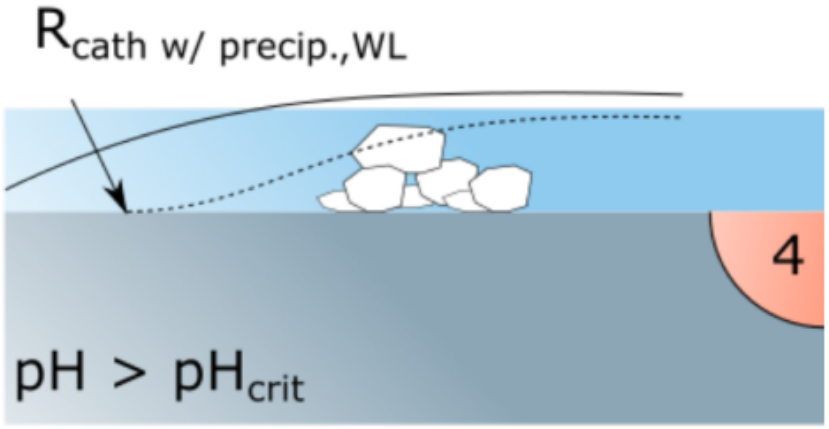
Improved Prediction for Maximum Pit Sizes

- Current model assumes constant cathode, however, direct observation of precipitates on surface of alloy

- Above pH_{crit} precipitation occurs and can cause:
  - Changes in conductivity
  - Changes in WL thickness
- Will directly impact cathodic kinetics

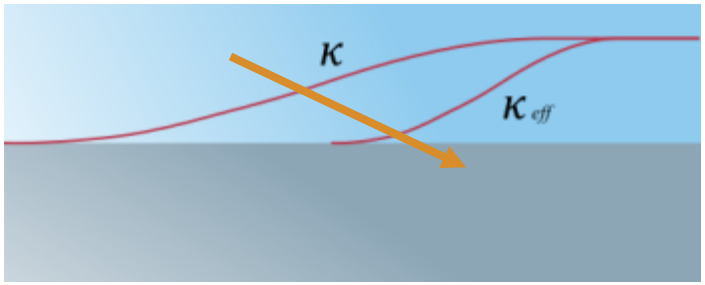


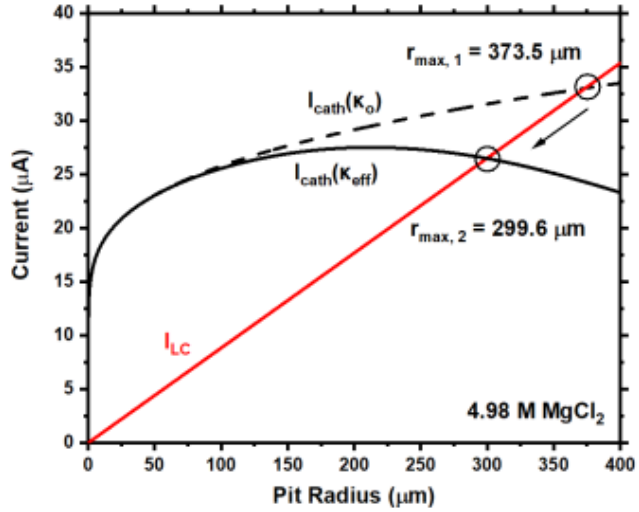
$$I_{c,max} \sim f(\kappa, WL, E_{OCP}, E_{RP}, r_a, i_{eq})$$

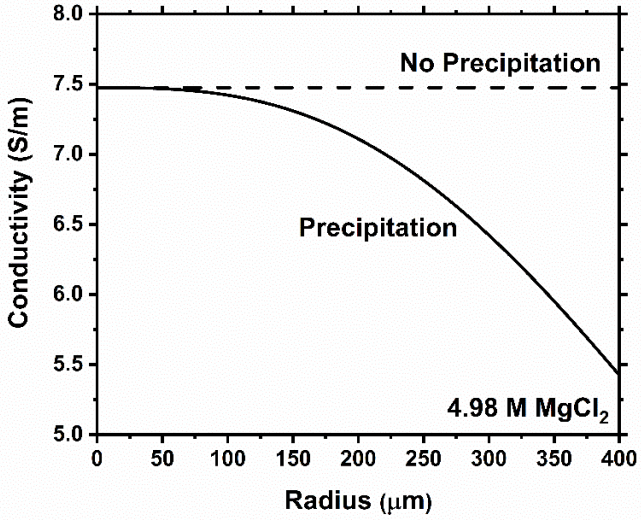


Influence of Precipitation on Max Pit Sizes

- Initially for $MgCl_2$ solutions
- Decrease in pit size by roughly 75 µm when considering precipitation
- Decrease in conductivity by roughly a factor of 1.5







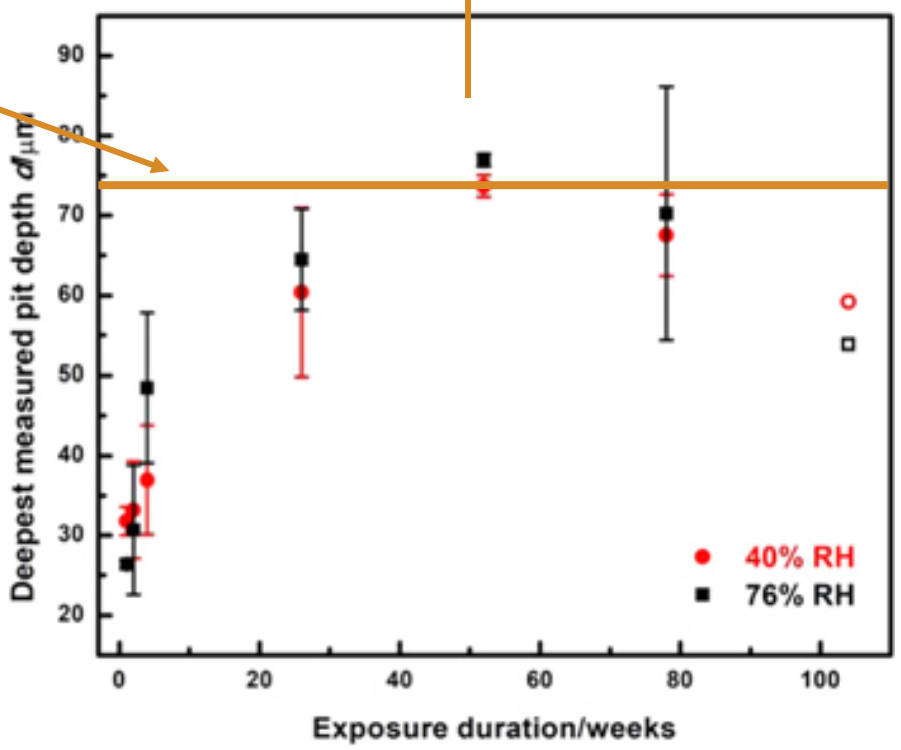
R.M. Katona, et al. Electrochim. Acta. 370 (2021) 137696.

Re-Comparison to Long Term Exposures

- When comparing to exposures, prediction of maximum pit sizes with precipitation is directly inline for 40% RH

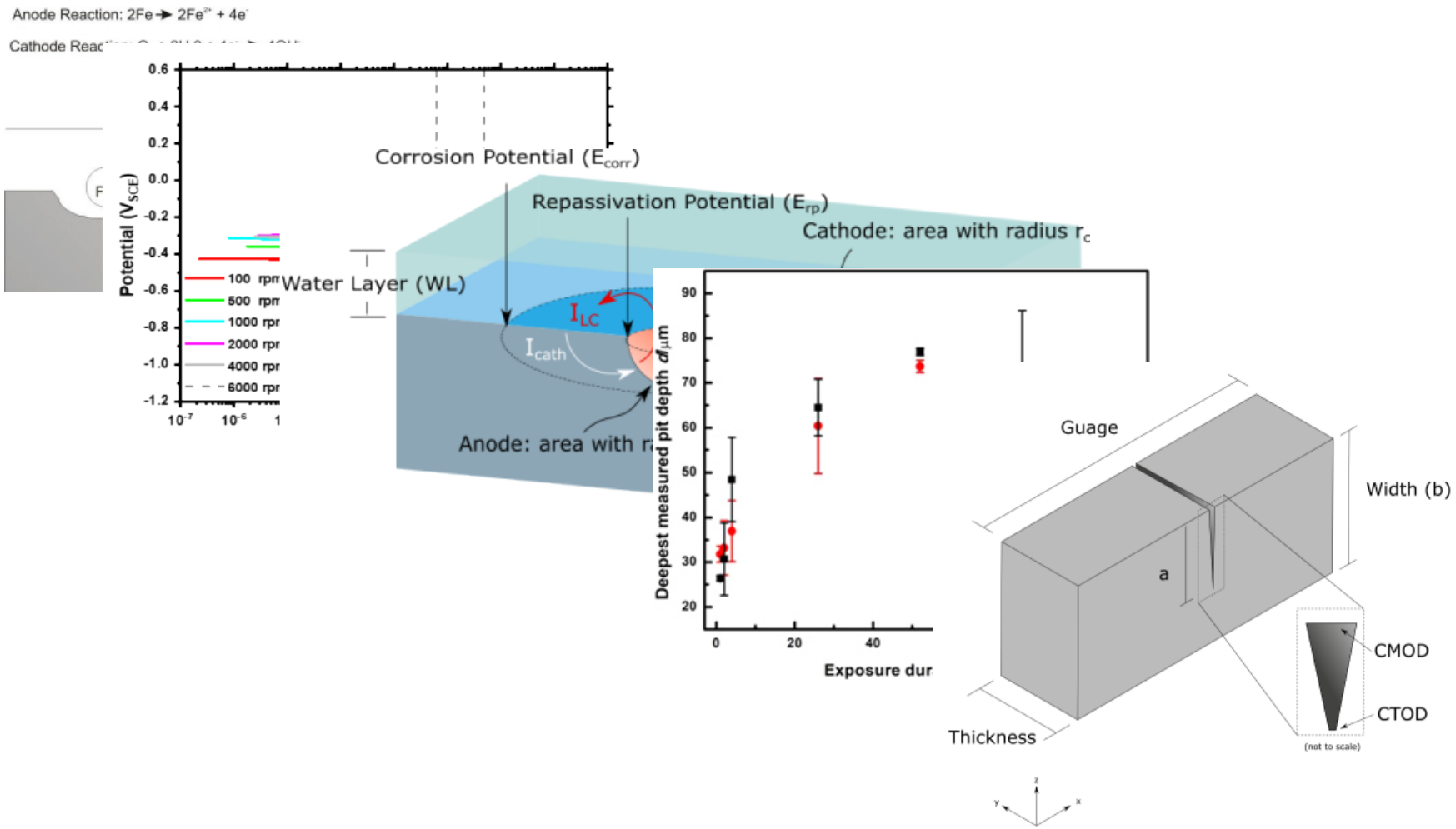
76 % Max Pit ~ 190 µm

40 % Max Pit ~ 74 µm

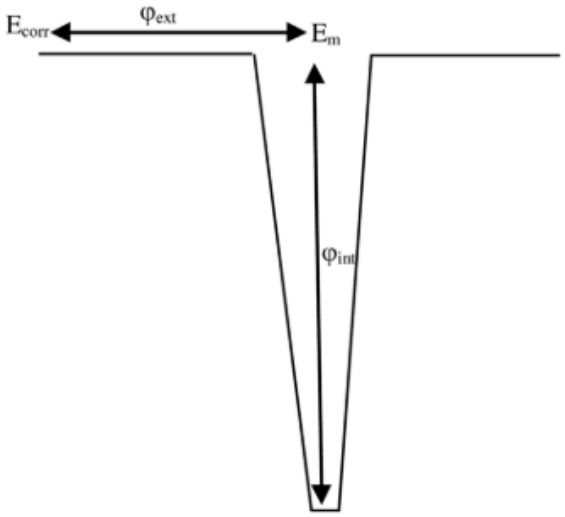


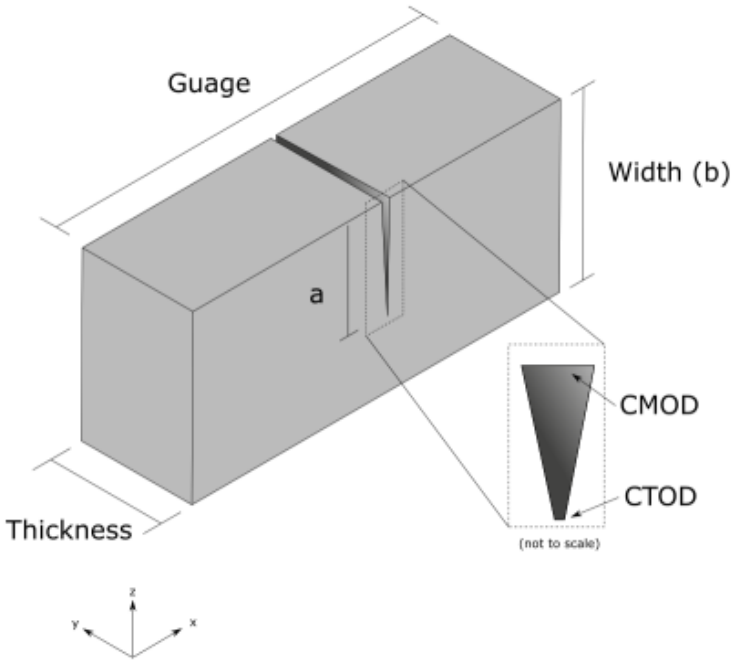
J. Srinivasan, et al. J. Electrochem. Soc. 168 (2021) 021501.

Overview


Anode Reaction: 2Fe → 2Fe2+ + 4e-
Potential (VSCE)
100 rpm
500 rpm
1000 rpm
2000 rpm
4000 rpm
6000 rpm
Corrosion Potential (Ecorr)
Repassivation Potential (Erp)
Cathode: area with radius rc
Water Layer (WL)
ILC
Icath
Anode: area with r
Deepest measured pit depth d µm
Exposure dur
Guage
Width (b)
a
CMOD
CTOD
Thickness
(not to scale)

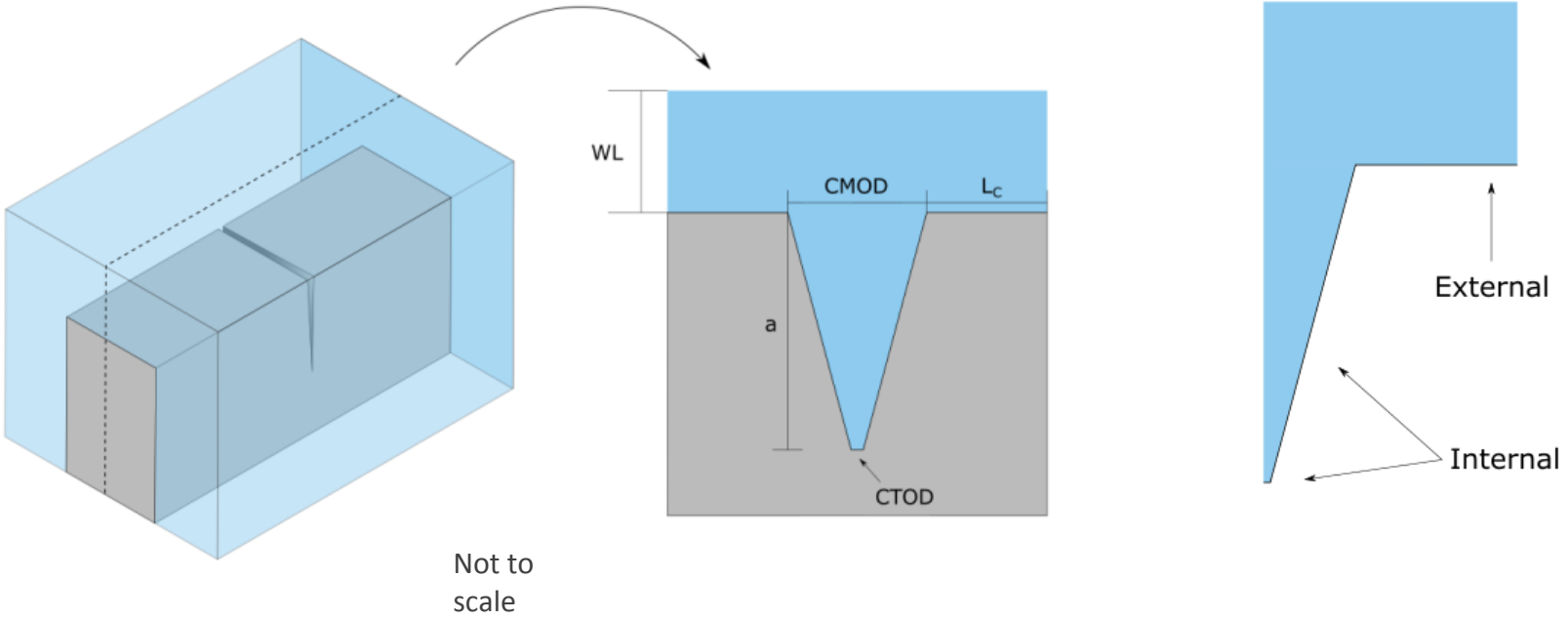
SCC Modeling





- Current models assume crack tip current density and external potentials to determine electrochemical conditions in the crack
- Presented model determines equilibrium conditions of the crack with chemistry dependent boundary conditions

SCC Modeling



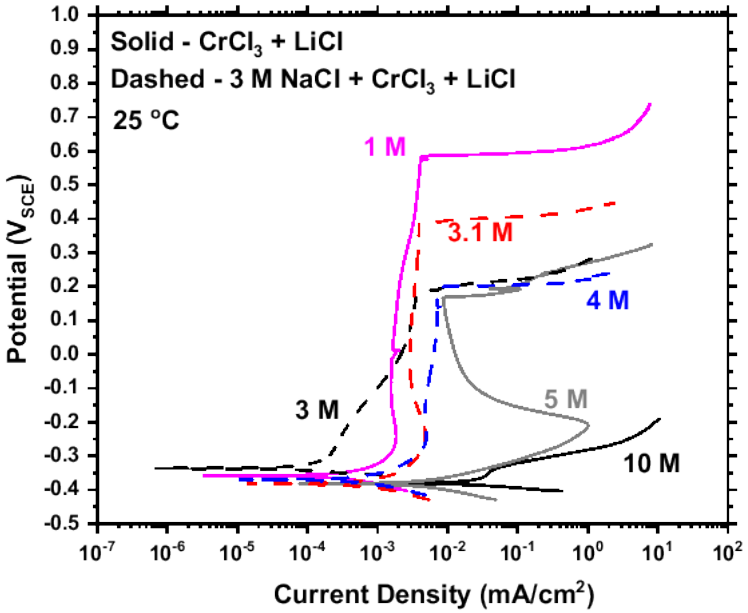
Not to scale

- Looking for trends in electrochemical parameters

- Inferences about crack growth rates

Solution dependent kinetics

- Performed anodic and cathodic polarizations as a function of metal chloride concentration



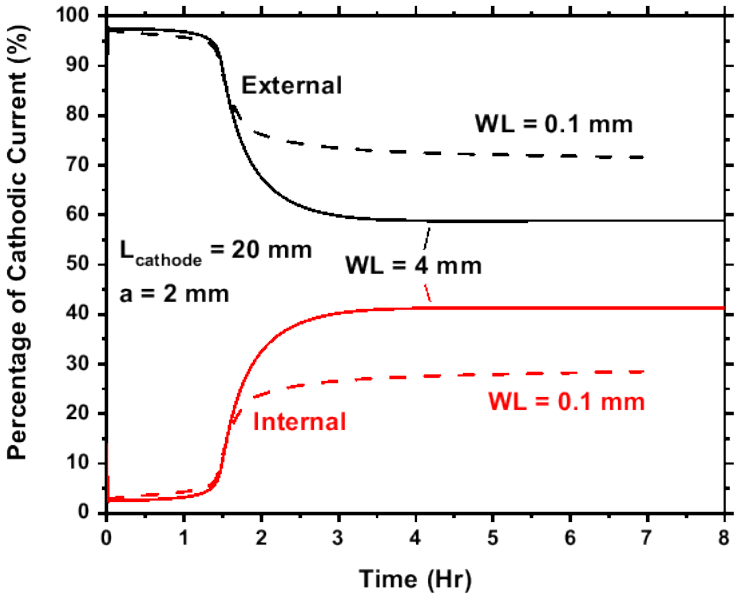
$$i_{act,M}([Cl^-]) = i_{o,Cl,M} \cdot 10^{\frac{\eta_M}{A_M}}$$

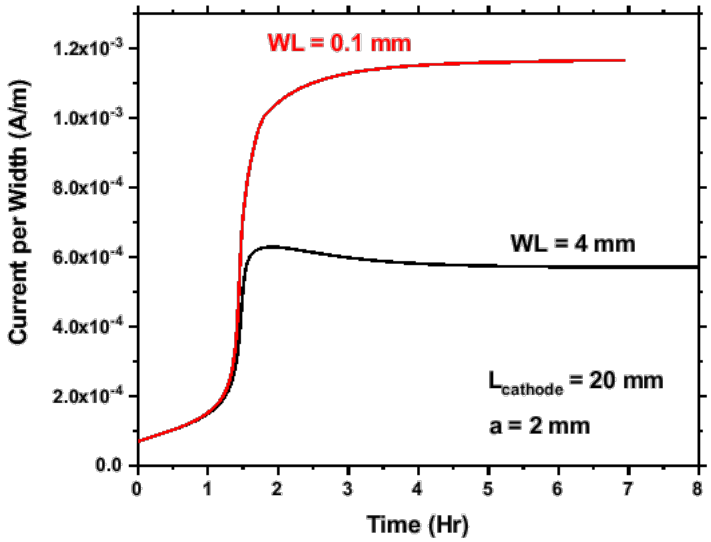
$$i_M([Cl^-]) = \frac{i_{act,M}}{1 + \frac{i_{act,M}}{i_{Cl,pass,M}}}$$

- Chemistry dependent equations for HER, ORR, and anodic dissolution

Influence of WL Thickness

- Decreasing WL thickness increases total cathodic per width

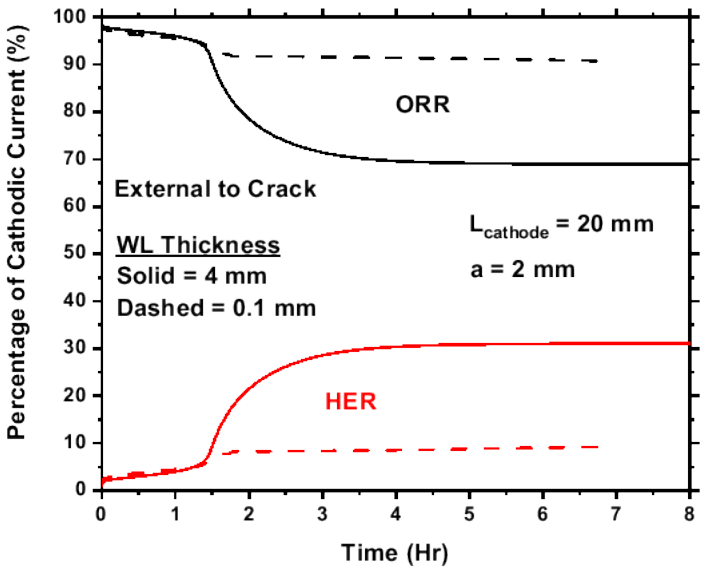


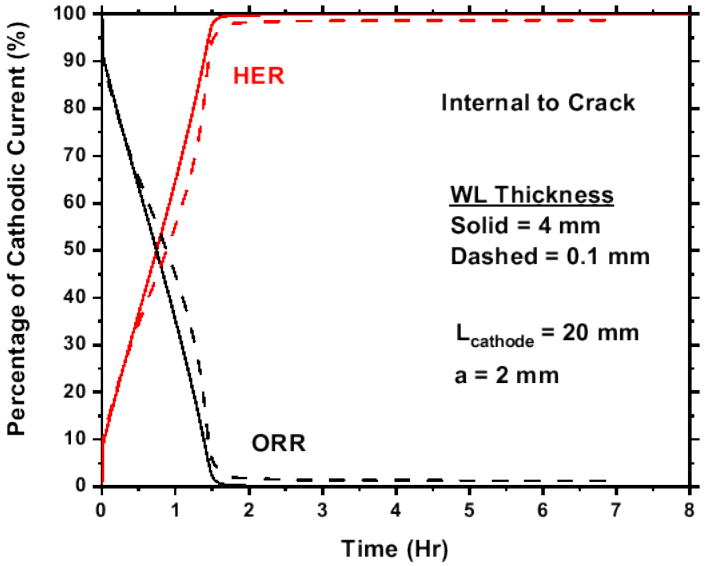


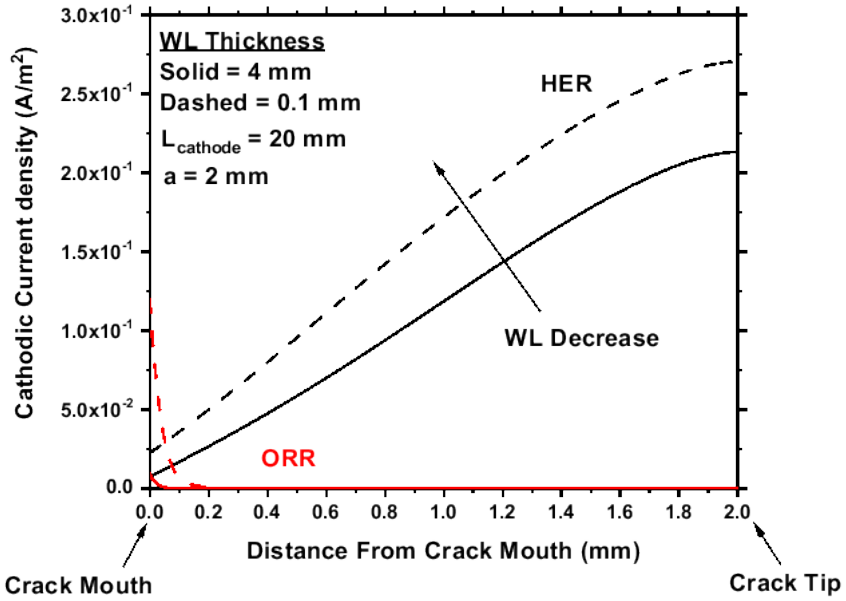
- Larger portion of the cathodic current on the external surface

Influence of WL Thickness

- Majority of external current is ORR
- Majority of internal current is HER
- ORR still present near crack mouth

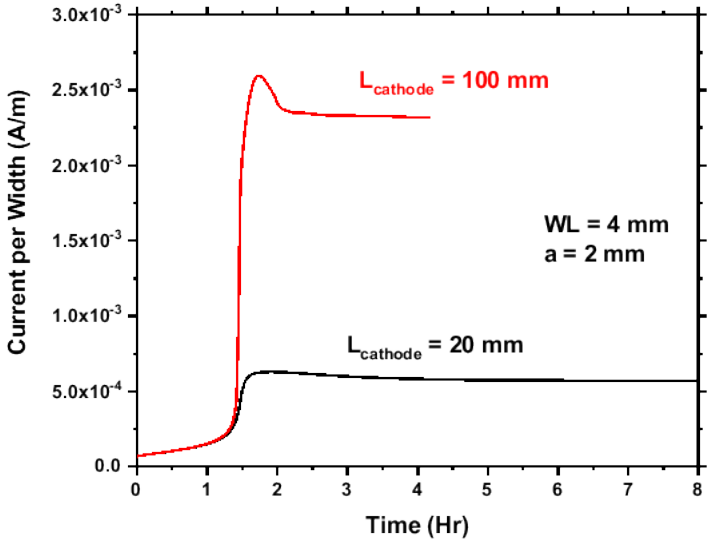


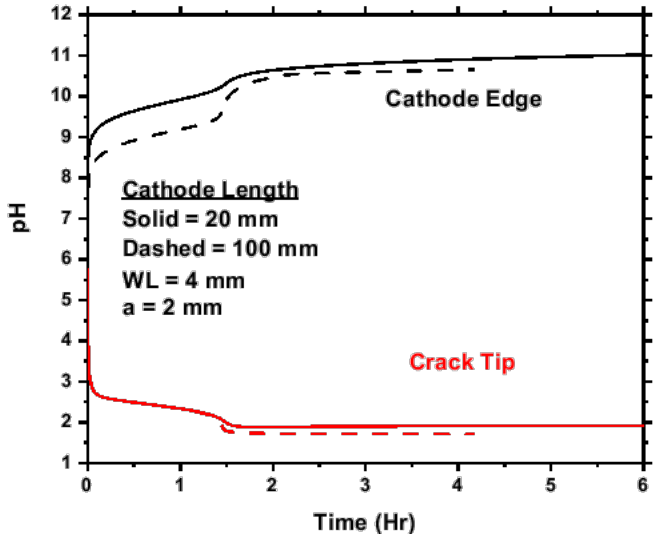


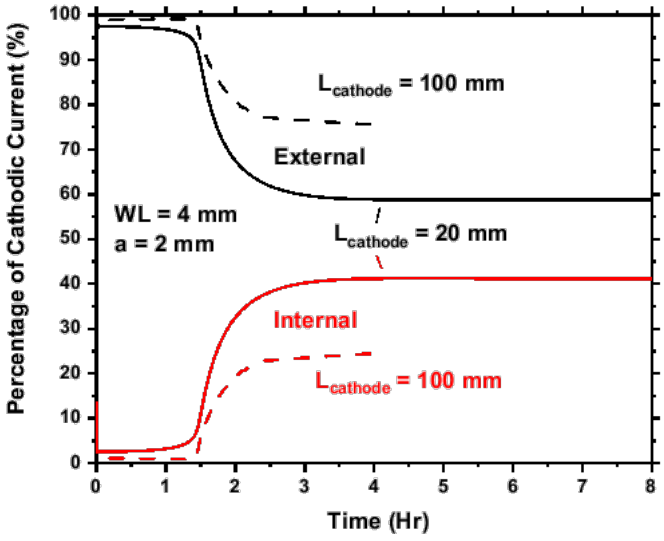


Influence Cathode Length

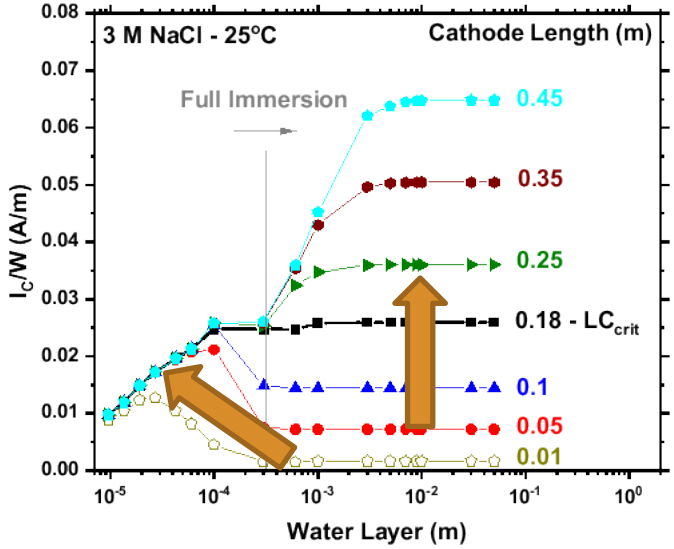
- Increasing cathode length increases the total current per width
- Cathodic current is more external
- pH lower at the crack tip

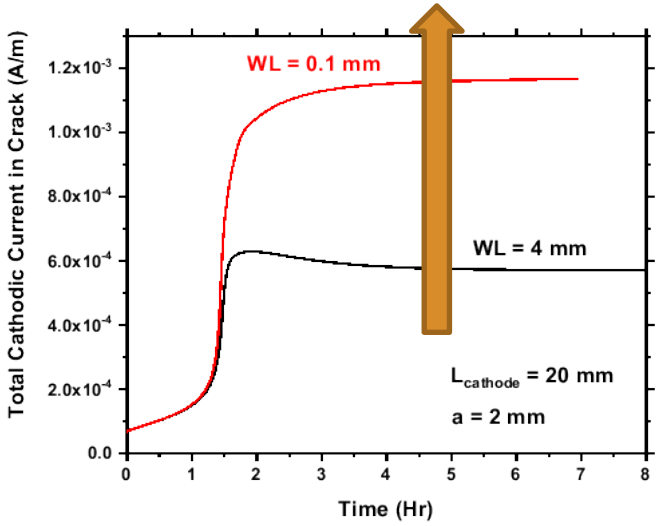


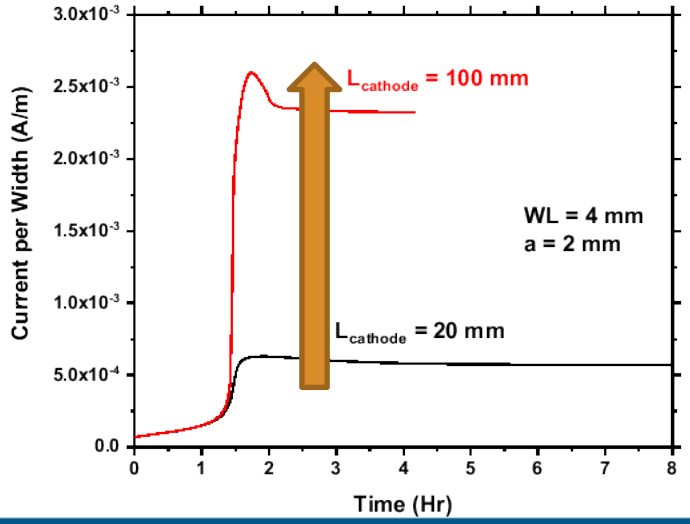




Interactions of WL and Cathode Length

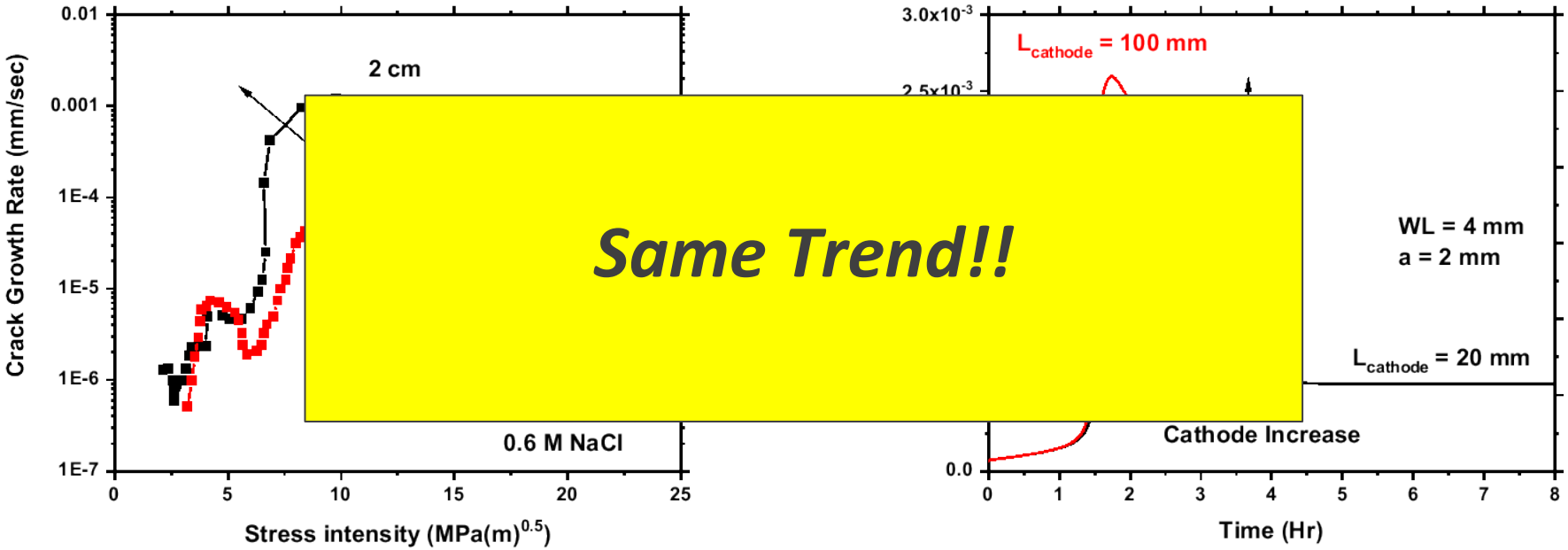






Comparison to literature

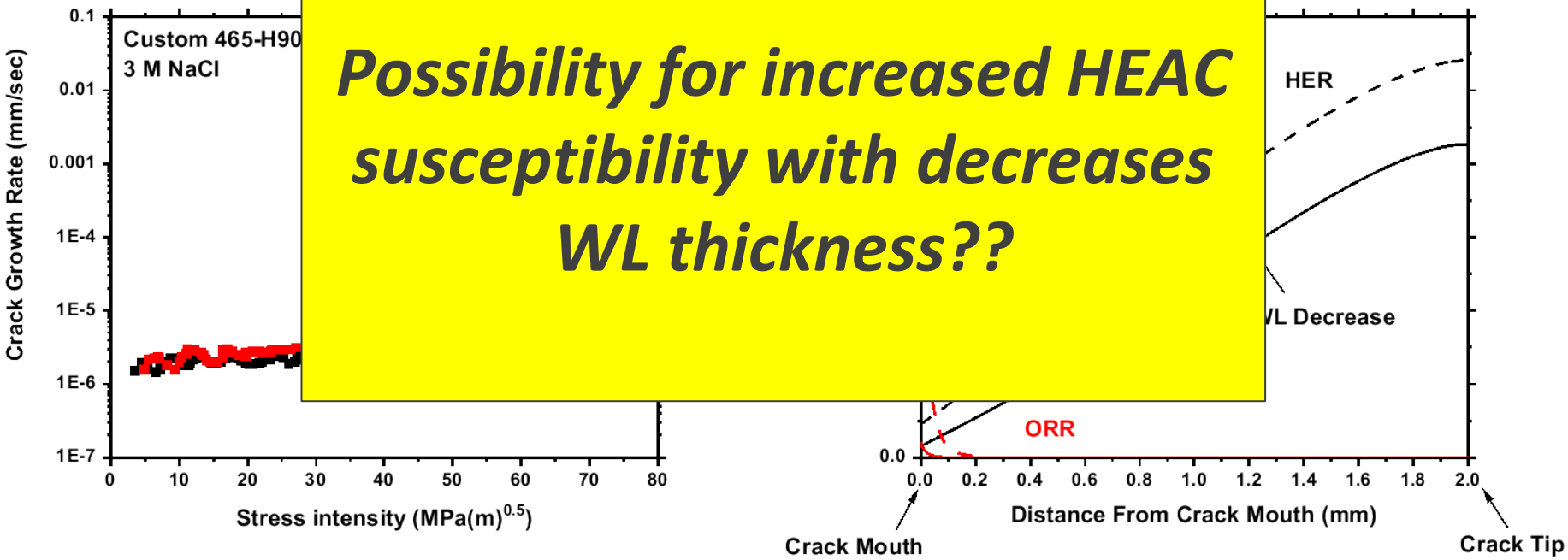
- Steiner et al. performed CGR experiments on AA alloy under full immersion conditions
- Painted different areas around crack tip to change cathodic area



P.J. Steiner, J.T. Burns, CORROSION. 74 (2018) 1117–1131.

Comparison to literature

- Harris et al. measured a decrease in threshold for CGR with decrease in WL thickness
- Decrease in pH and increase in HER near the crack tip

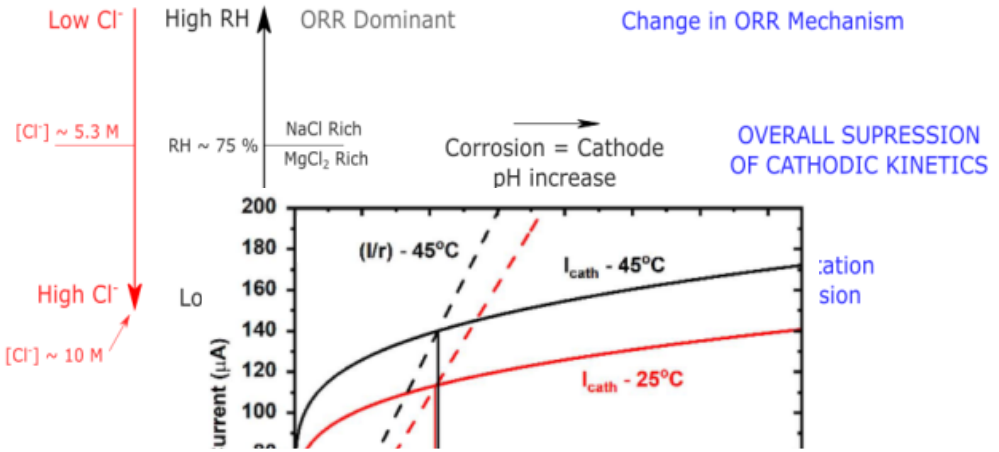


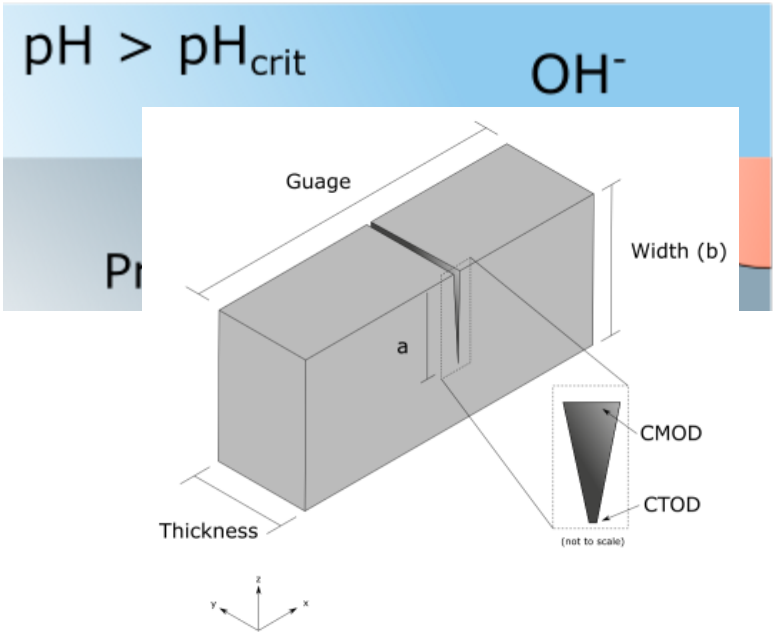
Possibility for increased HEAC susceptibility with decreases WL thickness??

Answered Questions

- What ***mechanisms control*** how external (solution composition, solution concentration, geometry, temperature) and internal (material) factors affect ***pitting and stress corrosion?***

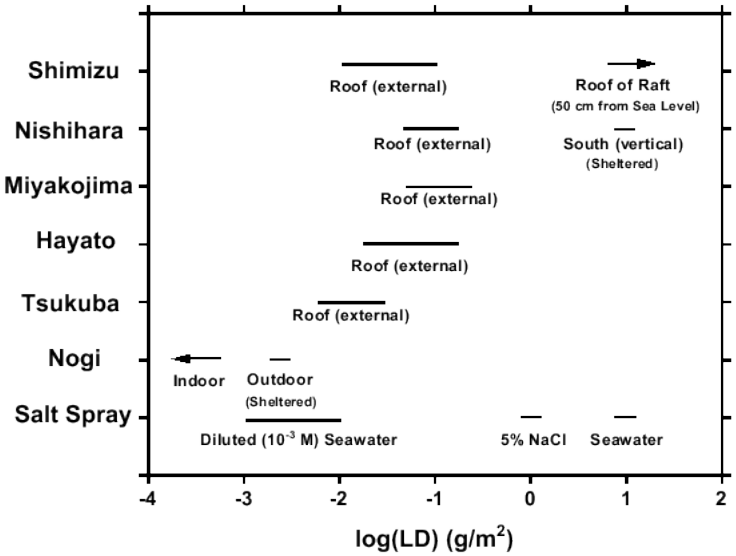
- To what extent can we ***predict damage from localized corrosion*** and stress corrosion cracking and what are ***the governing factors*** in these predictions?

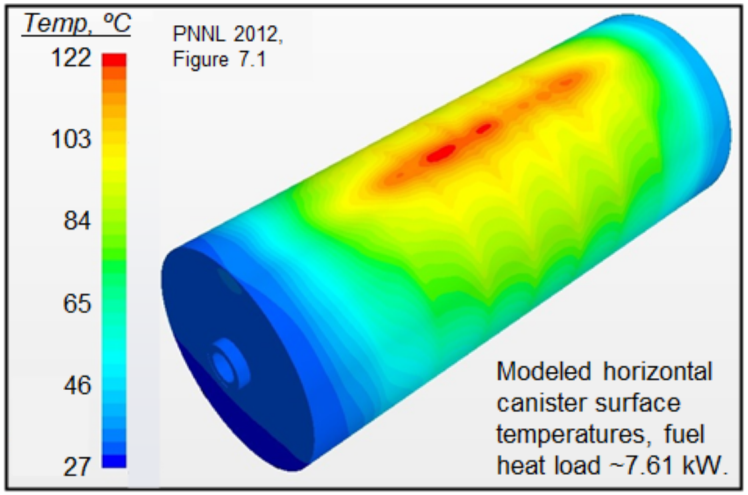




General Dissertation Question

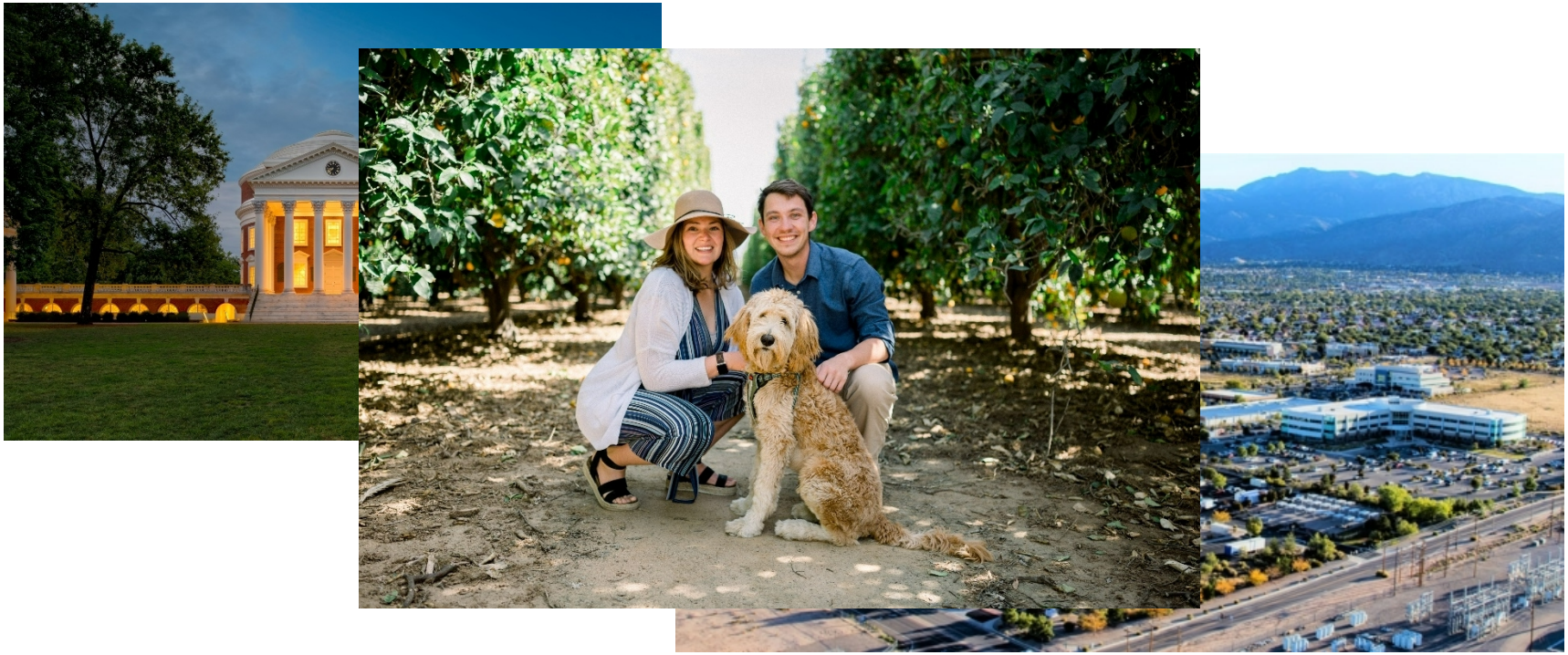
- Knowing pertinent weather and temperature related data, can we identify which regions/canisters that are potentially the worse for localized corrosion related scenarios?
- Can we understand effects of the environment on stress corrosion cracking?





Acknowledgements

- Robert Kelly, Kelly Research Group, Center for Electrochemical Science and Engineering
- Sandia Colleagues
- Parents and brother



Anodic and Cathodic Limitations on Localized Corrosion and Stress Corrosion Cracking Propagation of Stainless Steel 304L in Atmospheric Environments

R. M. Katona[1,2]

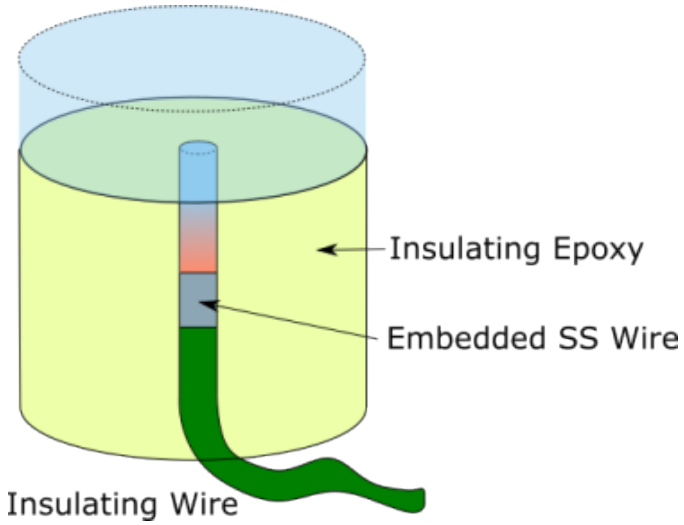
[1]Materials Science and Engineering, University of Virginia, Charlottesville, Virginia 22904

[2]Sandia National Laboratories, Albuquerque, New Mexico 87123, USA

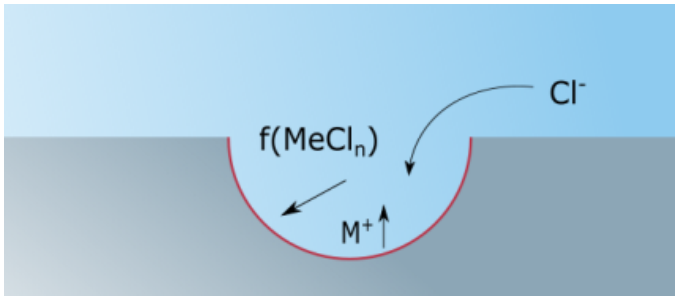
Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. Document: SAND####.

Supplemental

Background – Pit Propagation



Converted to hemisphere by a geometric factor of 3



- To sustain pitting, the current (I) at a given radius (r) must satisfy

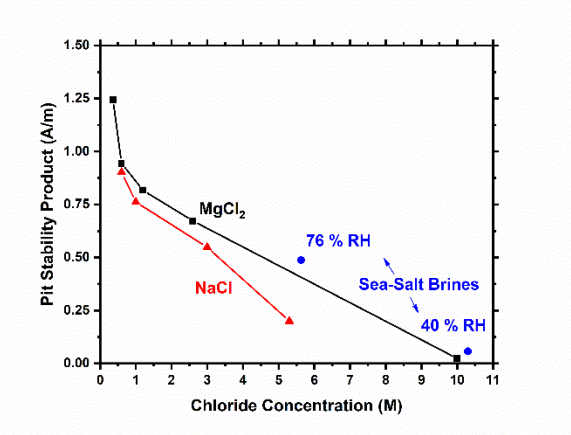
$$\left(\frac{I}{r}\right) \geq \left(\frac{I}{r}\right)_{crit}$$

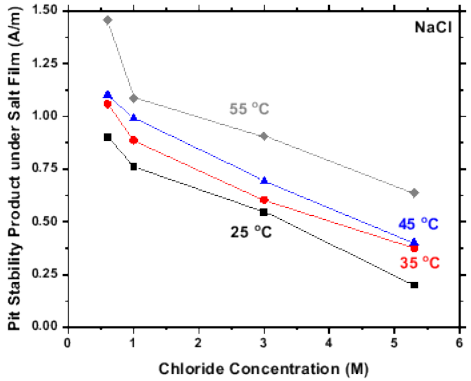
- Critical value ~50% of full saturation of salt film needed

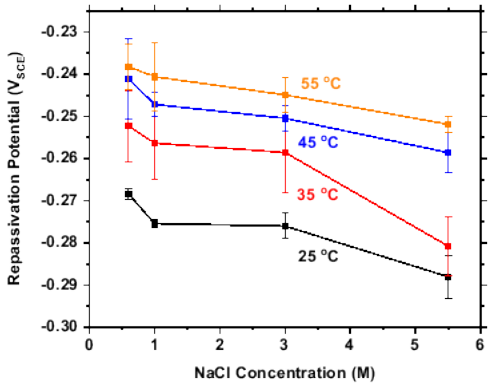
- Limiting anodic current demand (I_{LC}):

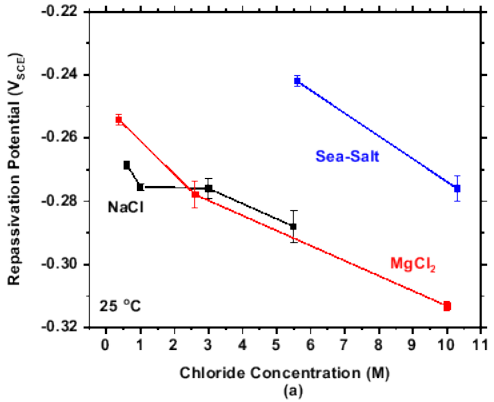
$$I_{LC} = \left(\frac{I}{r}\right)_{crit} r_{anode}$$

Anodic Kinetics

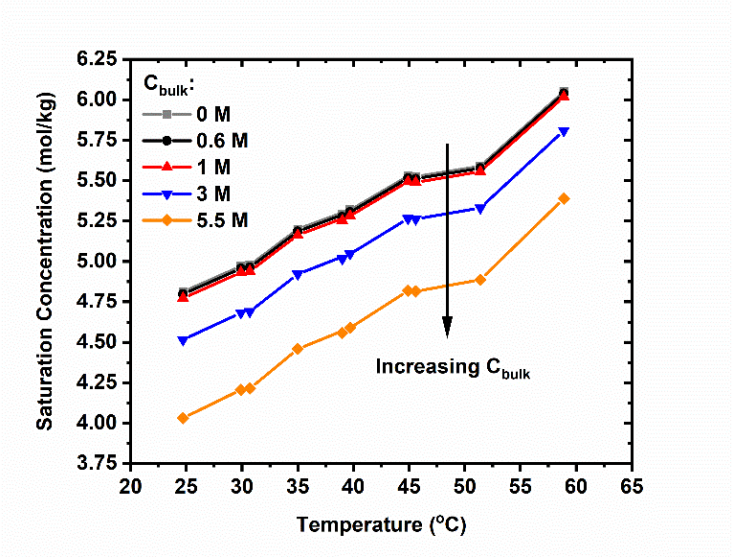








Anodic Kinetics



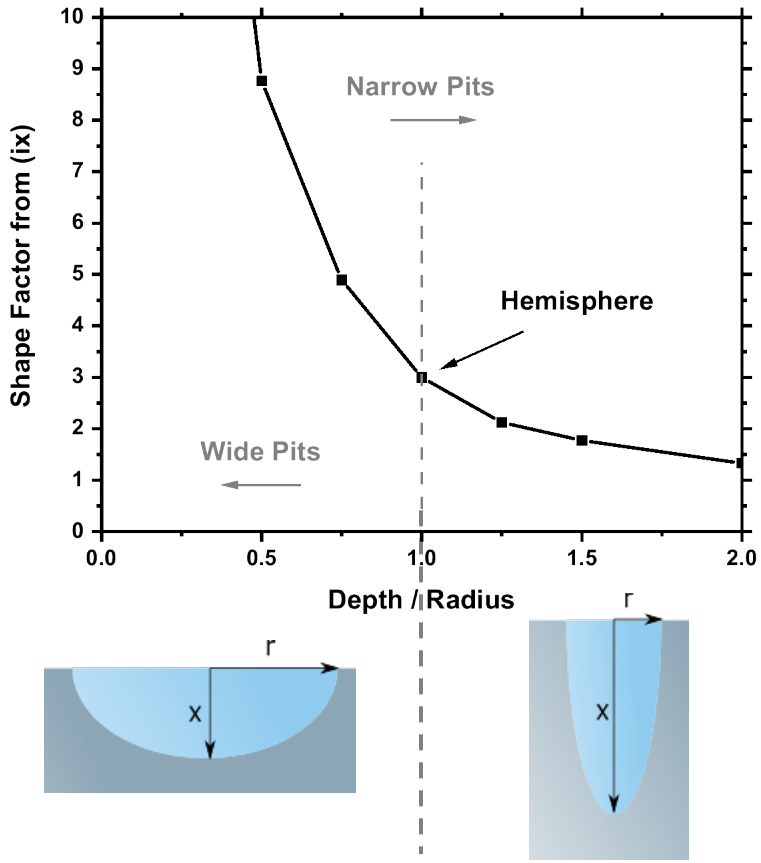
Shape Factor

- In order to determine the shape factor, the following ratio was taken:

$$Shape\ Factor = \frac{\left(\frac{I}{x}\right)}{(i * x)}$$

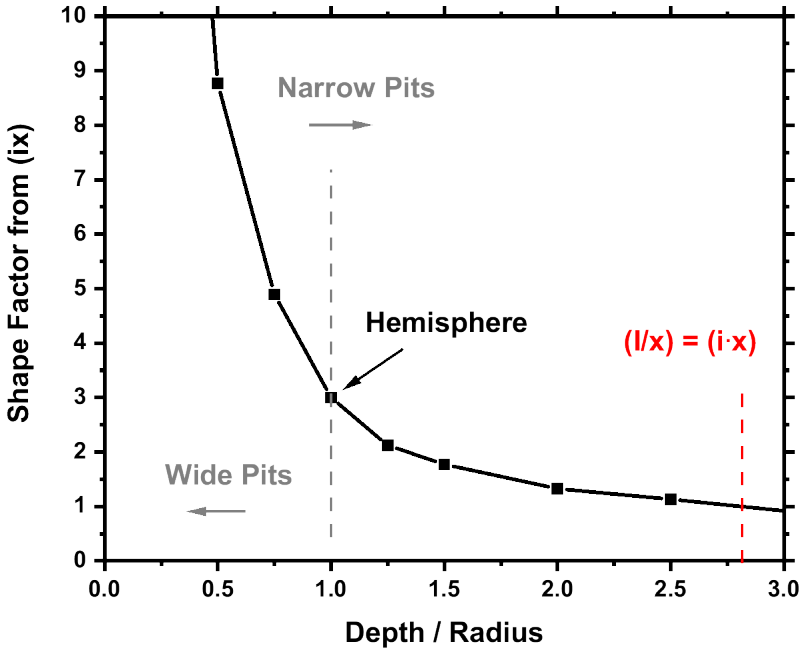
$\frac{I}{x}$ = total current needed at a given depth for ellipse

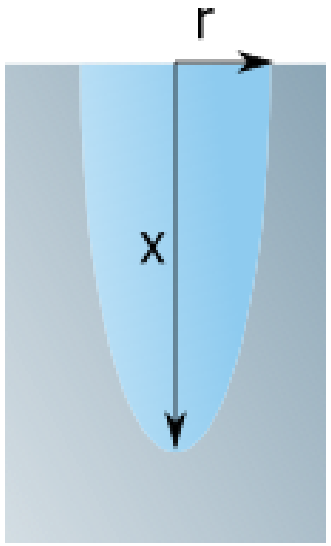
$(i * x)$ = current density at a given pit depth for 1-D pit

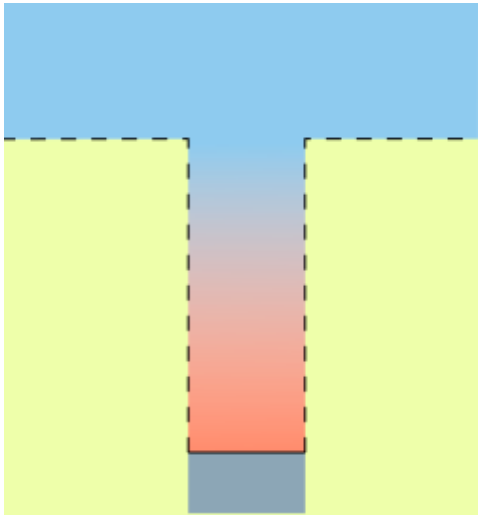


- For wide, shallow pits, diffusion begins to win out and you need more current to maintain the critical environment at the pit surface
- Conversely, diffusion is hindered by the geometry for narrow pits and thus less current is required to maintain critical environment

Shape Factor



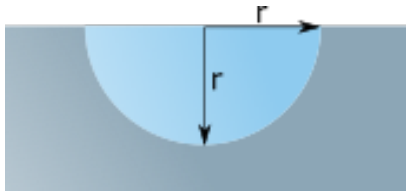




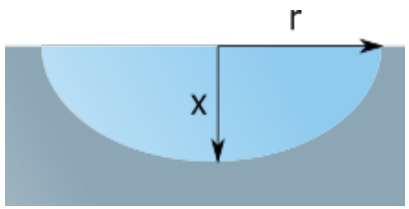
- At a certain point the value for I/x decreases below that of (·)
- Consequence of the entire pit surface being active in an ellipse however in a 1-D pit, only the bottom is active

Pit Size Increases with Increasing Aspect Ratio

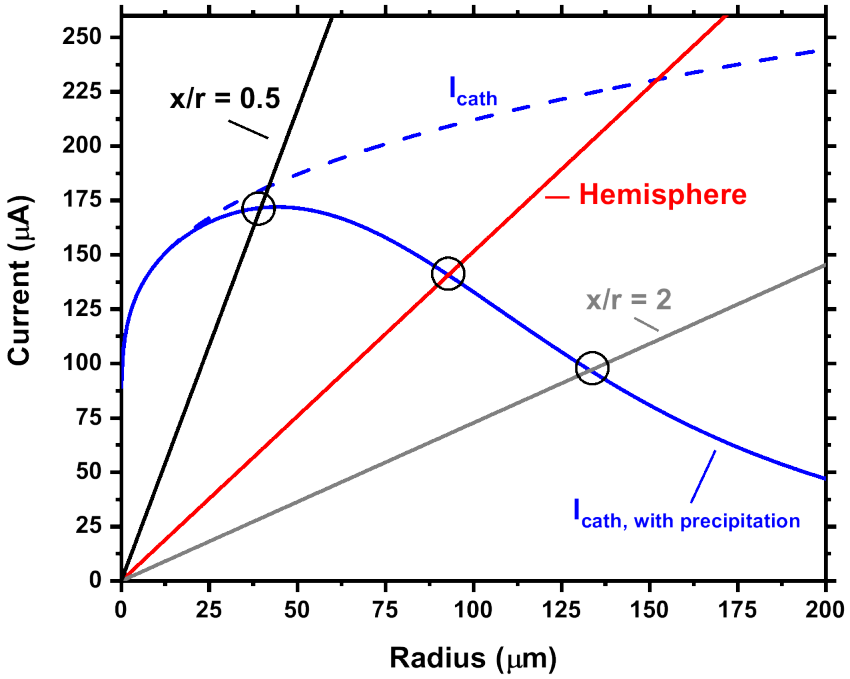
- Maximum pit at various aspect ratios taken at 50% saturation

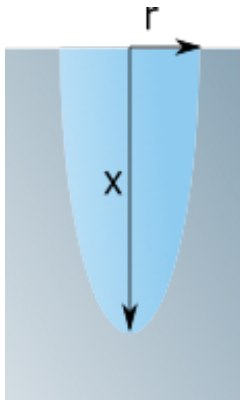


$= 92.8$



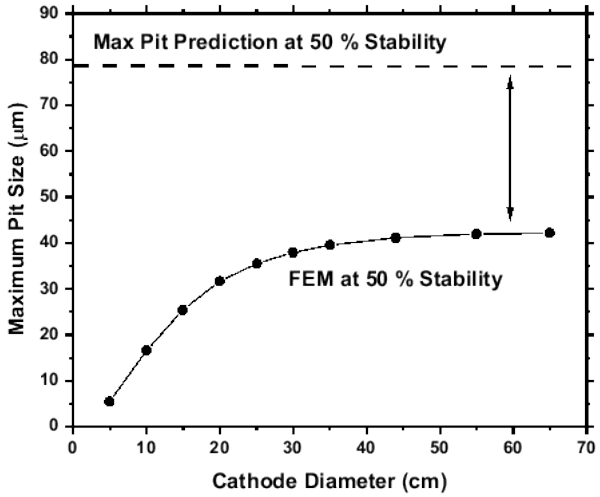
$= 39.7$





$= 133.2$

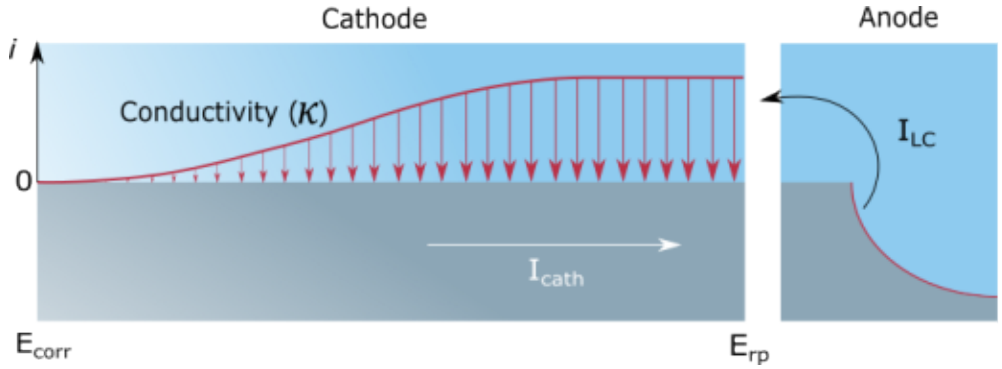
Ideal cathode assumption

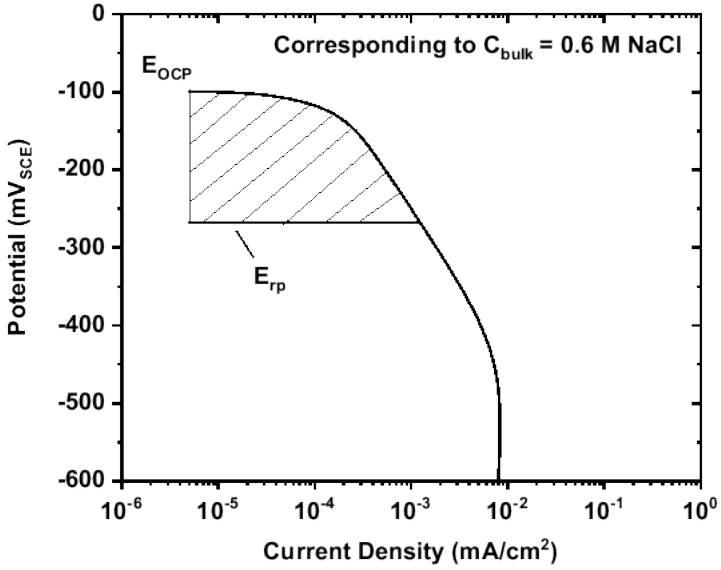


- Maximum pit with FEM comparison

Cathode Supply

- Ohmic drop in cathode governed by current densities, water layer thickness, and conductivity





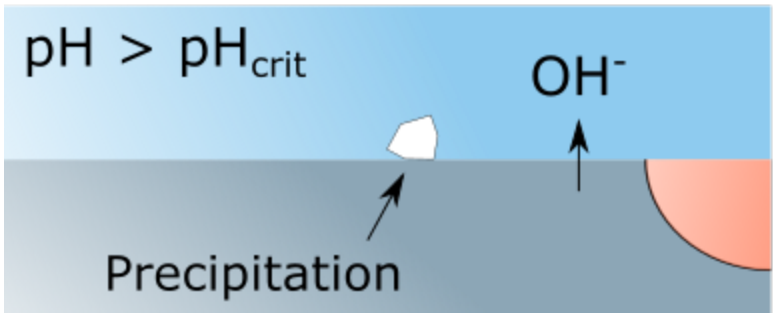
$$I_{c,max} \sim f(\kappa, WL, E_{OCP}, E_{RP}, r_a, i_{eq})$$

$$\ln I_{cath} = \frac{4\pi\kappa WL\Delta E}{I_{cath}} + \ln\left[\frac{\left(\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (i_c - i_p)dE\right)}{\Delta E}\right]$$

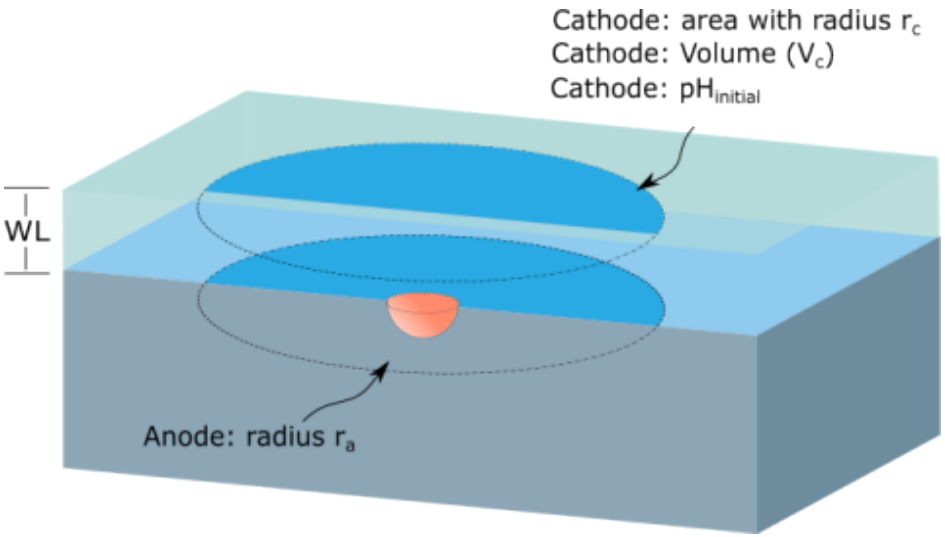
- Cathode current function of conductivity, WL, electrochemical potentials, anode radius, and equivalent current density

Modeling Cathode Precipitates

- Cathodic reactions cause pH rise
- Can calculate OH^- production at a given pit depth and convert to a pH



$$M_{OH^-} = \frac{\left[\frac{2}{3}(r_a)^3\right]\left[\frac{\rho_{SS} * e^-_{SS}}{MW_{ss}}\right]}{V_{cath}}$$

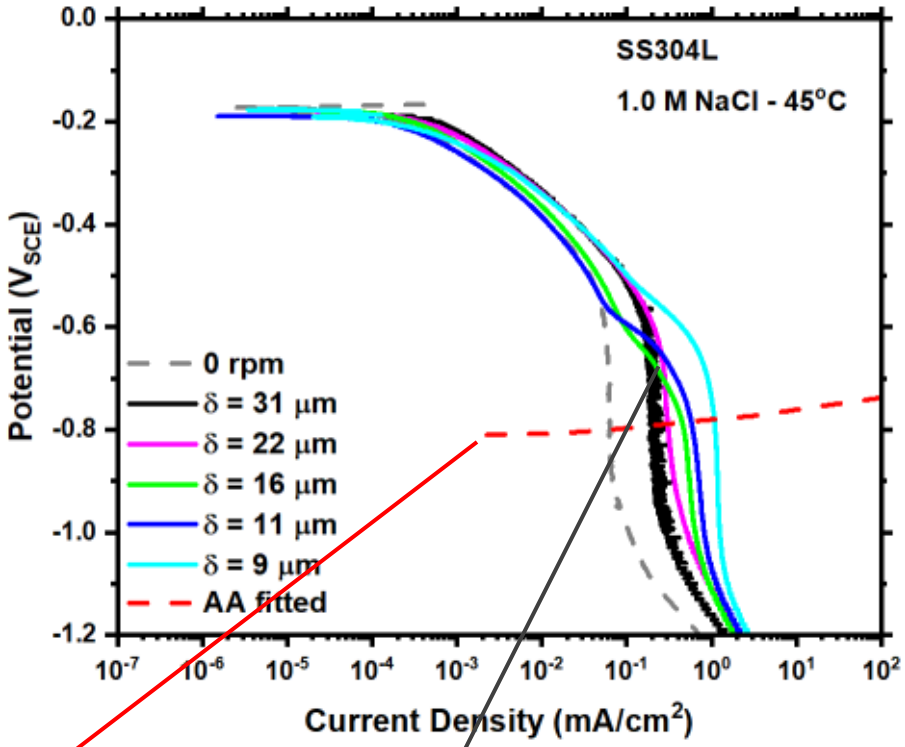


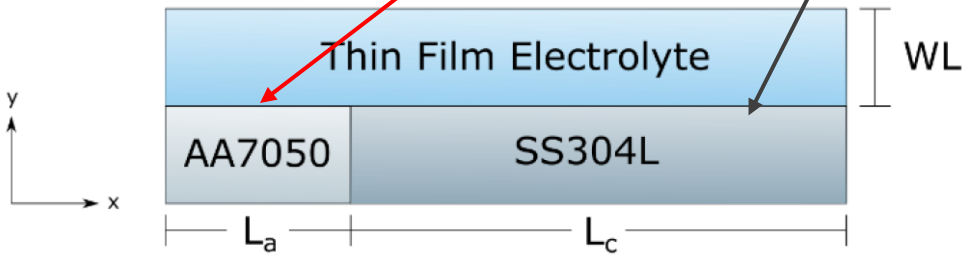
$$\kappa_{eff} = k\left(1 - \frac{V_{precip}}{V_{solution} + V_{precip}}\right)^{\frac{3}{2}}$$

$$I_{cath,updated} = f(\kappa_{eff})$$

Modeling in a Galvanic Couple

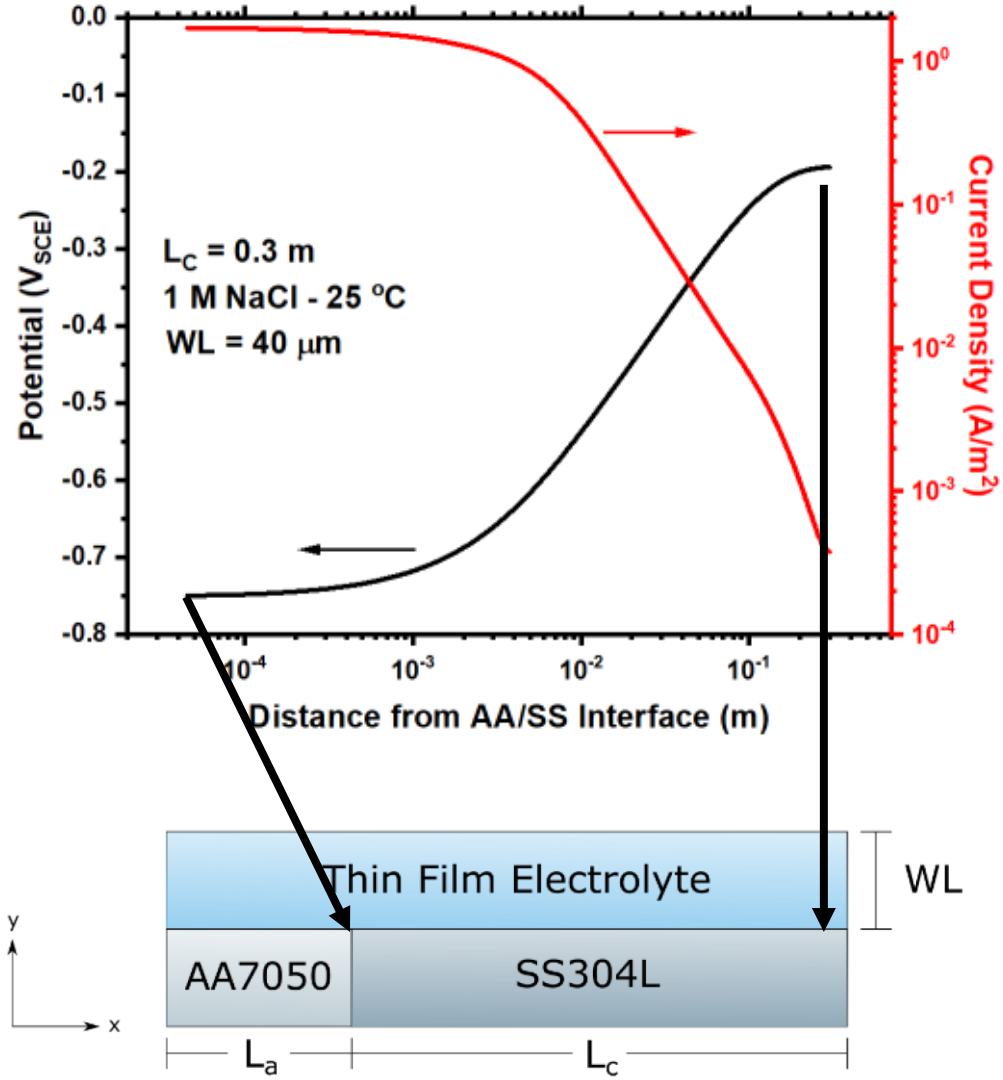
- Assign the polarization scan to respective anode or cathode
  - Anything greater than δ_{nc} utilizes quiescent polarization scan
- Input solution conductivity
- Variable cathode length (L_C) and WL thickness
- Evaluate current per width (I_C/W)





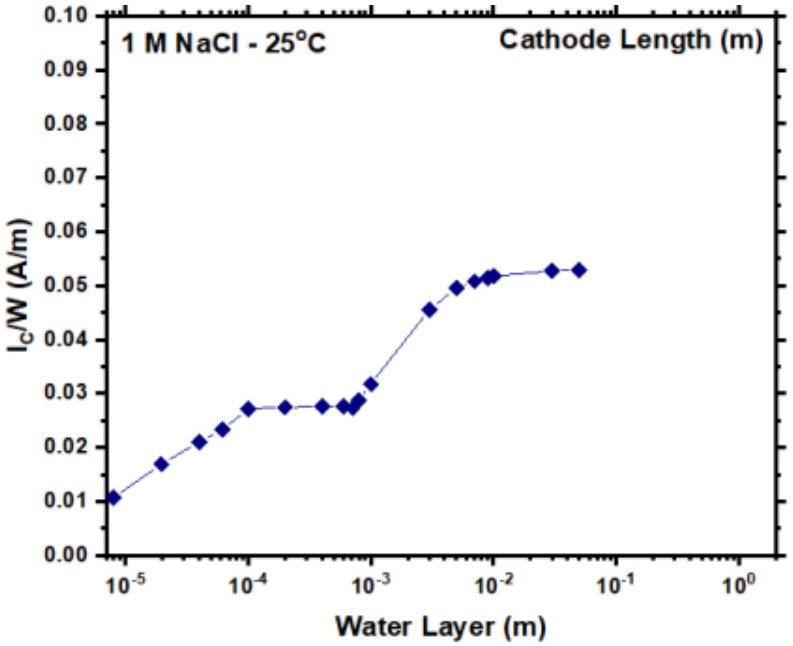
Modeling in a Galvanic Couple

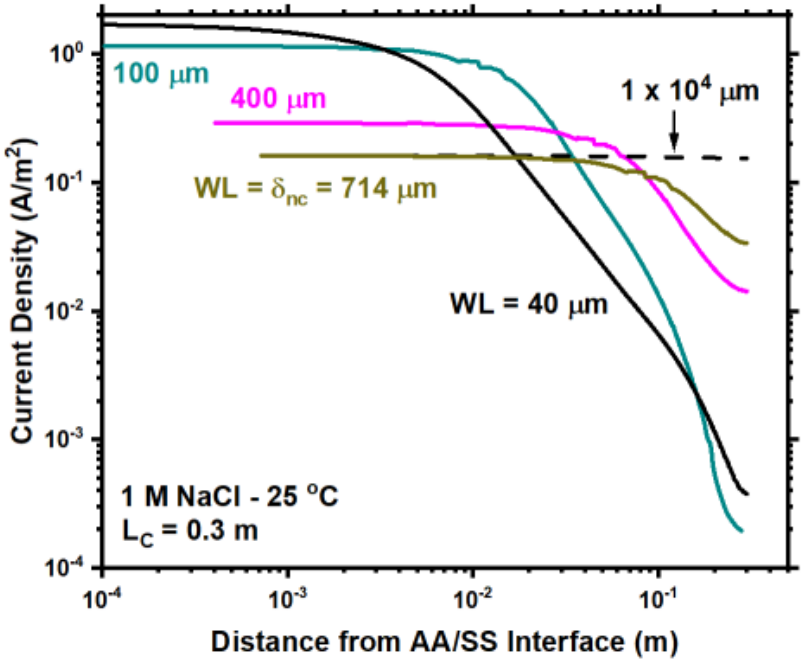
- Potential at the interface is the AA/SS304L coupling potential
- Potential far away from interface is OCP of SS304L
- Current density high near the interface and decays when moving from the interface
- Evaluate I_C/W by integrating current along the cathode



Increasing WL Thickness

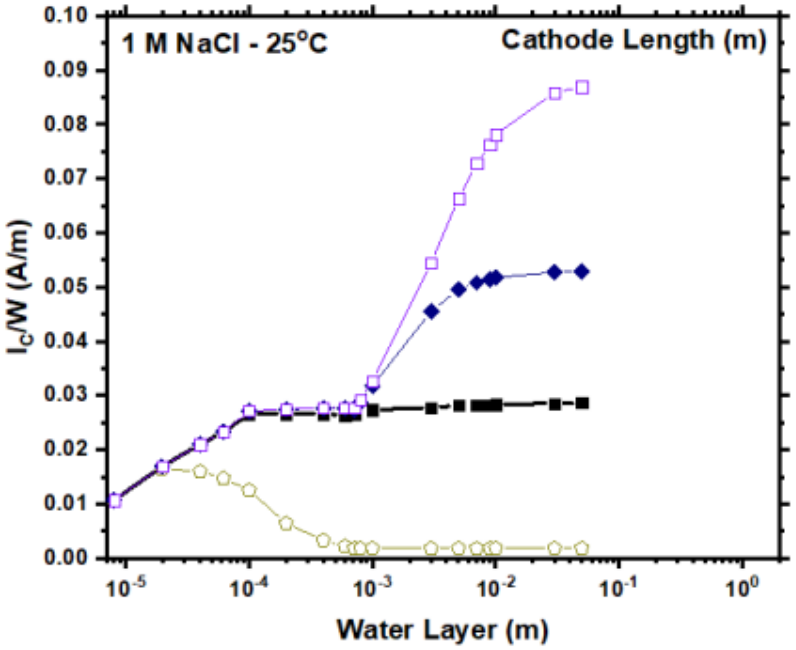
- Continuously increasing the WL at the same cathode size will not increase the current
- Current is now fully limited by the cathode size

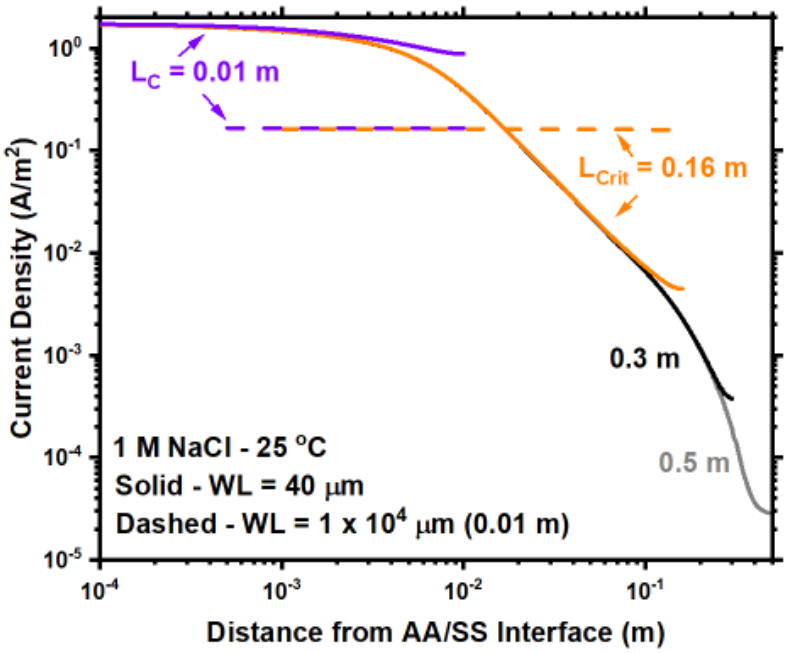




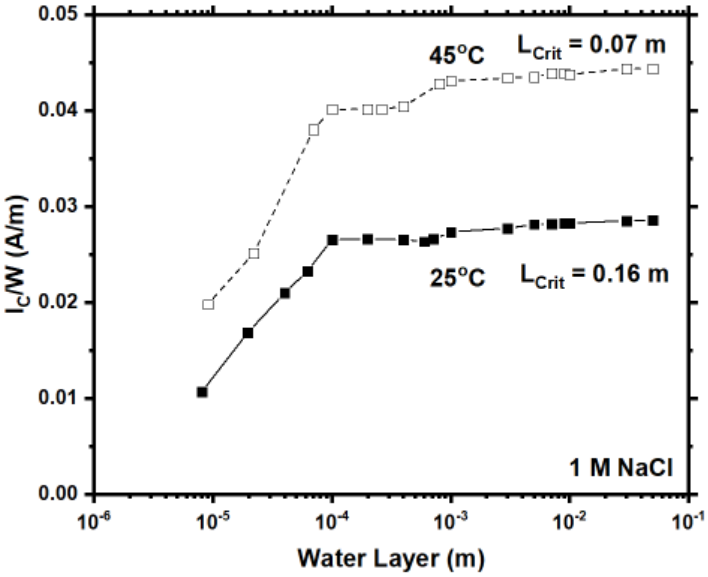
Increasing Cathode Length and WL

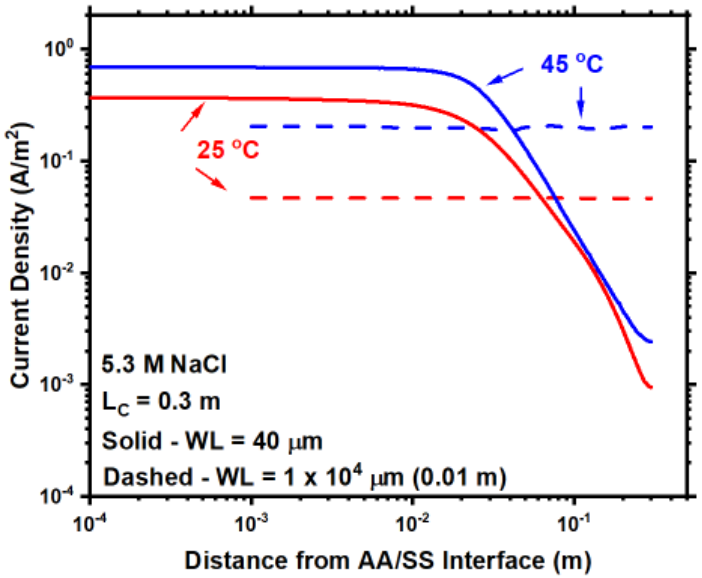
- Further increasing cathode length increases I_C/W
- I_C/W scales with cathode size

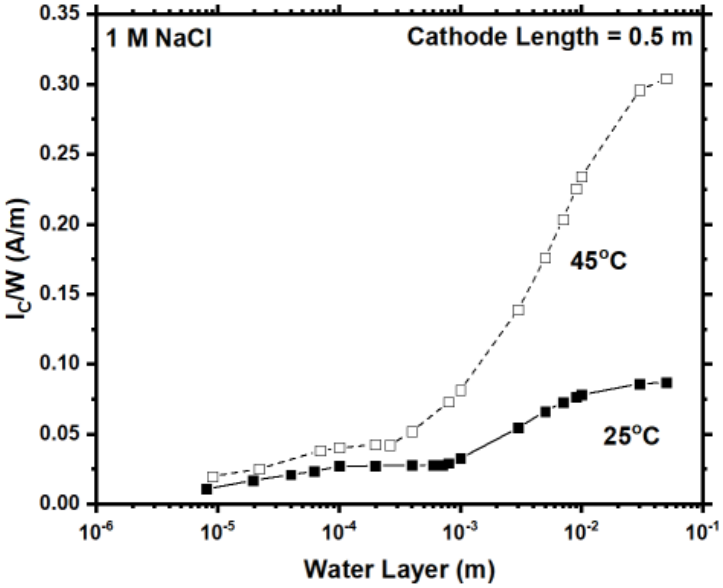




Increasing Temperature

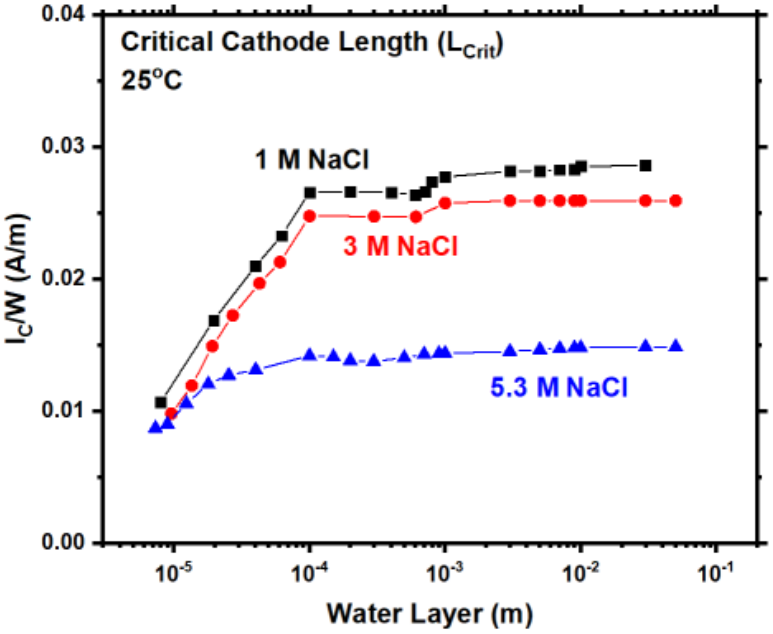


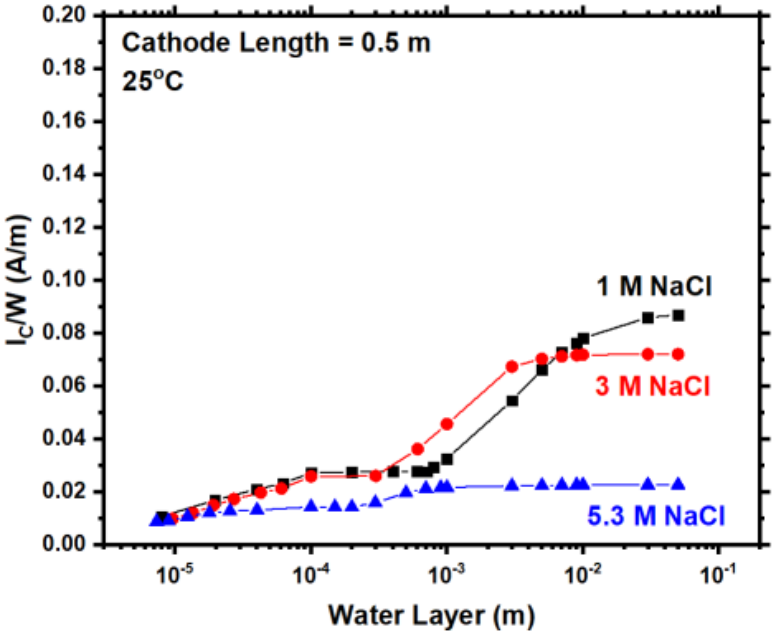




- Increasing temperature increases I_C/W
- Increasing temperature increases κ and i_{lim}

Increasing Chloride Concentration



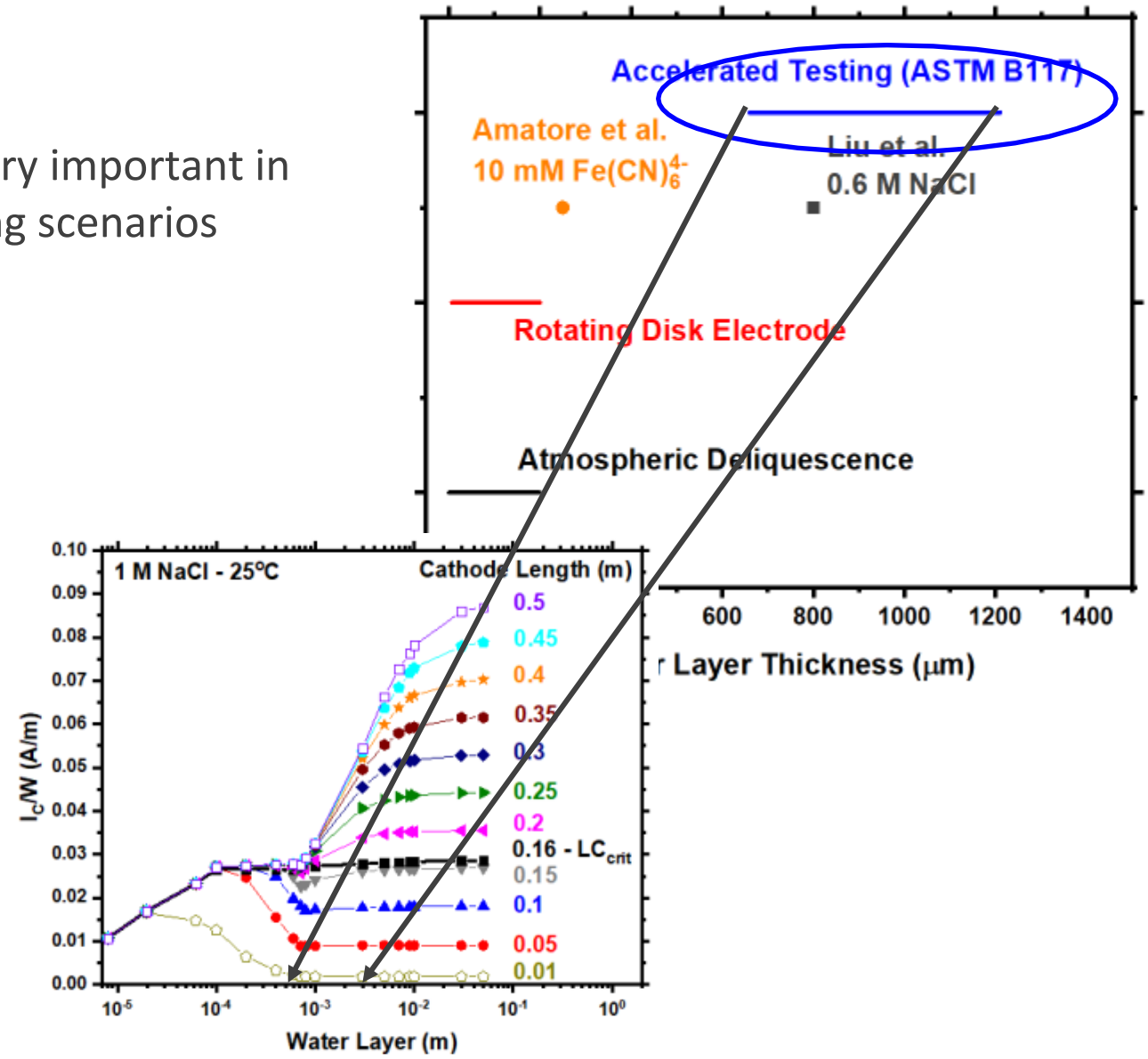


- Increasing chloride concentration decreases I_C/W in most cases
- Shouldn't current increase? -> More corrosion damage?
- Limited by the mass transport in the system

$$i_{lim} = 0.62nF D_{O_2}^{2/3} \nu^{-1/6} C_{O_2,bulk} \omega^{1/2}$$

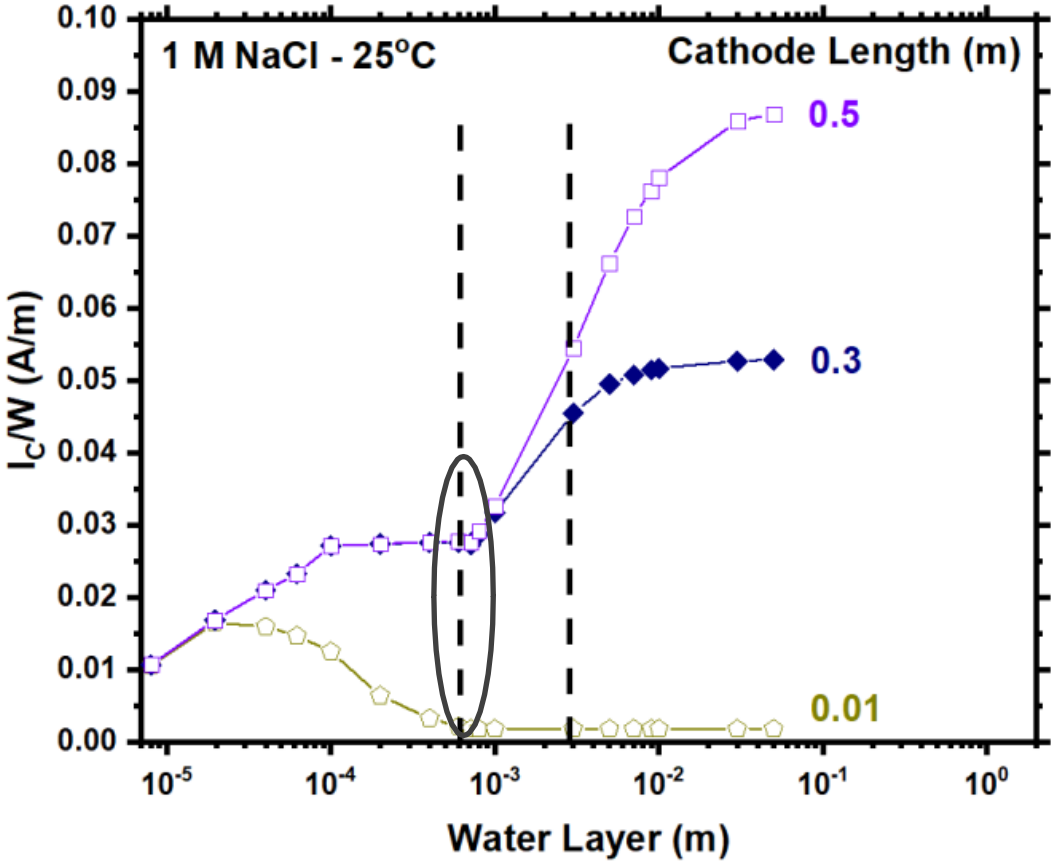
Implications

- Cathode size is very important in accelerated testing scenarios



Implications

- Cathode size is very important in accelerated testing scenarios
- Using small cathodes severely underestimates corrosion damage
  - I_C/W is 15 times greater at the lower angle for the larger cathodes (0.3 and 0.5 m) in comparison to the smaller cathode (0.01 m)



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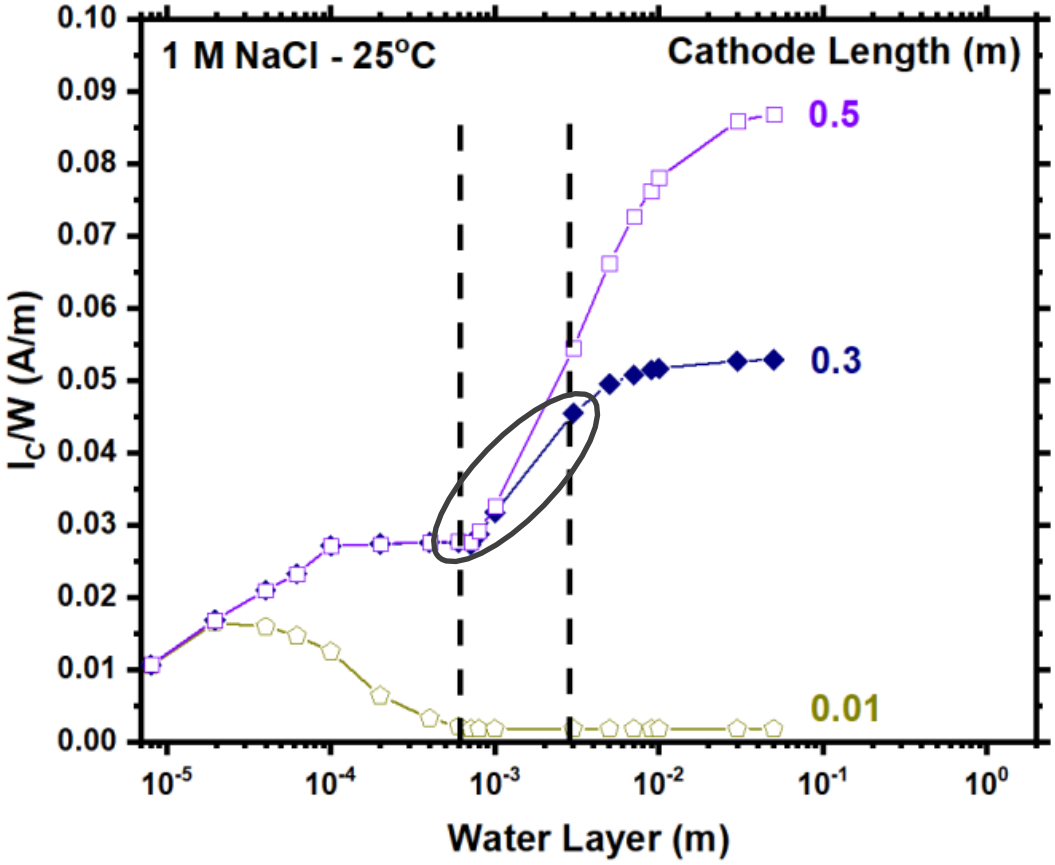
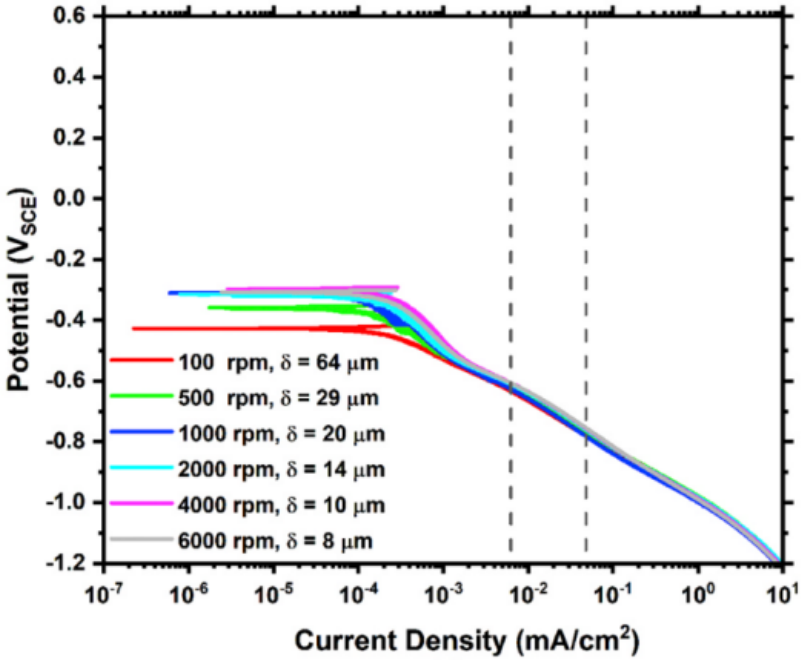
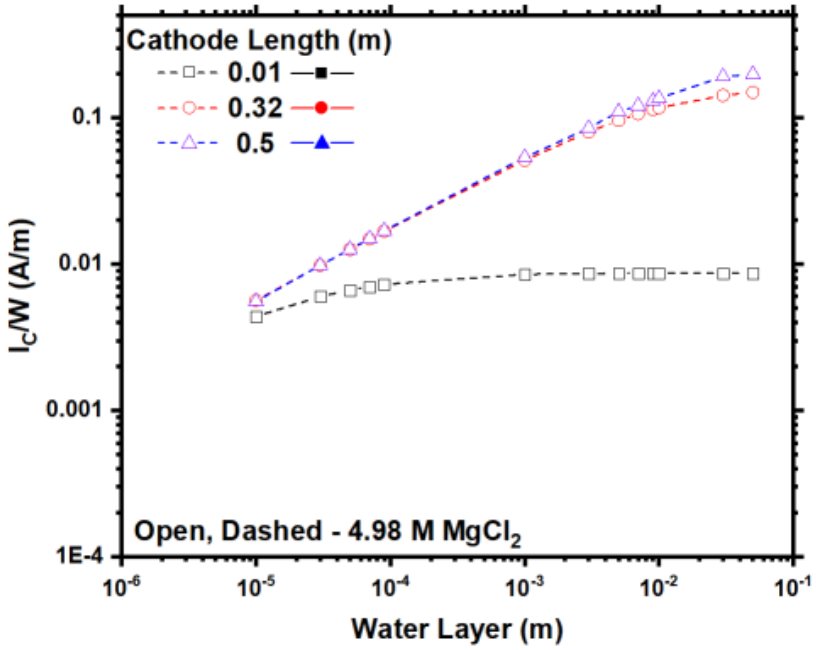


- Same cathode length at different angles will experience different corrosion damage
  - Tests experience large test-to-test and chamber-to-chamber variability
- Difficult to extrapolate corrosion damage to real life scenarios

Changing Solution

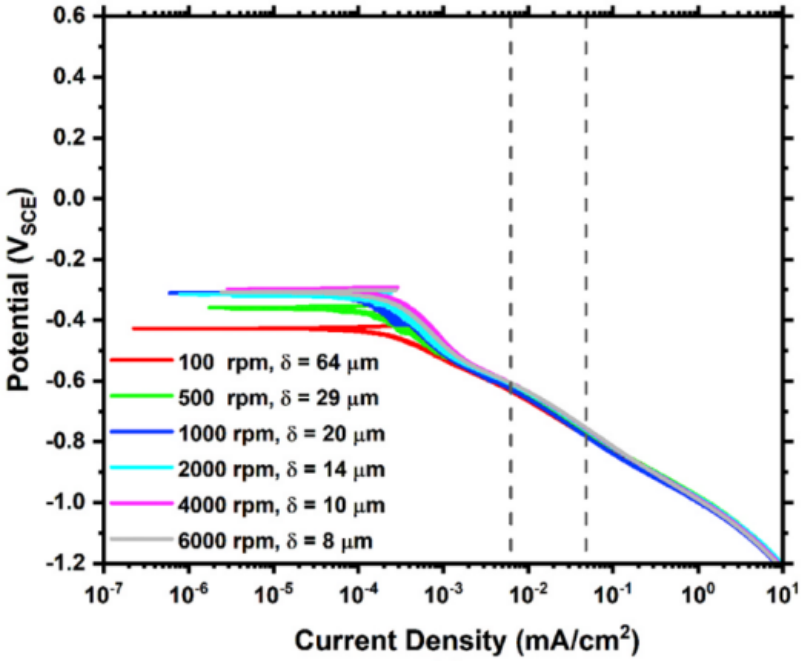


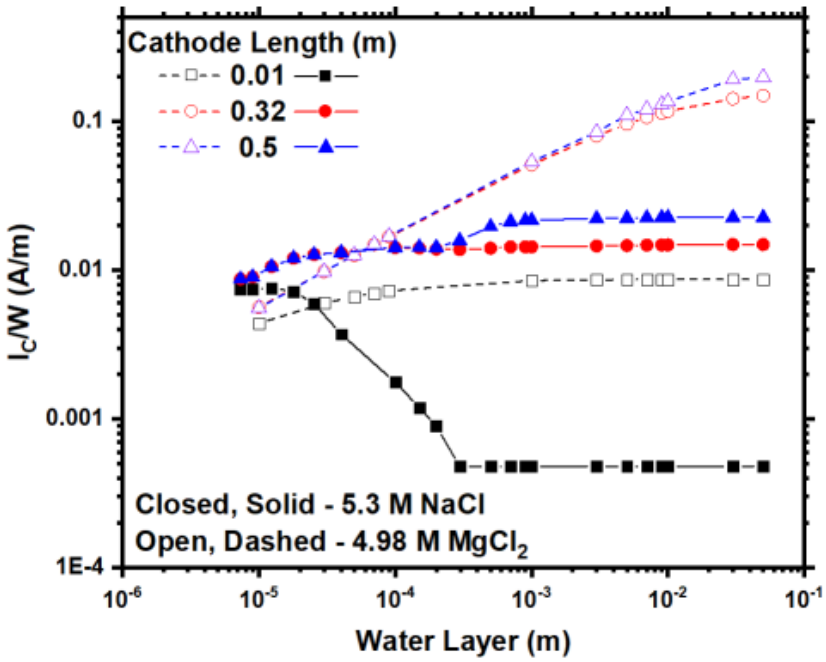


- $MgCl_2$ solutions exhibit no rotational dependence when using an RDE
- I_C/W only increases with increasing WL
  - Ohmic control
  - No M-T limitations

R.M. Katona, J.C. Carpenter, A.W. Knight, C.R. Bryan, R.F. Schaller, R.G. Kelly, E.J. Schindelholz, Corros. Sci. 177 (2020) 108935.

Changing Solution





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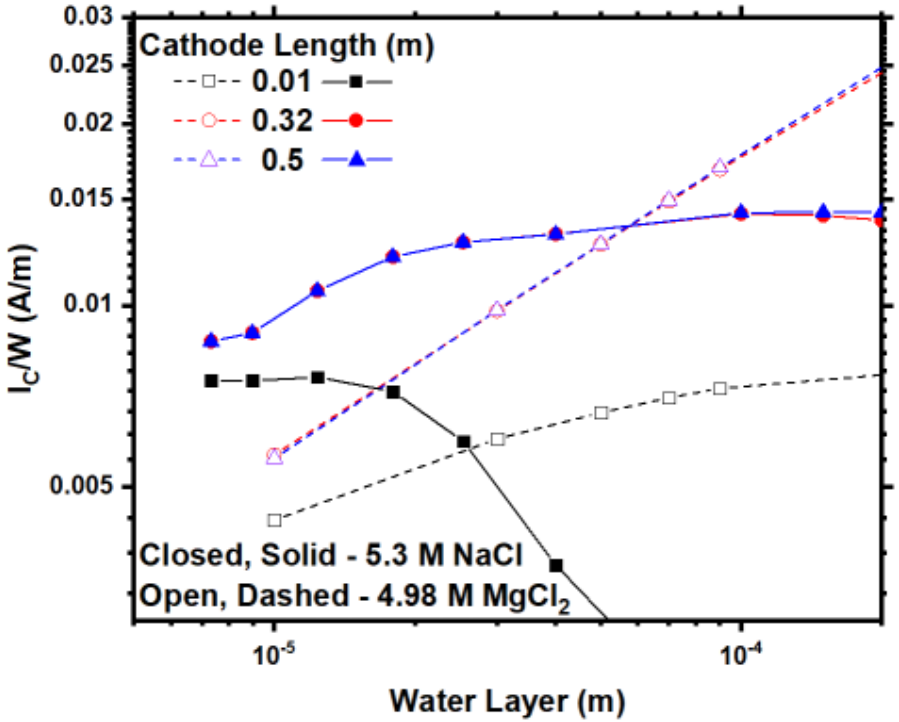
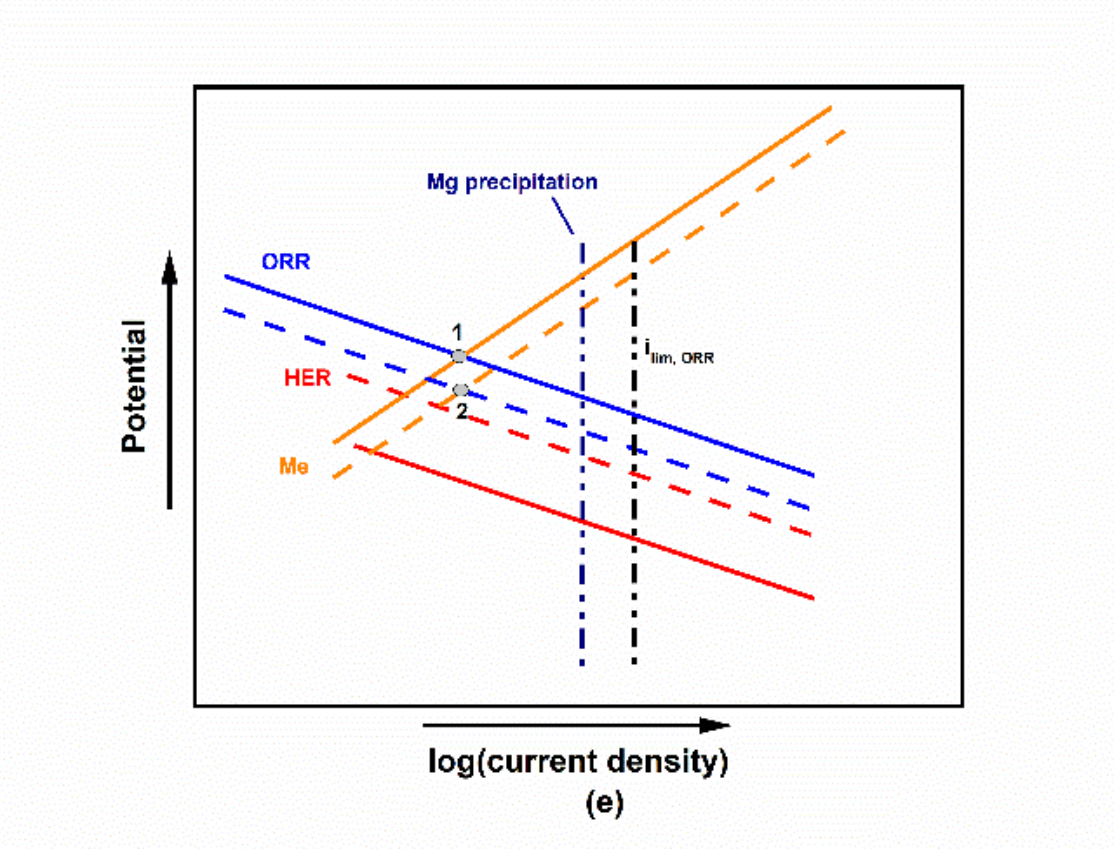


- At small WL, NaCl has a higher I_C/W
  - Due to current density dependence on WL
- When increasing WL, NaCl experiences more M-T limitations whereas $MgCl_2$ does not due to a lack of WL dependence on the cathodic kinetics

R.M. Katona, J.C. Carpenter, A.W. Knight, C.R. Bryan, R.F. Schaller, R.G. Kelly, E.J. Schindelholz, Corros. Sci. 177 (2020) 108935.

$MgCl_2$ Cathodic Kinetics



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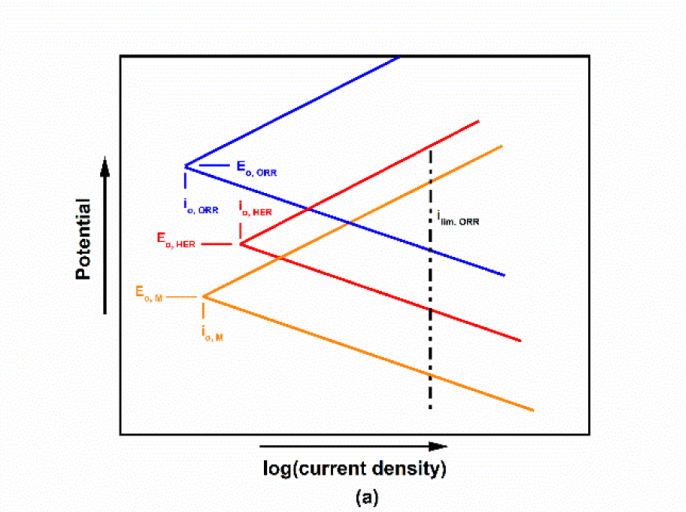
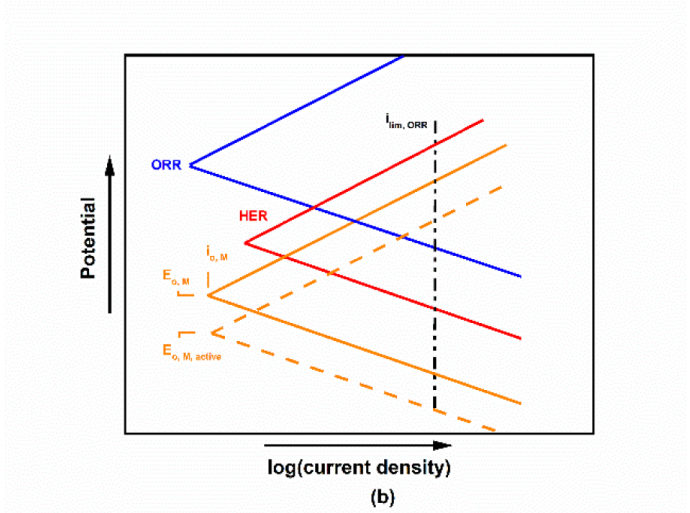
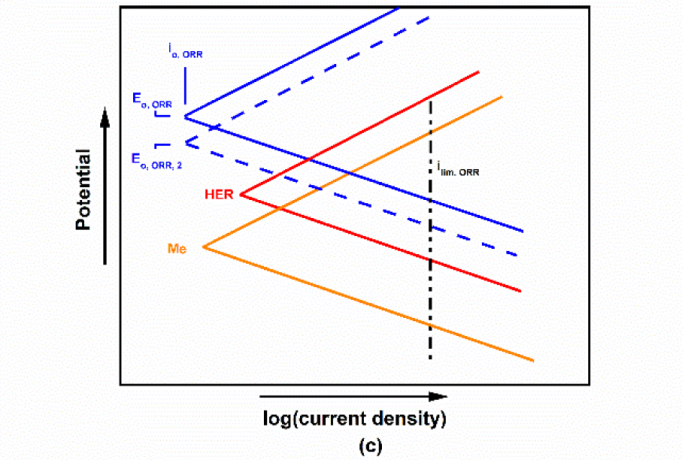
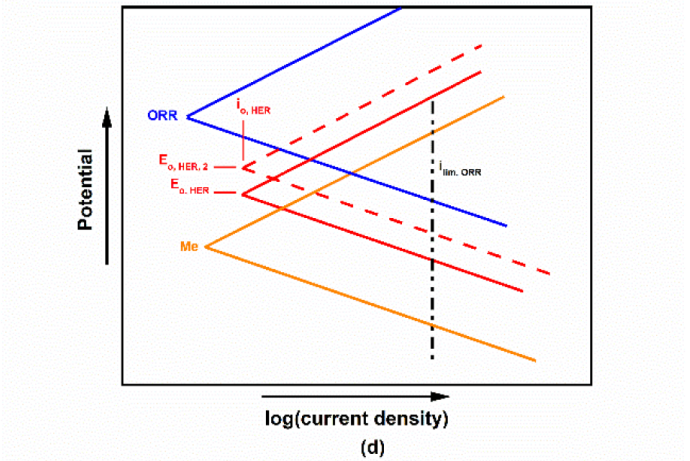
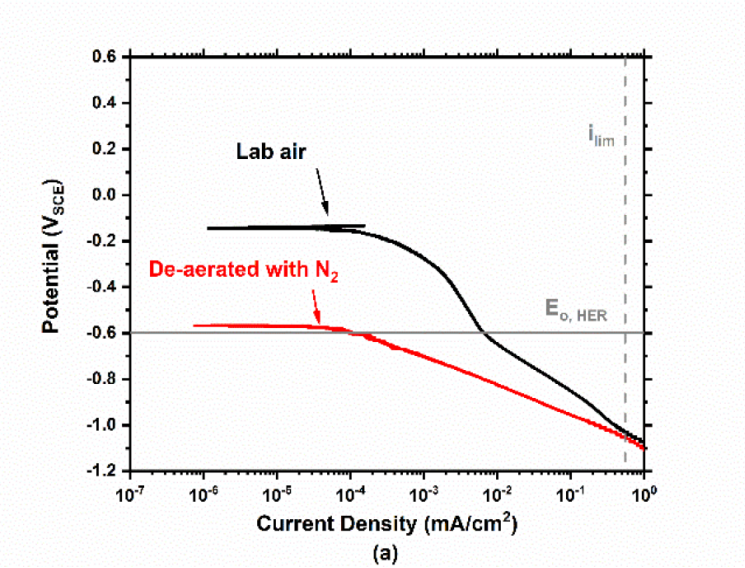


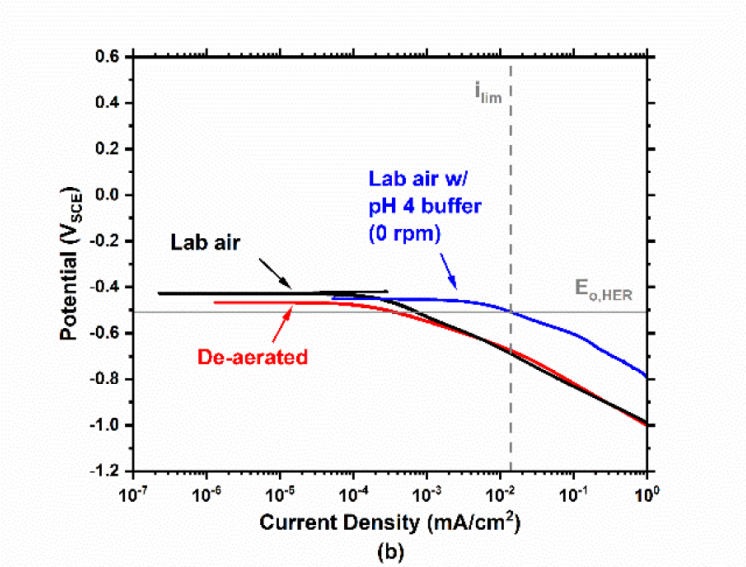






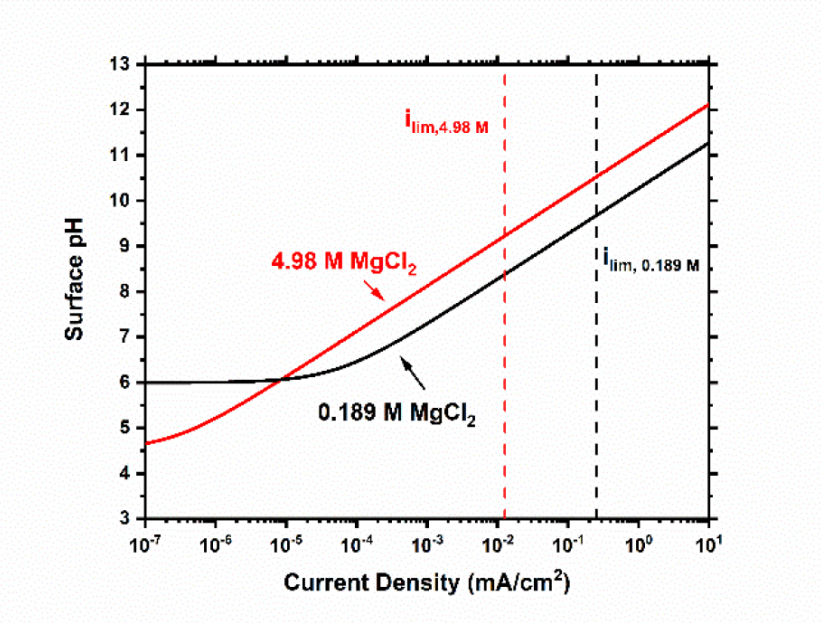
$MgCl_2$ cathodic kinetics





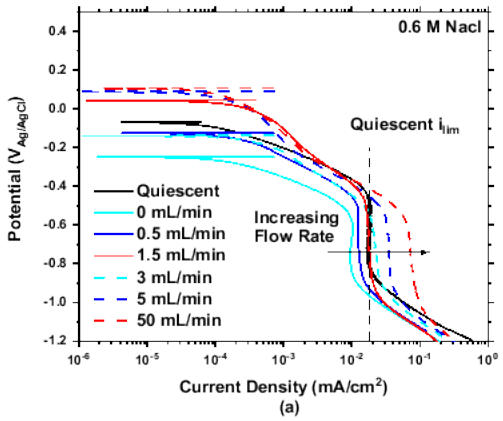
- Comparison of cathodic polarization scans on SS304L in aerated and N_2 de-aerated solutions for (a) 0.189 and (b)4.98 M $MgCl_2$ at 25°C and 500 rpm. Also shown in (b) is a polarization scan with an acetic acid buffer added to solution. Nernst potentials are calculated for a pH of (a) 6 and (b) 4.5 through Equation 11.

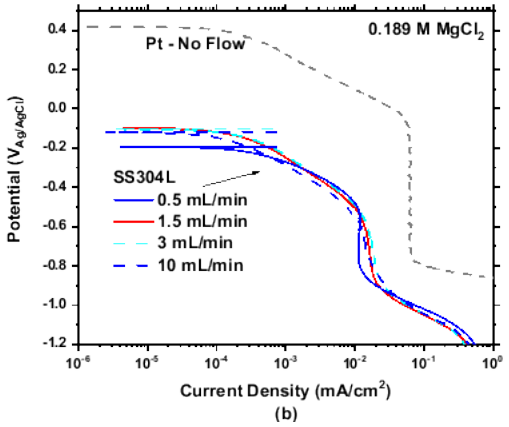
$MgCl_2$ cathodic kinetics



- Surface pH for SS304L at δ=20 and 19 µm in 0.189 M and 4.98 M MgCl2 respectively, calculated using Equation 10. The vertical dashed line labeled ilim corresponds each δ calculated from Equation 3 using data from Figure 2.

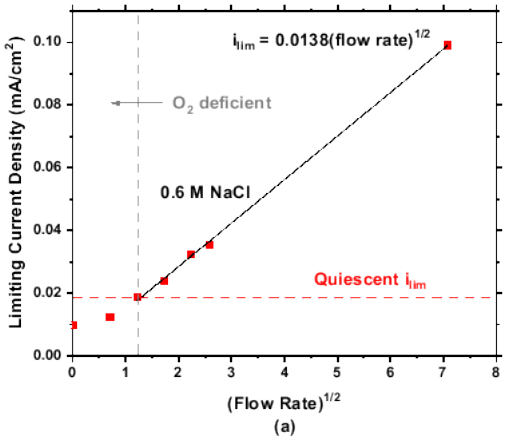
In-situ Raman

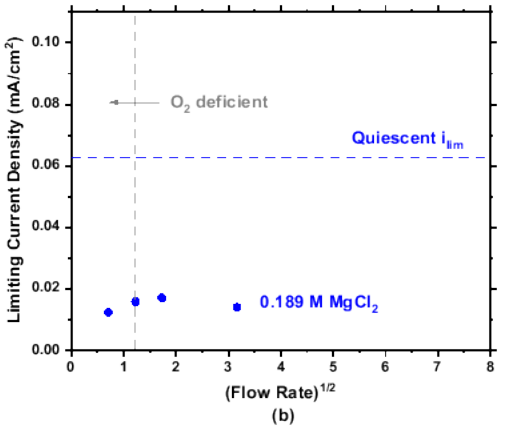


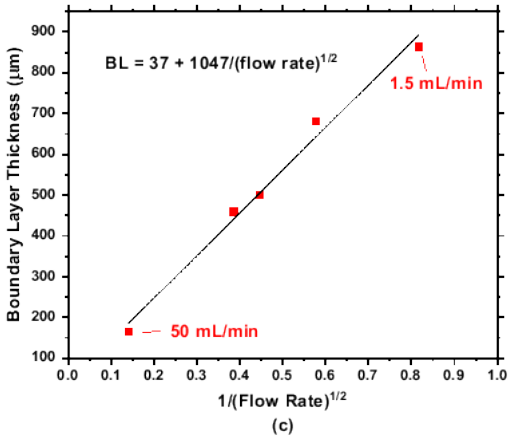


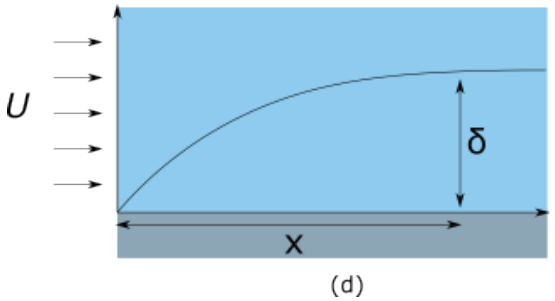
- Effect of solution flow rate on the cathodic polarization of 304L SS in (a) 0.6 M NaCl and (b) 0.189 M $MgCl_2$ in the flow cell. Also in (b) is a polarization scan for Pt alloy under quiescent conditions [9].

In-Situ Raman



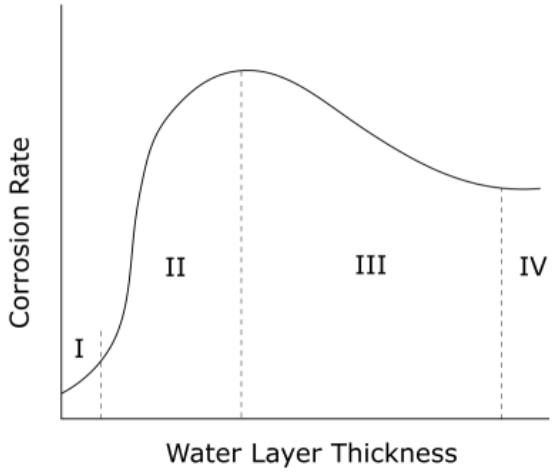






- Influence of Q on the limiting current density of SS304L for (a) 0.6 M NaCl and (b) 0.189 M $MgCl_2$. (c) Calculated effective boundary layer thicknesses as a function of flow rate for 0.6 M NaCl solutions. (d) Schematic for boundary layer thicknesses

WL thickness influences



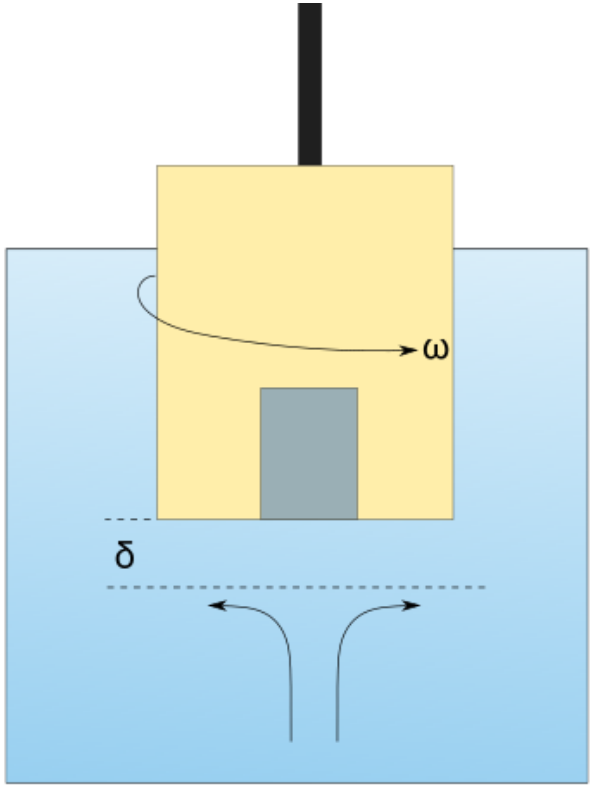
N.D. Tomashov, CORROSION. 20 (1964) 7t-14t.

Putting the WL into Perspective

- When using a rotating disk electrode (RDE) a hydrodynamic boundary layer can simulate WL thicknesses

$$\delta \propto \frac{D^{1/3}\nu^{1/6}}{\omega^{1/2}}$$

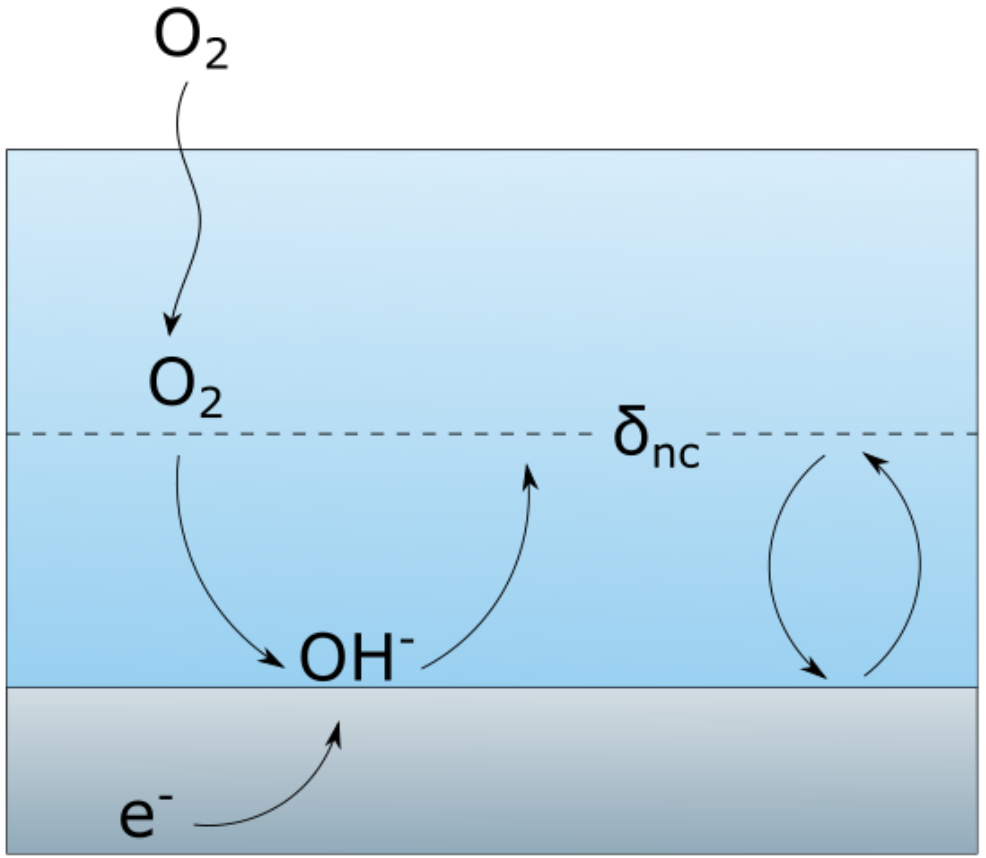
- Dependent upon diffusion coefficient (D), kinematic viscosity (ν) and the rotation rate (ω)
- Values range from ~7 to 200 µm depending on solution values and rotation rate



Natural Convection Boundary Layer

- Natural convection occurs in solutions that have thermally or compositionally driven spatially inhomogeneous density distributions
- When oxygen is being reduced:

$$O_2 + 2H^+ + 4e^- \rightarrow 4OH^-$$



- **<u>Determines the transition between atmospheric and bulk conditions</u>**

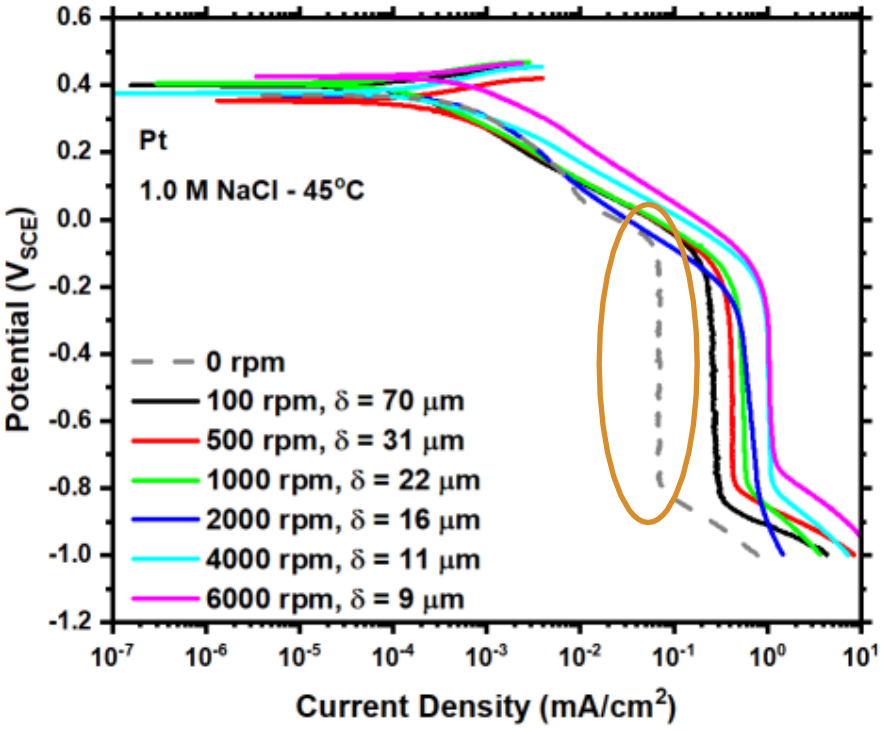
Natural Convection Boundary Layer

- Limiting current densities can be predicted based on Fick's first law:

$$i_{lim} = \frac{nFD(C_{bulk} - C_{surface})}{\delta}$$

- If there was no natural convection creating a boundary layer,

$$\delta \rightarrow \infty \qquad i_{lim} \rightarrow 0$$

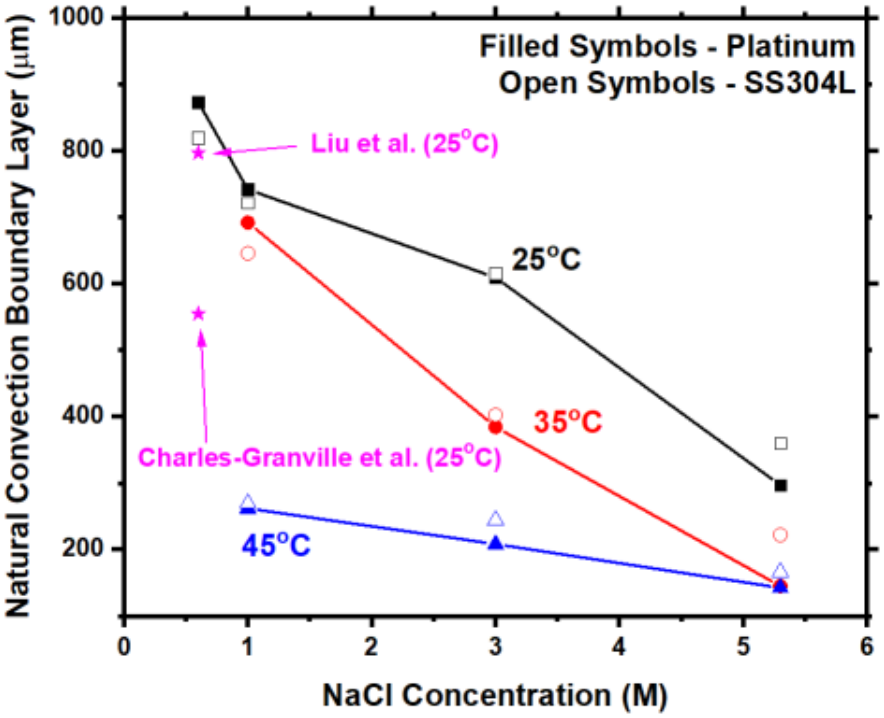


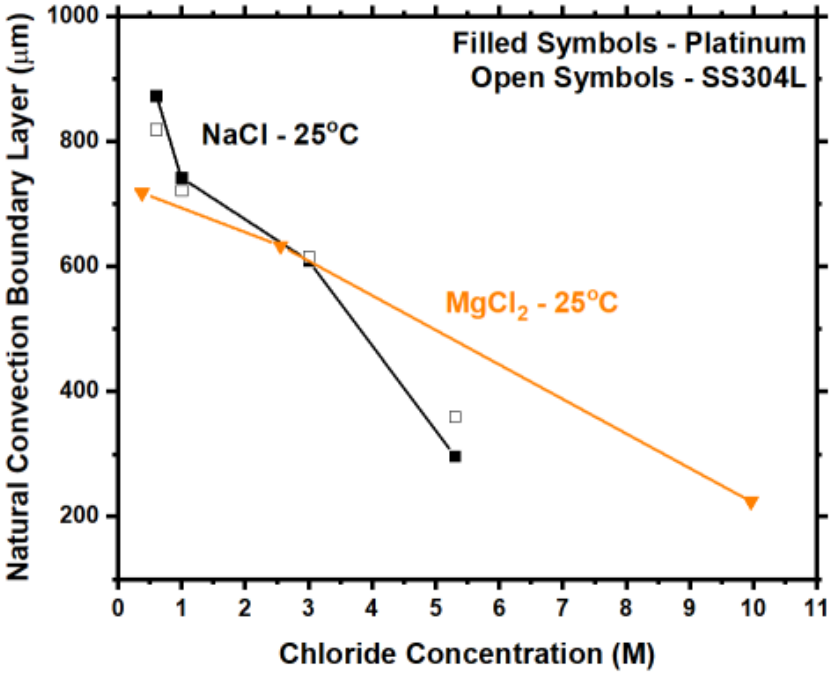
- Liu et al. determined the natural convection boundary layer to be roughly 800 μm in 0.6 M NaCl

C. Liu, J. Srinivasan, R.G. Kelly, J. Electrochem. Soc. 164 (2017) C845–C855.

Natural Convection Boundary Layer

- Increasing NaCl concentration decreases δ_{nc}
- Increasing temperature decreases δ_{nc}





- Trends hold for $MgCl_2$ solutions

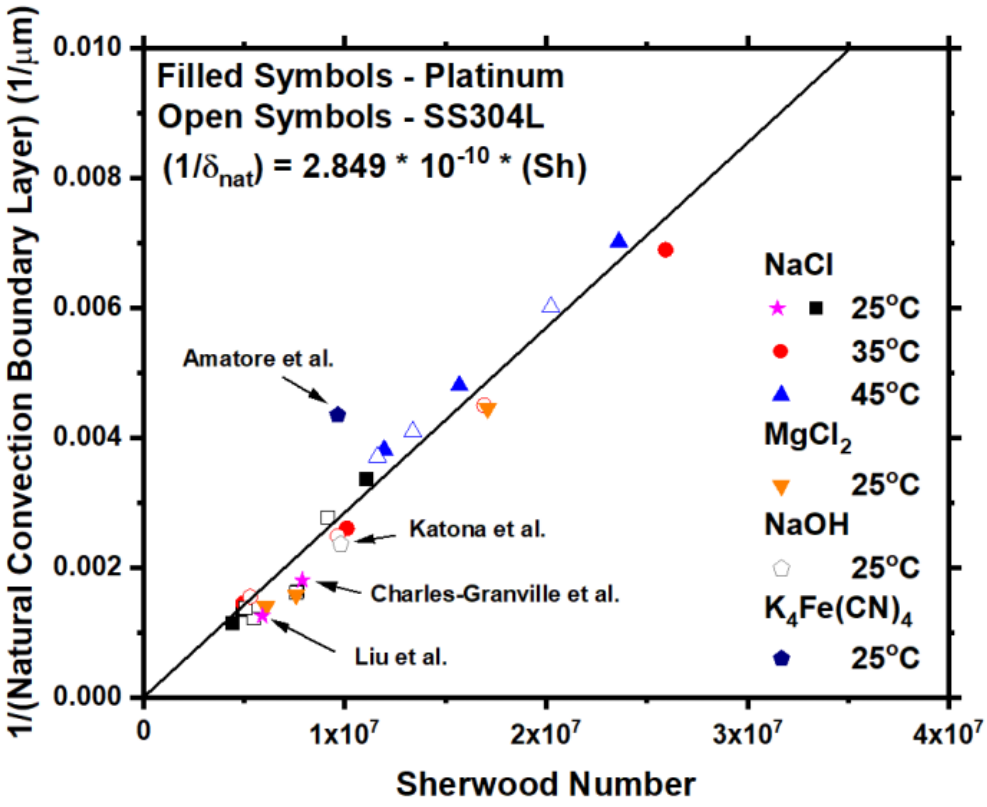
R.M. Katona, J.C. Carpenter, A.W. Knight, C.R. Bryan, R.F. Schaller, R.G. Kelly, E.J. Schindelholz, Corros. Sci. 177 (2020) 108935.

Can we predict δ_{nc}?

- δ_{nc} does not scale with i_{lim} or any other singular solution property ($C_{O_2}, D_{O_2}, etc.$)
- Mass transport in electrochemical systems can be described with dimensionless values

$$K = \frac{i_{lim}}{nFC_{bulk}}$$

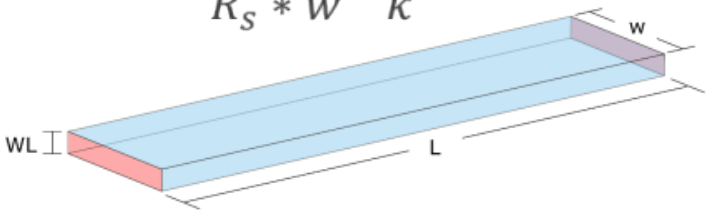
$$Sh = \frac{K}{D/d}$$

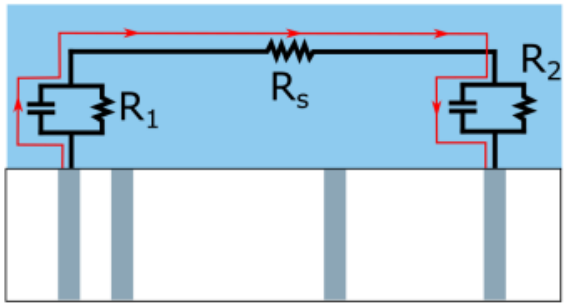


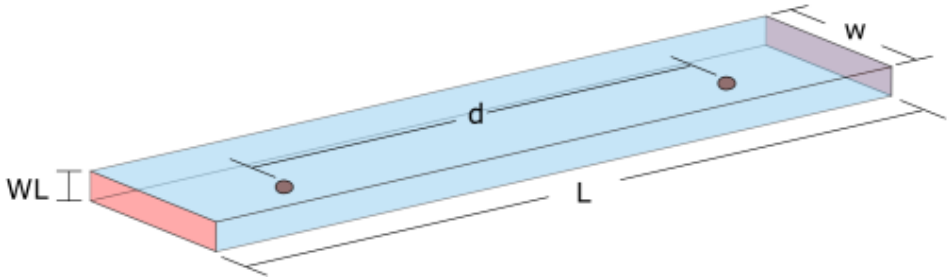
- Literature results match well with fit

Measuring WL thicknesses

$$WL = \frac{L}{R_s * w} * \frac{1}{\kappa}$$



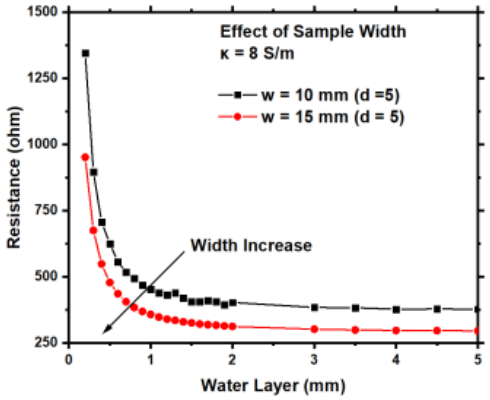


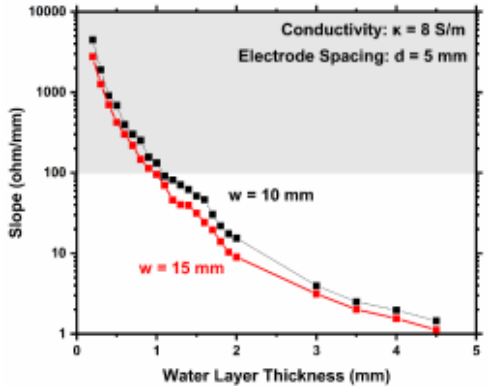


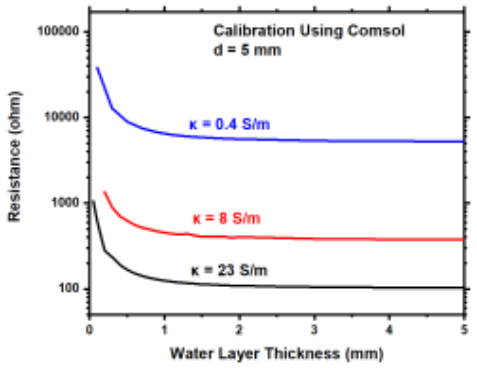
$$R_s = \frac{\Delta V}{\int I}$$

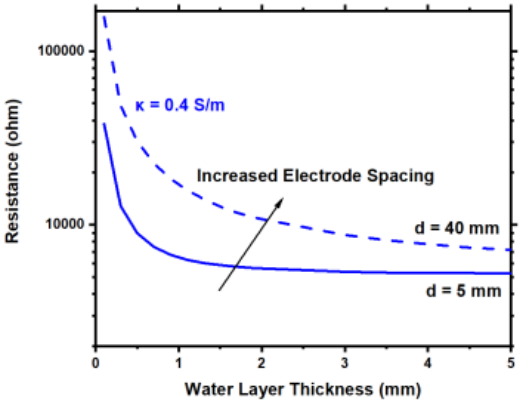
- a

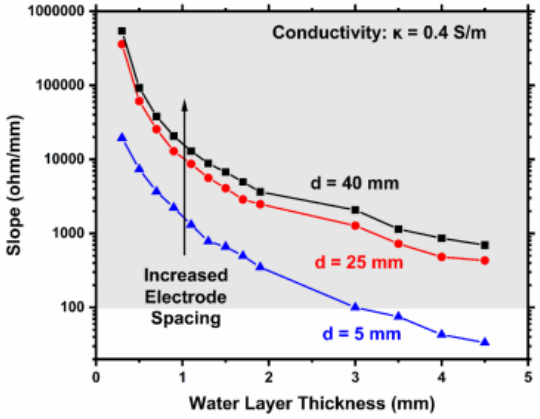
Measuring WL thicknesses

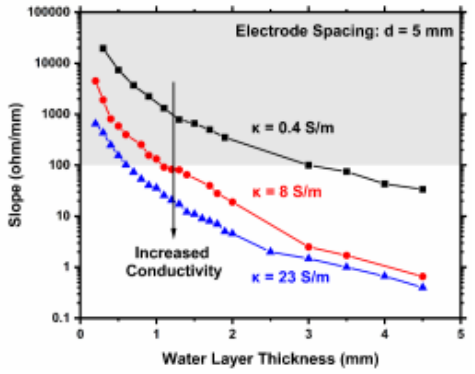




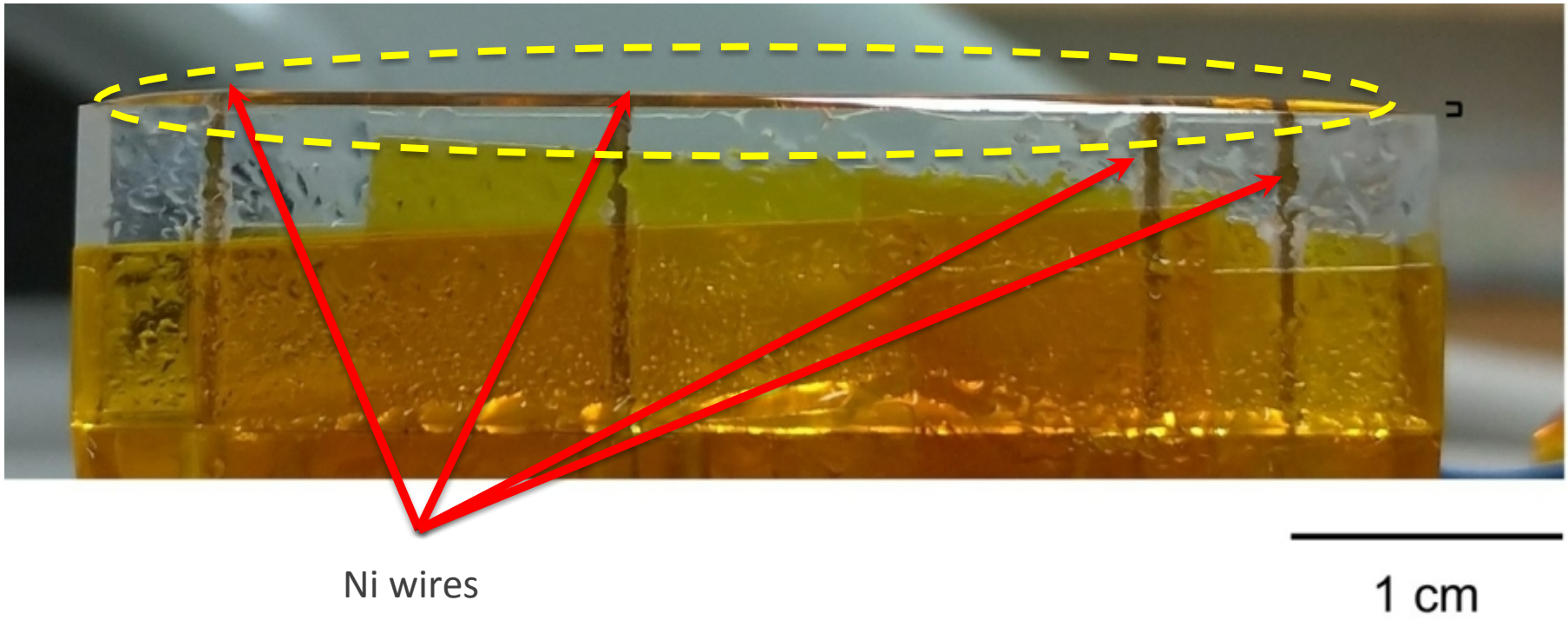








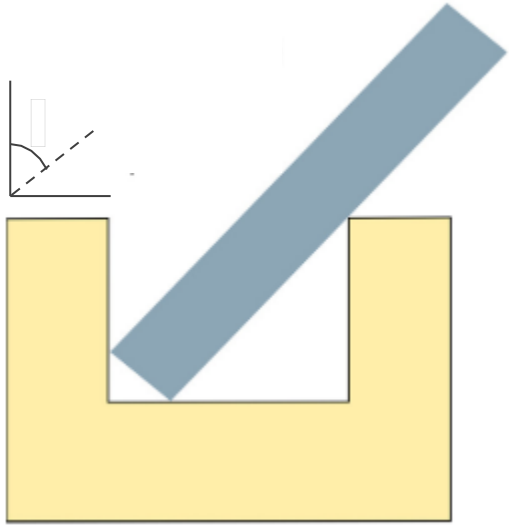
Measuring WL thickness

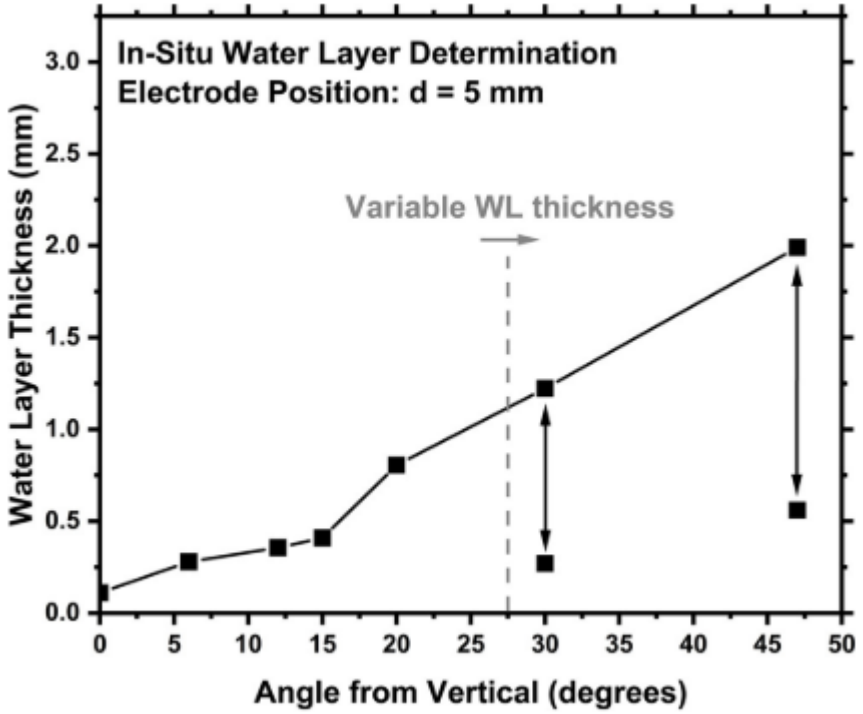


- s

Putting the WL into Perspective

- In accelerated corrosion scenarios, WL thicknesses are based on angle of exposure



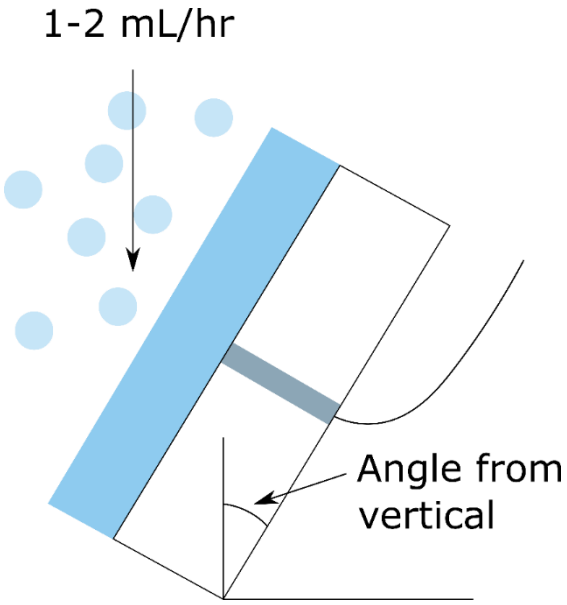


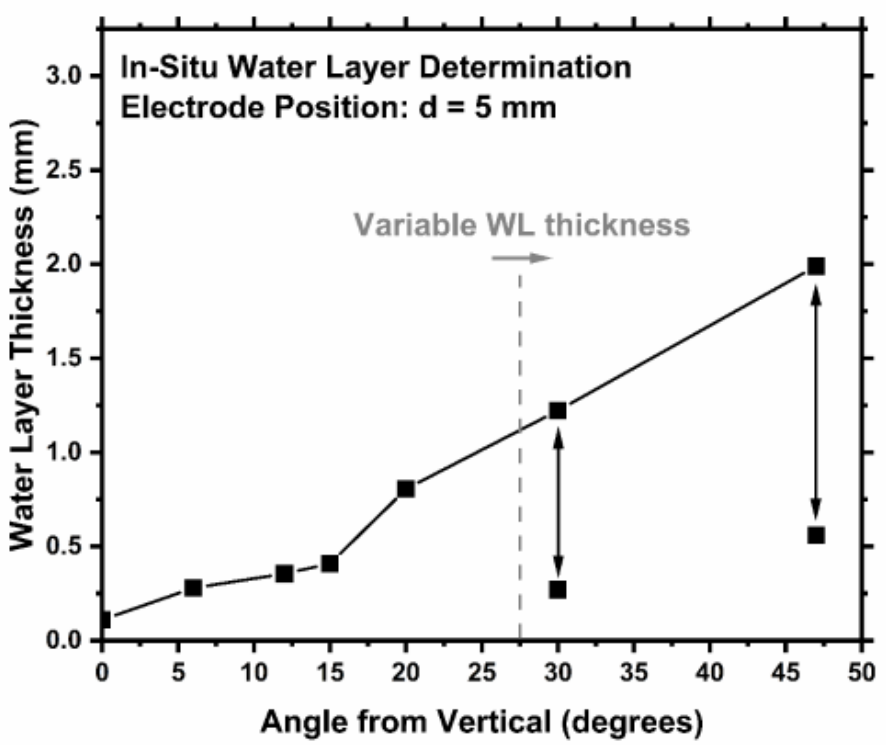
- Under ASTM B117 (15 – 30˚), WL varies from 660 – 1210 µm
- Transient WL present at certain angles of exposure

R.M. Katona, S. Tokuda, J. Perry, R.G. Kelly, Corros. Sci. 175 (2020) 108849.

Angle of exposure varies WL thickness significantly

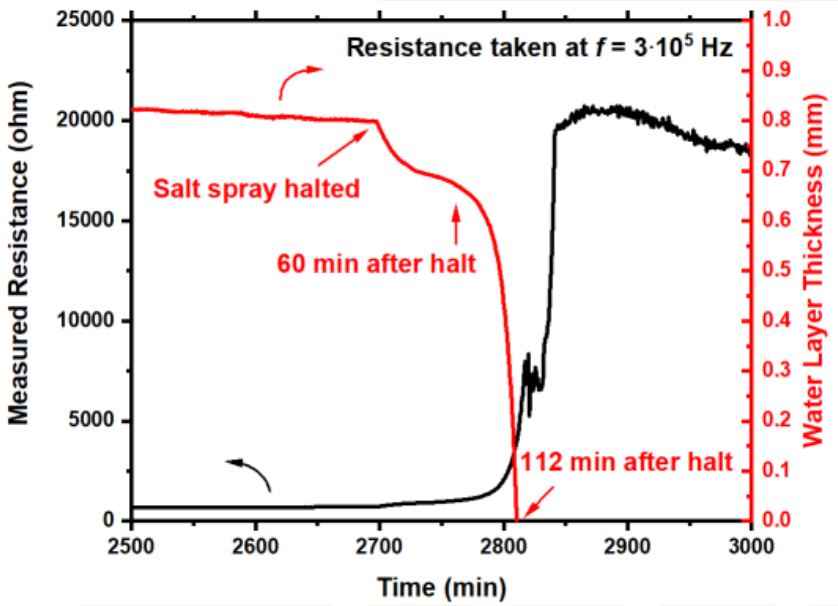
- Increasing angle of exposure increases WL thickness





Evaporation occurs during shut-off periods

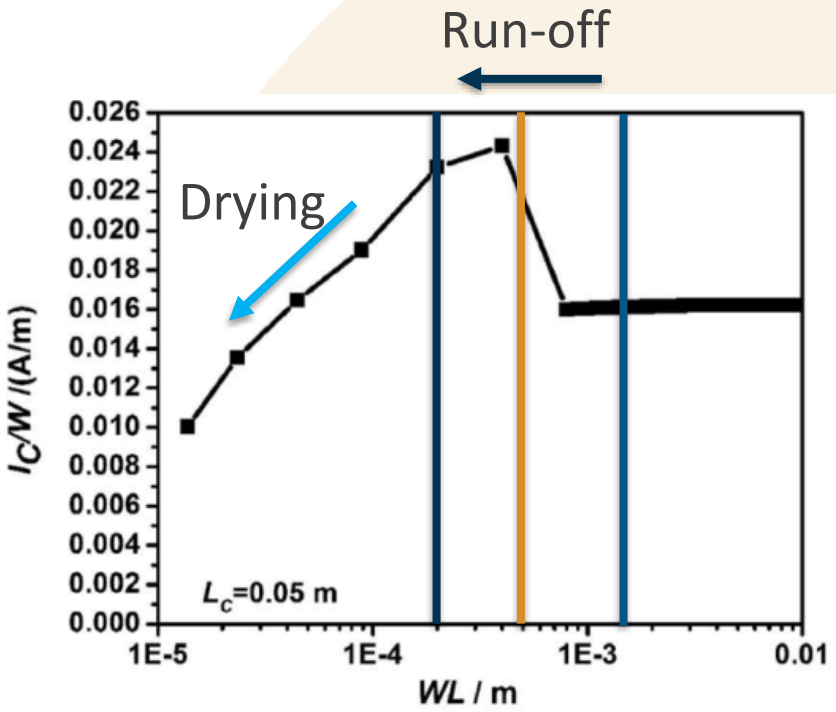
- Salt spray was stopped after roughly 45 hours of exposure and measurements were continuously taken
- Lid of chamber was left shut but fan started
- Within 1 hour of the shut-off, the WL thickness decreased 0.15 mm (18.5%)
- No WL after 112 min



Angle of sample and test interruptions are allowable within ASTM standards can drastically influence WL thickness and corrosion rate

Water layer and cathode length impact cathodic current in a galvanic couple

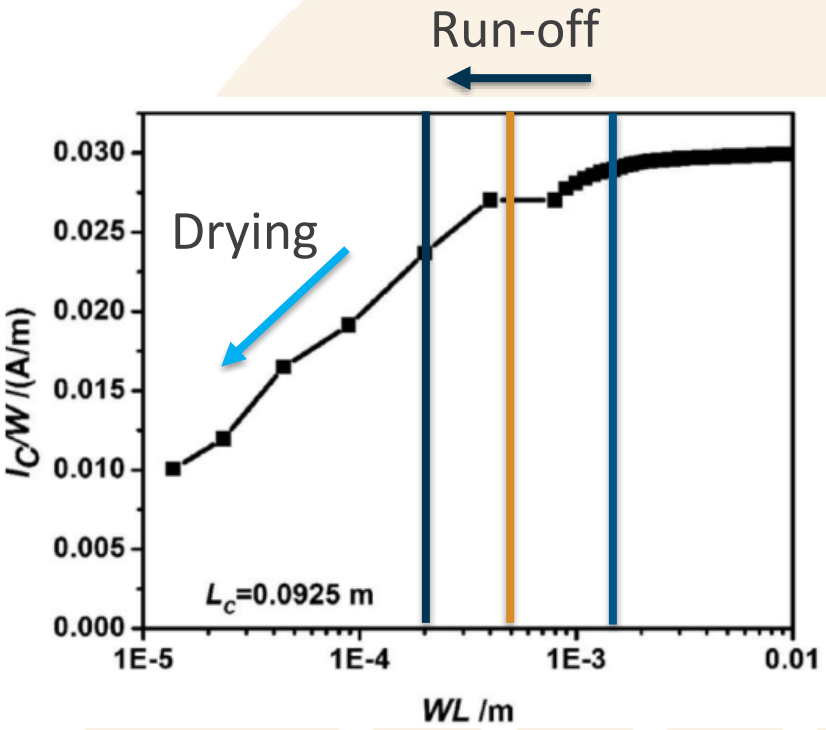
- Increased current seen at 15˚
- Mass transport limitations on current calculated at a WL corresponding to an angle of exposure of 30˚
- But remember, there is run-off at high angles of exposure
- Drying will further decrease WL and current



C. Liu et al., J. Electrochem. Soc. 164 (2017) C845–C855.

Water layer and cathode length impact cathodic current in a galvanic couple

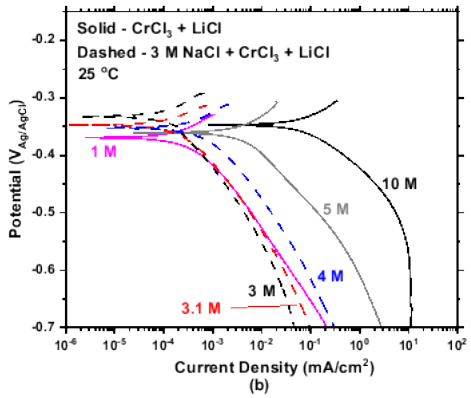
- Highest current seen at an angle of exposure of 30˚
- Decreasing angle to 15˚ decreases current
- Run-off and drying further decrease current

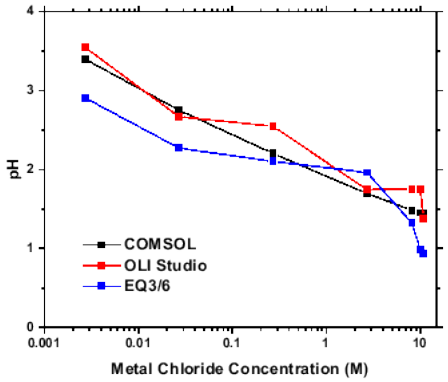


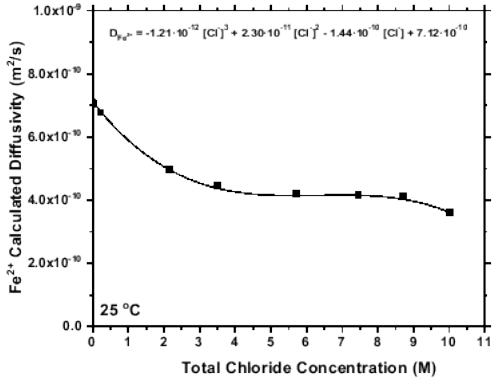
C. Liu et al., J. Electrochem. Soc. 164 (2017) C845–C855.

CGR Modeling

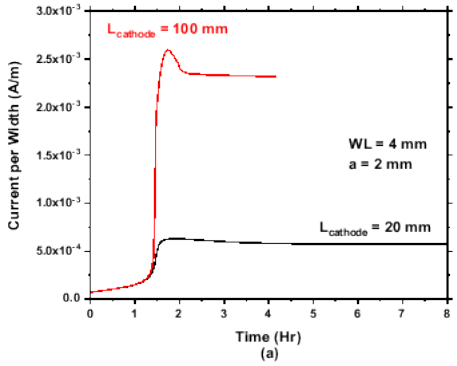
- Boundary conditions

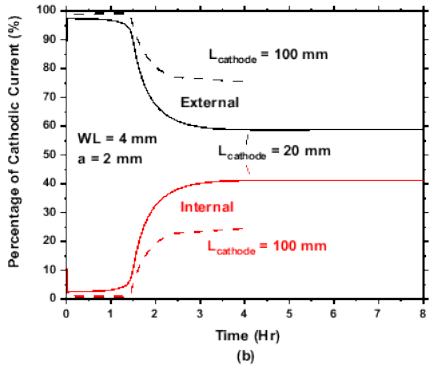


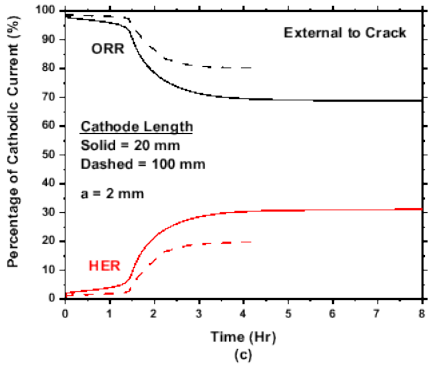


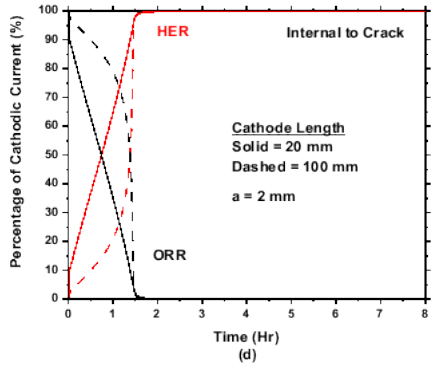


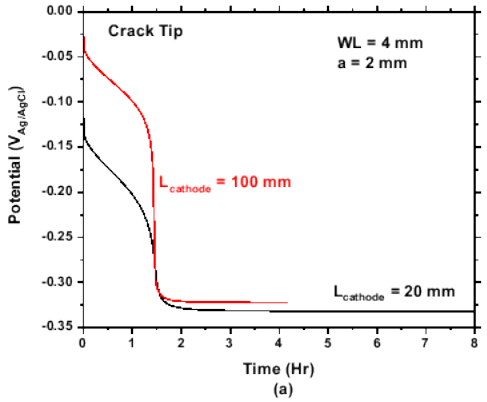
Cathode Length

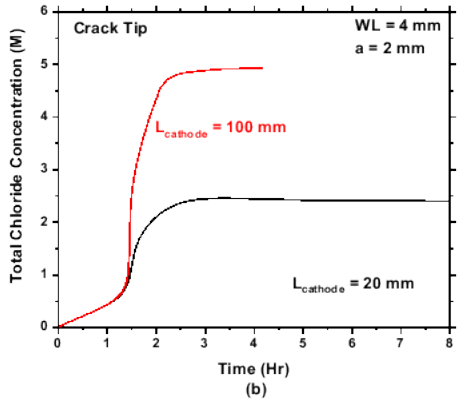


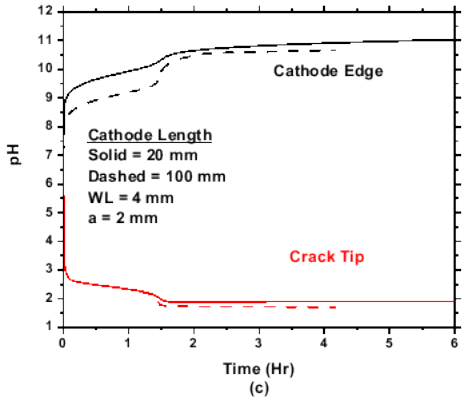




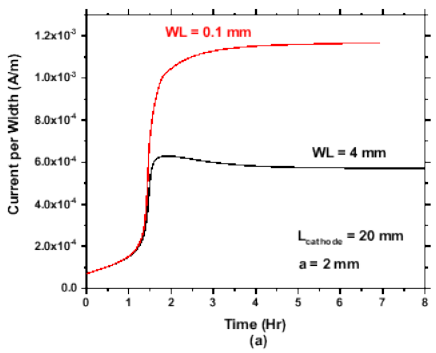


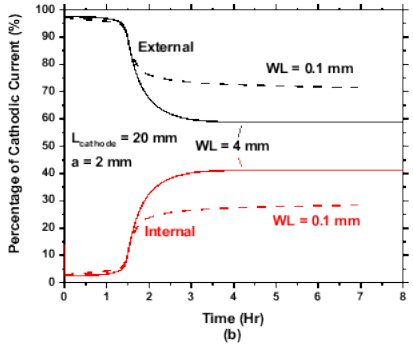


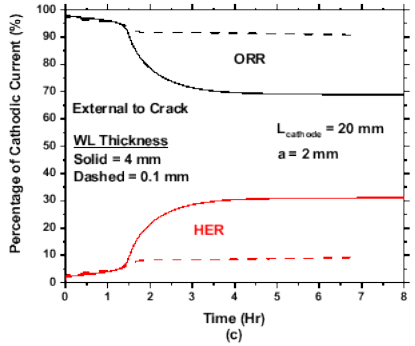


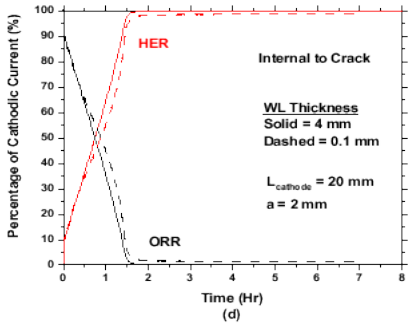


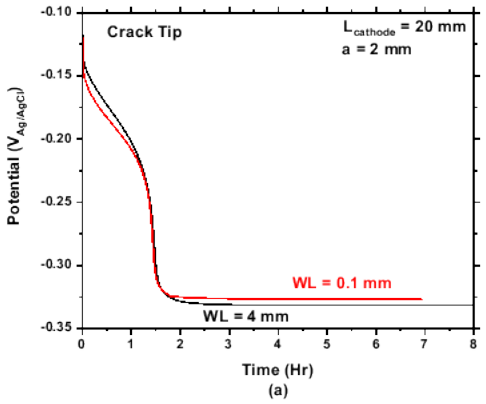
WL thickness

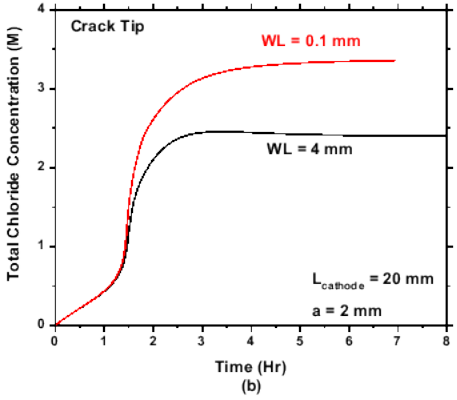


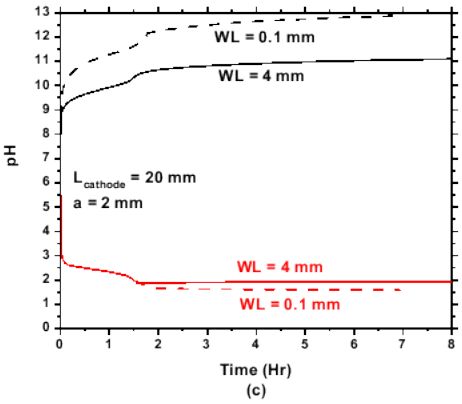




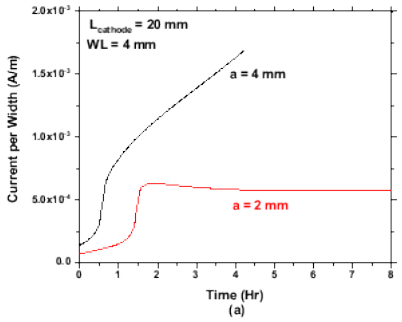


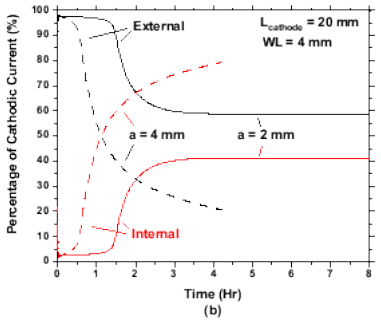


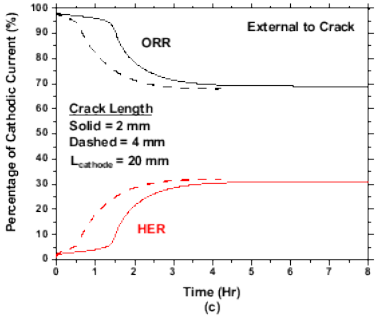


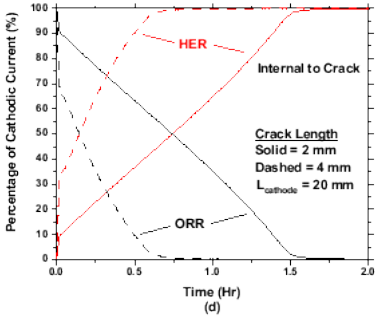


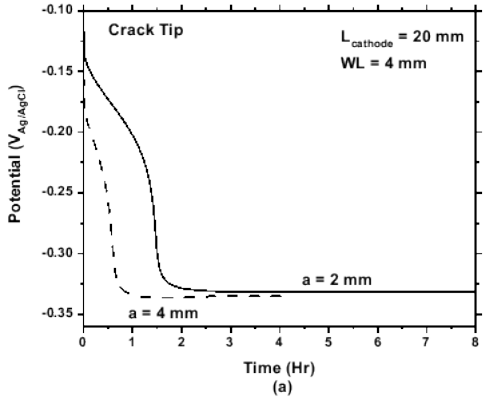
Crack Length

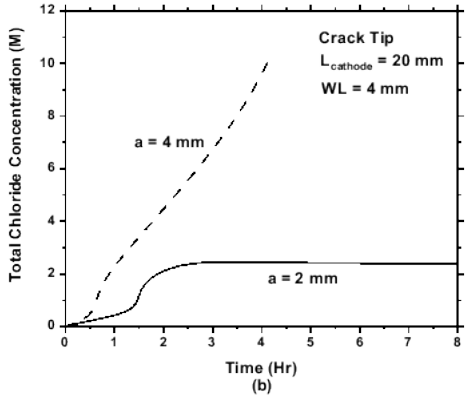


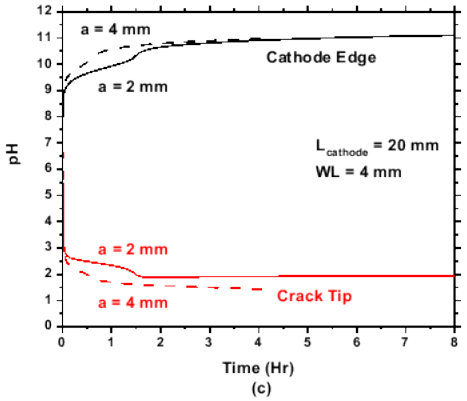




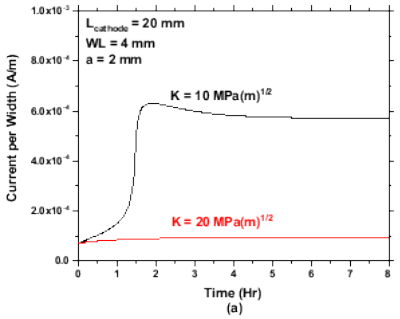


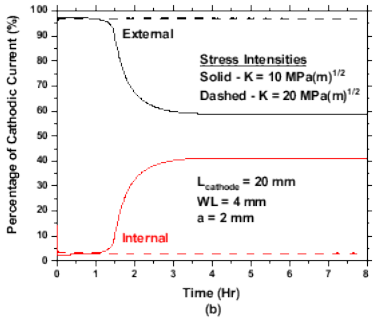


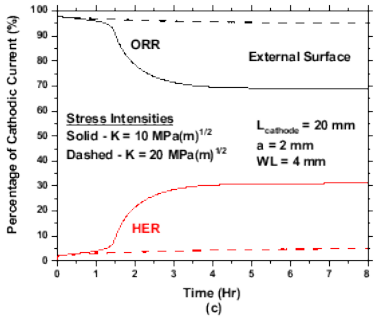


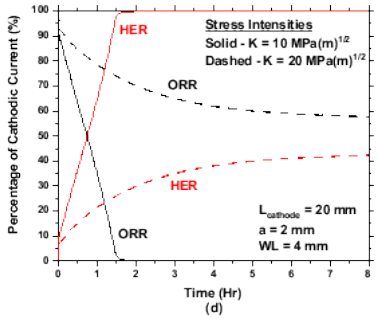


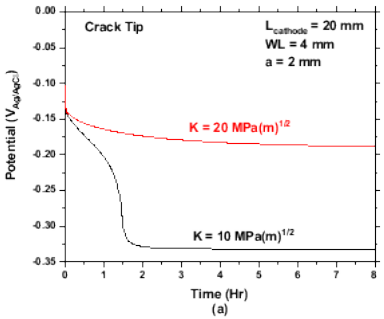
Stress intensity

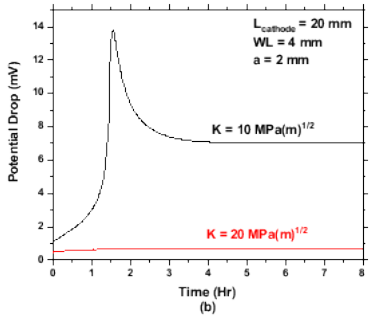


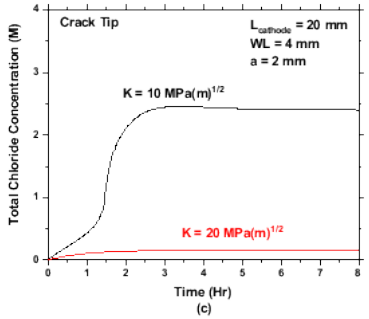


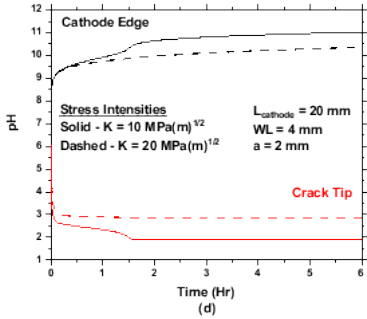




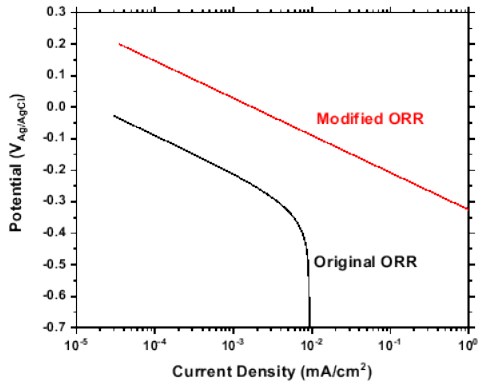


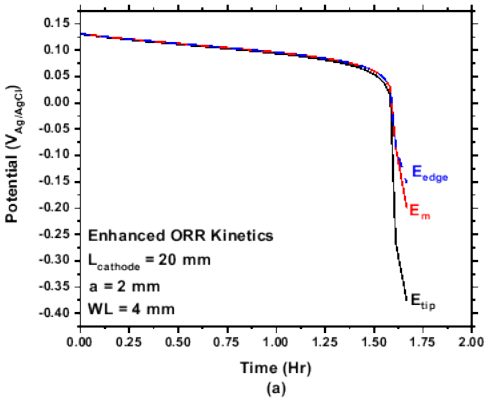


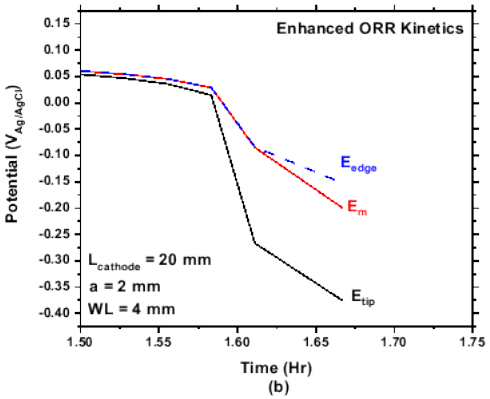


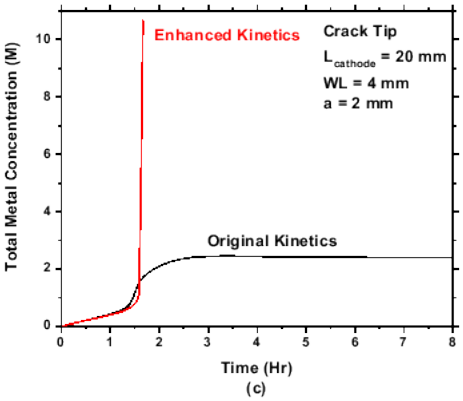


Modified ORR

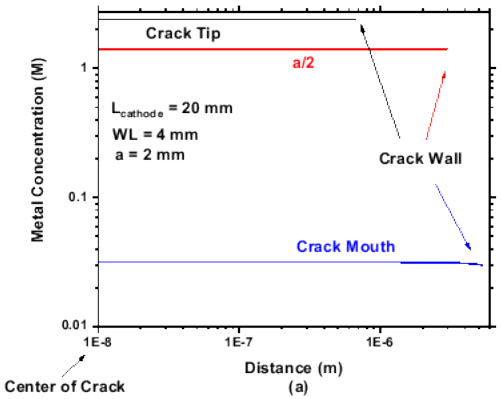


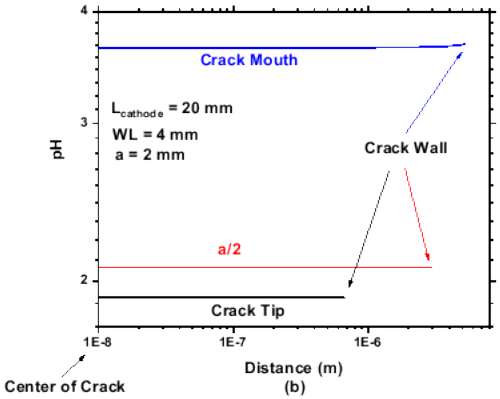


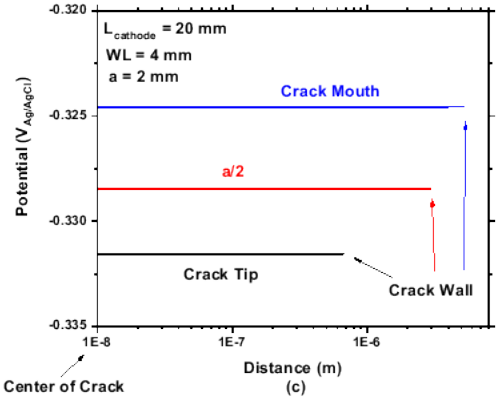




Distributions across a crack







Influence of crack geometry

$K\ (MPa\sqrt{m})$	Geometry	Crack Width (m)	$E_{tip}\ (V_{Ag/AgCl})$	pH_{tip}	$Cl_{tip}\ (M)$
10	Parallel-sided	$\frac{CTOD + CMOD}{2}$	-0.219	4.64	0.33
10	Trapezoidal	$CTOD$ to $CMOD$	-0.332	1.92	2.41