SAND2021-4820PE

Understanding Governing Factors of Localized Corrosion in Marine Environments

R. M. Katona[1,2]

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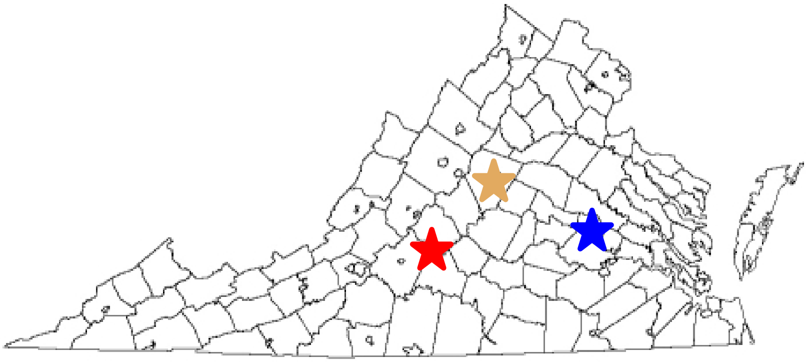
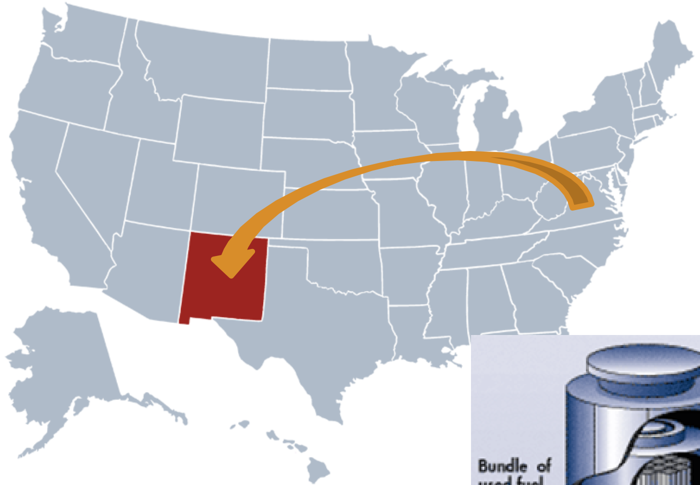
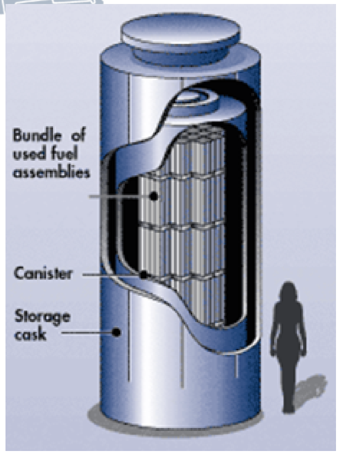
About me

- From right outside Richmond, VA
- Bachelor of Science in Physics and Mathematics – 2017
  - University of Lynchburg (VA)
- Master of Engineering in Materials Science and Engineering – 2019
  - University of Virginia (UVA)
- PhD in Materials Science and Engineering – Expected Summer 2021
  - Anodic and Cathodic Limitations on Localized Corrosion and Stress Corrosion Cracking Propagation of Stainless Steel 304L in Atmospheric Environments
- Graduate Student Intern
  - Storage and Transportation technology

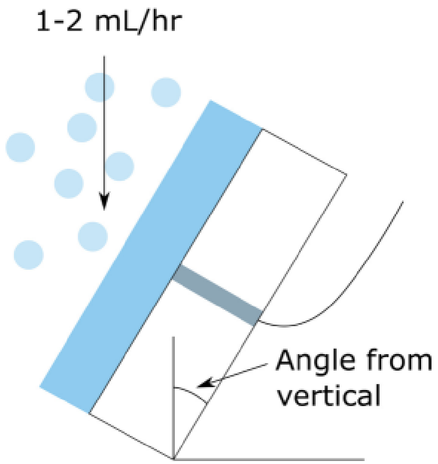






About Graduate School

- Advisor: Dr. Robert Kelly
- Center for Electrochemical Science and Engineering (CESE)
- Outreach
  - Creation of 3D printing class for 4-5TH graders ay the UVA Curry School for Education
- Consulting at UVA
  - Assisted in creating a Virtual Twin for a spent nuclear fuel canister
  - Incorporation of pit modeling into twin to identify potentials for materials degradation
- Highlighted Research (not presented today)
  - Creation of sensor to determine water layer thickness in accelerated testing
- Publication record
  - 9 publications accepted/submitted (7 first author)



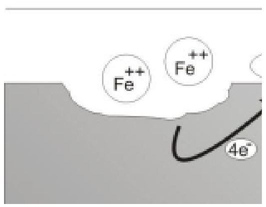
At Sandia

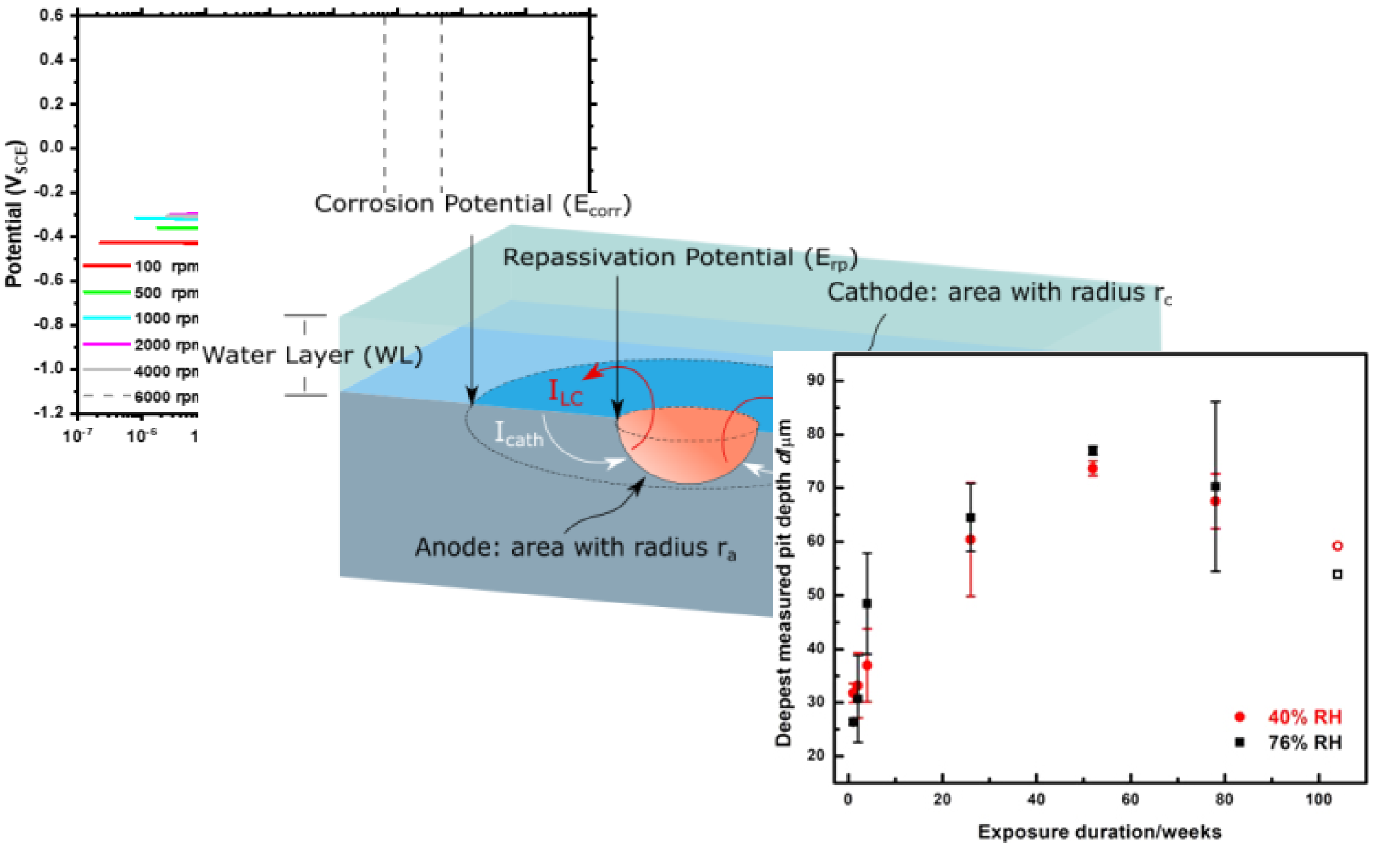
- Advisor: Dr. Rebecca Schaller (Materials Reliability)
  - Previously Dr. Eric Schindelholz
- Working in Storage and Transportation Technology
- Proposals
  - Three proposals written with one successfully funded
- Creation of laboratory space
  - Lead environmental assessments, failure modes analysis, and created working documents
- Experimental design and testing on electromechanical and hydraulic fracture mechanics load frames
- Advised multiple undergraduate students from University of New Mexico
  - Taught fundamentals of electrochemistry
  - Helped create posters for presentation at conferences

Overview

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

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

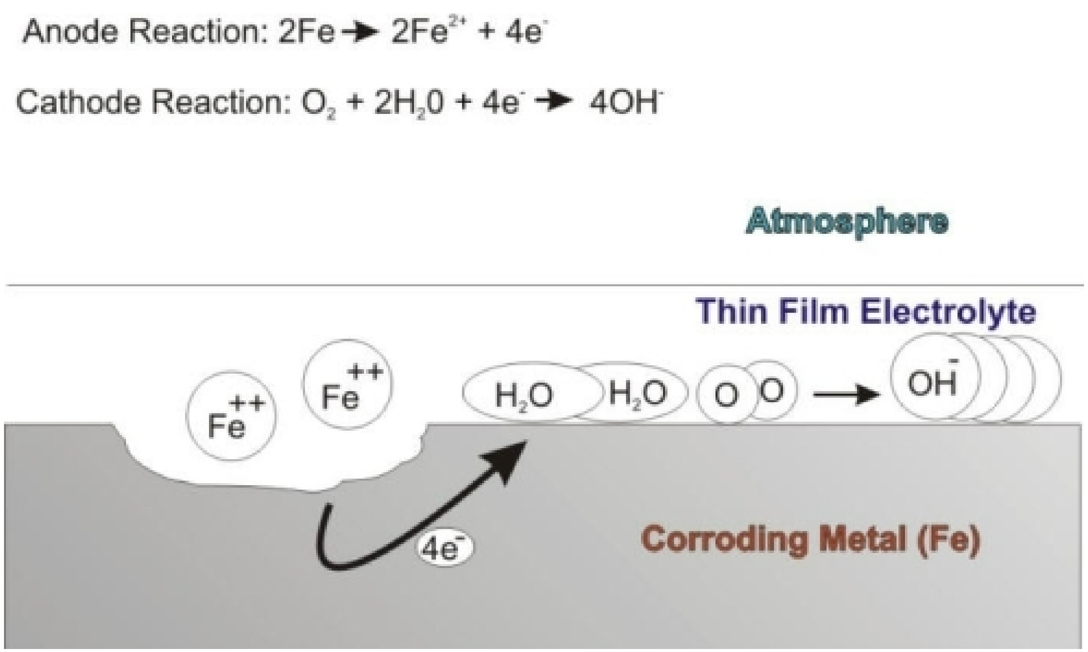




Atmospheric corrosion

- 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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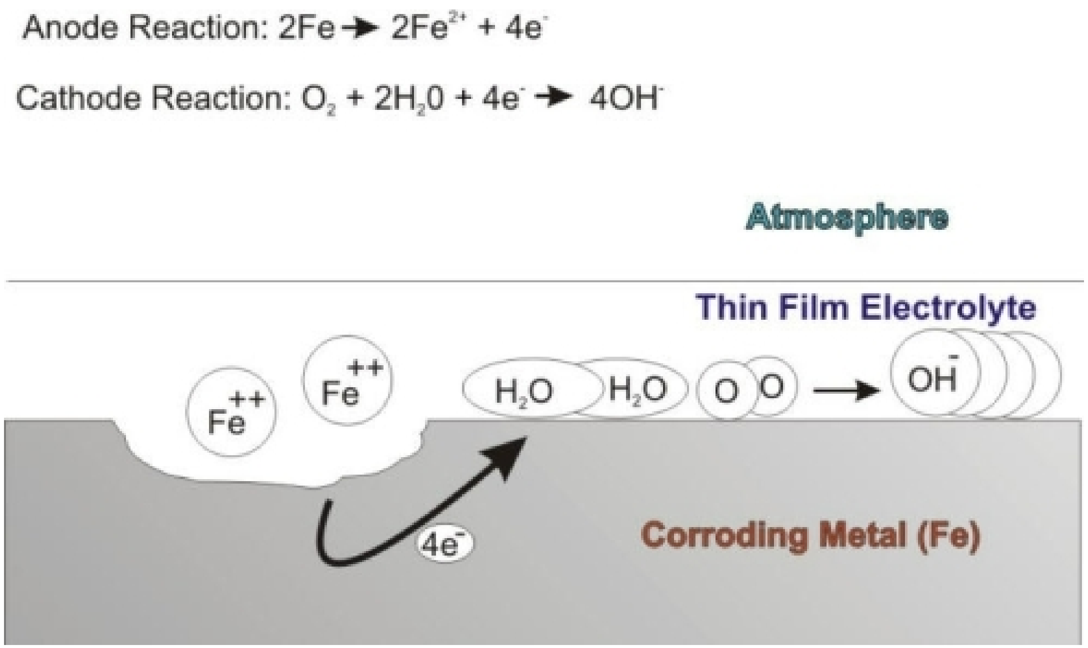
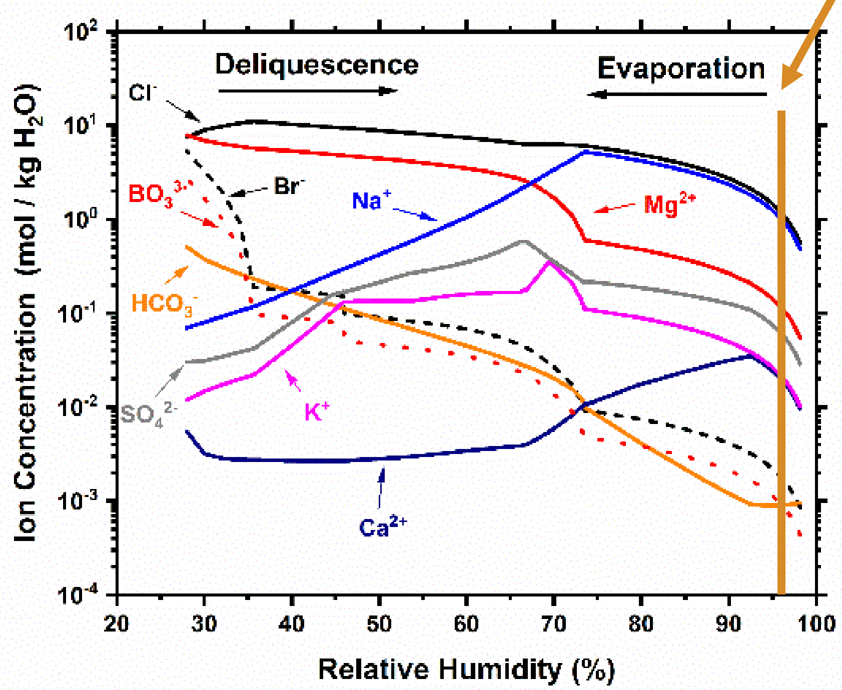


Atmospheric Brines

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

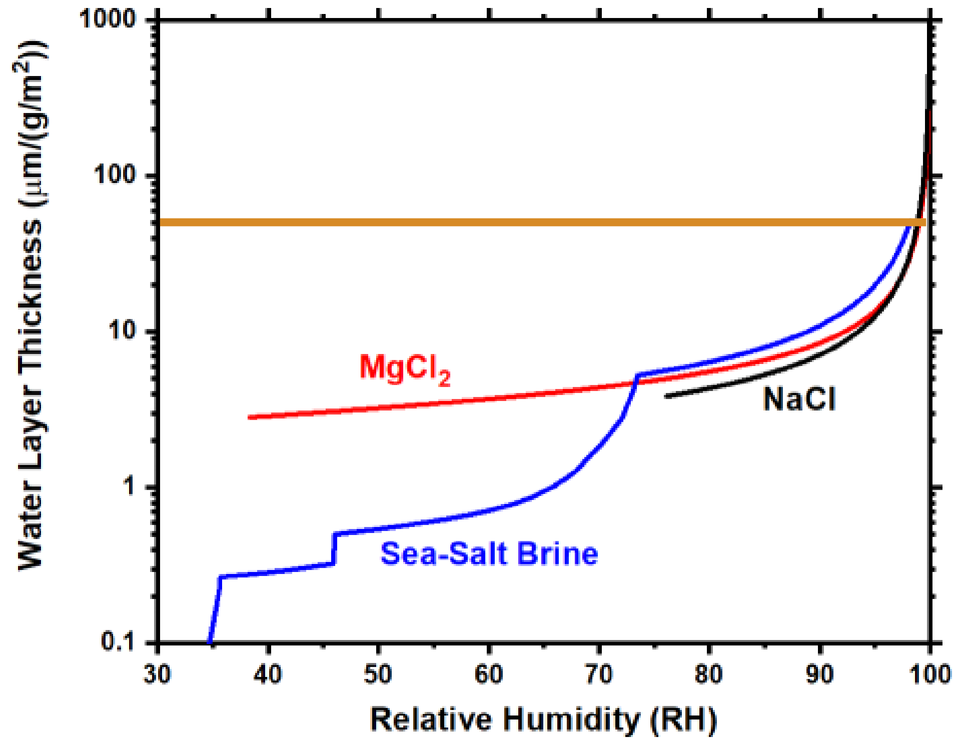
98 % RH ~ 0.6 M NaCl



Thin Atmospheric Water Layers

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

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



- Under typical conditions a WL < 200 μm is expected
- Due to condensation, rain, or salt spray, WLs above 1,000 μm are likely, at least transiently

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

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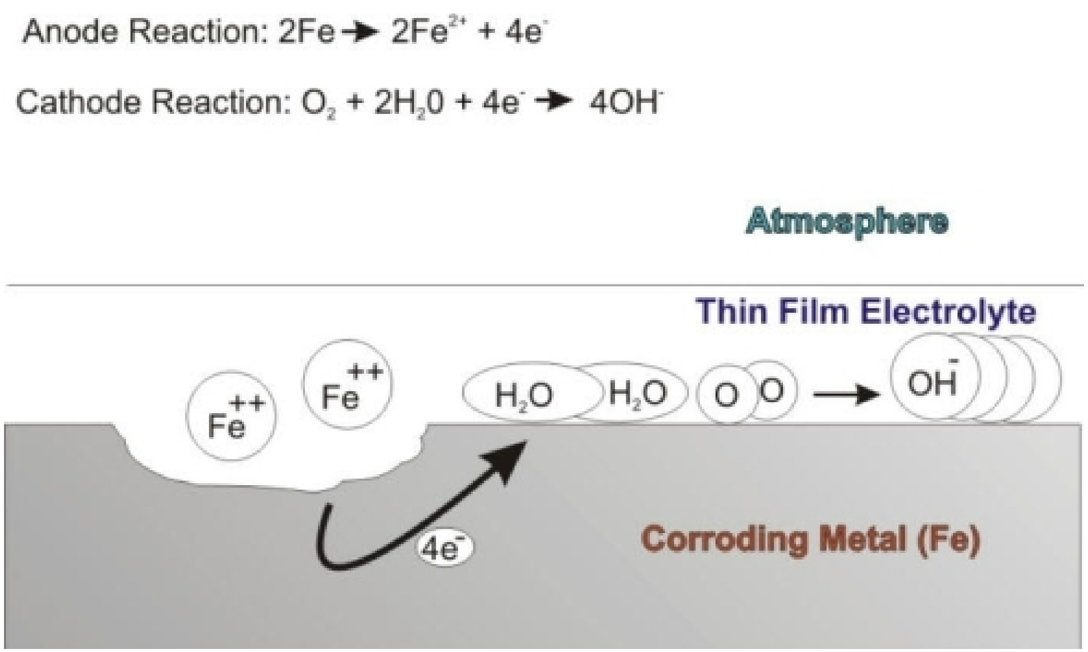
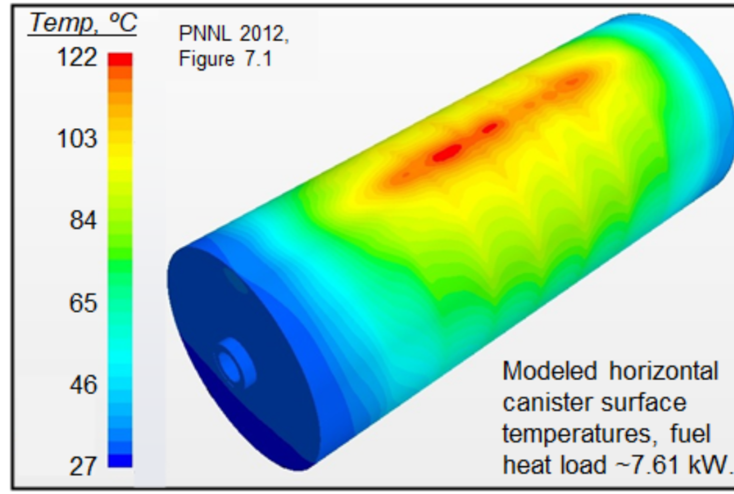
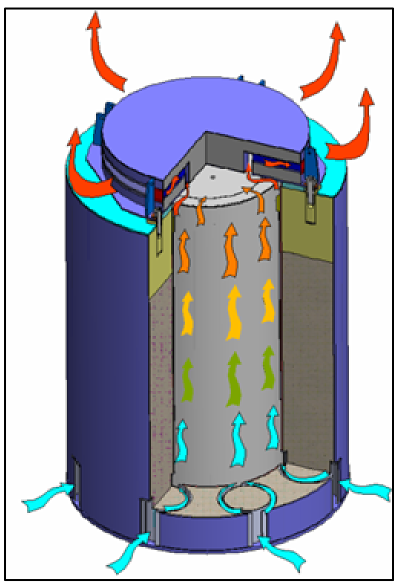


Temperatures

- 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

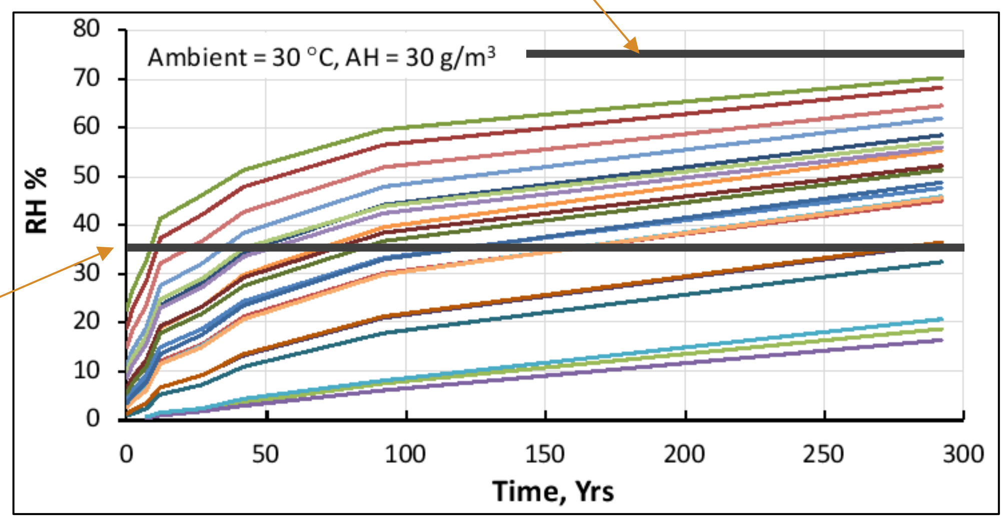




FCRD-UFD-2012-000114 Figure 7.3

NaCl Deliquescence

$MgCl_2$ Deliquescence



Atmospheric corrosion

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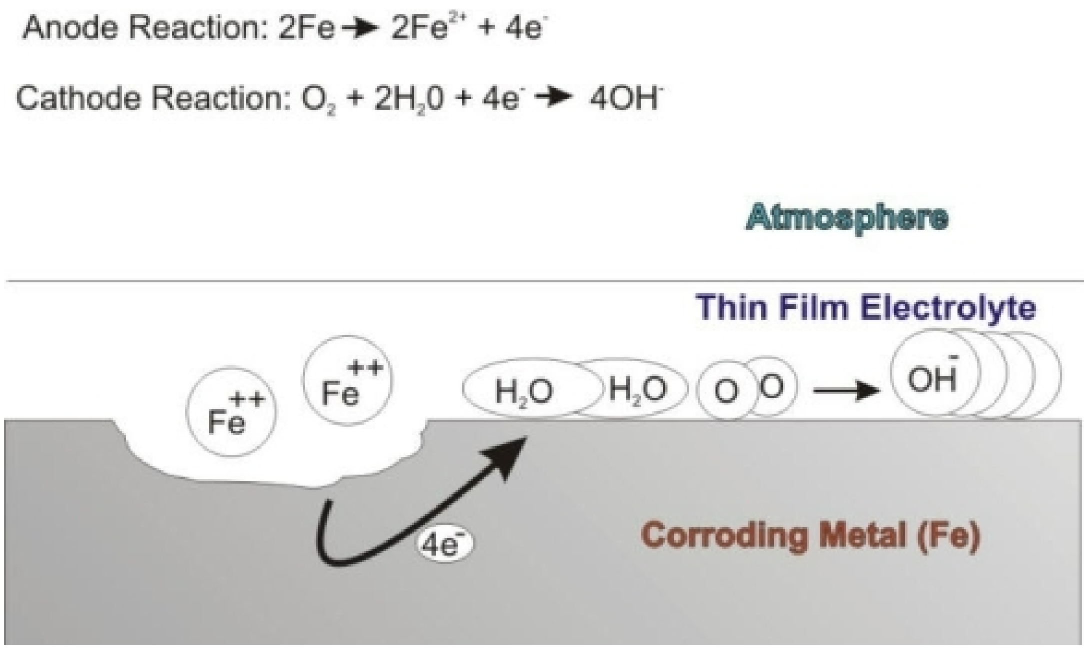
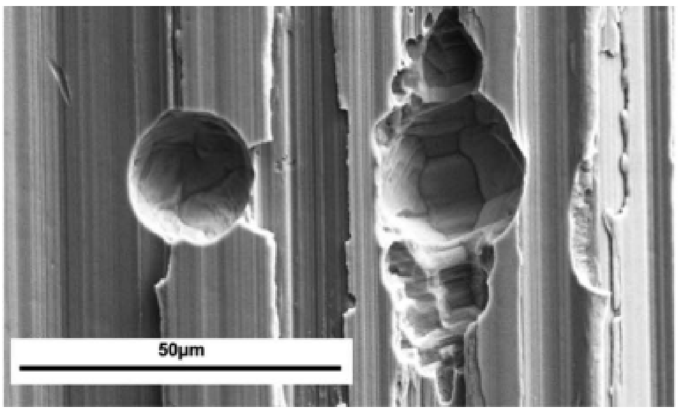
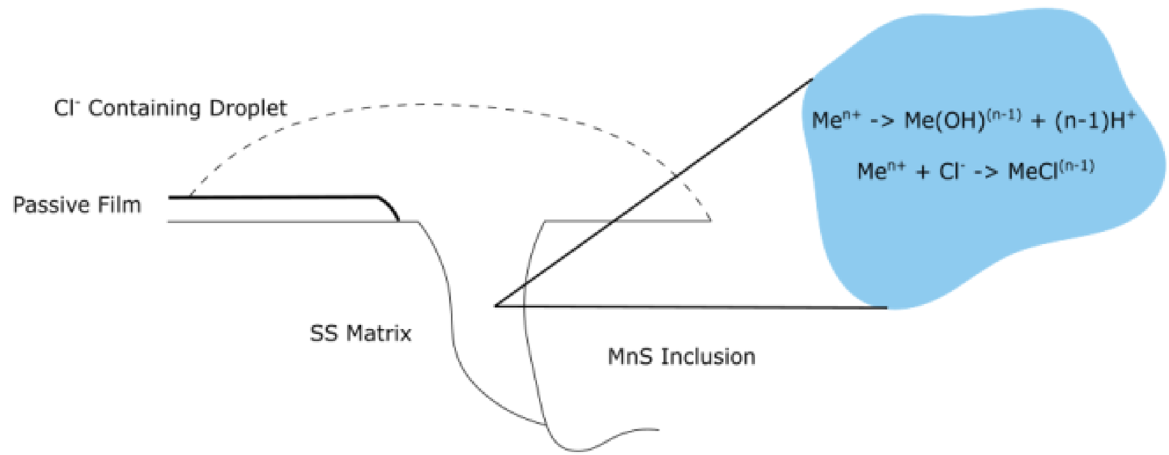
  - *Solution composition*
  - *Solution concentration*
  - Temperature
  - ***Alloy***
  - ***Reaction mechanisms***



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





UNIVERSITY of VIRGINIA

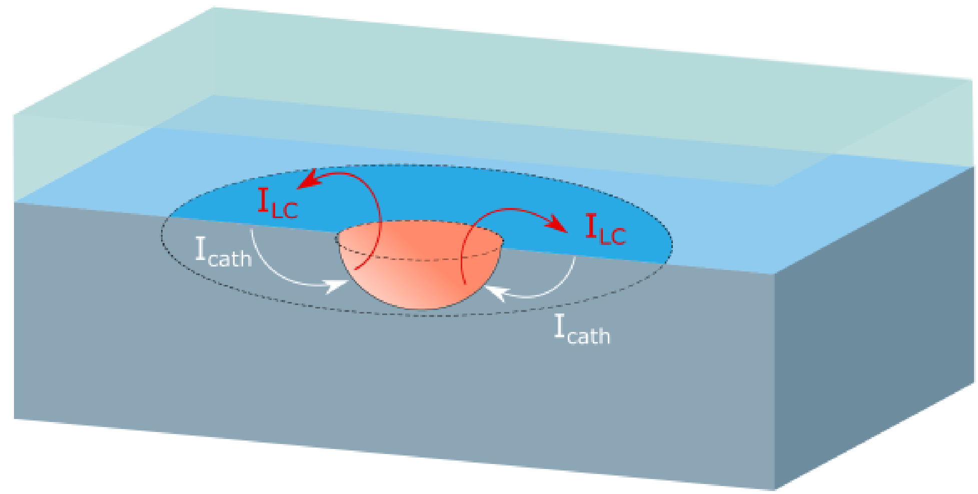
T.D. Weirich, et al., J. Electrochem. Soc. 166 (2019) C3477–C3487.

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

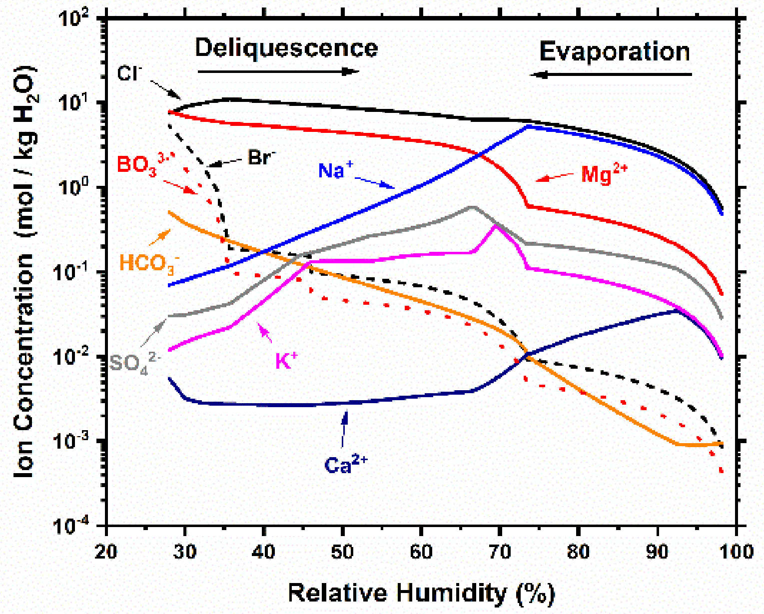
$$\square_2 + 2\square^+ + 4\square^- \rightarrow 4\square\square^-$$

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



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?

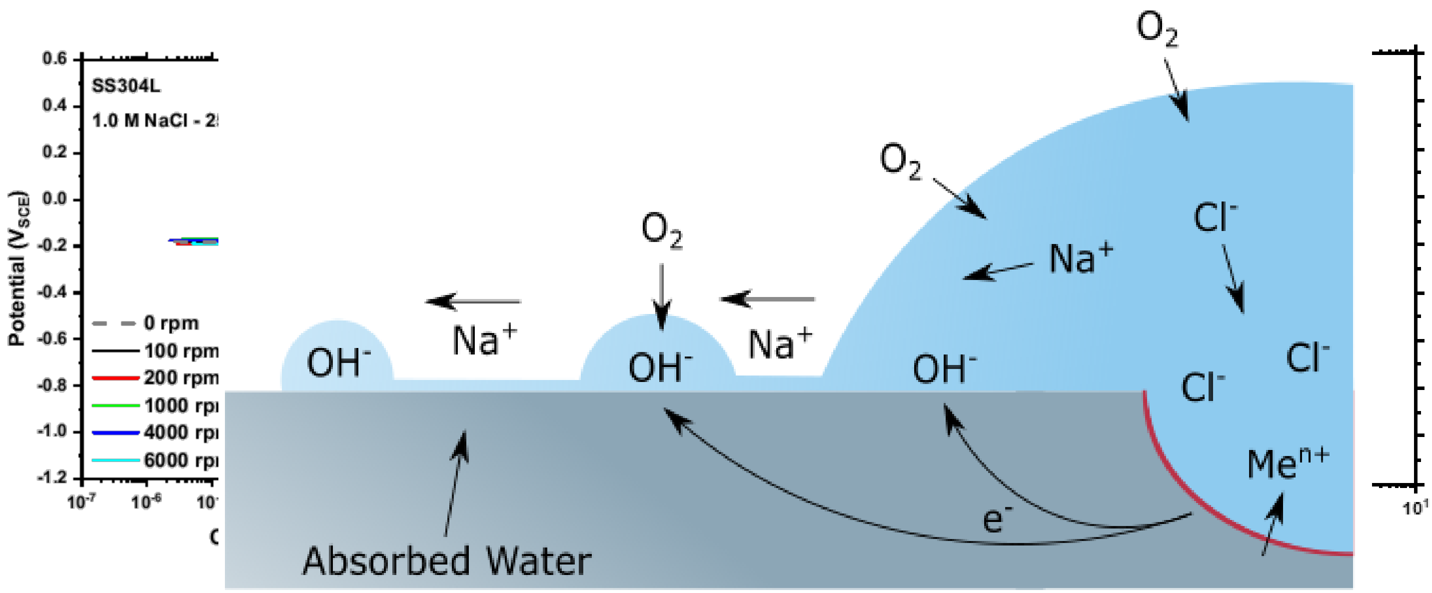
Critical Dissertation Questions

- 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?

Cathodic Reaction Mechanisms

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

$$_2 + 2\;^{+} + 4\;^{-} \rightarrow 4\;^{-}$$

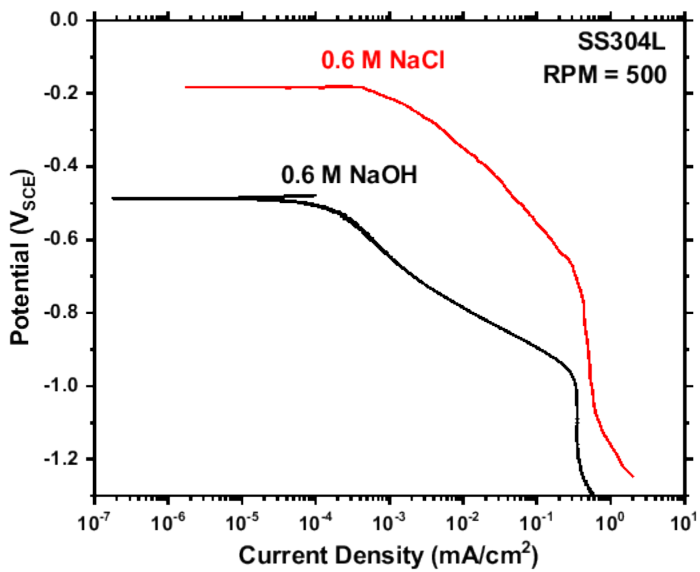


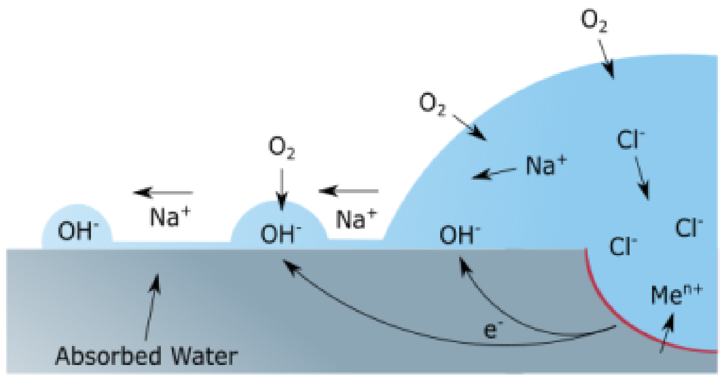
- Holds for all concentrations (0.6 – 5.3 M) and temperatures (25-45 ˚C) of NaCl explored

Cathodic Reaction Mechanisms

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

$$\square_2 + \square^- \leftrightarrow \square_2^-$$

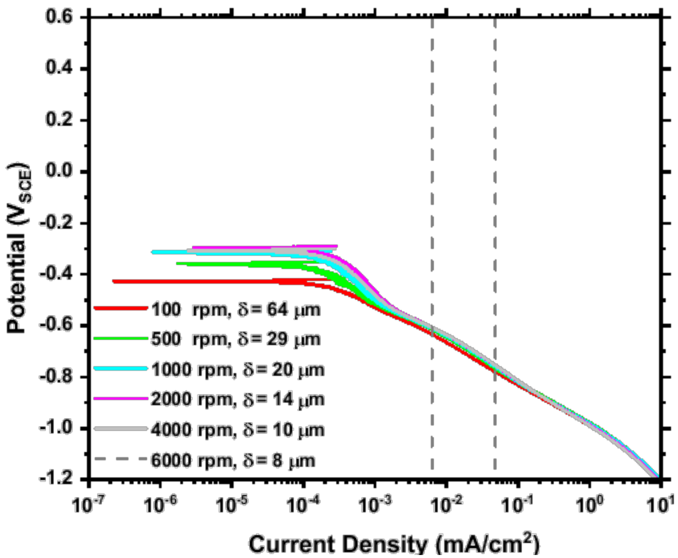


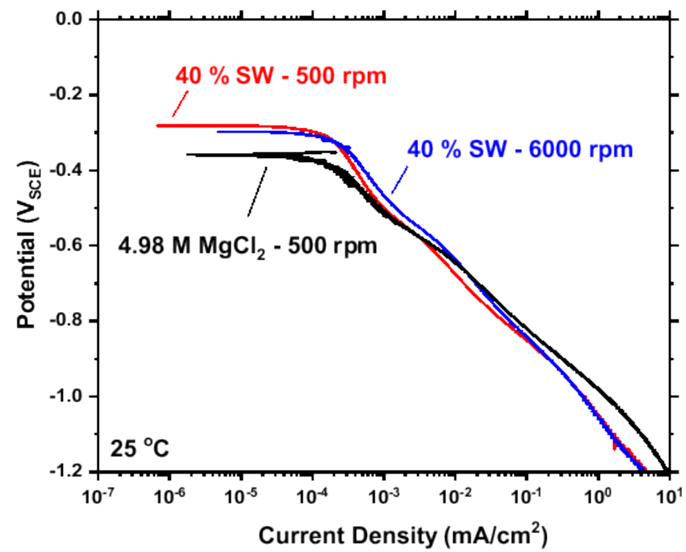


- ORR suppression in NaOH solutions
- Decrease in current density in NaOH solution in comparison to NaCl solutions

Cathodic Reaction Mechanisms

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



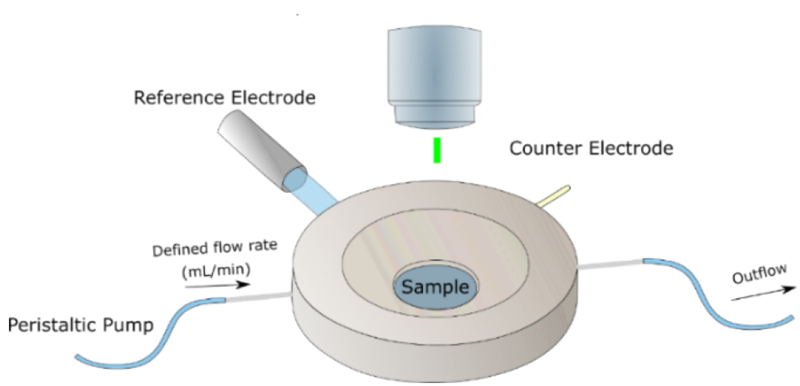


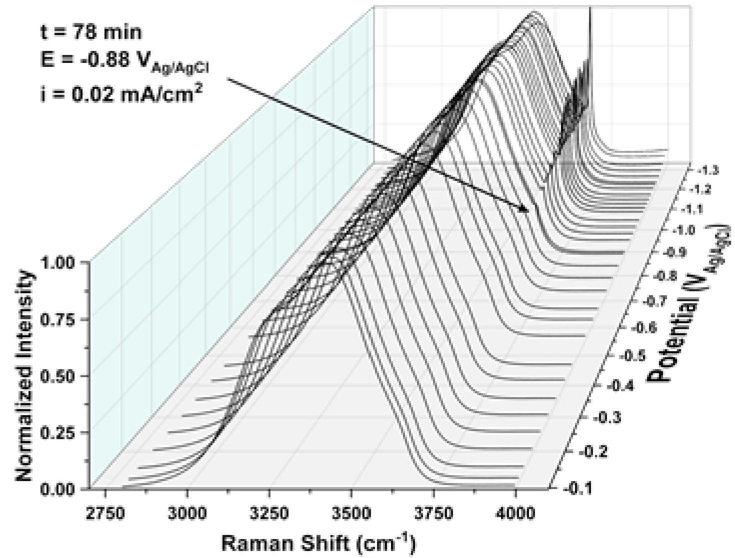
- Proposed HER due to ORR suppression due to precipitate formation in brine and localized corrosion

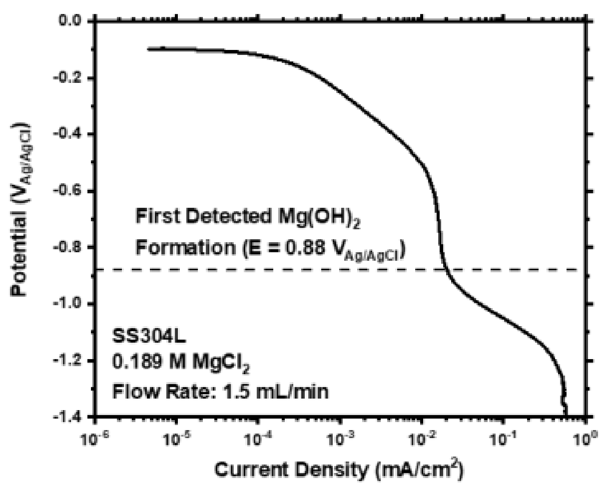
R.M. Katona, et al., Corros. Sci. 177 (2020) 108935.

In-situ Spectroelectrochemistry

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



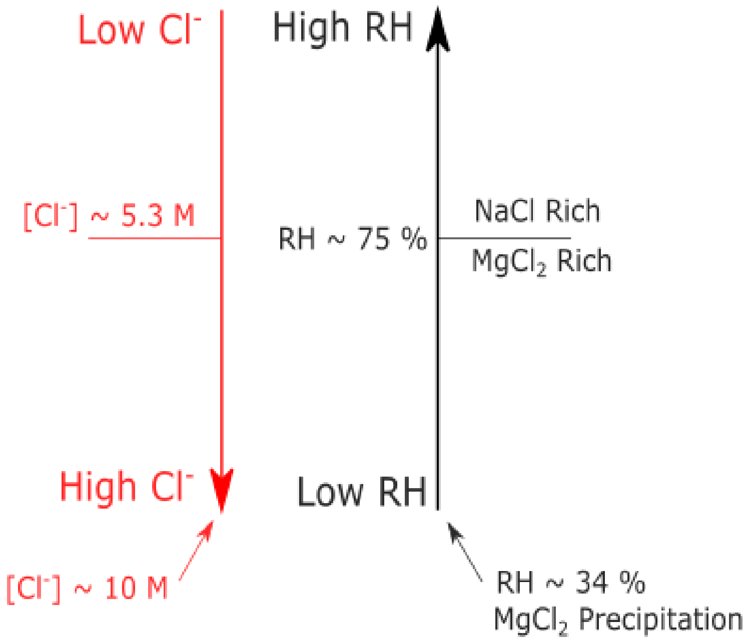




- $Mg(OH)_2$ identified
  - ORR suppression
  - $MgCO_3$ not kinetically stable
- Technique development to control boundary layer with flow rate

Cathodic Kinetics Summary

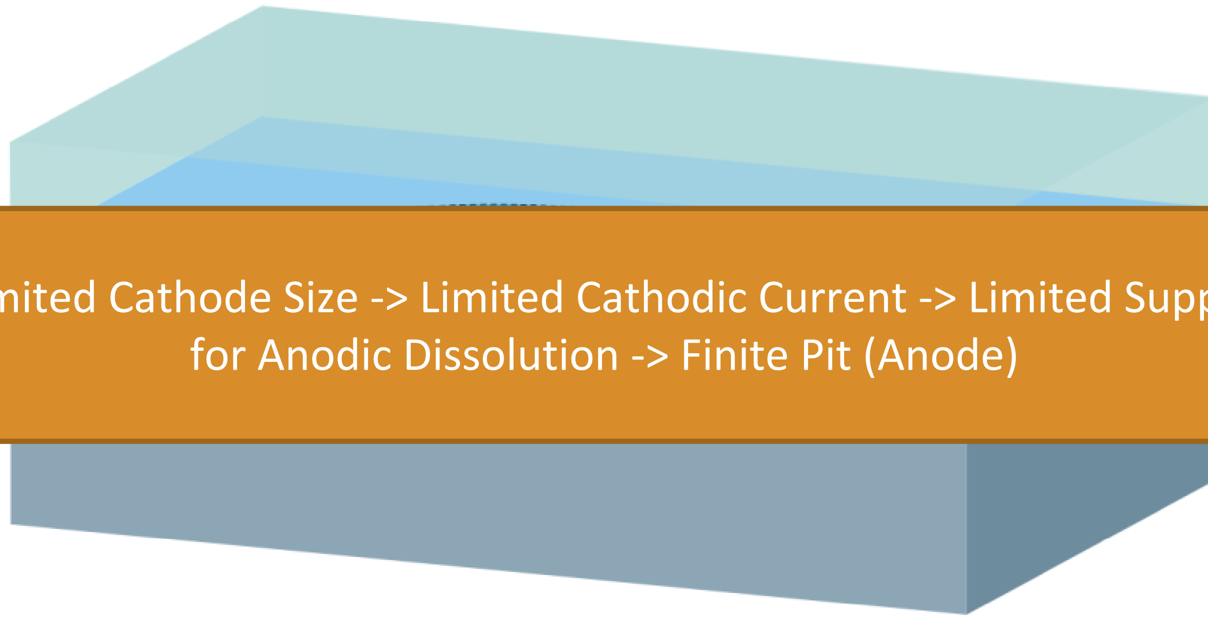
- Across wide range of solutions, various mechanisms are dominant



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

Modeling Localized Corrosion

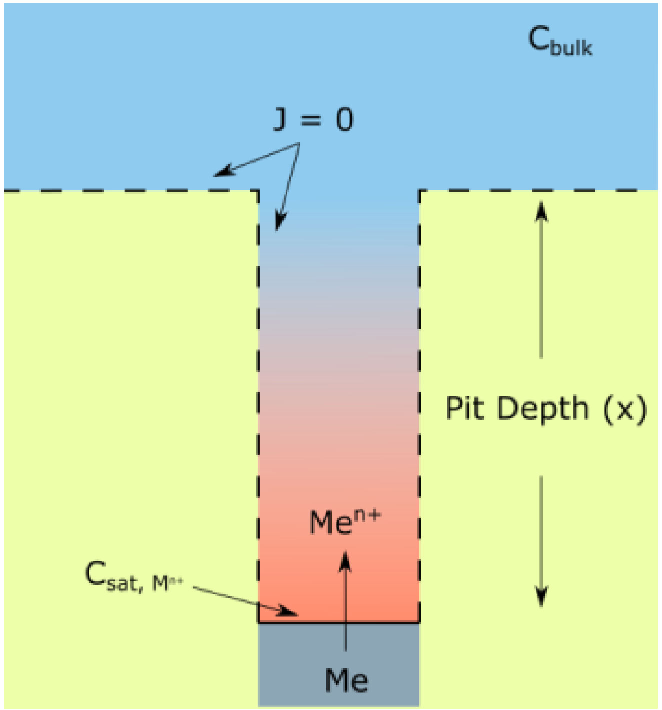
- In chloride environments, pitting is highly probable, therefore worried about **maximum extent of corrosion**
- Pits (anode) are inherently coupled to the surrounding cathode



Limited Cathode Size -> Limited Cathodic Current -> Limited Supply for Anodic Dissolution -> Finite Pit (Anode)

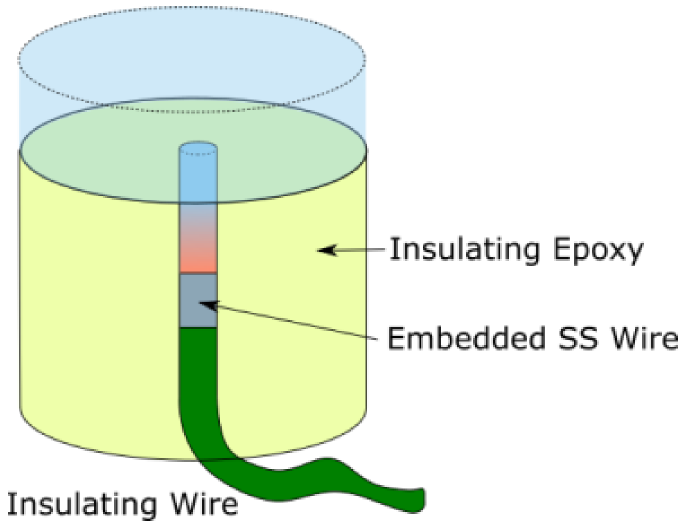
- Anode can only grow if sufficient supply from cathode
- Cathode current limited by reaction mechanism and physical geometry (water layer, sample size, etc.)

Background – Pit Propagation



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

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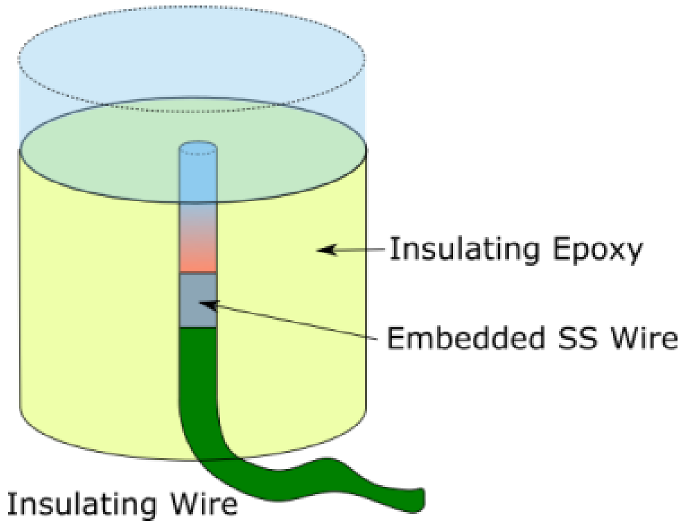
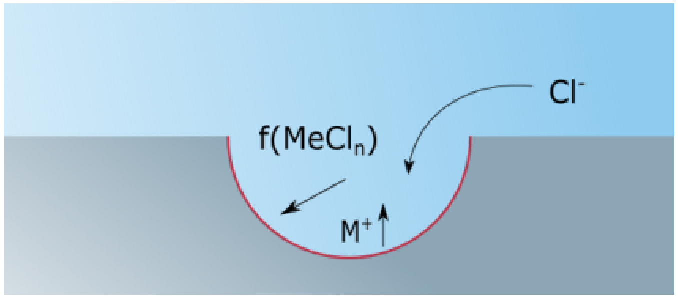


Converted to hemisphere by a geometric factor of 3



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

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

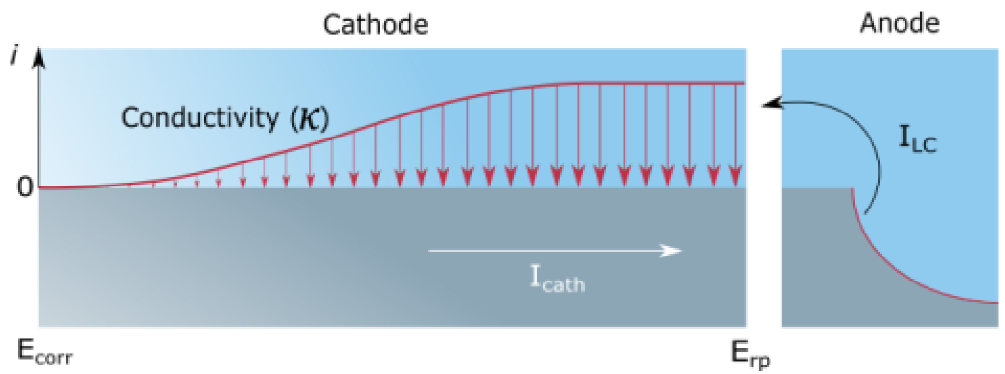
- Critical value ~50% of full saturation of salt film needed

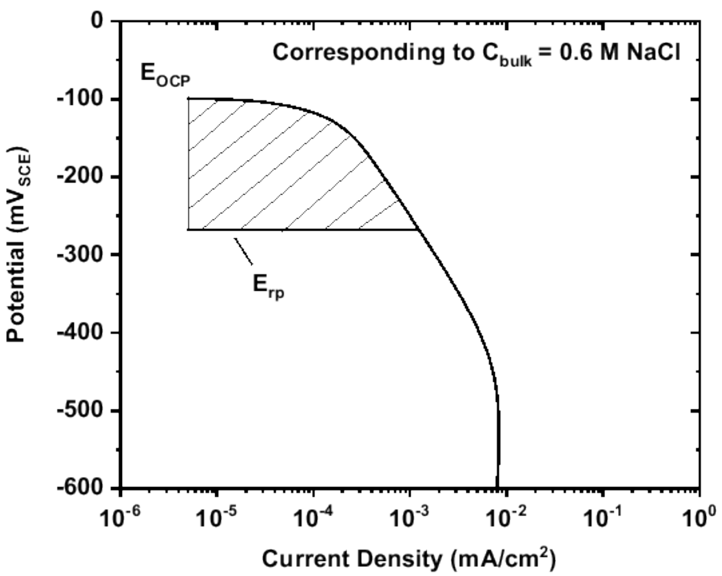
- Limiting anodic current demand (I_{LC}):

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

Cathode Supply

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



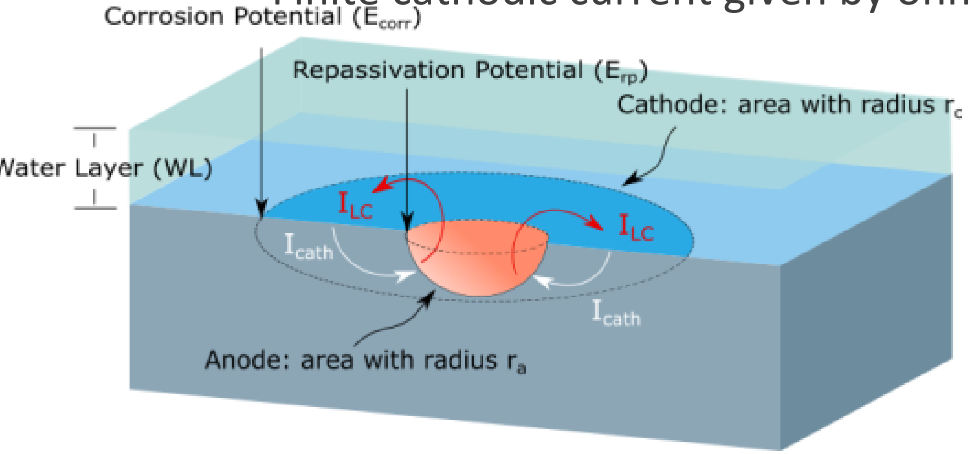


$$I_{c,max} \sim f(\kappa, WL, E_{OCP}, E_{RP}, r_a, i_{eq})$$

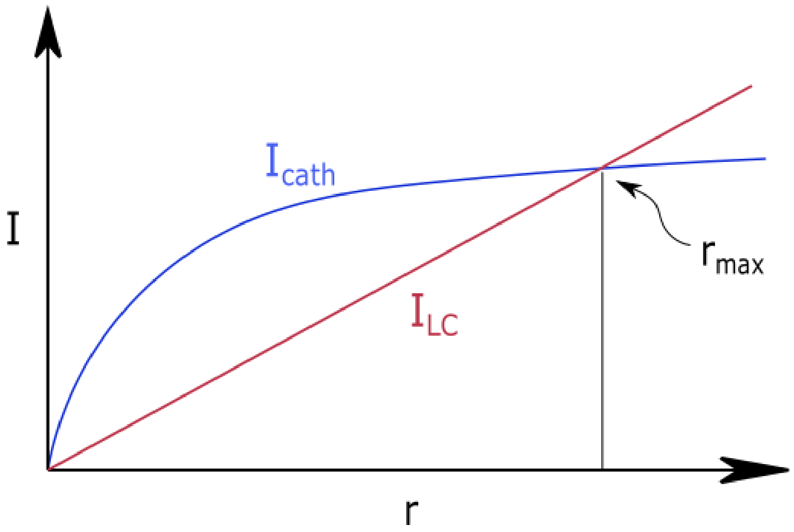
- Cathode current function of conductivity, WL, electrochemical potentials, anode radius, and equivalent current density

Modeling Localized Corrosion

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

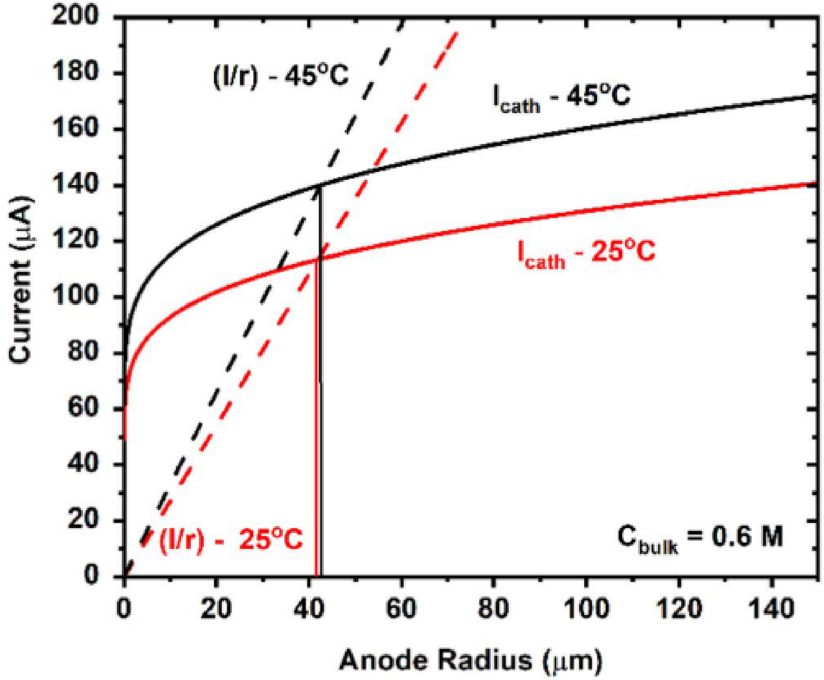


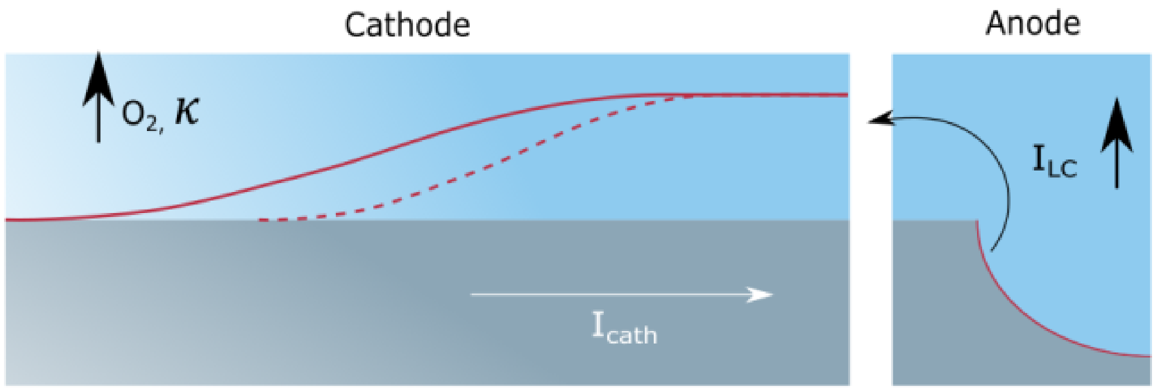
Anodic Demand = Cathodic Supply -> Max pit



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

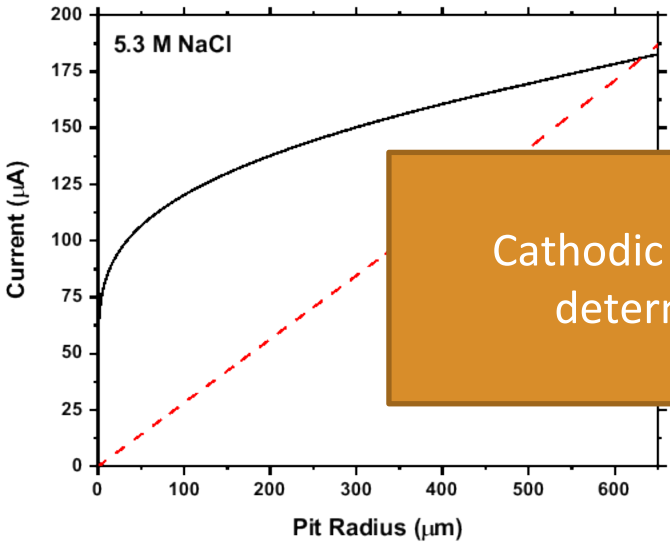




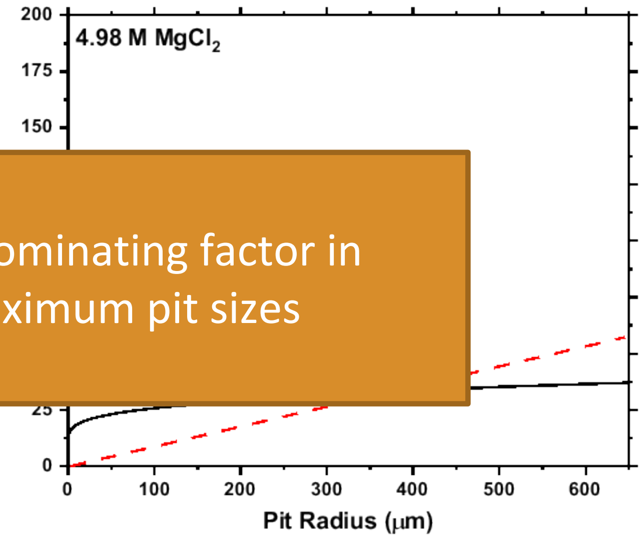
R.M. Katona, et al., J. Electrochem. Soc. 166 (2019) C3364–C3375.

Change in Solution Composition

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



Cathodic current dominating factor in determining maximum pit sizes



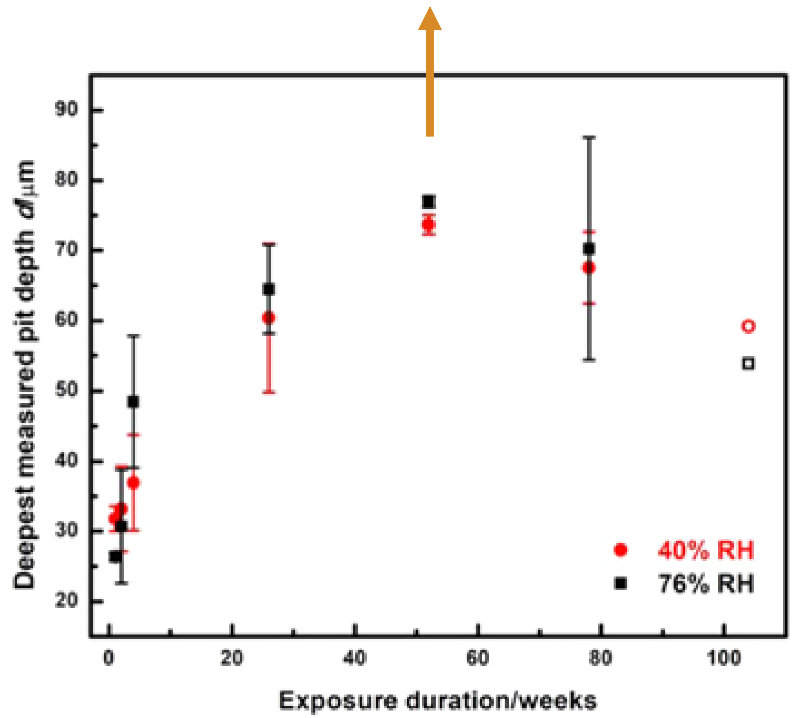
- $MgCl_2$ experiences ORR suppression and decreased conductivity
- $MgCl_2$ increased demand for anodic dissolution potentially due to common ion effect

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

76 % Max Pit ~ 230 µm

40 % Max Pit ~ 110 µm

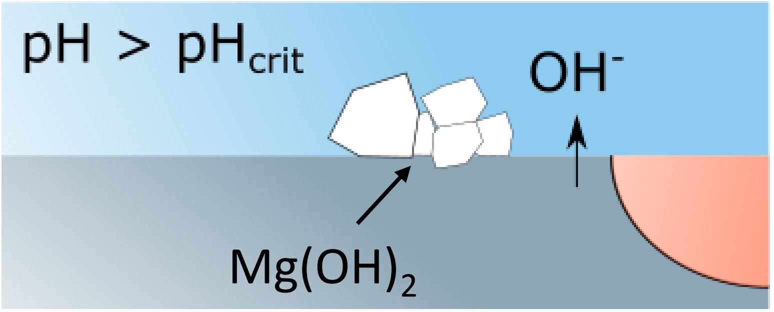


Can we decrease the error in our predicted maximum pit sizes?

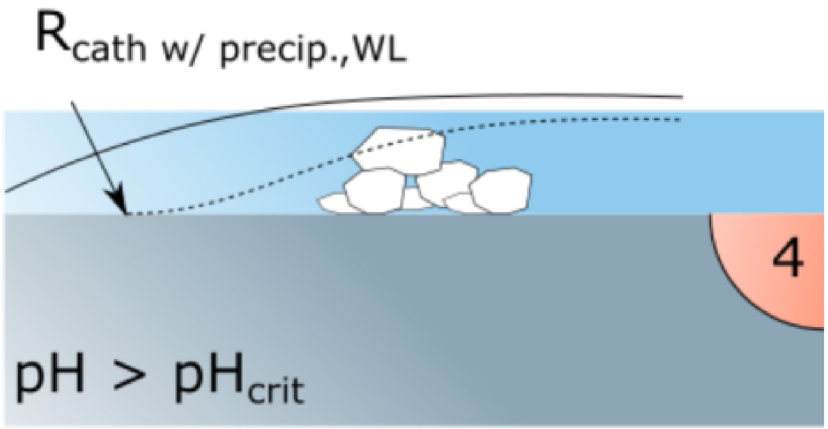
J. Srinivasan, et al. J. Electrochem. Soc. 168 (2021) 021501.

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

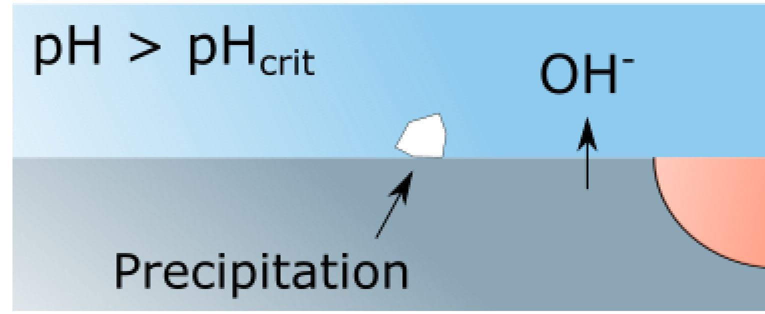


$$I_{c,max} \sim f(\kappa, WL, E_{OCP}, E_{RP}, r_a, i_{eq})$$

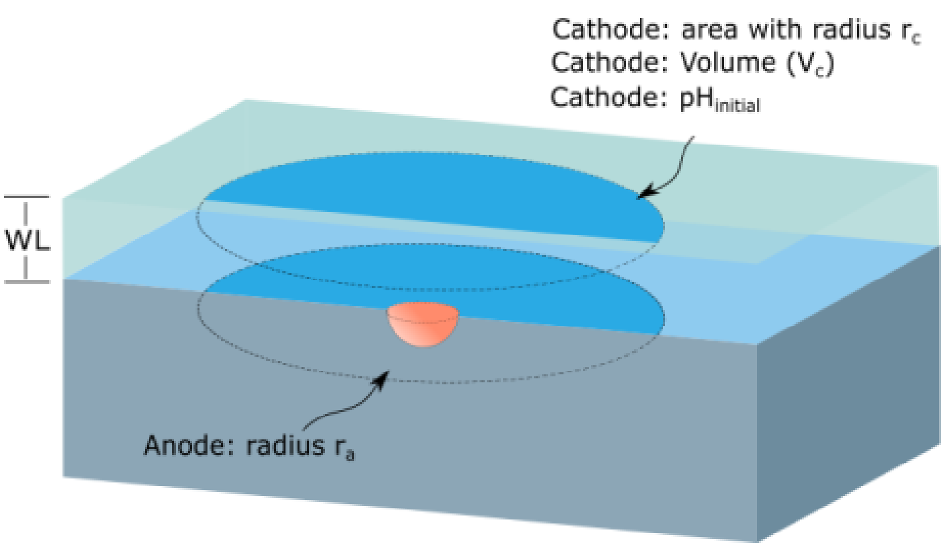


Modeling Cathode Precipitates

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



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

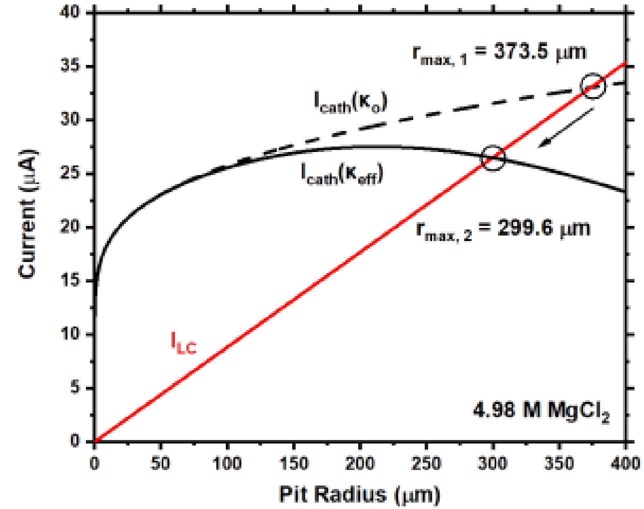


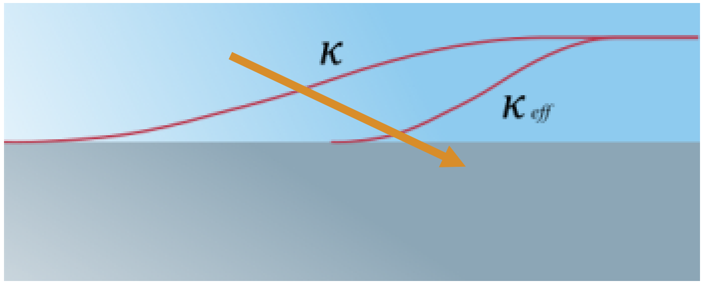
$$\kappa_{eff} = k\left(1 - \frac{V_{precip}}{V_{solution} + V_{precip}}\right)^{\frac{3}{2}}$$

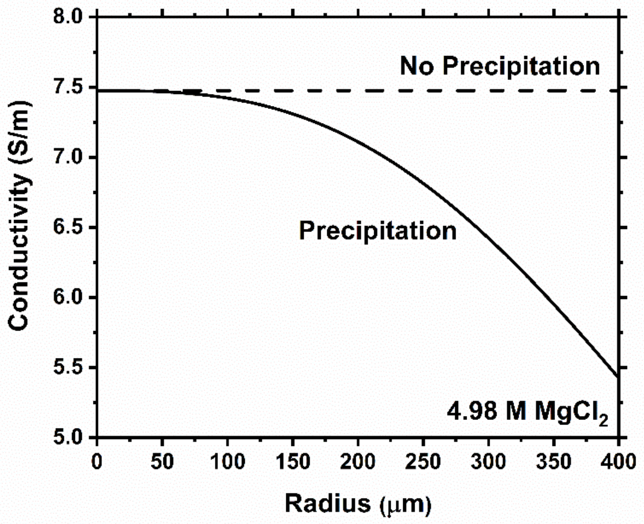
$$I_{cath,updated} = f(\kappa_{eff})$$

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

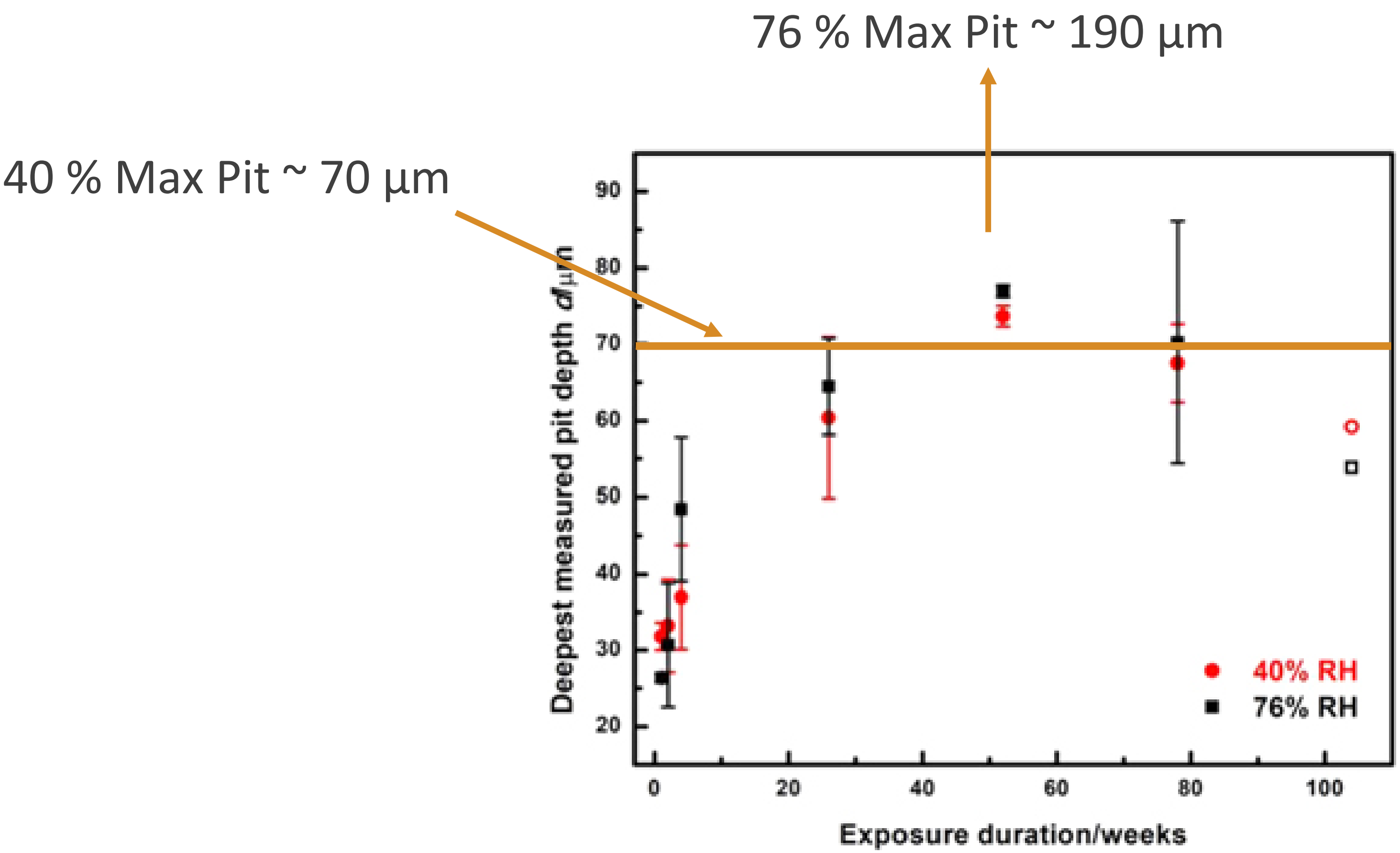






Re-Comparison to Long Term Exposures

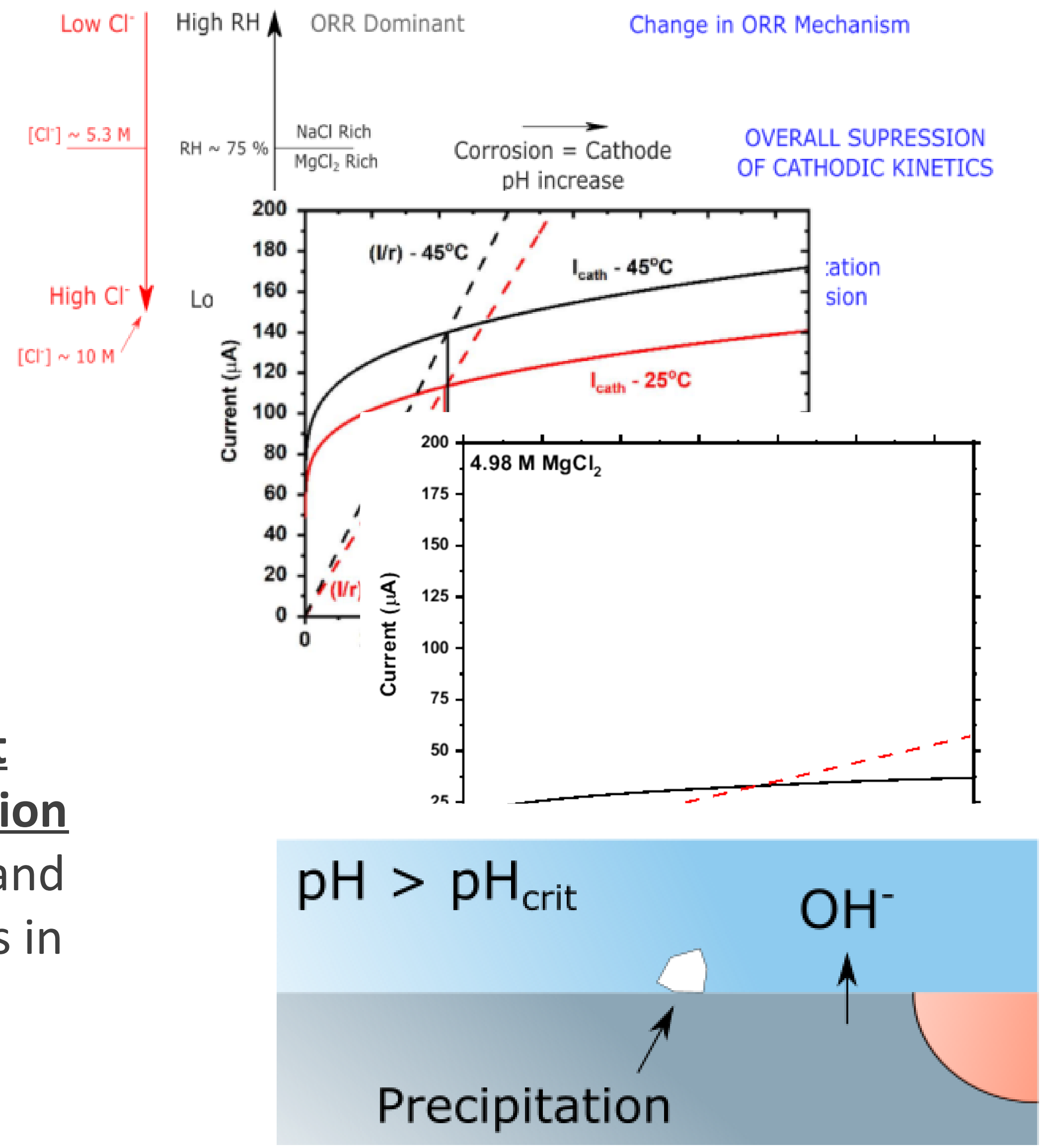
- When comparing to exposures, prediction of maximum pit sizes with precipitation is directly inline for 40% RH



Answered Questions

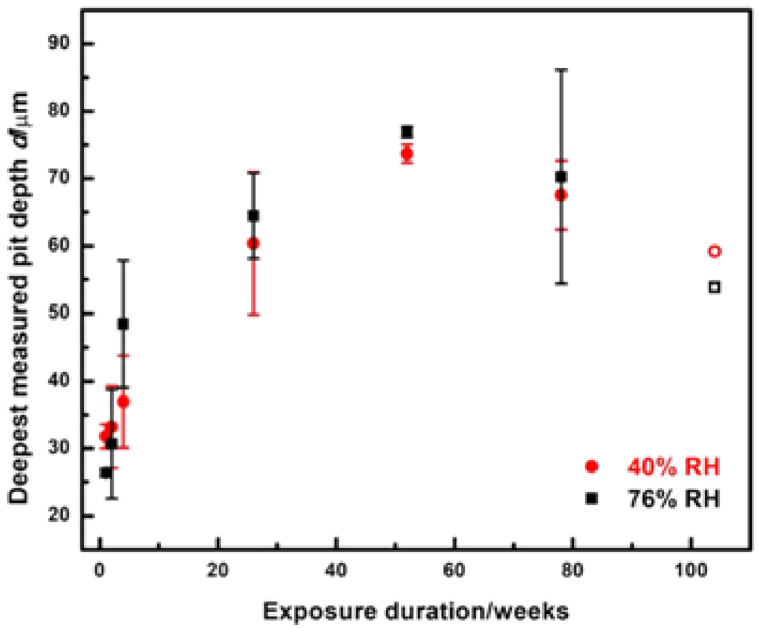
- What **mechanisms control** how ***external*** (solution composition, solution concentration, geometry, temperature) and ***internal*** (material) factors **affect pitting and stress corrosion**?

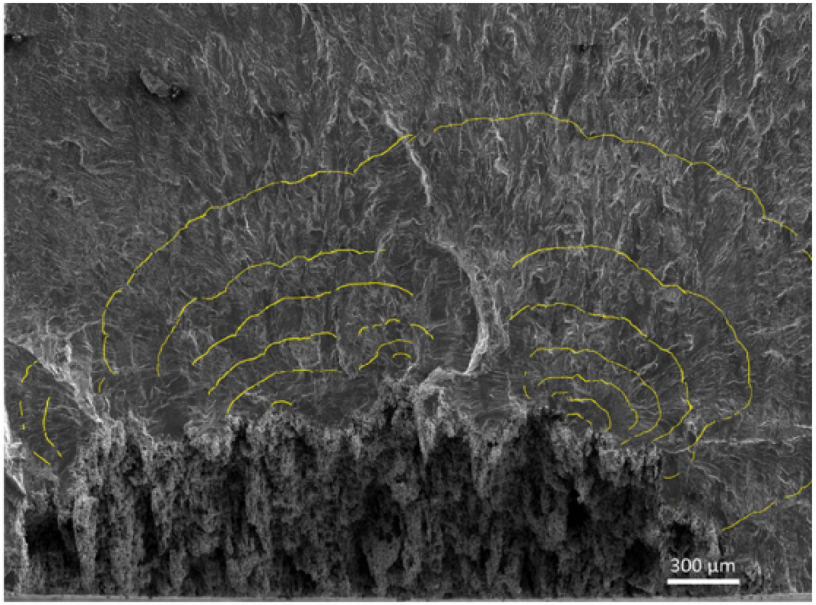
- To what extent can we **predict damage from localized corrosion** and stress corrosion cracking and what are the governing factors in these predictions?



What is still missing?

- Kinetics of pit growth and metastable pitting
- Pit to crack transition





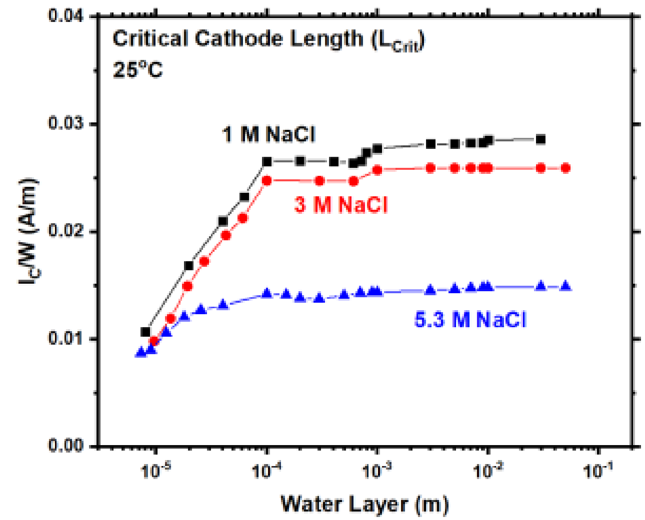
- Stress Corrosion Cracking
  - In-situ crack growth rate measurements in atmospheric conditions
  - Understanding crack tip electrochemistry

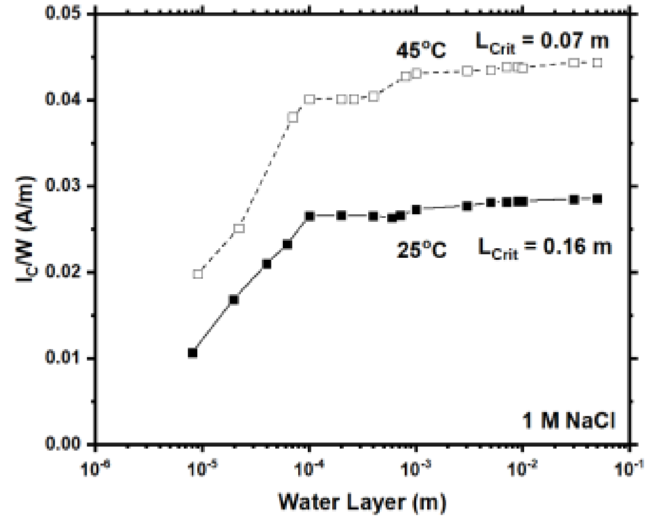
J. Srinivasan, et al. J. Electrochem. Soc. 168 (2021) 021501.
N.E.C. Co, J.T. Burns, Int. J. Fatigue. (2017).

Extension of Work, Future Work, and Potential Applications

Extension of Work to Galvanic Modeling

- Finite Element Modeling in a galvanic couple
- Many trends with temperature and chloride concentration hold in galvanic couple





Journal of The Electrochemical Society, 2021 **168** 031512

CrossMark

EDITORS' CHOICE

Editors' Choice—Natural Convection Boundary Layer Thickness at Elevated Chloride Concentrations and Temperatures and the Effects on a Galvanic Couple

R. M. Katona,[1,2,*,z] J. C. Carpenter,[1] A. W. Knight,[1] R. S. Marshall,[2,*] B. L. Nation,[1] E. J. Schindelholz,[3,**] R. F. Schaller,[1,**] and R. G. Kelly[2,***]

[1] *Sandia National Laboratories, Albuquerque, New Mexico 87123, United States of America*
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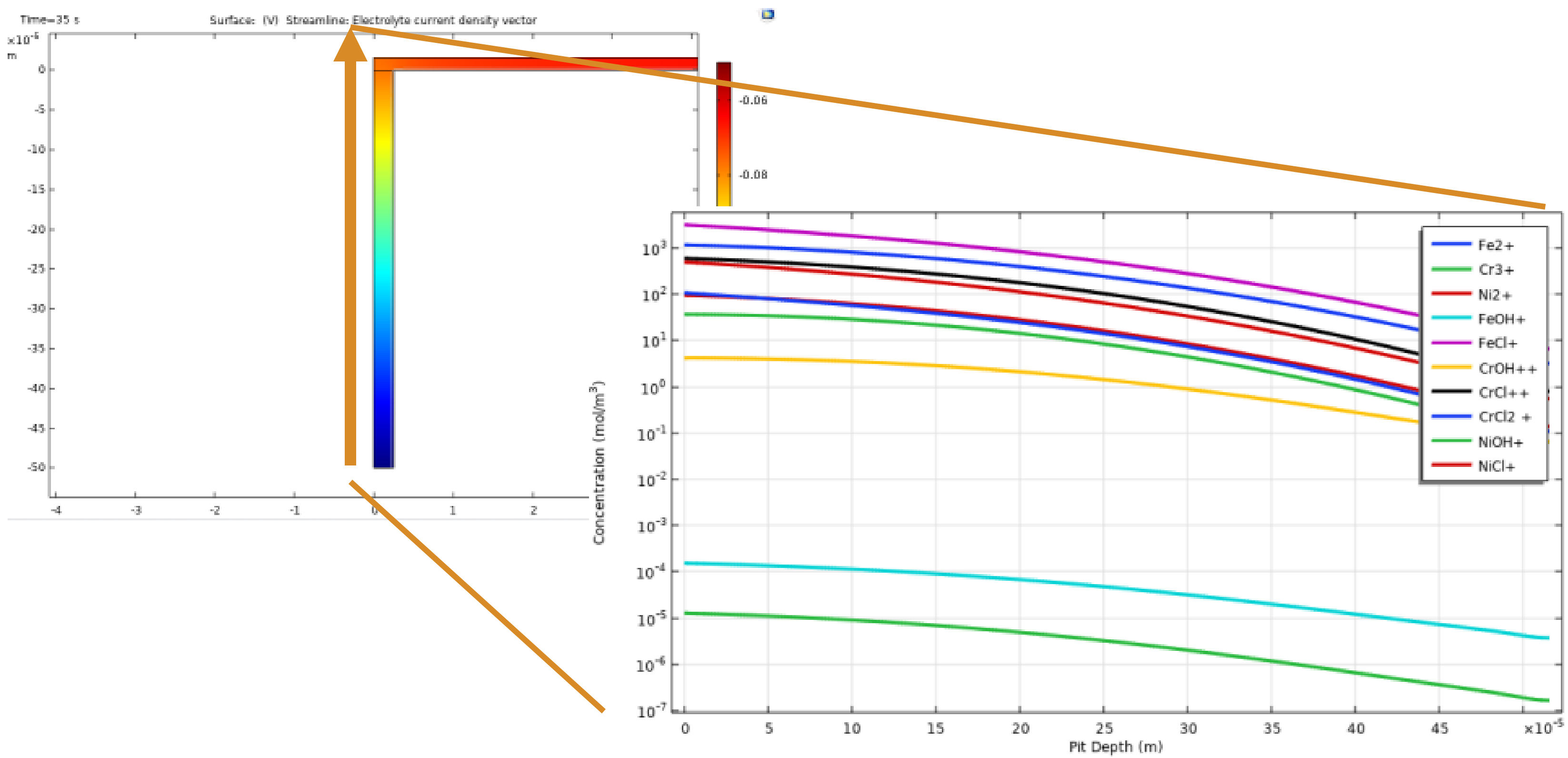
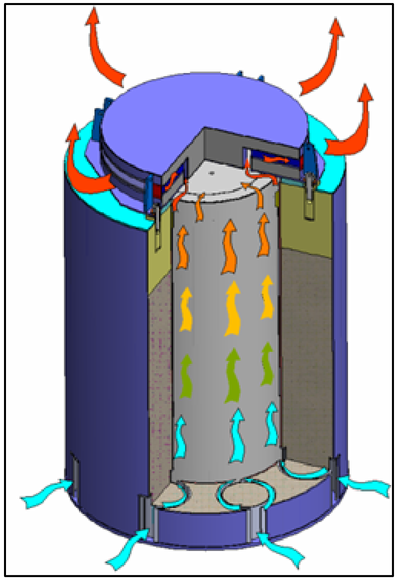
Future work

- Enhanced modeling tracking pH and chemical speciation using finite element modeling techniques

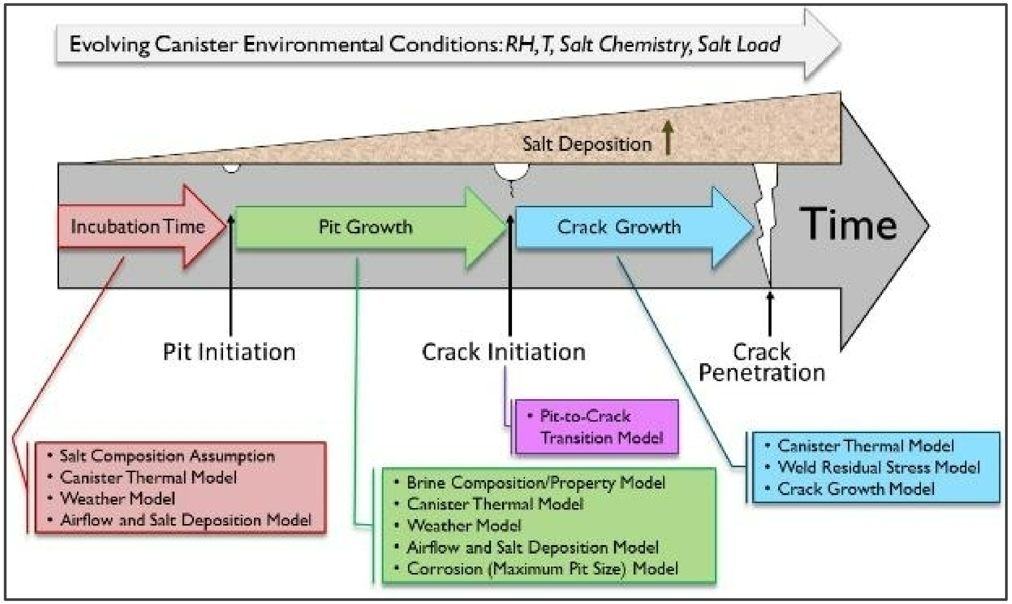


Modeling in Consulting

- Overall project was supporting modeling efforts to help identify potential materials degradation for spent nuclear fuel canisters
- Goal to help identify potential hot spots for materials degradation (local to canister and around the country)

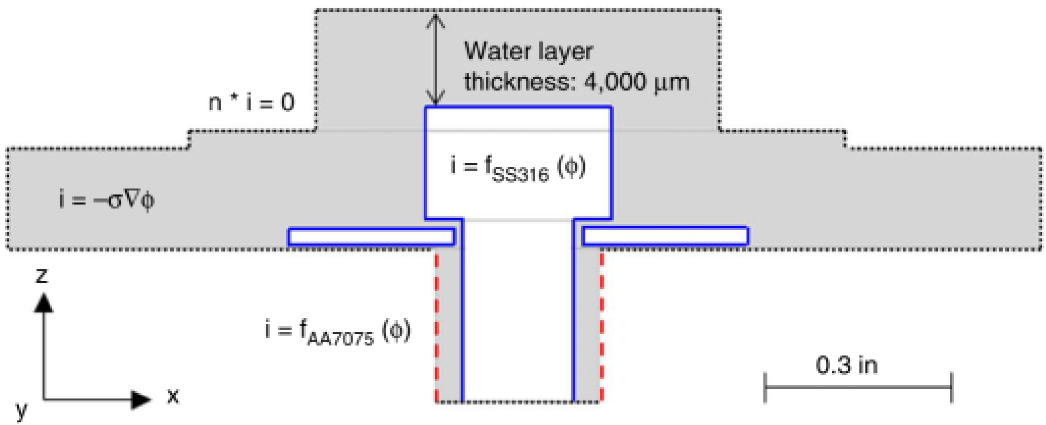


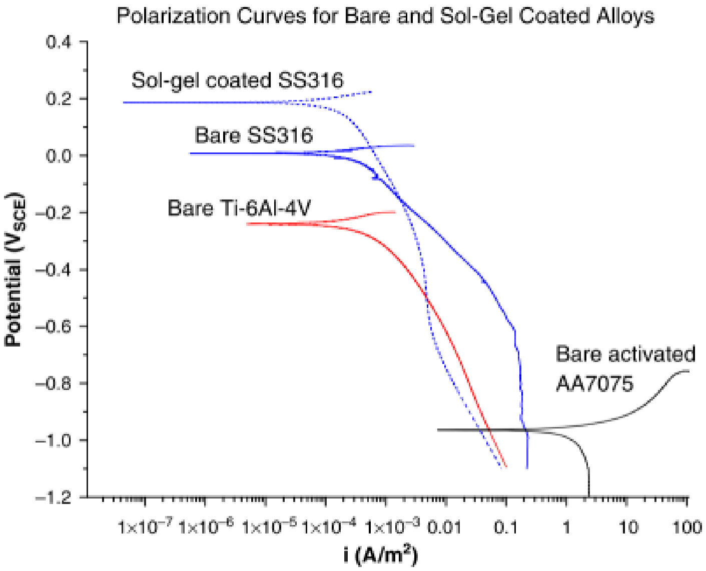
FCRD-UFD-2012-000114 Figure 7.3



Modeling in Consulting

- Utilizing Finite Element Modeling in order to inform upon coating efficacy and potential failure

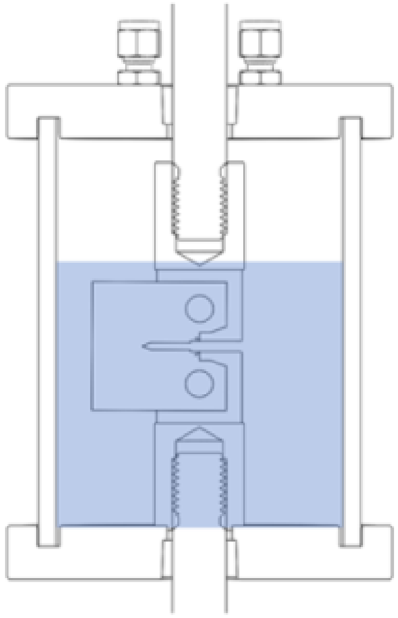


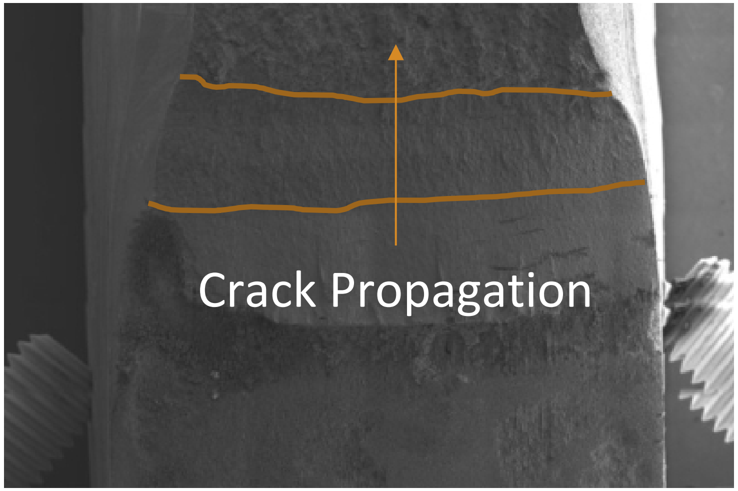


- Identify potential areas for failure in different geometries

Failure Analysis

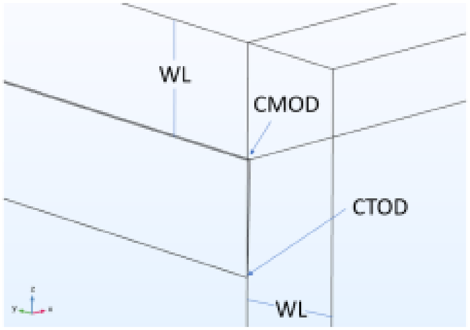
- Assessing failure mechanisms by *in-situ* crack growth rate
- Performing ex-situ microscopy in order to help determine stress corrosion cracking morphologies





- Combine with modeling to get overall picture of cracking mechanisms

FEM Schematic of Crack



Acknowledgements

- Robert Kelly, Kelly Research Group, Center for Electrochemical Science and Engineering
- Rebecca Schaller, Charles Bryan, Sylvia Saltzstein, Jacob Carpenter, Andrew Knight, Eric Schindelholz

Understanding Governing Factors of Localized Corrosion in Marine Environments

R. M. Katona[1,2]

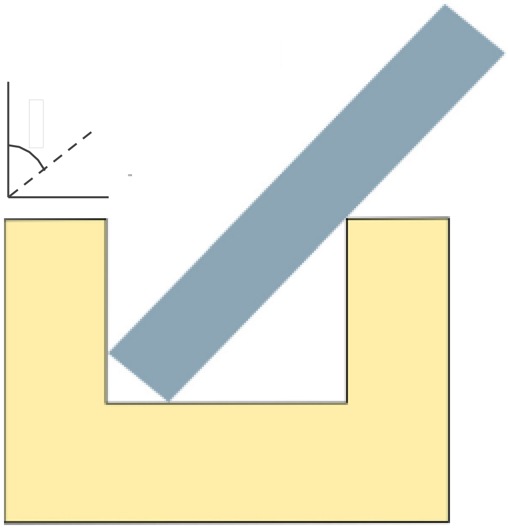
[1]Materials Science and Engineering, University of Virginia, Charlottesville, Virginia 22904

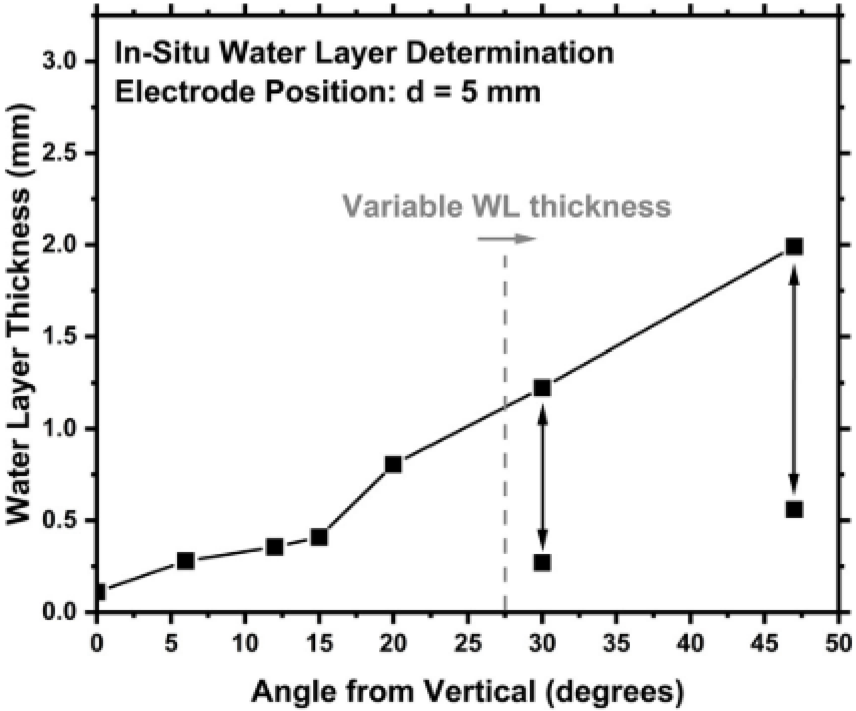
[2]Sandia National Laboratories, Albuquerque, New Mexico 87123, USA

Supplemental

Putting the WL into Perspective

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





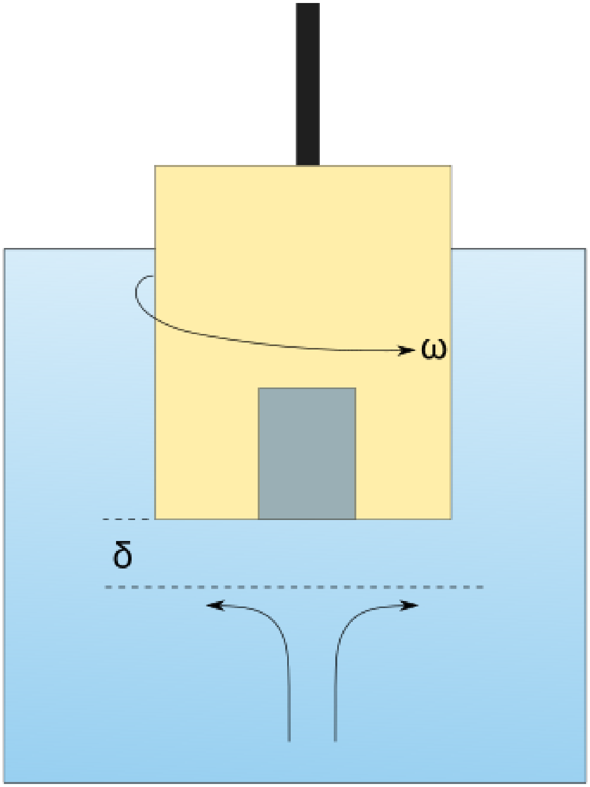
- Under ASTM B117 (15 – 30˚), WL varies from 660 – 1210 µm
- Transient WL present at certain angles of exposure

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

Putting the WL into Perspective

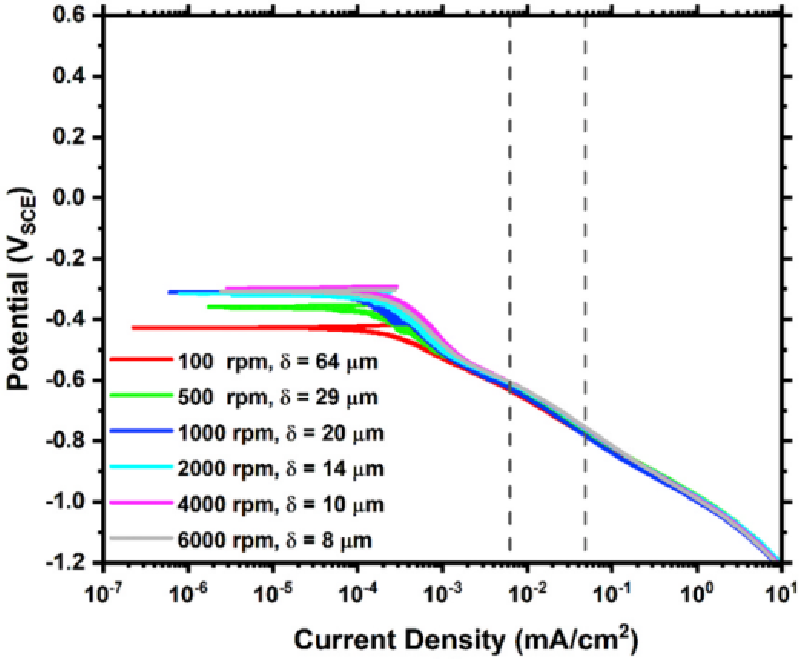
- When using a rotating disk electrode (RDE) a hydrodynamic boundary layer can simulate WL thicknesses

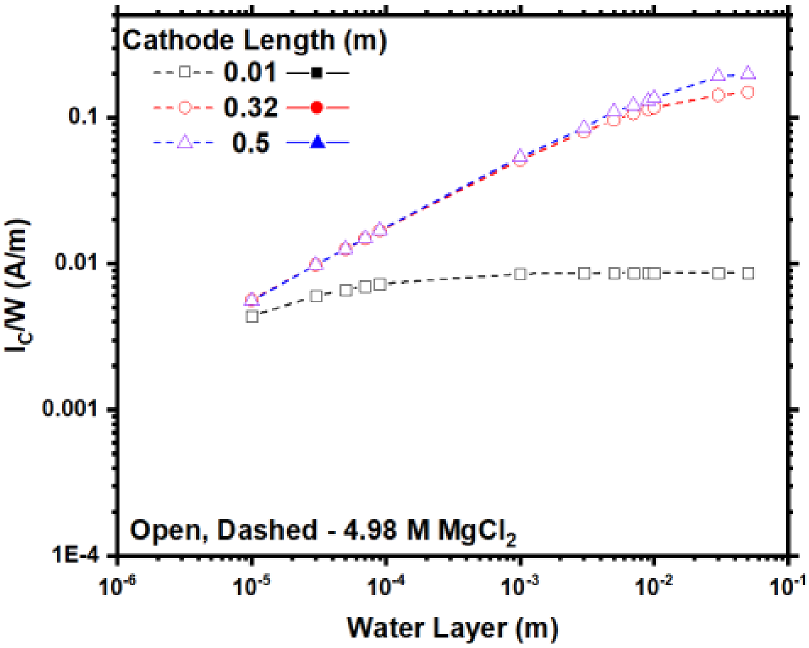
$$\delta \propto \frac{D^{1/3}\nu^{1/6}}{\omega^{1/2}}$$



- 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

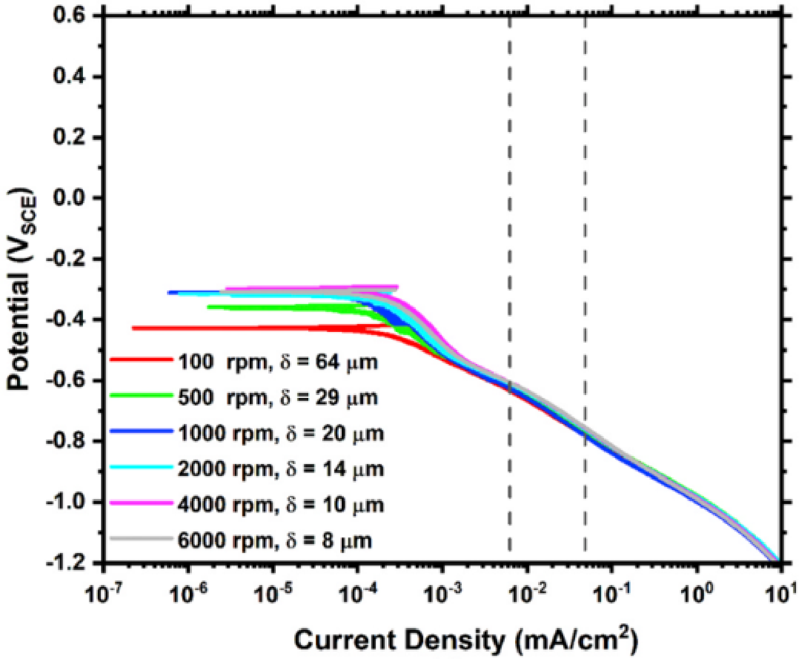
Changing Solution

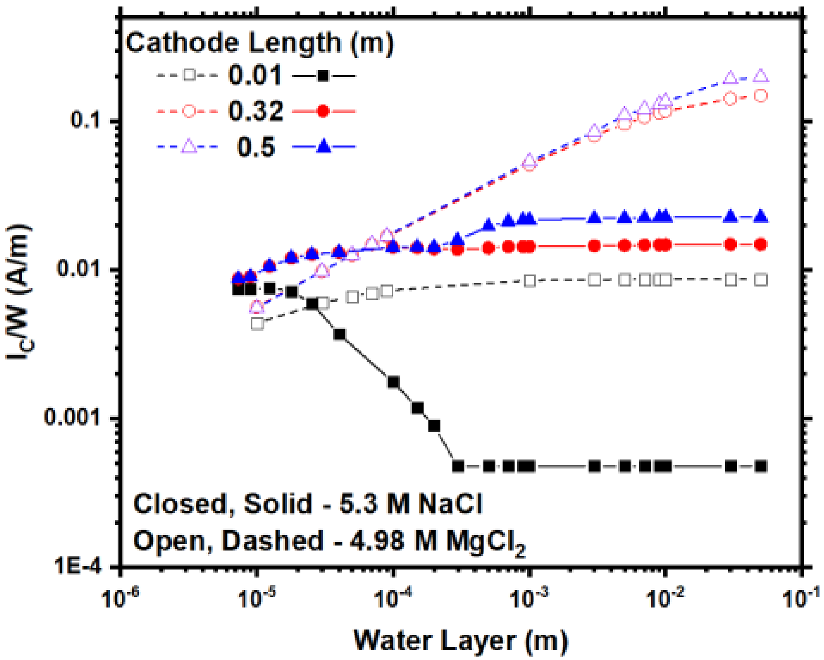




- $MgCl_2$ solutions exhibit no rotational dependence when using an RDE
- I_C/W only increases with increasing WL
  - Ohmic control
  - No M-T limitations

Changing Solution





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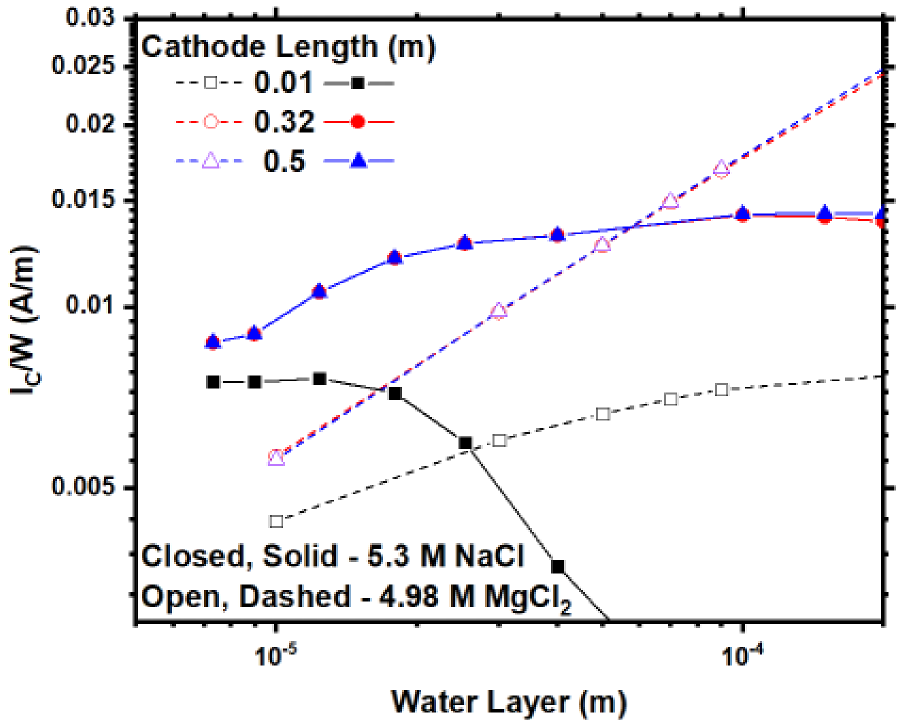
R.M. Katona, J.C. Carpenter, A.W. Knight, C.R. Bryan, R.F. Schaller, R.G. Kelly, E.J. Schindelholz, Corros. Sci. 177 (2020) 108935.

Changing Solution



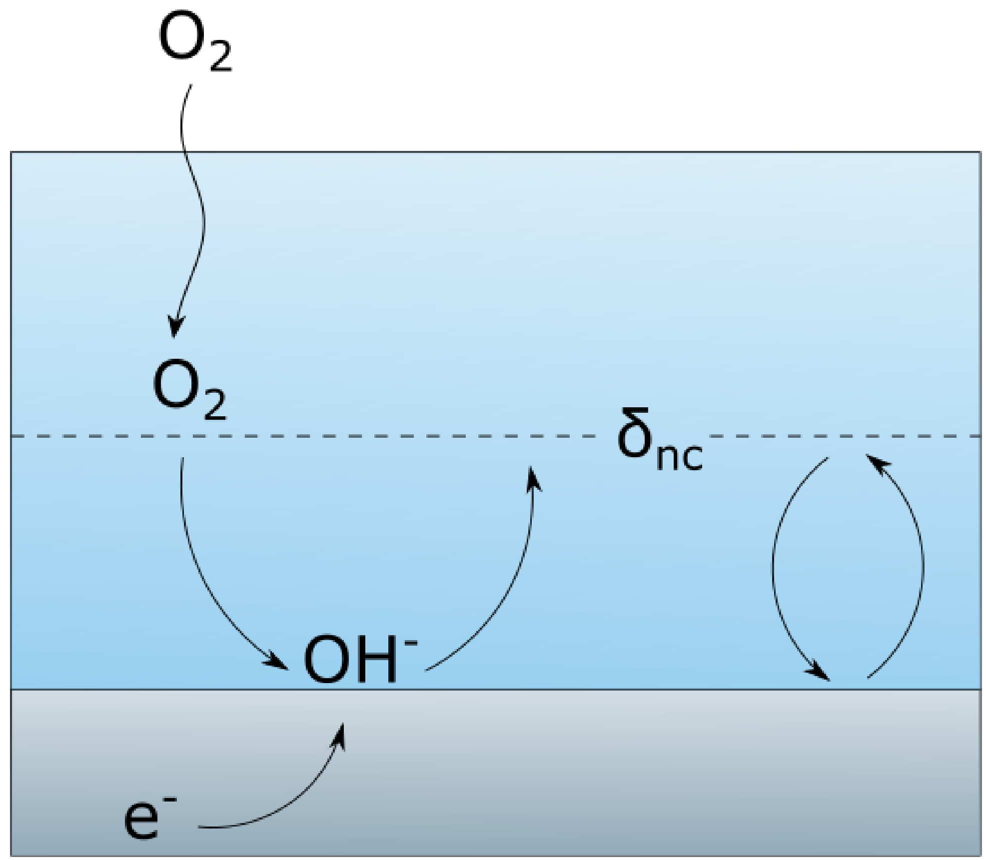
- At small WL, NaCl has a higher I_C/W
  - Due to current density dependence on WL
- When increasing WL, NaCl experiences more M-T limitations whereas $MgCl_2$ does not due to a lack of WL dependence on the cathodic kinetics

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.

Natural Convection Boundary Layer

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

$$\square_2 + 2\square^{+} + 4\square^{-} \rightarrow 4\square\square^{-}$$



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

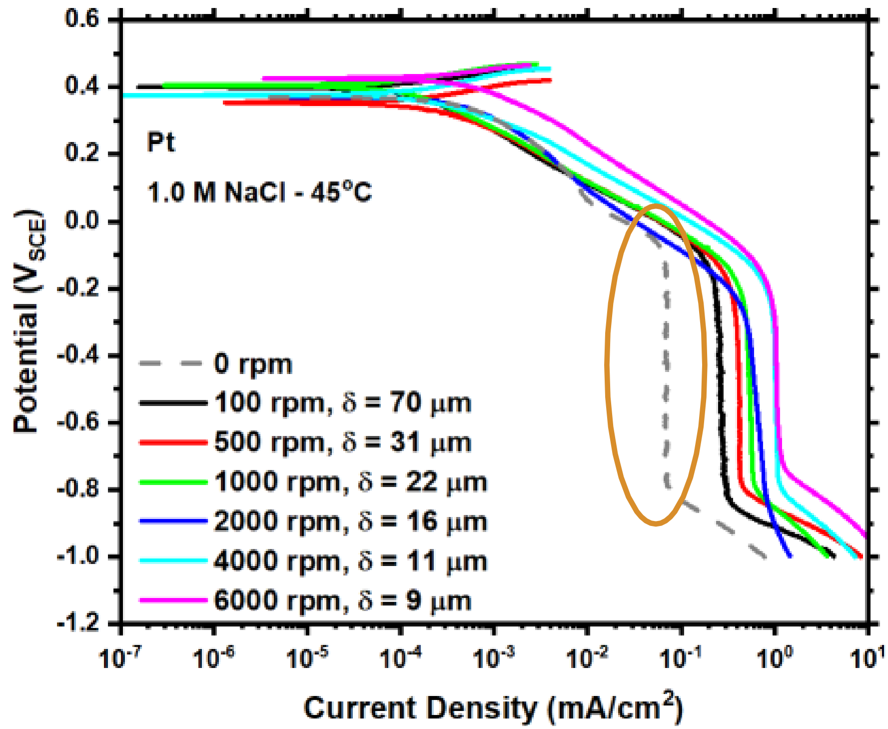
Natural Convection Boundary Layer

- 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,

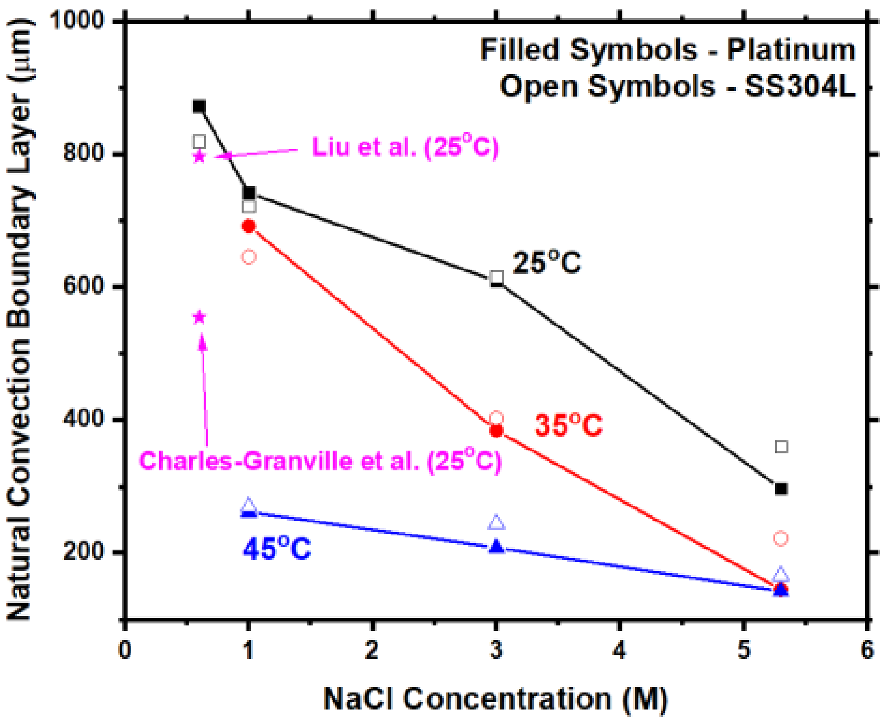
$$\delta \to \infty \qquad \to 0$$

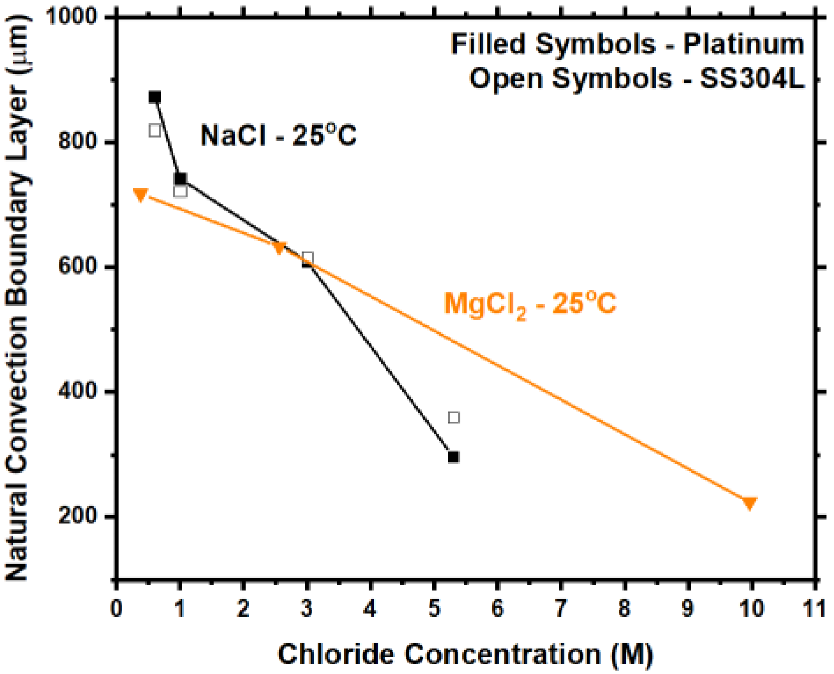


- Liu et al. determined the natural convection boundary layer to be roughly 800 μm in 0.6 M NaCl

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.

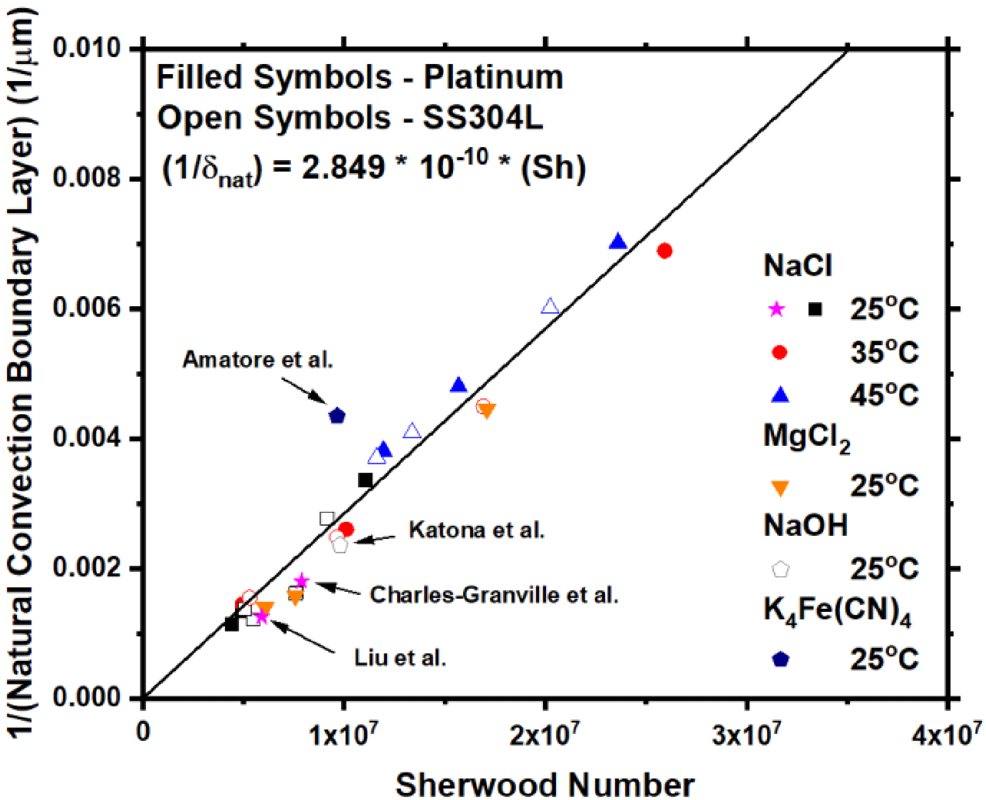
Can we predict δ_{nc}?

- 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

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

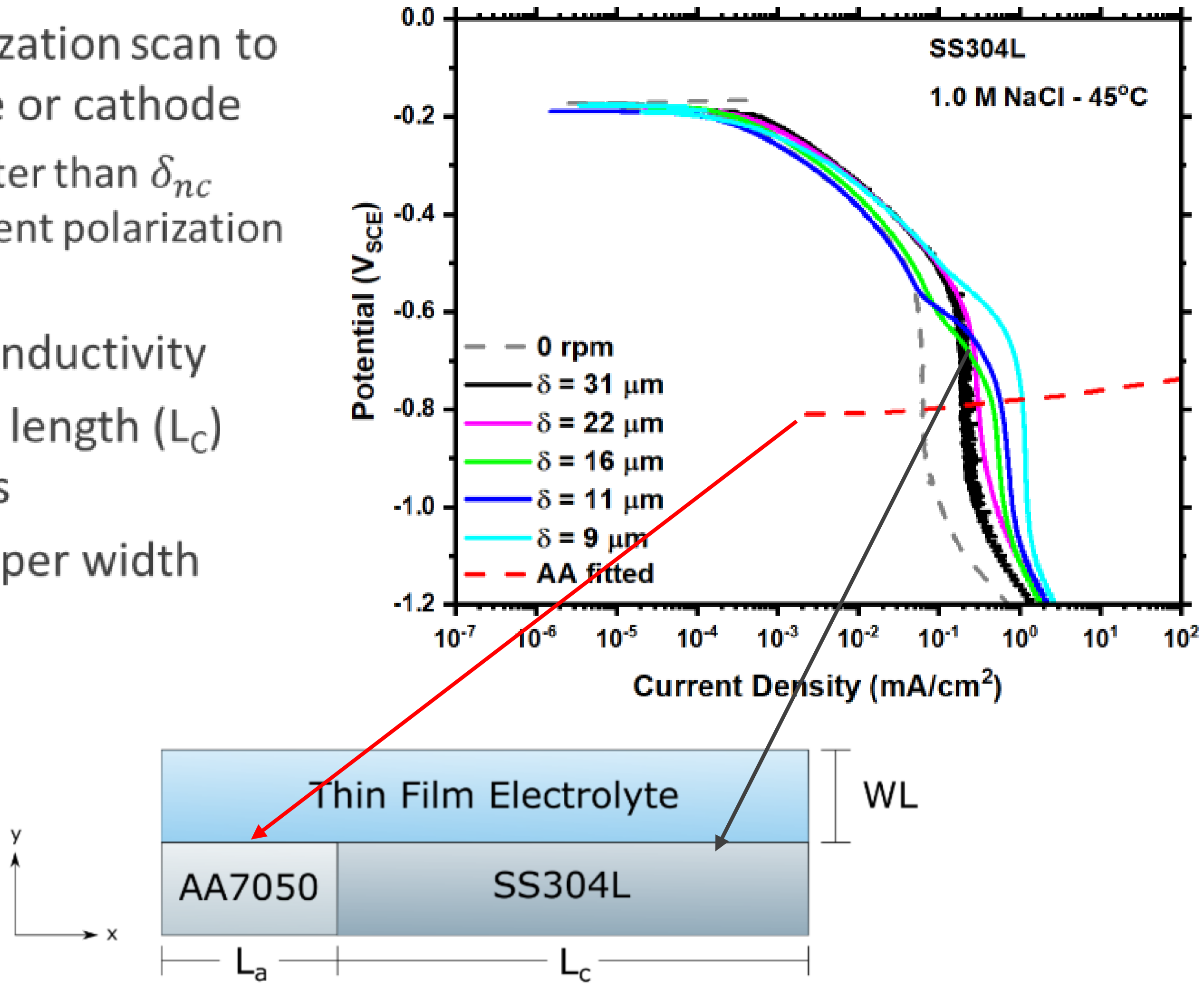
$$Sh = \frac{K}{D/d}$$



- Literature results match well with fit

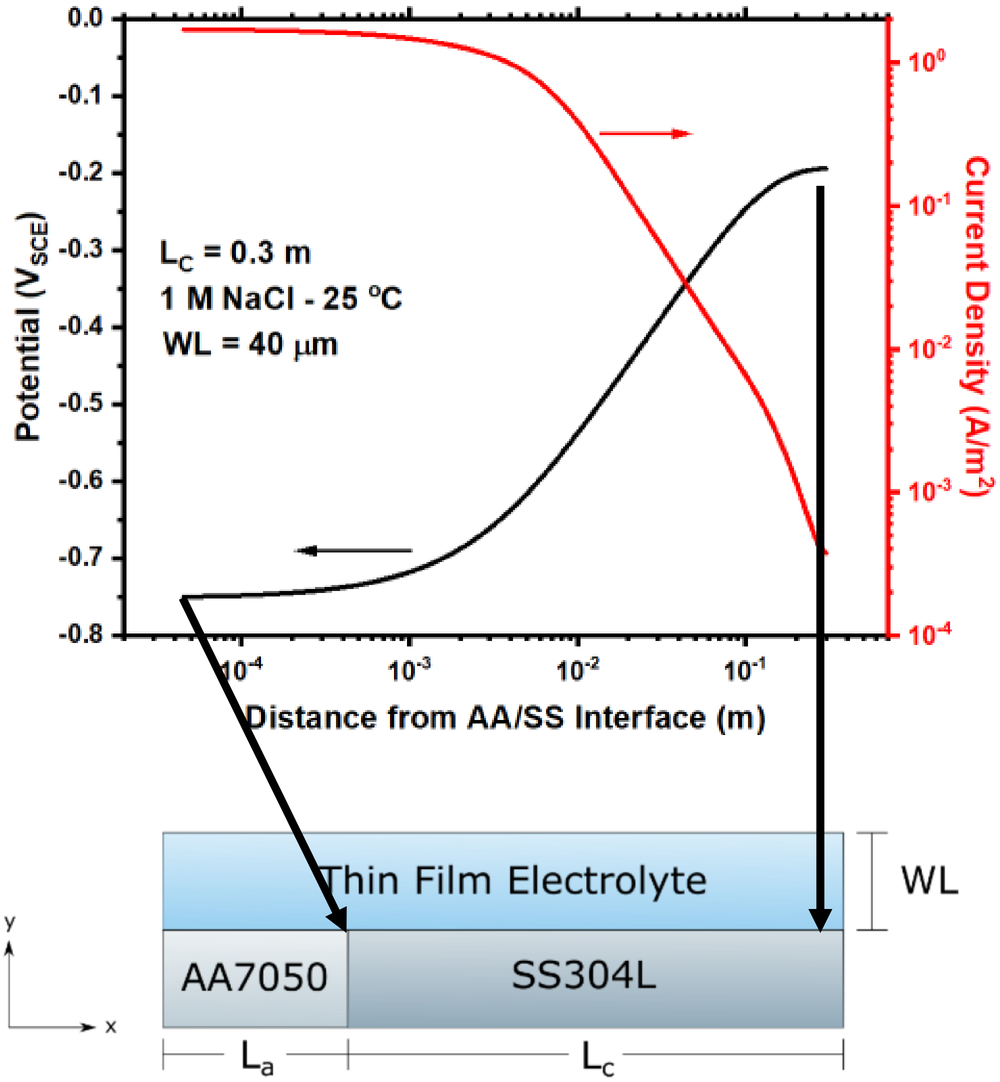
Modeling in a Galvanic Couple

- 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)



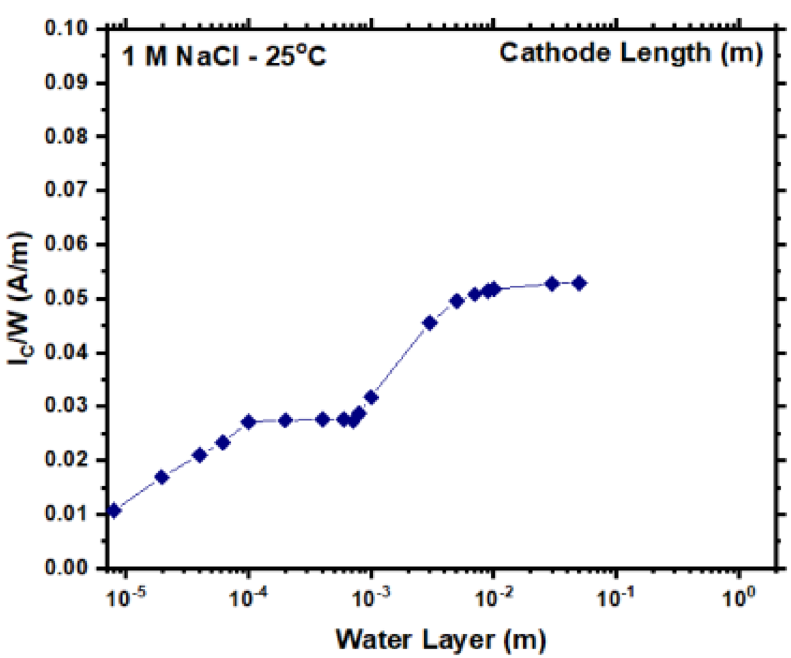
Modeling in a Galvanic Couple

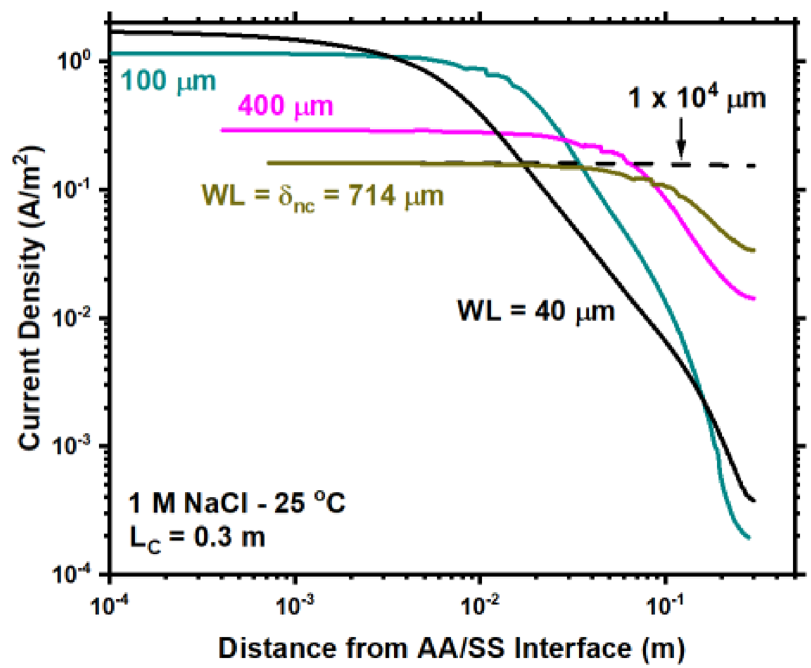
- Potential at the interface is the AA/SS304L coupling potential
- Potential far away from interface is OCP of SS304L
- Current density high near the interface and decays when moving from the interface
- Evaluate I_C/W by integrating current along the cathode



Increasing WL Thickness

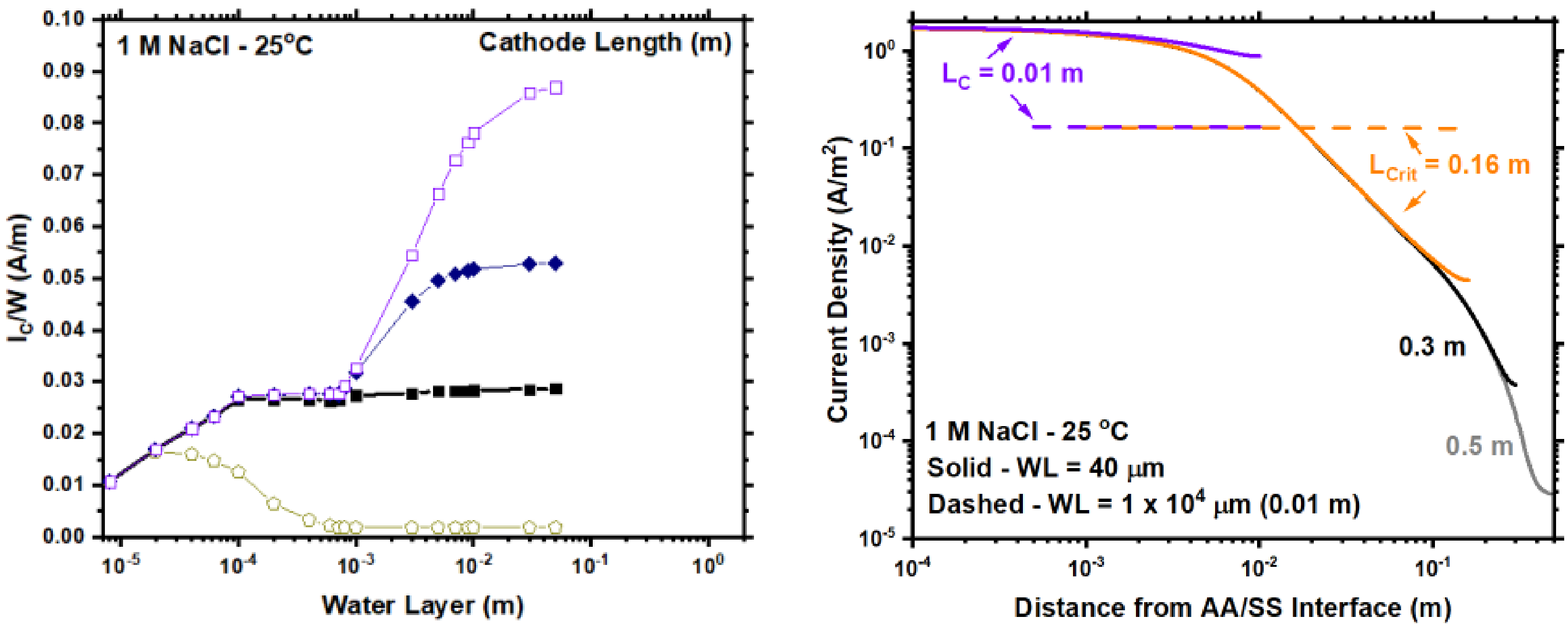
- Continuously increasing the WL at the same cathode size will not increase the current
- Current is now fully limited by the cathode size



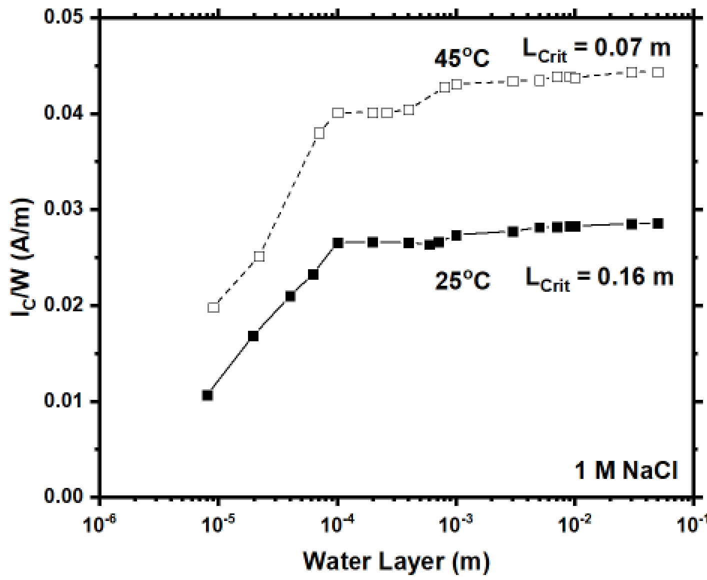


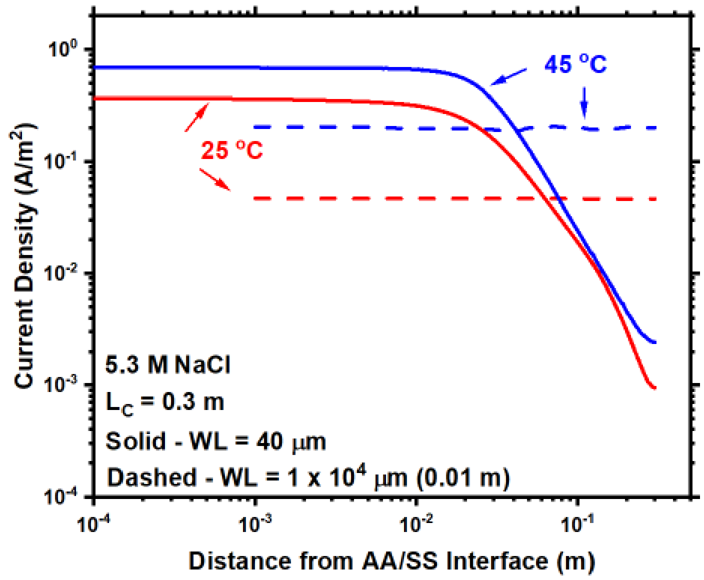
Increasing Cathode Length and WL

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

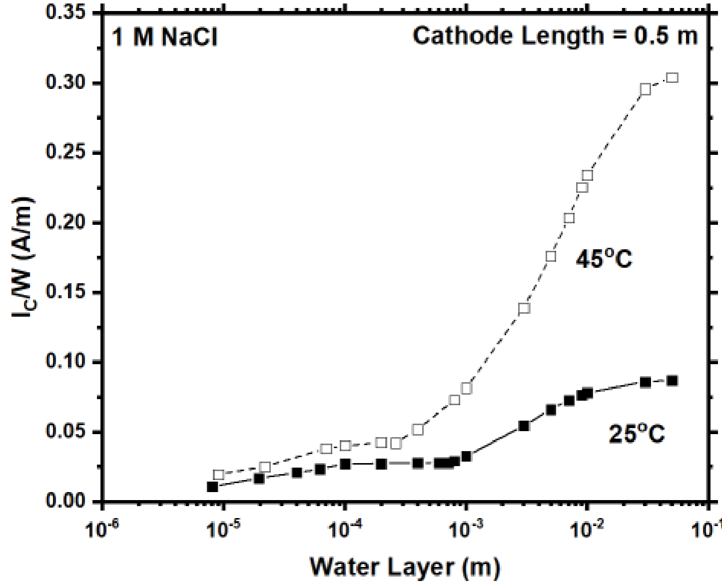


Increasing Temperature

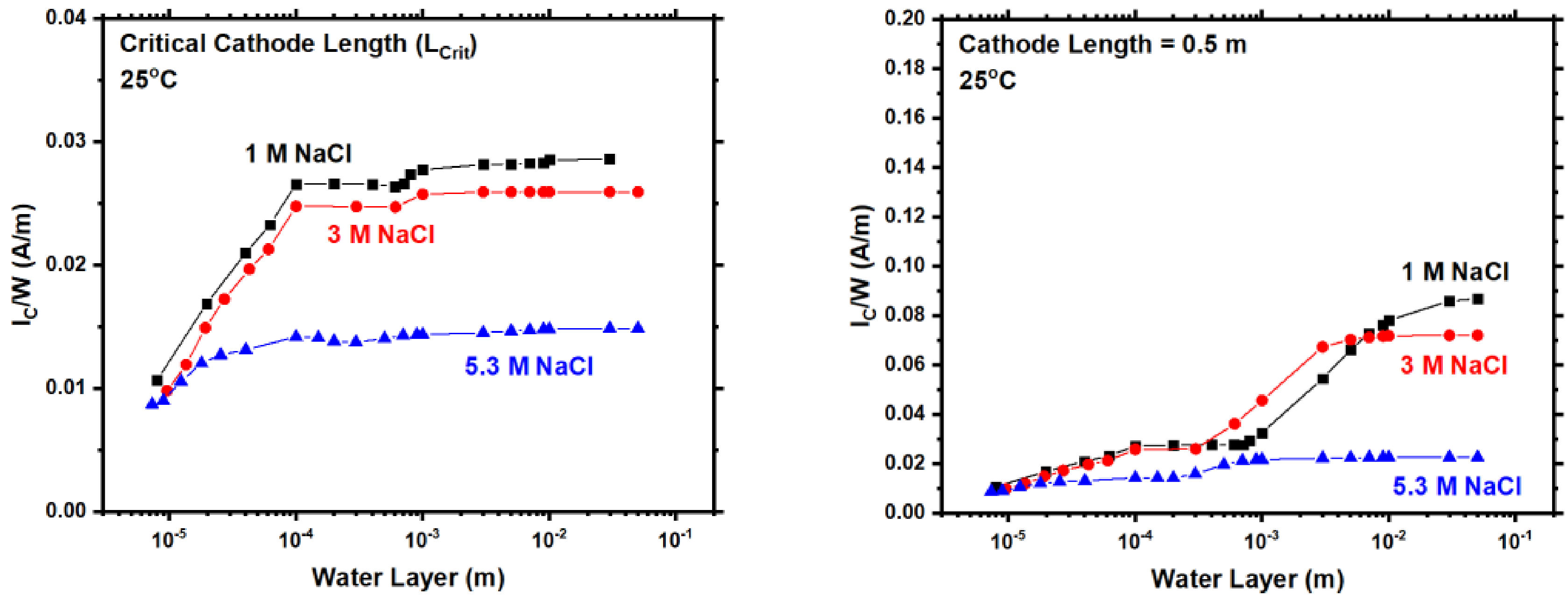




- Increasing temperature increases I_C/W
- Increasing temperature increases κ and i_{lim}



Increasing Chloride Concentration

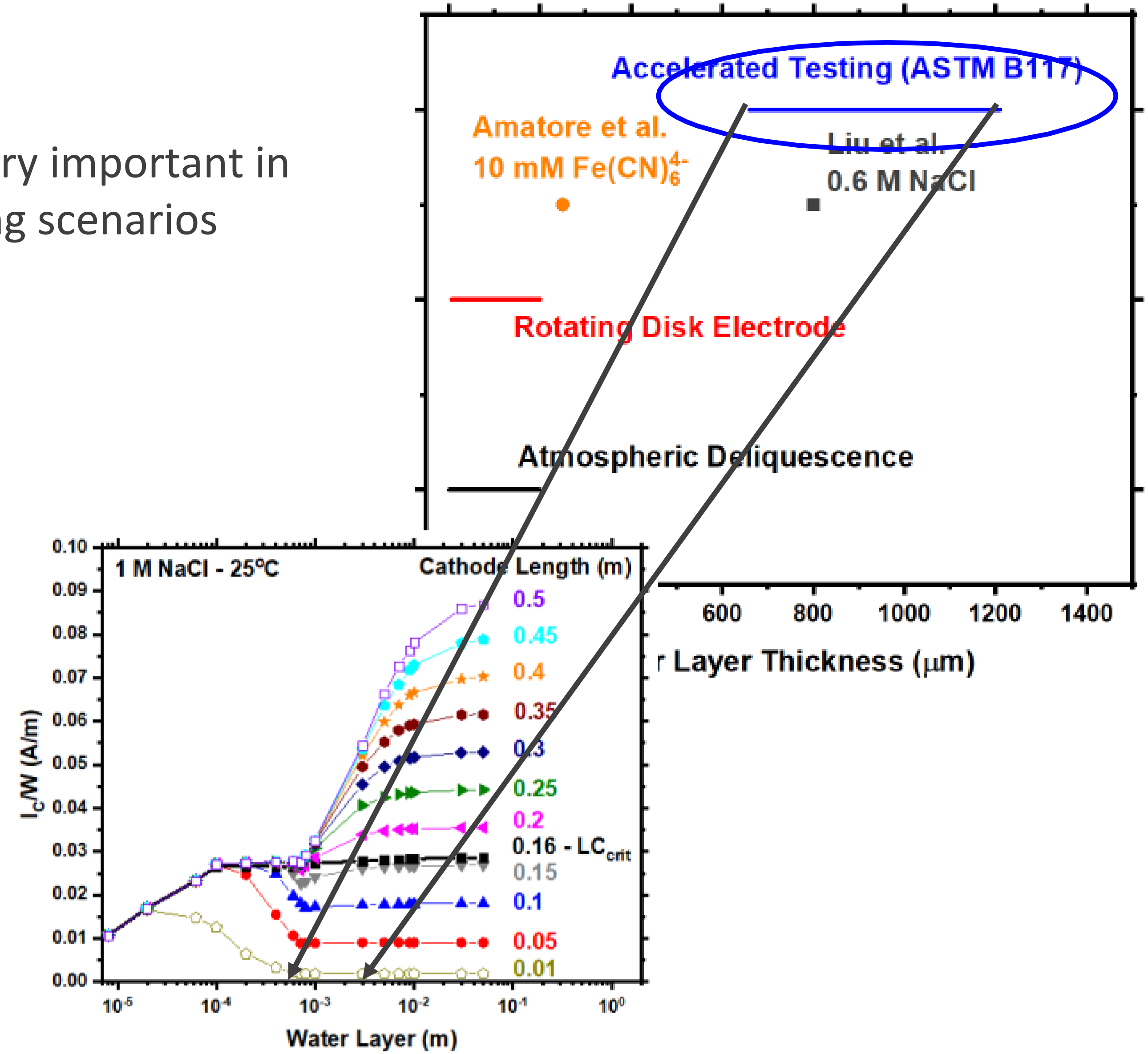


- Increasing chloride concentration decreases I_C/W in most cases
- Shouldn't current increase? -> More corrosion damage?
- Limited by the mass transport in the system

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

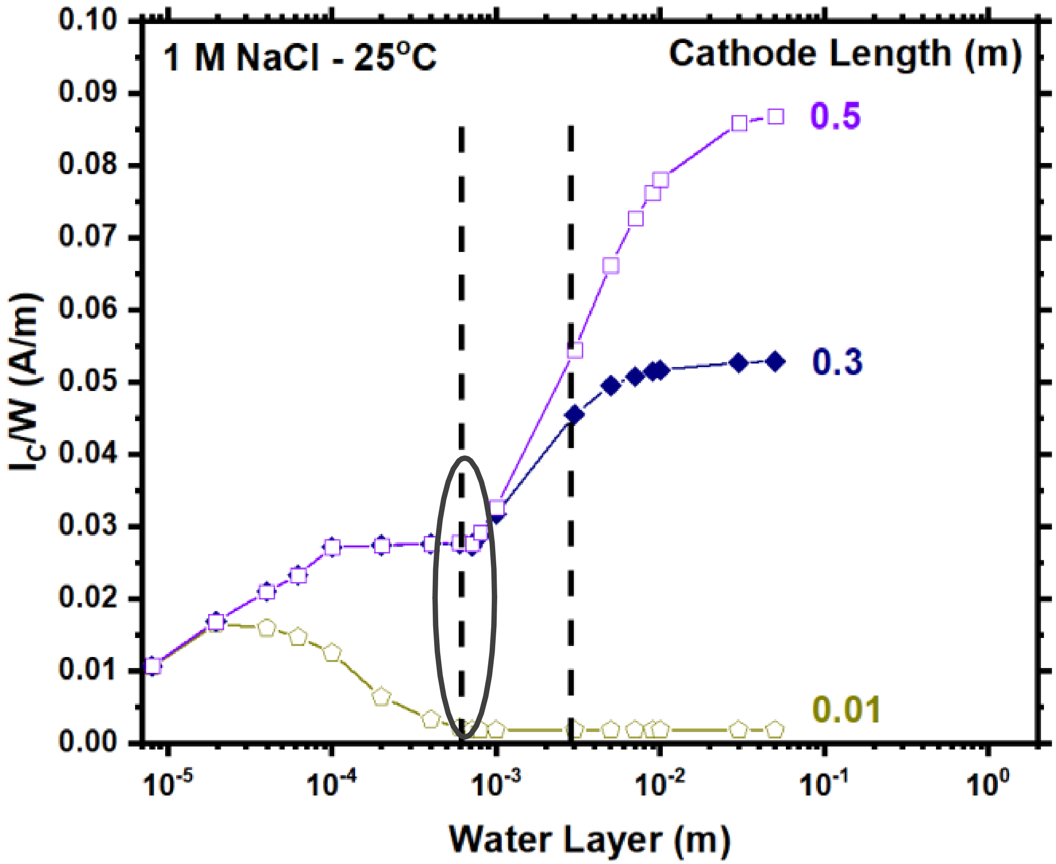
Implications

- 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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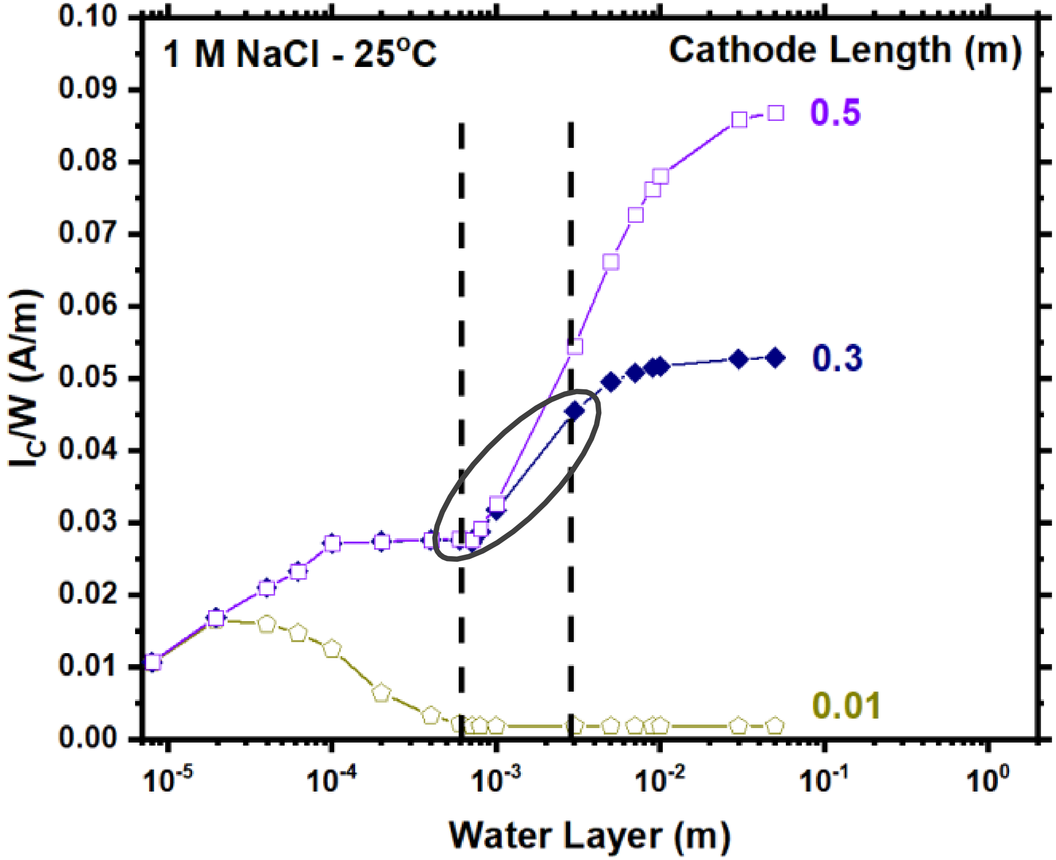

- Same cathode length at different angles will experience different corrosion damage
  - Tests experience large test-to-test and chamber-to-chamber variability
- Difficult to extrapolate corrosion damage to real life scenarios

$MgCl_2$ Cathodic Kinetics