SAND2021-12076C

Predicting Stress Corrosion Crack Tip Electrochemical Conditions and the Influence of Exposure Environment

R. M. Katona[1,2], R. S. Marshall[2], C. V. Moraes[2], Z. D. Harris[2], J. T. Burns[2], C.R. Bryan[1], R. F. Schaller[1], and R. G. Kelly[2]

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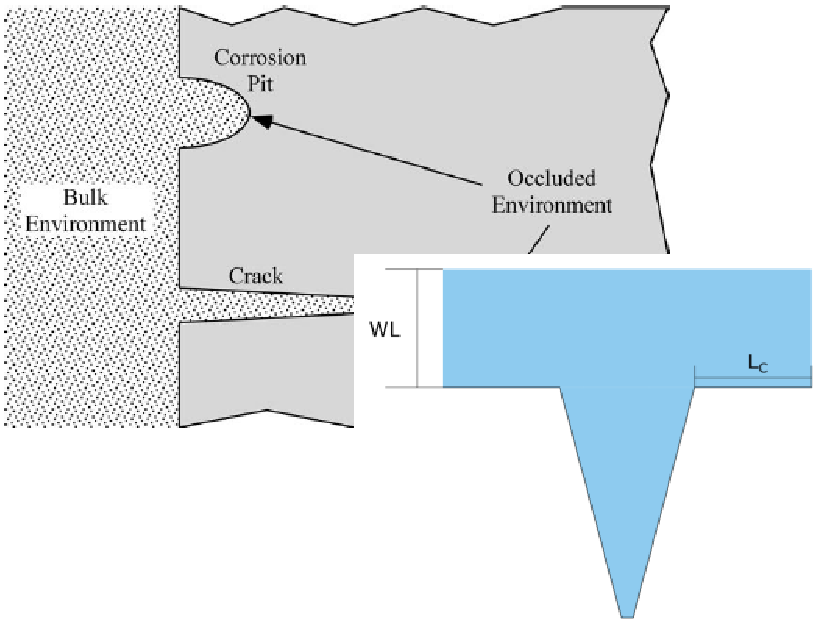
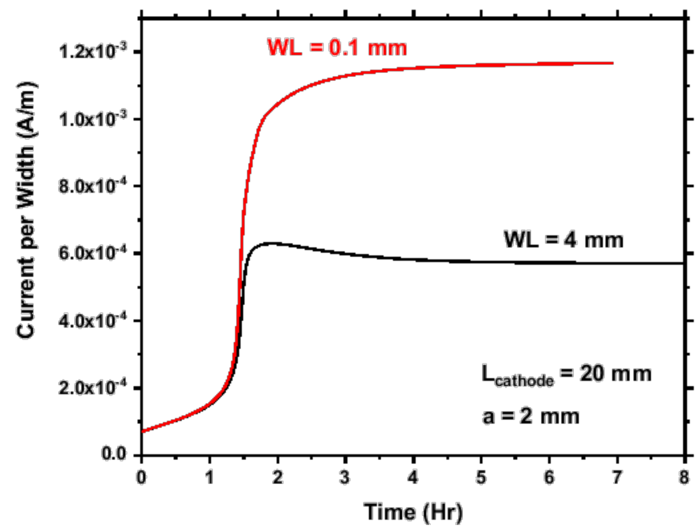
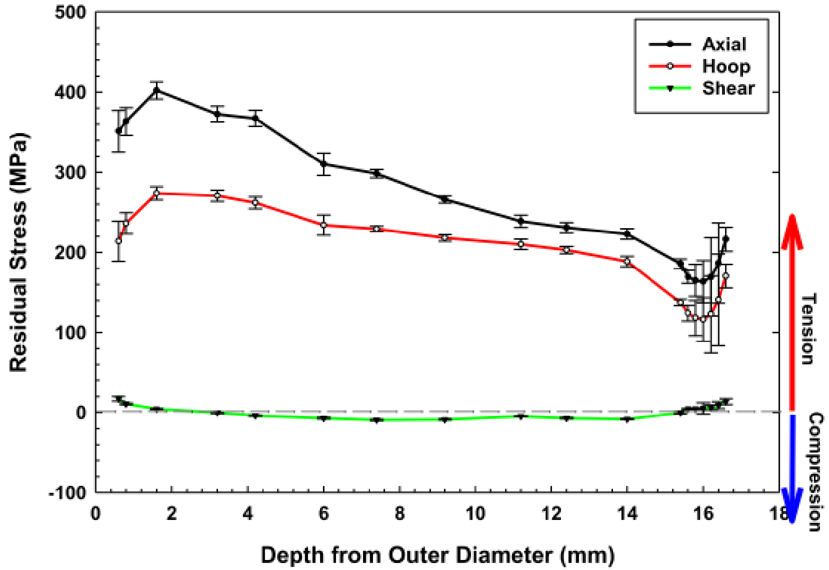
Overview


Corrosion
Pit
Occluded
Environment
Bulk
Environment
Crack
WL
L_C

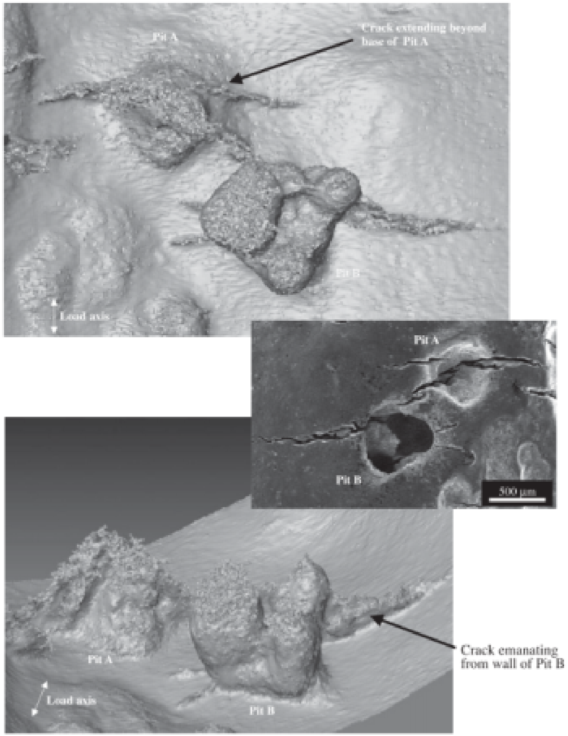

WL
L_C


WL = 0.1 mm
WL = 4 mm
$L_{cathode}$ = 20 mm
a = 2 mm
Current per Width (A/m)
Time (Hr)
1.2x10^{-3}
1.0x10^{-3}
8.0x10^{-4}
6.0x10^{-4}
4.0x10^{-4}
2.0x10^{-4}
0.0
0 1 2 3 4 5 6 7 8

Stress Corrosion Cracking



Residual stress in SS304L canister for SNF applications [1]



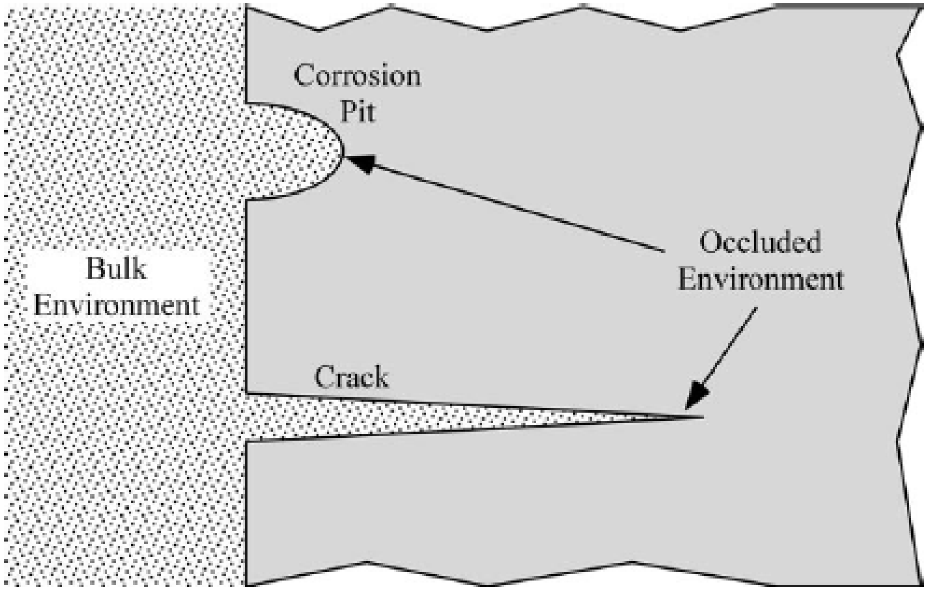
Cracks immerging from pitting corrosion damage [2]

- 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

Current SCC Modeling

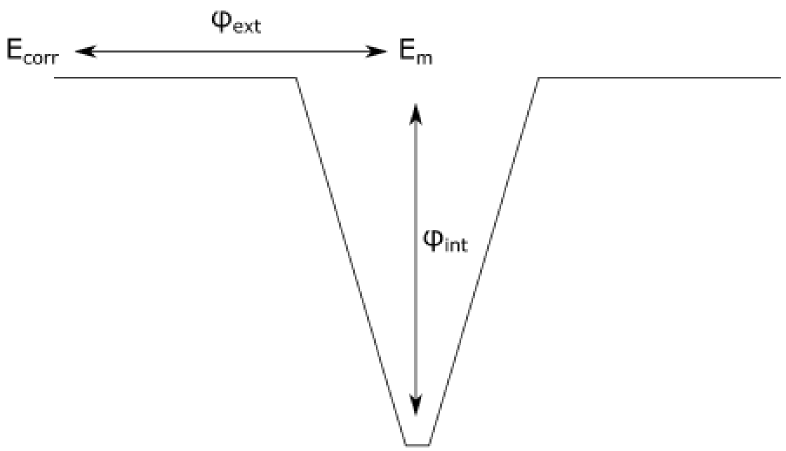


Figure adapted from [1]

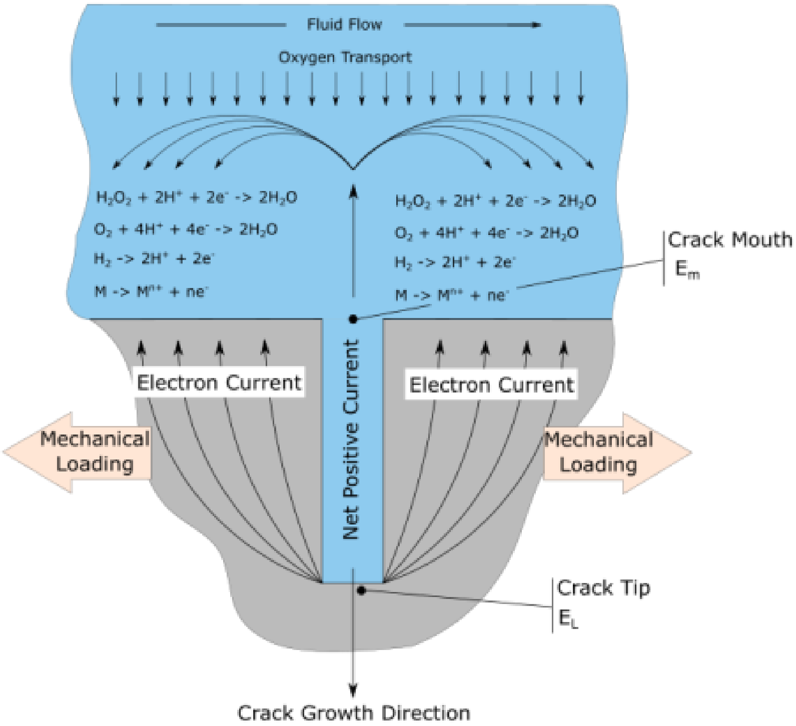


Figure adapted from [2]

- Current models assume crack tip current density and external potentials to determine electrochemical conditions in the crack
  - ***Static boundary conditions***
- Size of external cathode and WL not explicitly considered
- No consideration of diffusion limited oxygen reduction reaction (ORR)

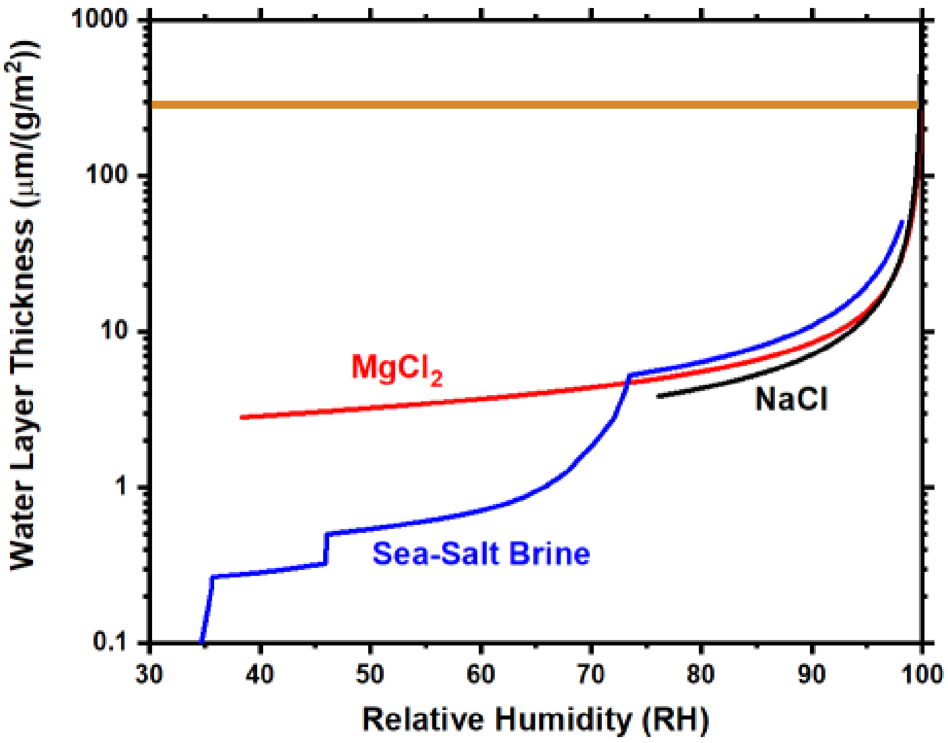
[1] A. Turnbull. Corrosion. 57 (2001) 175–189.
[2] M.P. Manahan, et al., Corros. Sci. 37 (1995) 189–208.

Salt enable deliquescence possible in atmospheric scenarios

- 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

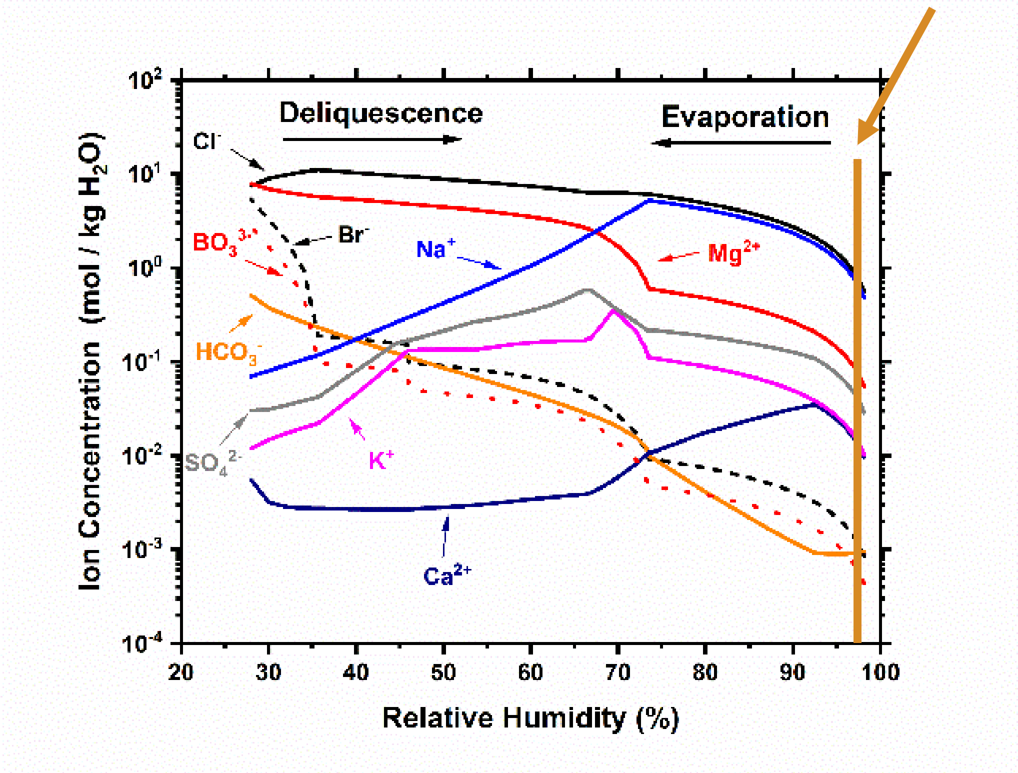


R.M. Katona, A.W. Knight, E.J. Schindelholz, C.R. Bryan, R.F. Schaller, R.G. Kelly. Electrocimicha Acta. Accepted. (2020).

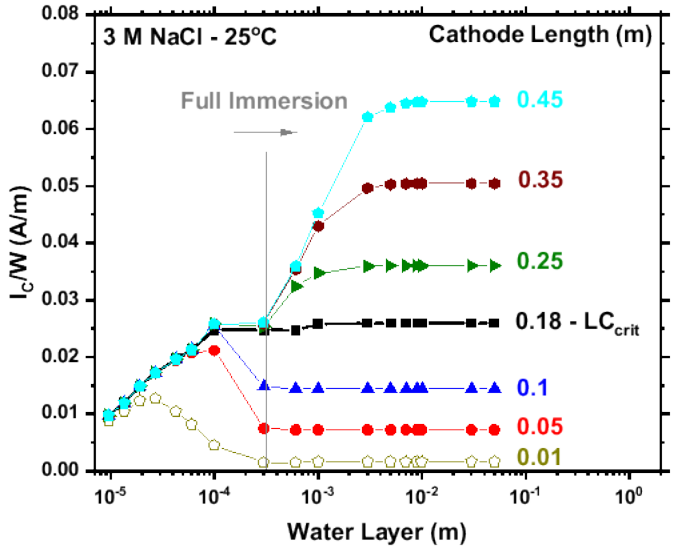
Dehydration of sea-salt brine varies in composition

- Important relative humidities:
  - Precipitation of NaCl ~ 75 % RH
  - Precipitation of $MgCl_2$ ~ 35 % RH

98 % RH ~ 0.6 M NaCl



What we know from galvanic couples



- Galvanic coupling model with fixed boundary conditions
- Modeling indicates strong coupling of the WL thickness and cathode length
- Delineation between thin film and bulk conditions

What's missing in SCC models?

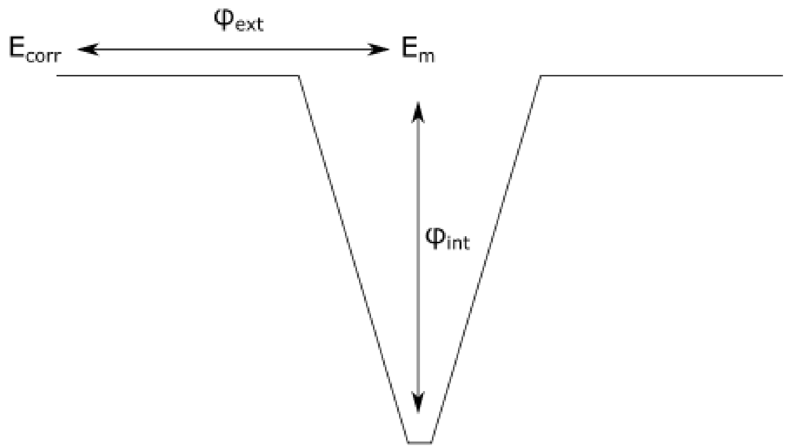
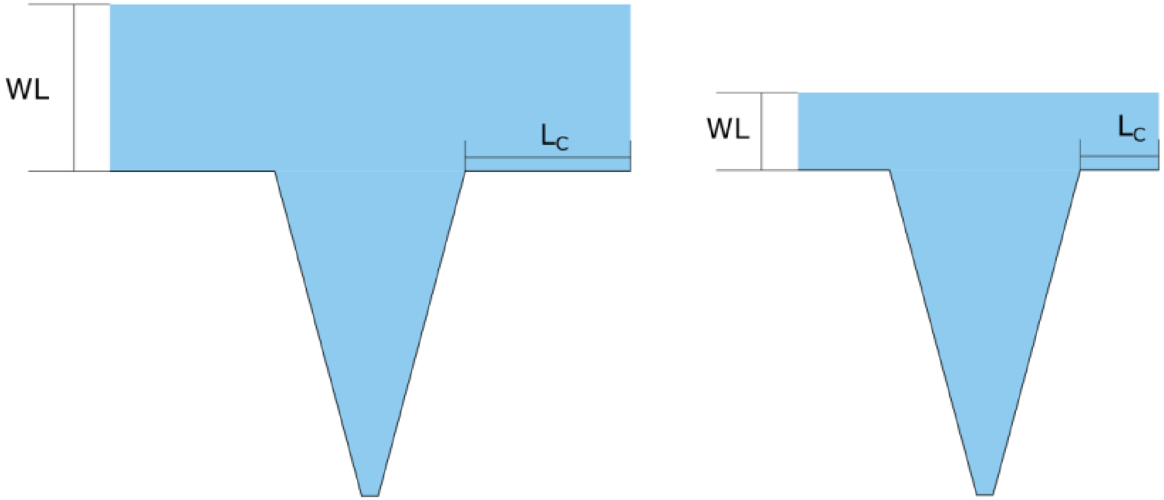


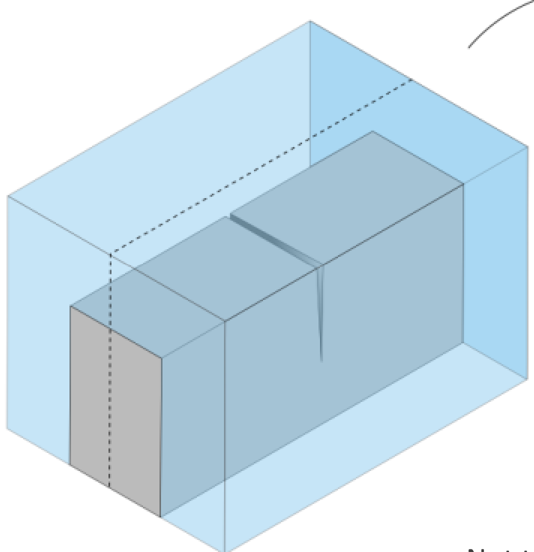
Figure adapted from [1]

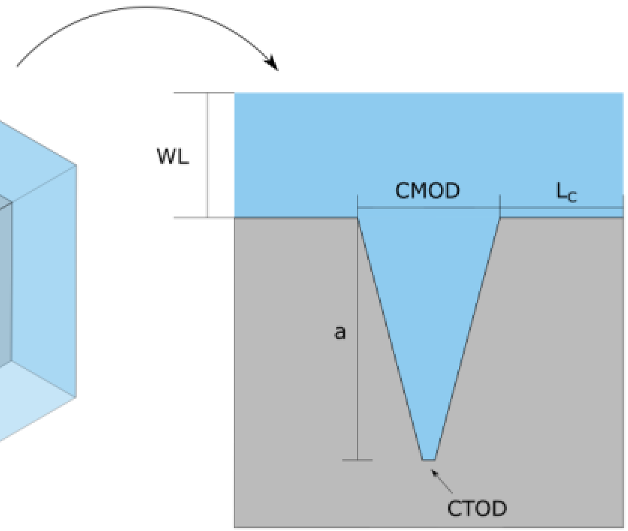
- Chemistry dependent boundary conditions
- Diffusion limited ORR not considered
- Influence of external environment
    - Size sample
    - Water layer thickness



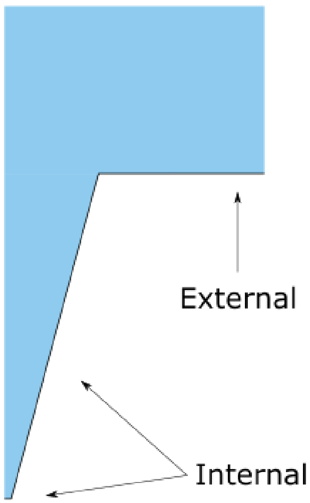
[1] A. Turnbull. Corrosion. 57 (2001) 175–189.

SCC Modeling





Not to
scale

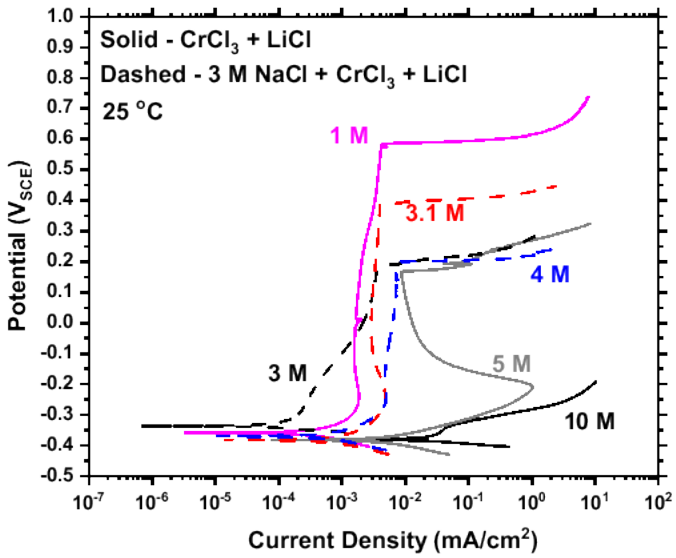


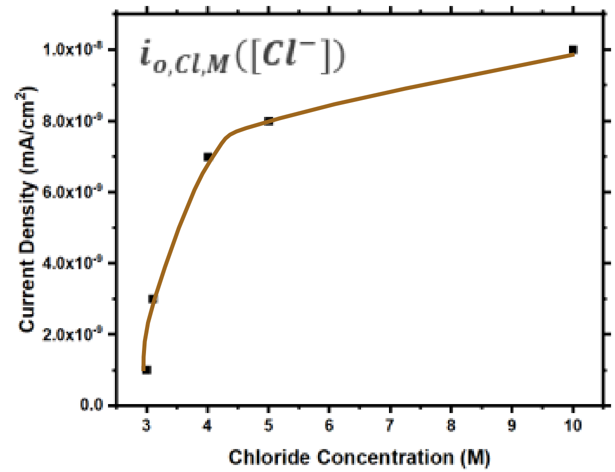
- Finite element reactive transport model (COMSOL) looking for trends in electrochemical parameters

- Inferences about crack growth rates

Solution dependent kinetics

- Anodic and cathodic polarizations as a function of metal chloride concentration





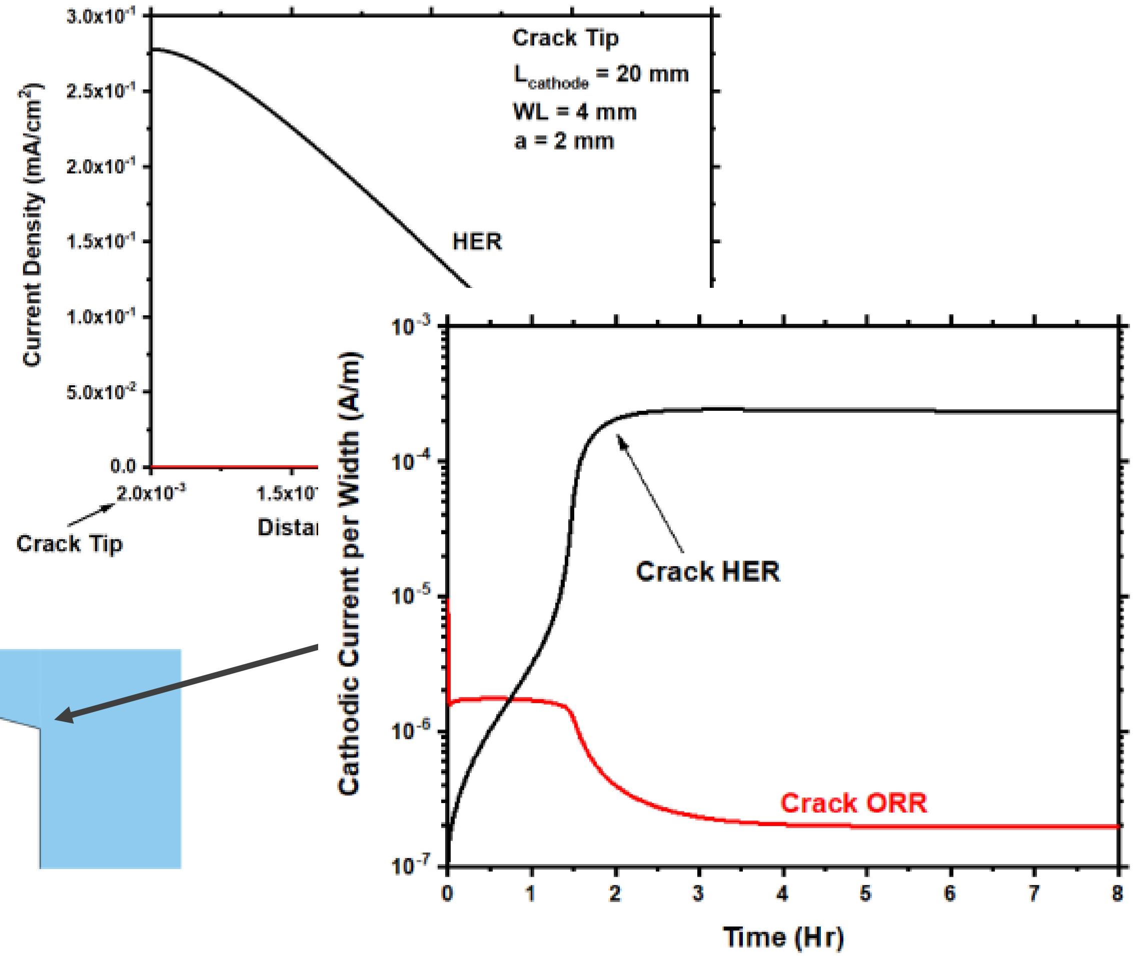
$$i_{act,M}([\mathrm{Cl}^-]) = \boldsymbol{i_{o,Cl,M}} \cdot 10^{\frac{\eta_M}{A_M}}$$

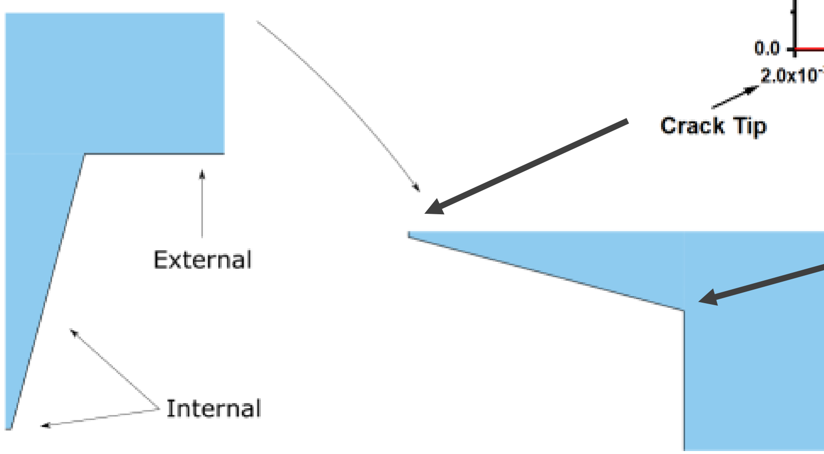
- Chemistry dependent equations for HER, ORR, anodic dissolution, and passive current density
- Mass transport model with hydrolysis and metal salt formation

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

Current per Width Allows Evaluation Over Time

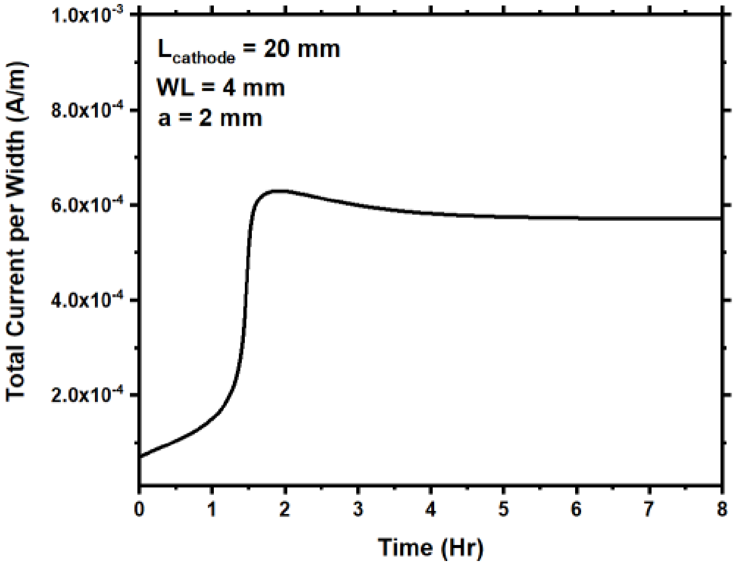
- Evaluate current density along surface

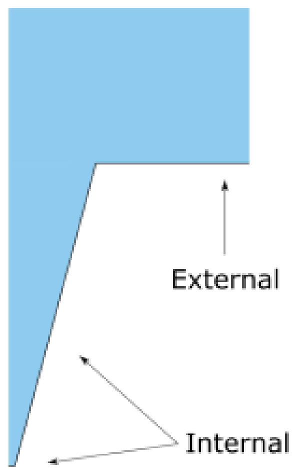


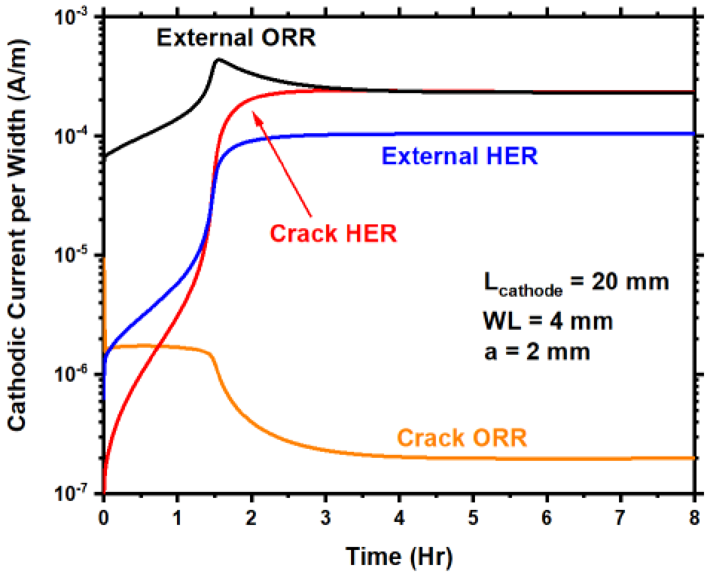


- Integrate to get current per width of a surface

External ORR and internal HER dominant cathodic reactions

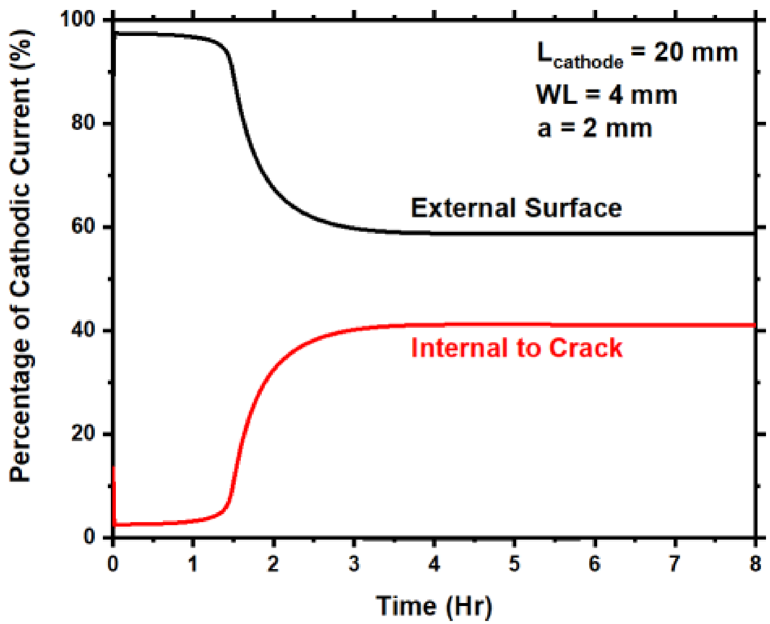


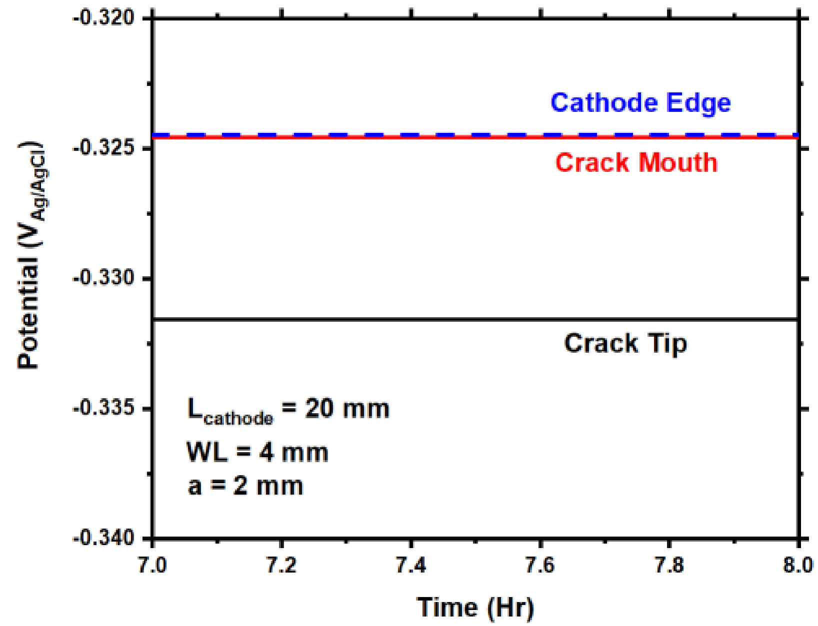




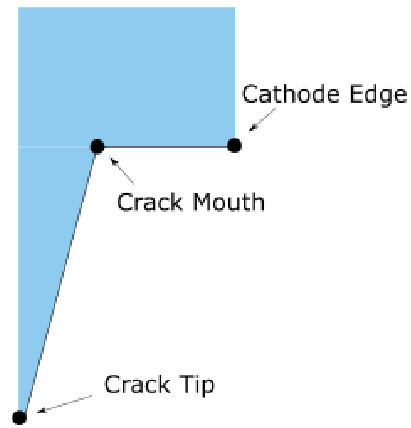
- Total current per width increases until steady state value at roughly 4 hours
- External ORR and internal HER dominant cathodic reactions
  - External HER is still prominent

Majority of cathodic current external to crack





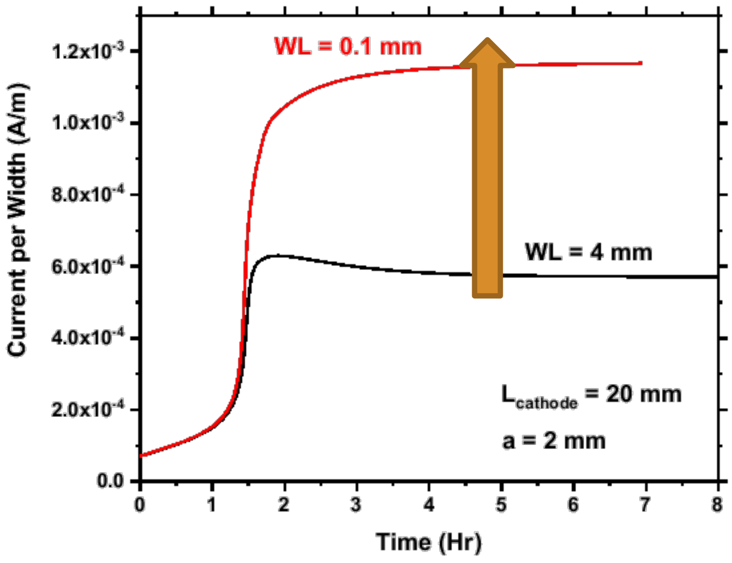
- Strong coupling of external surface similar to initial observations of CEFM [1]
- Potential drop external to the crack minimal
  - $E_m \approx E_{edge}$
  - Due to ***high conductivity***, ***bulk conditions***, and ***finite sample*** dimensions

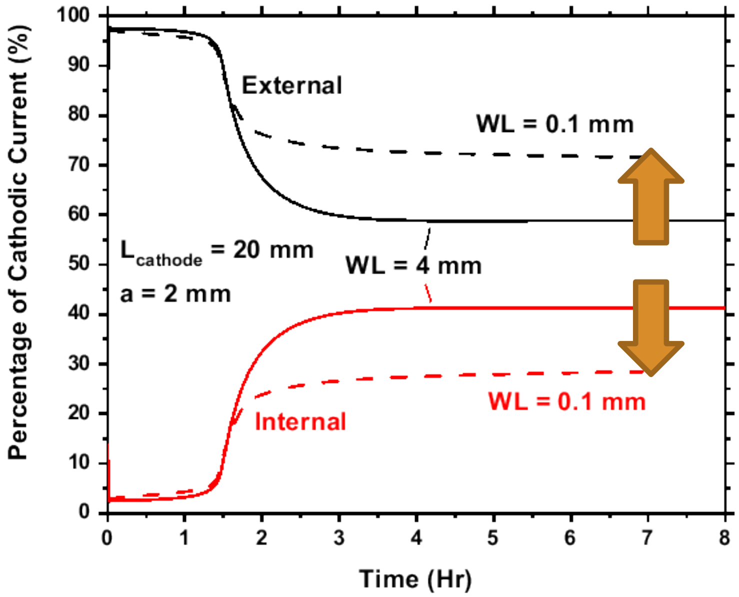


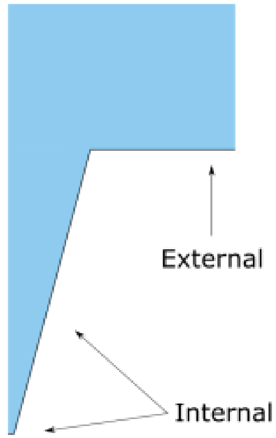
[1] M.P. Manahan, et al., Corros. Sci. 37 (1995) 189–208.

Decreasing WL thickness increases electrochemical severity

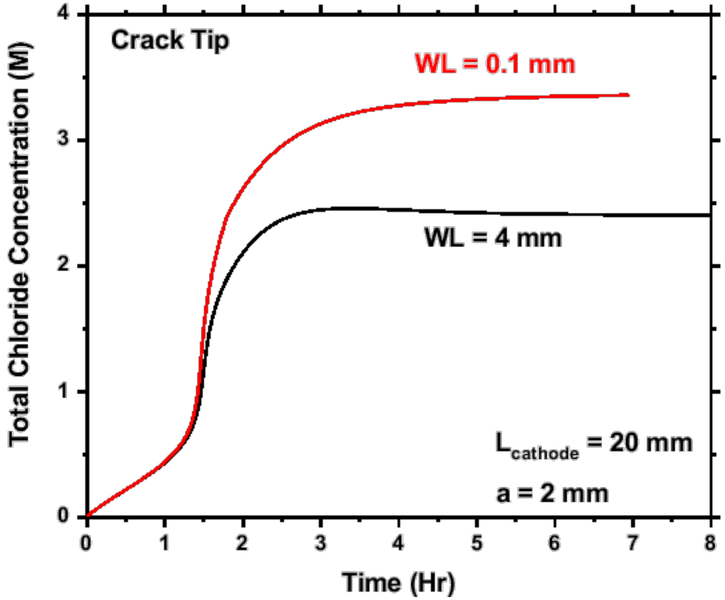
- Decreasing WL thickness increases total cathodic current per width
- Larger portion of the cathodic current on the external surface



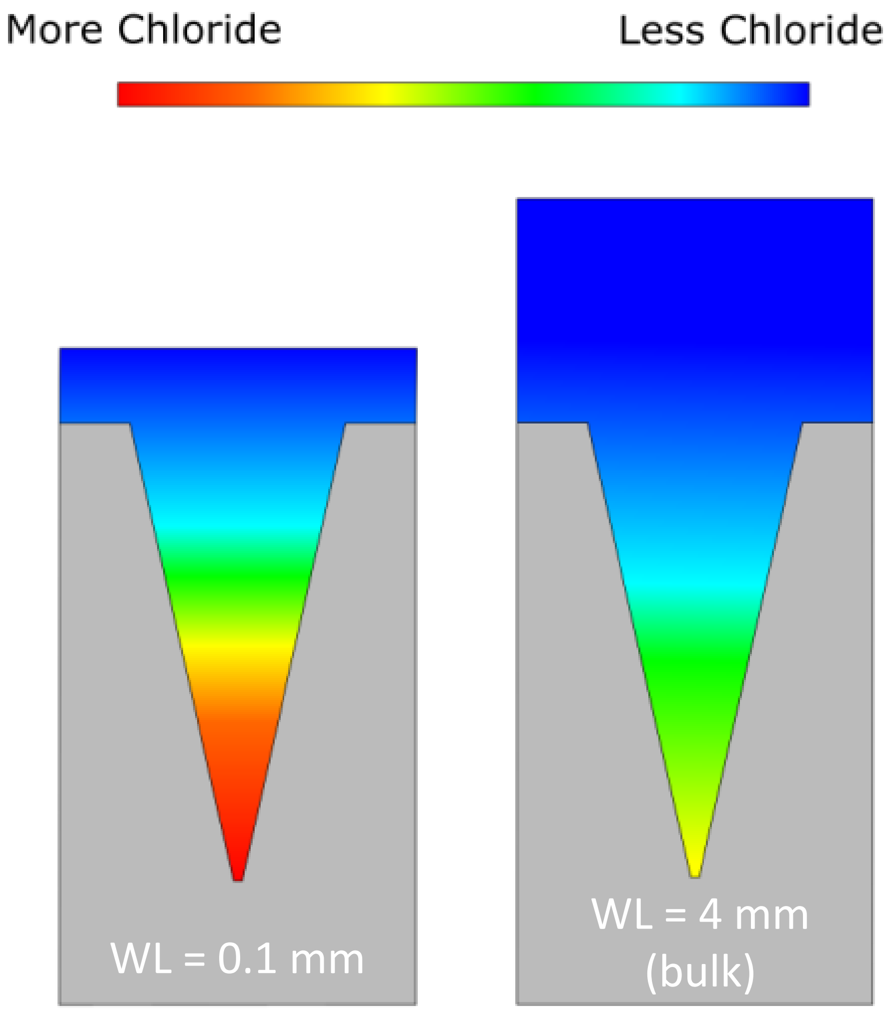




Chloride concentration at the crack tip increases with decreasing WL thickness

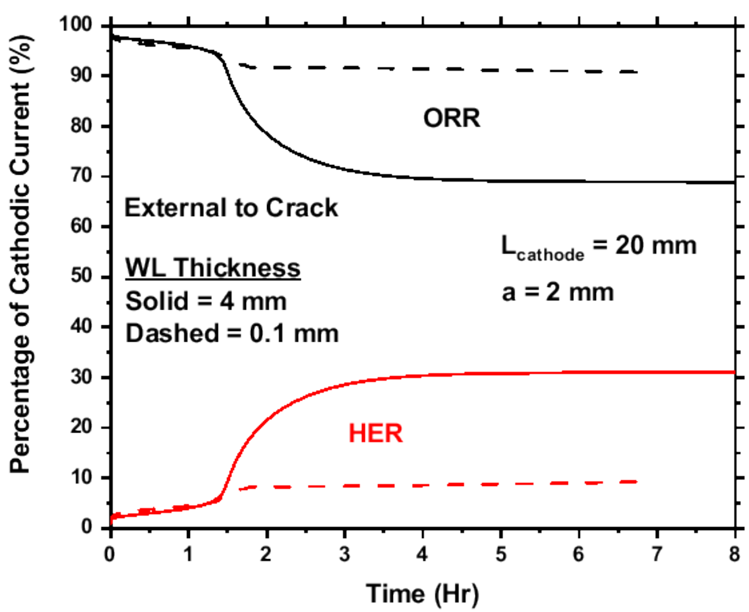


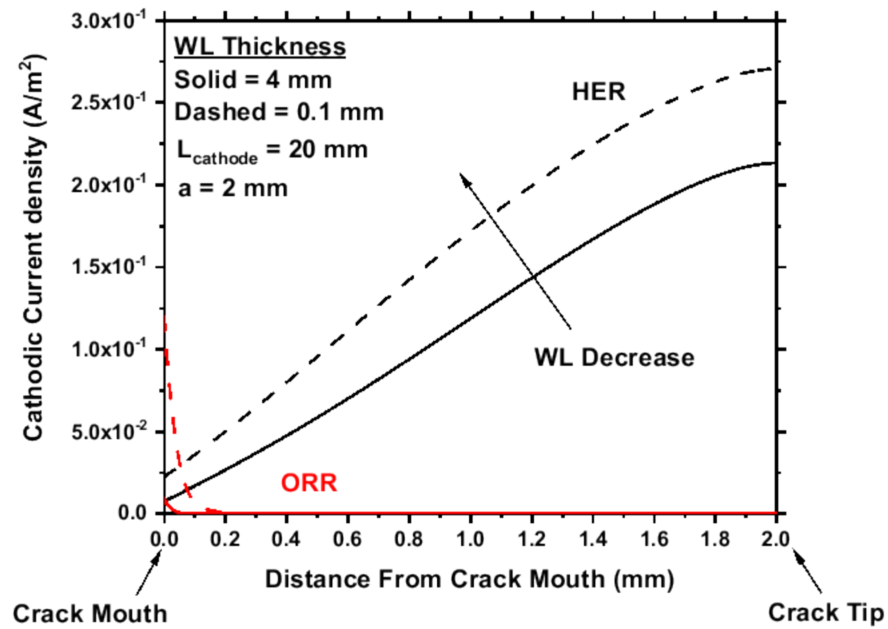
- Increased current per width with decreased WL thickness increases chloride concentration at the crack tip due to electromigration



Decreasing WL thickness increases electrochemical severity

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

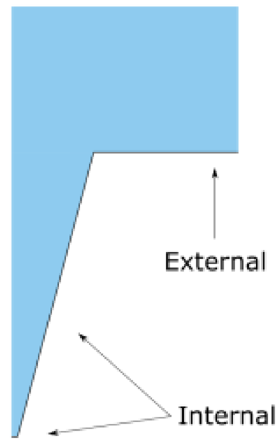


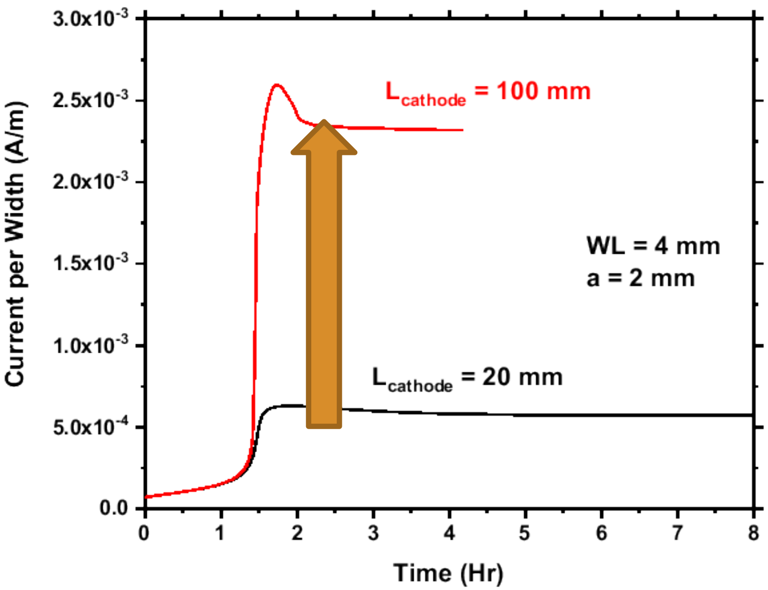


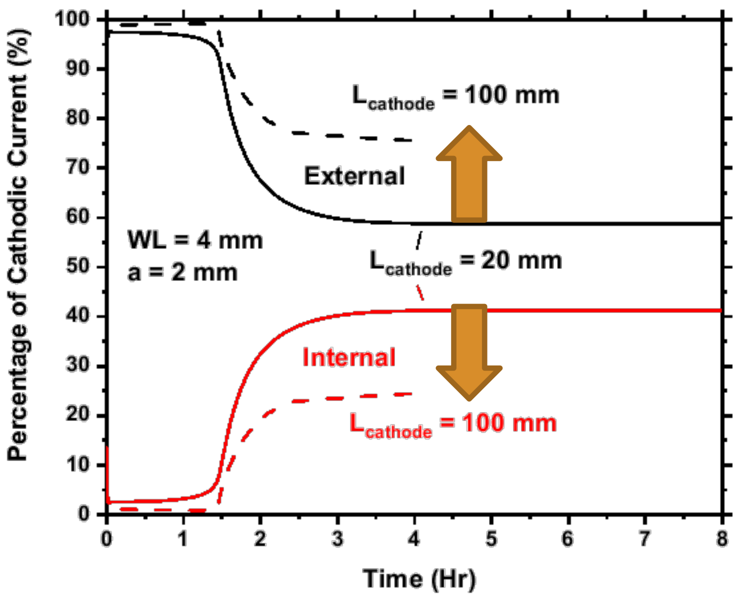
Higher total current (Ext. ORR enhanced) → Greater anodic dis. (lower pH, higher Cl^-) → Increased HER in crack

Increasing cathode length increases electrochemical severity

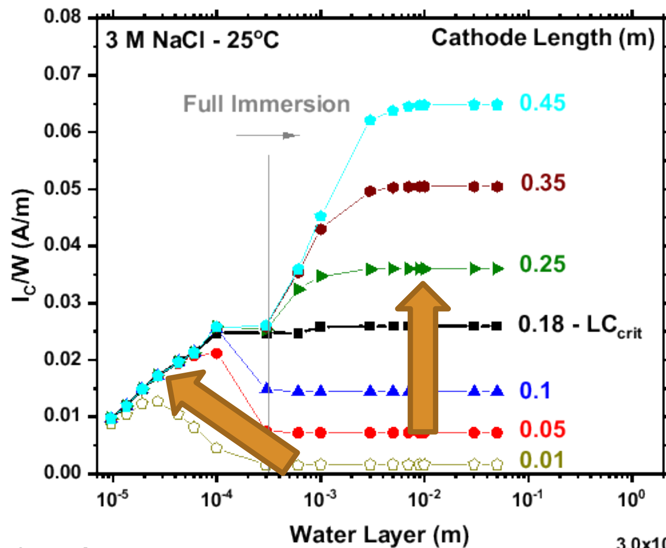
- Increasing cathode length increases the total current per width
- Cathodic current is more external
  - Roughly 75 % external

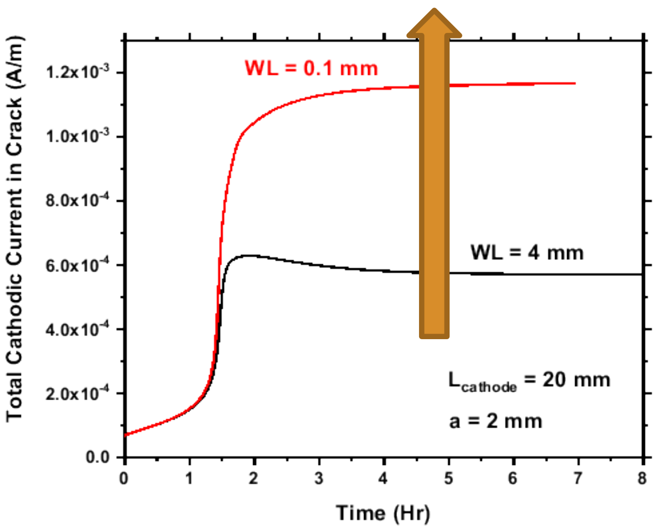


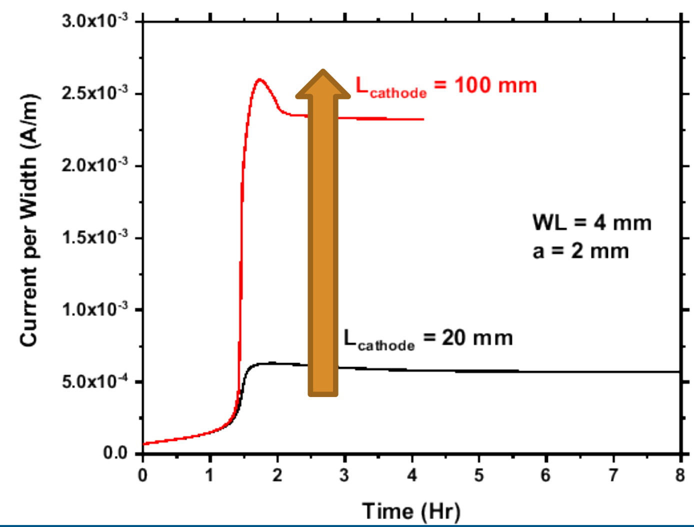




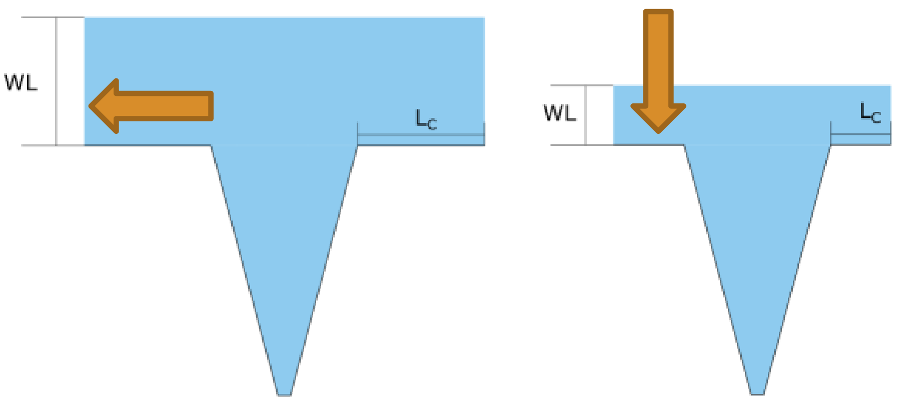
Coupling of cathode size and WL thickness similar between SCC and galvanic couple

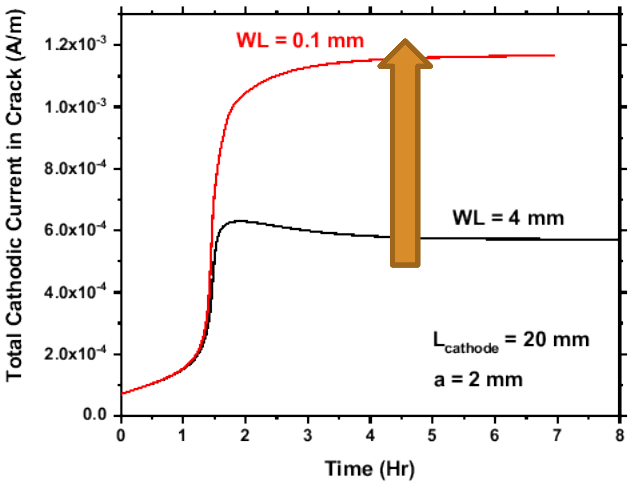


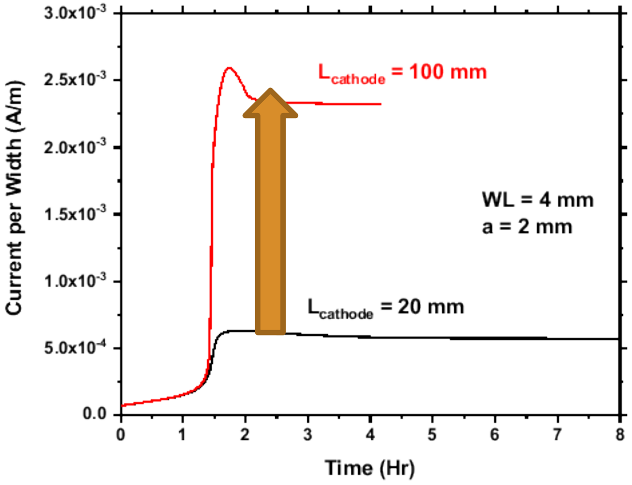




External environment strongly influences electrochemical conditions at the crack tip



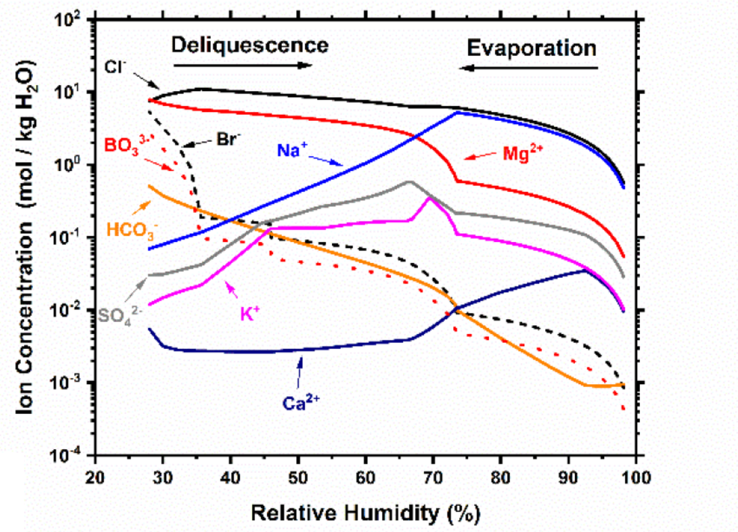


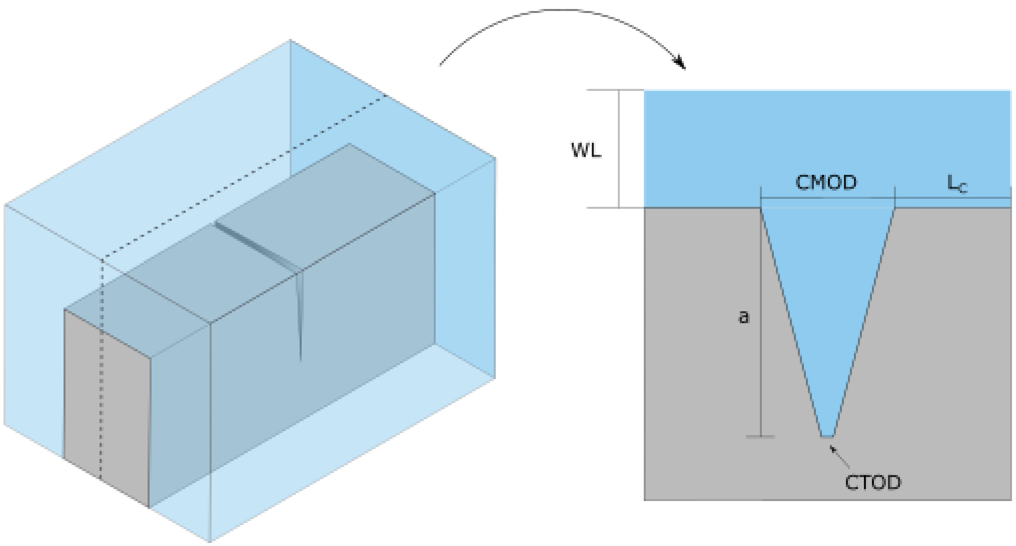


- Decreasing WL thicknesses and increasing cathode length increases electrochemical severity at the crack tip

Future Work

- Exploration of solution composition influences
- Expand work to 3-Dimensional modeling
- Experimental validation of trends





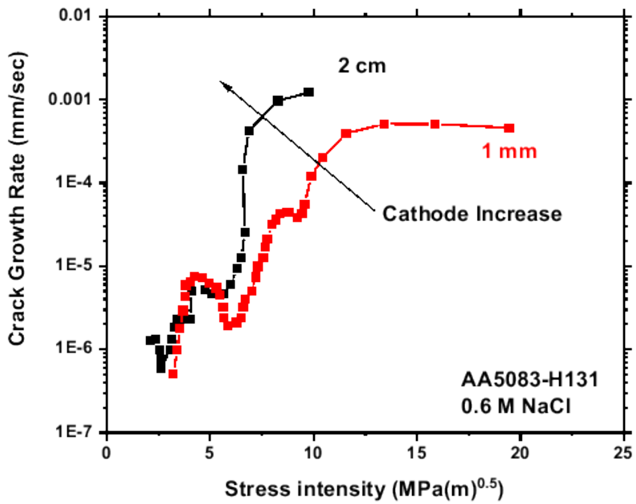


Figure adapted from [1]

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

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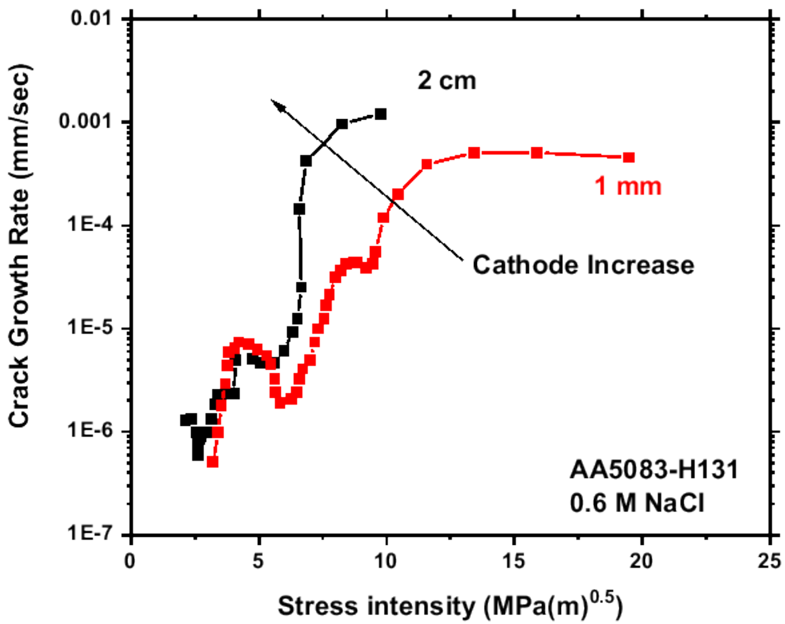
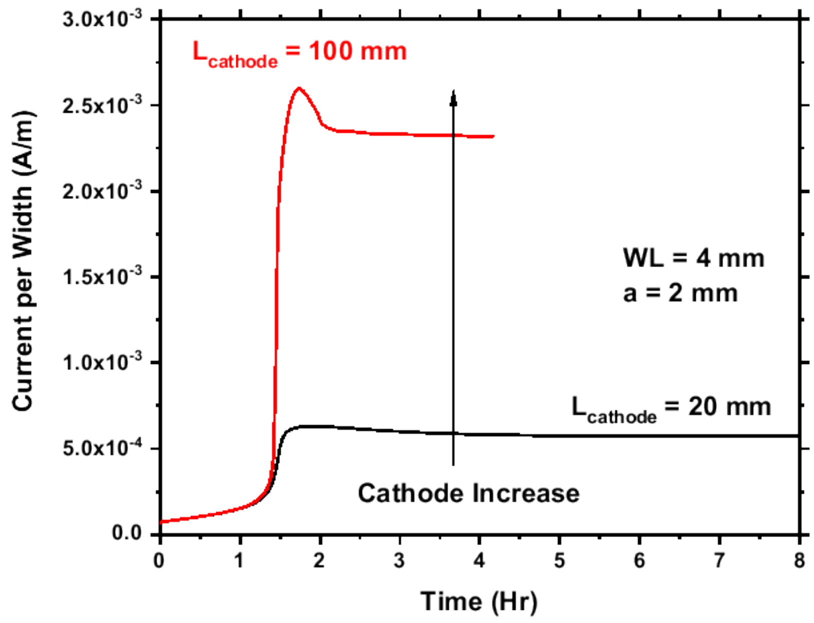
Supplemental

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

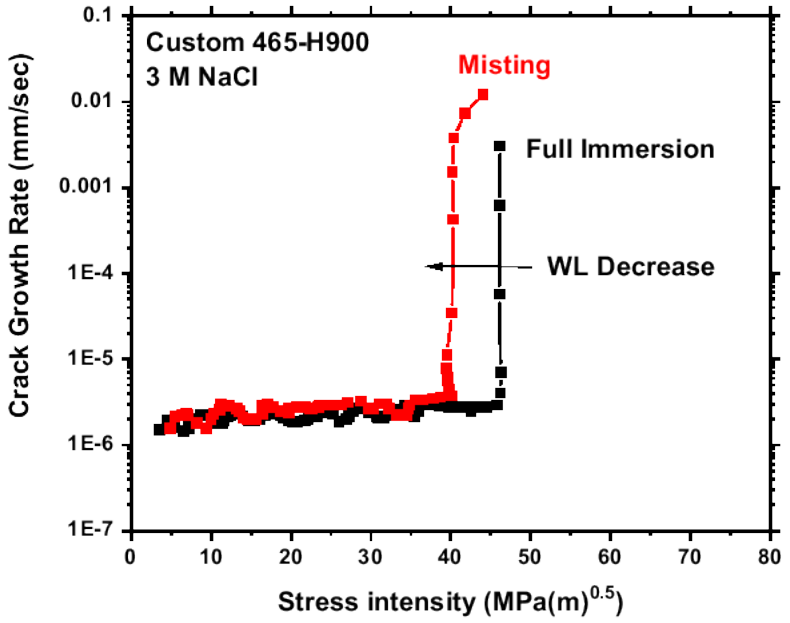


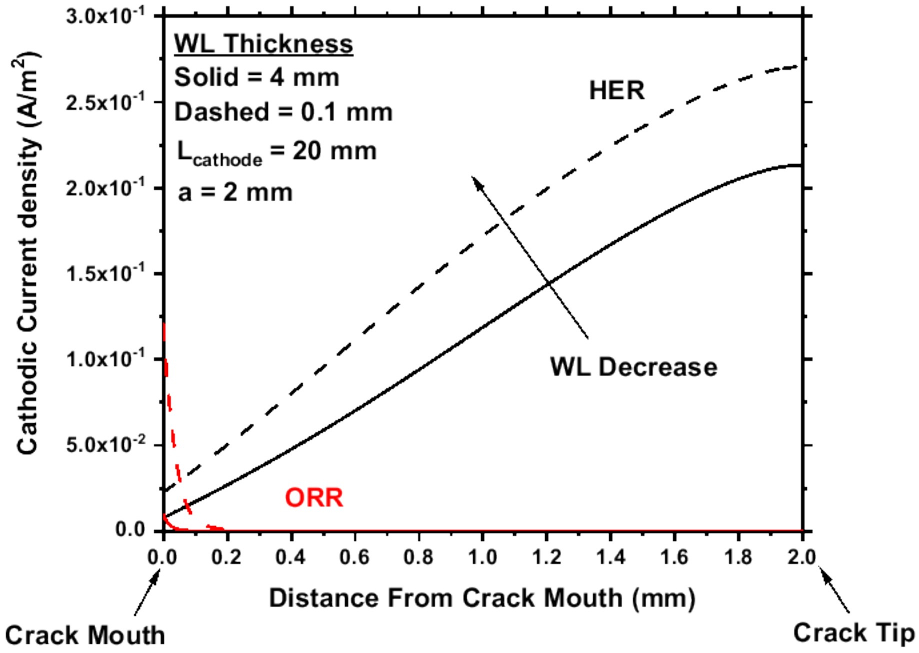


- Increase in crack growth rate and increase in overall current

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

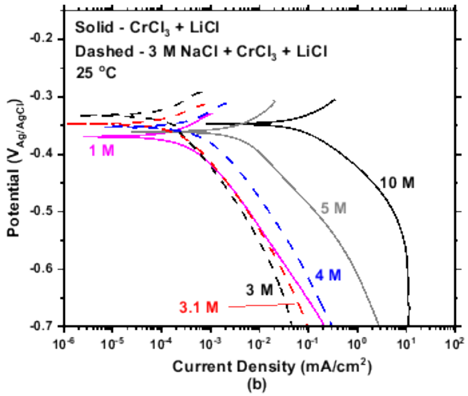


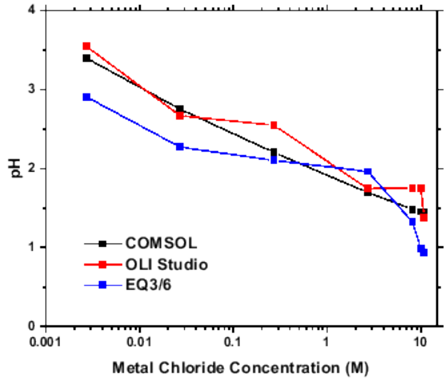


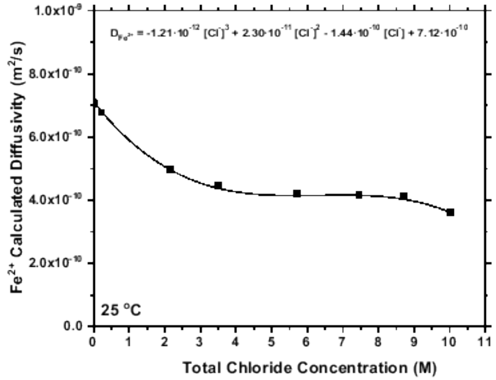
Z.D. Harris, et al. in: TMS 2020, San Diego, CA, 2020.

CGR Modeling

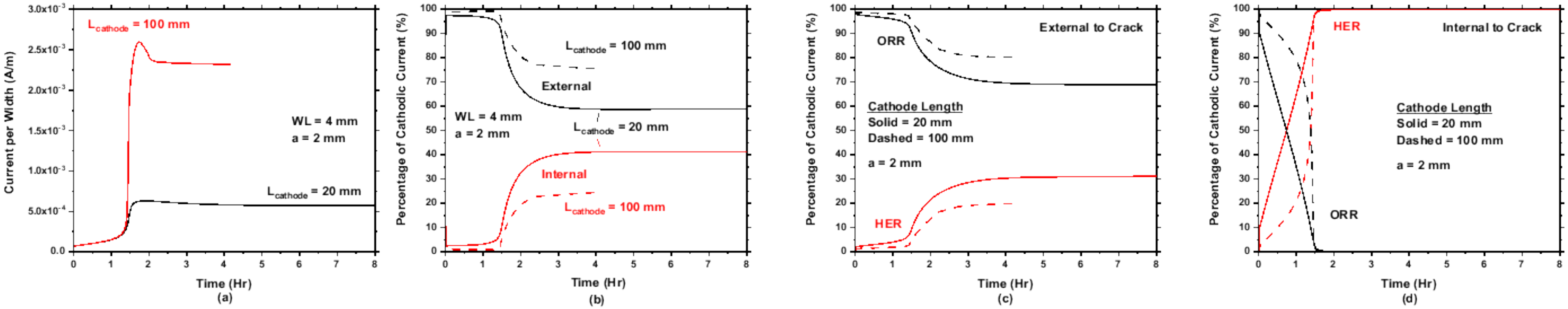
- Boundary conditions

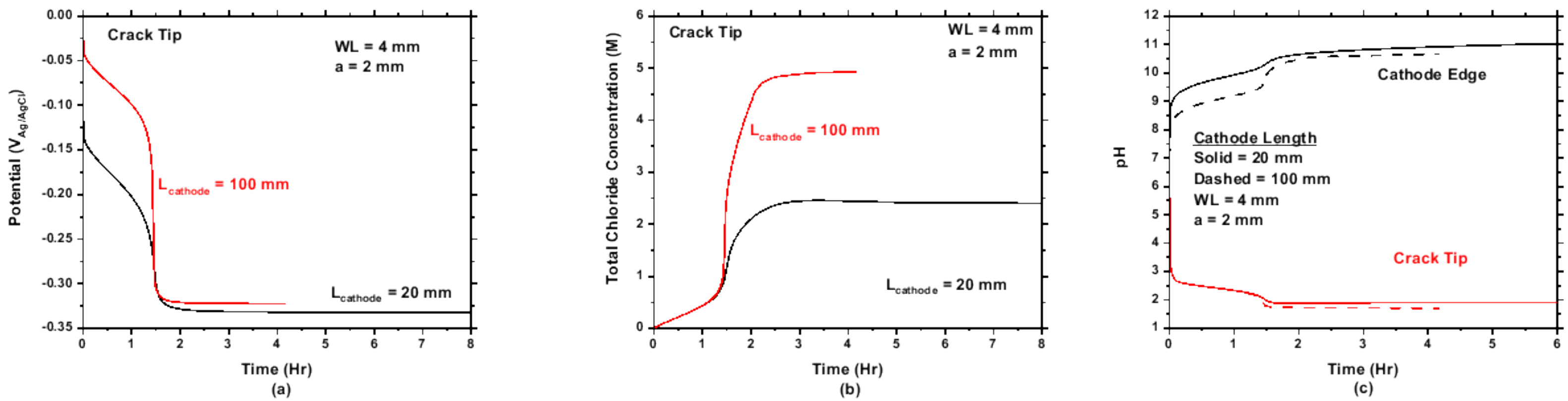




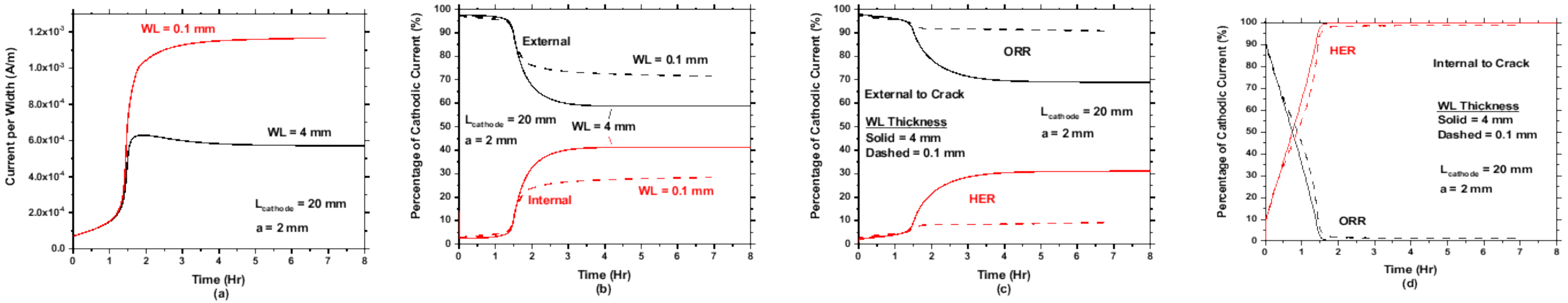


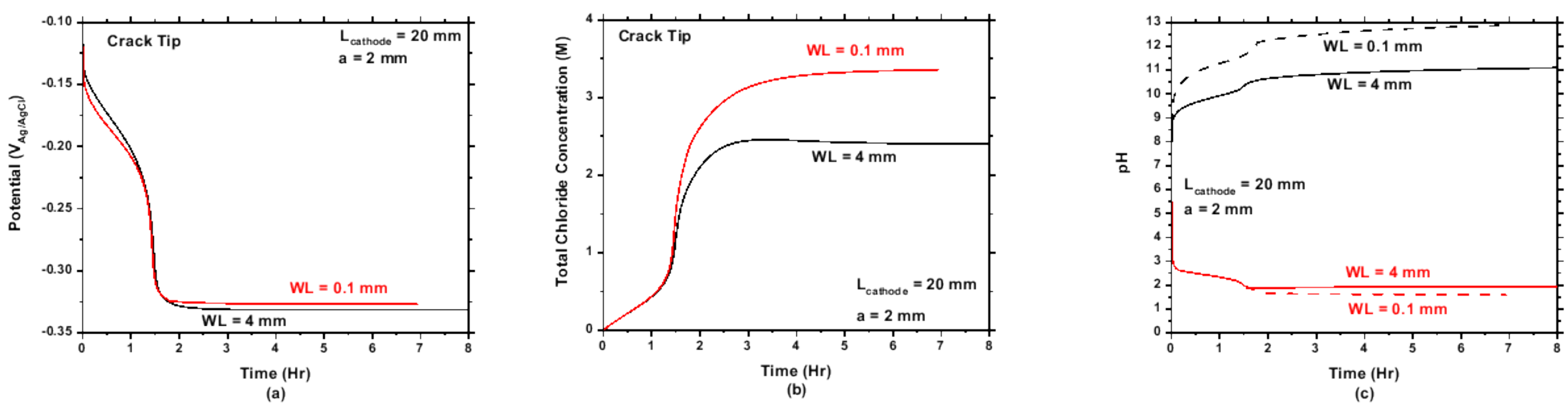
Cathode Length



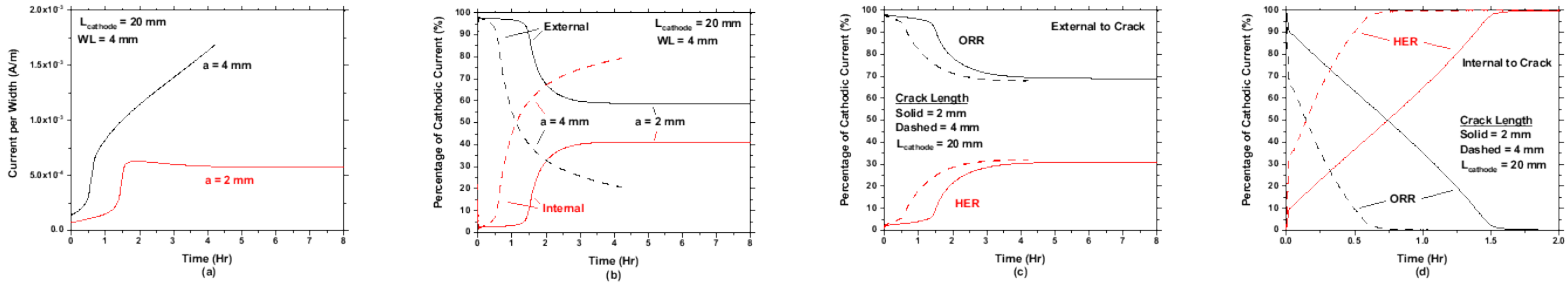


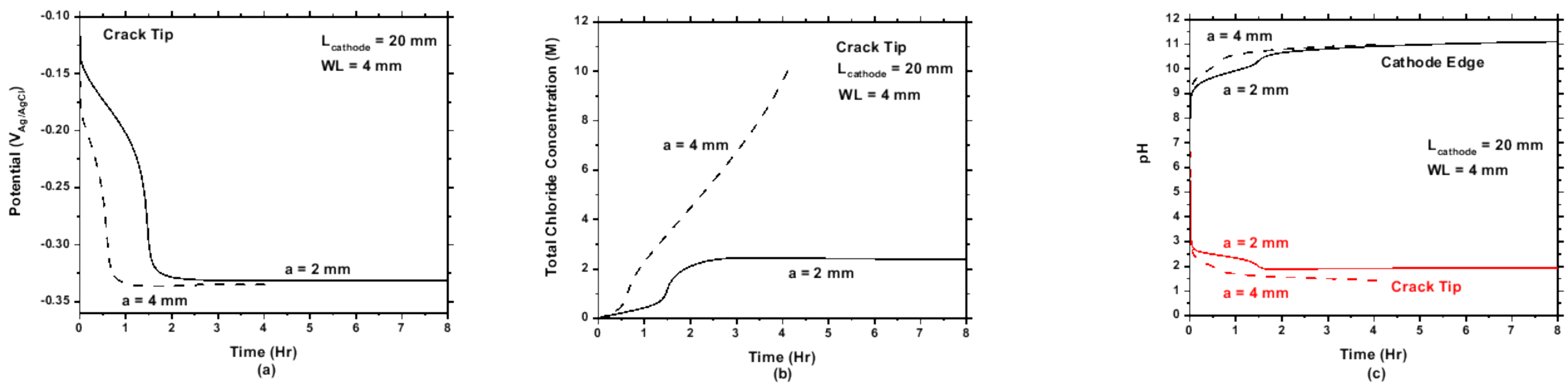
WL thickness



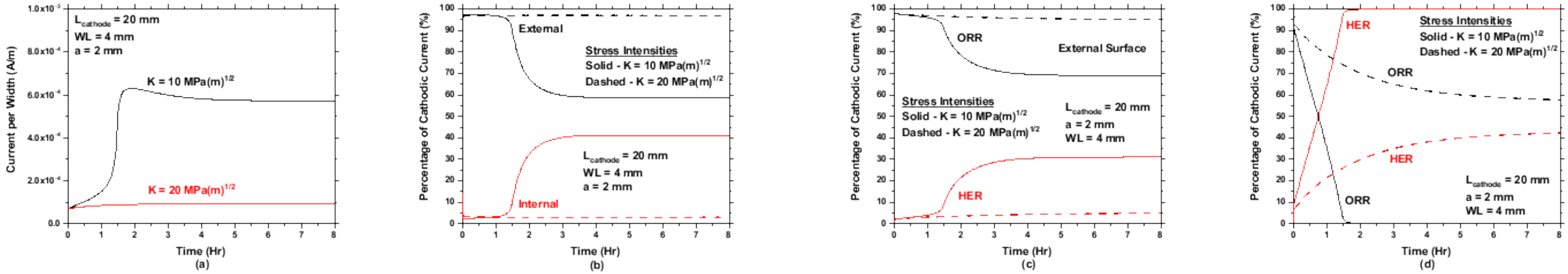


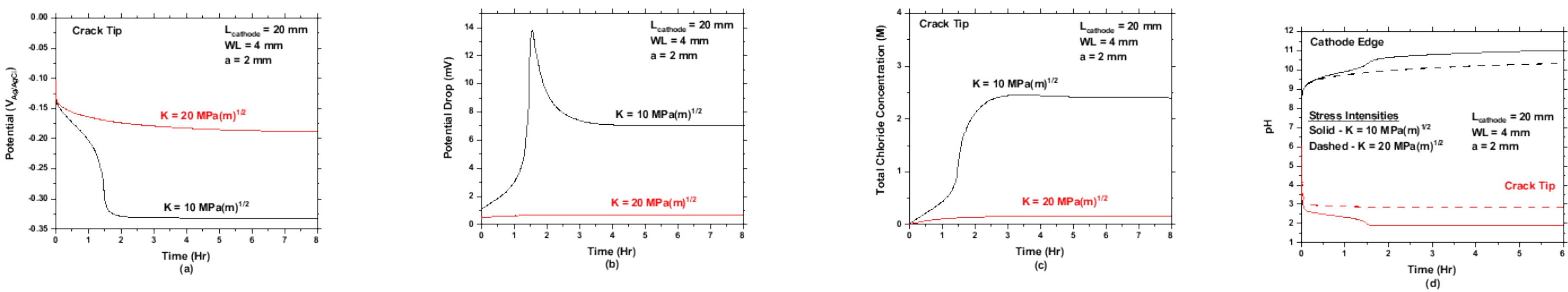
Crack Length



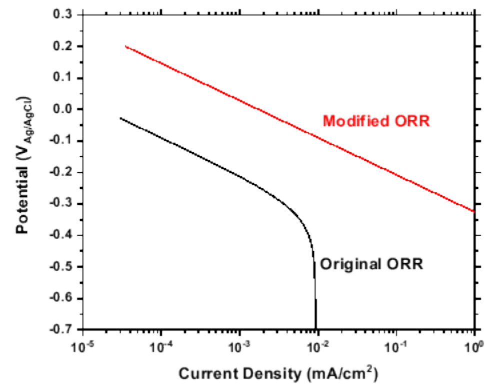


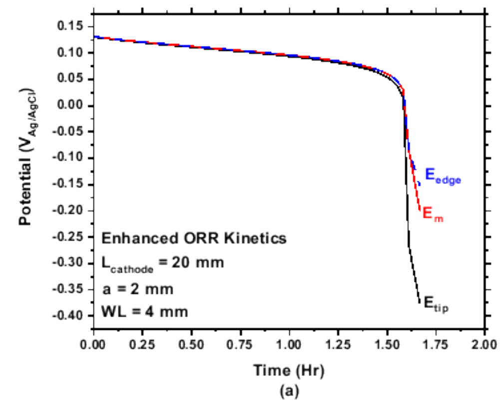
Stress intensity

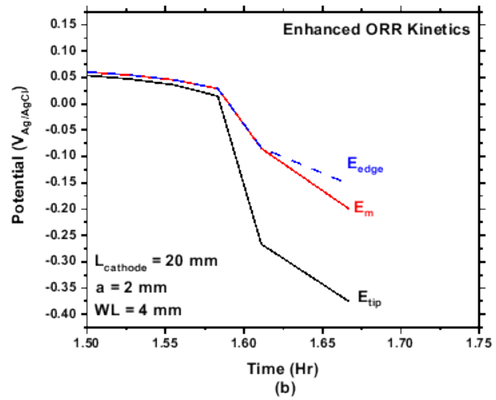


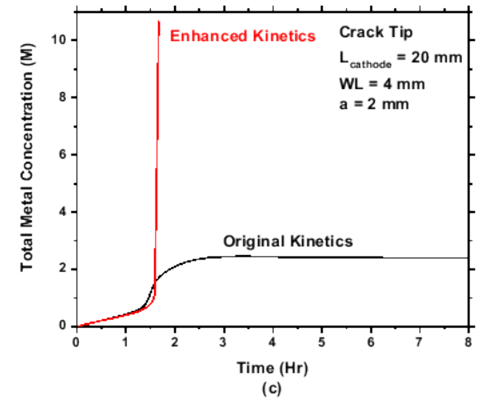


Modified ORR

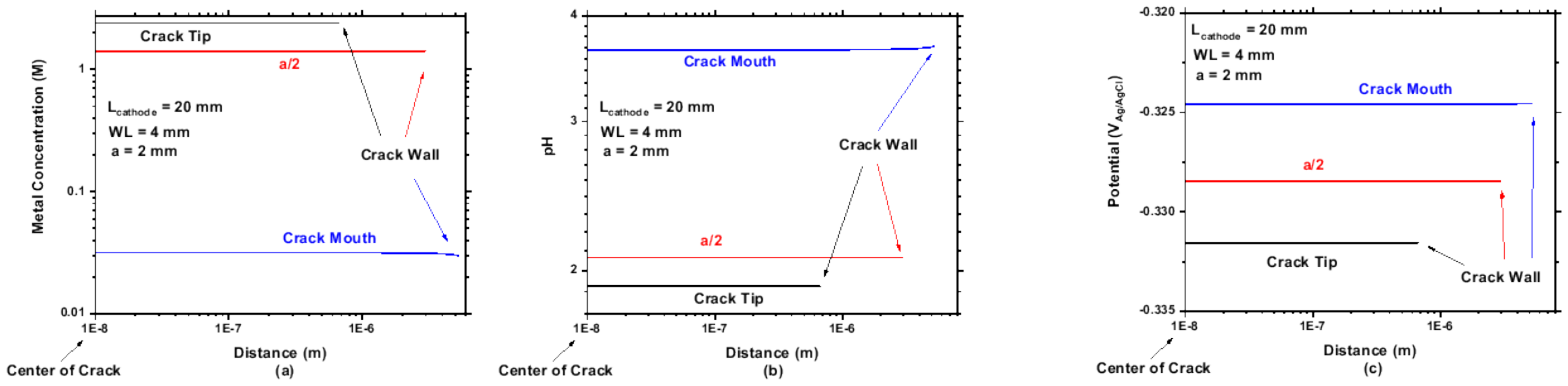








Distributions across a crack



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