SAND2022-1980C

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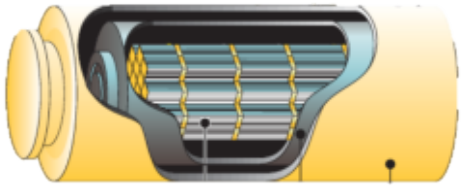
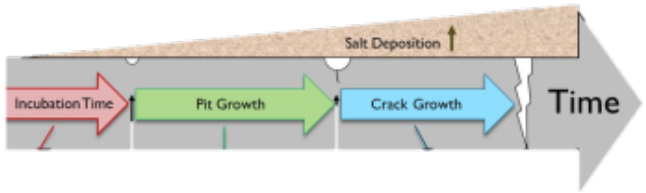
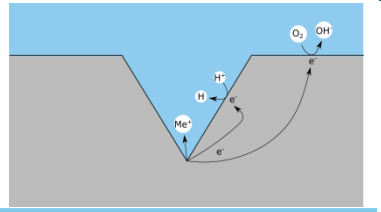
Predicting Electrochemical Conditions in a Stress Corrosion Crack Tip and the Influence of Exposure Environment







PRESENTED BY

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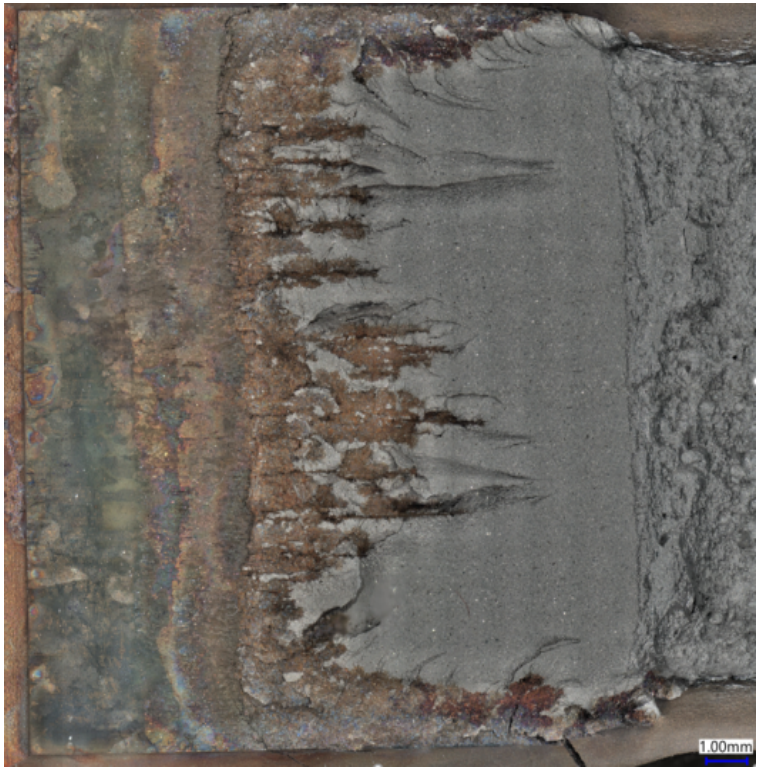
U.S. DEPARTMENT OF ENERGY NNSA

Need to understand crack chemistry and trends with changes in environment and sample

Saturated NaCl

Saturated $MgCl_2$



- Preliminary laboratory tests at ~ 55 ˚C in compact tension specimens show differences in crack morphologies
  - Could be due to differences in crack tip environment
- **Here we are building model to accommodate changes in sample size, external environment (WL thickness and solution) and sample geometry**

Past SCC Models of Interest

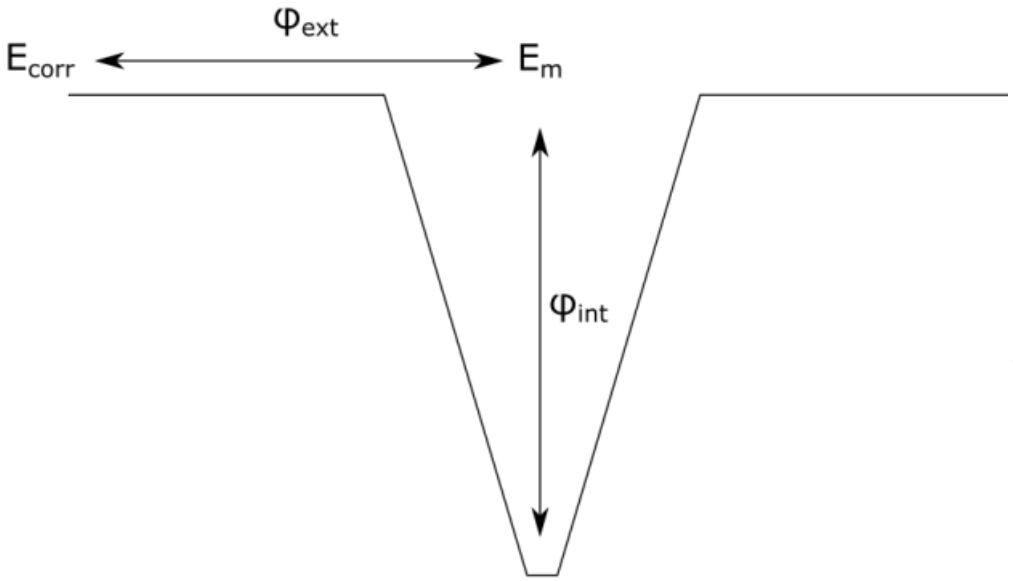


Figure adapted from Turnbull

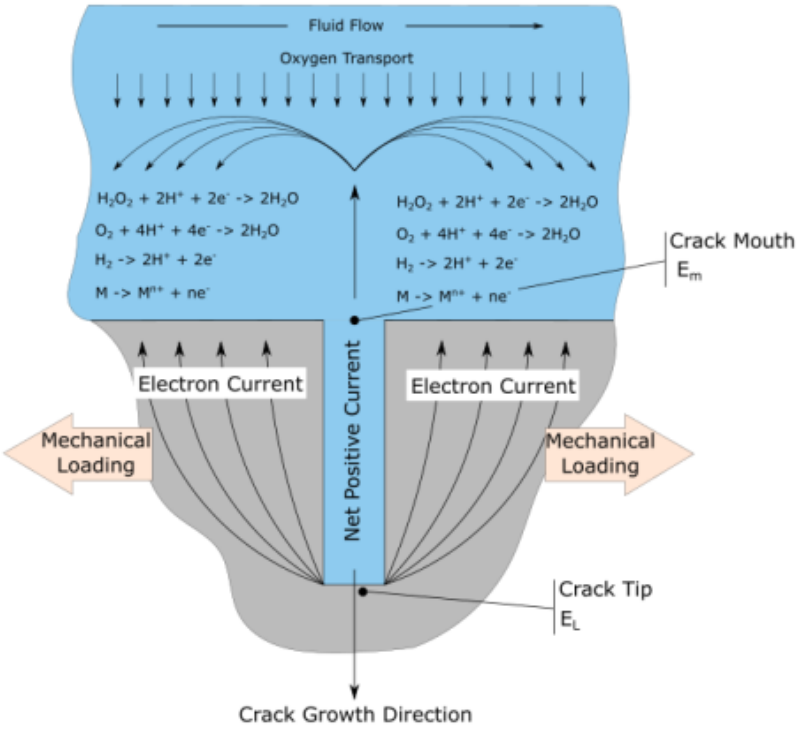


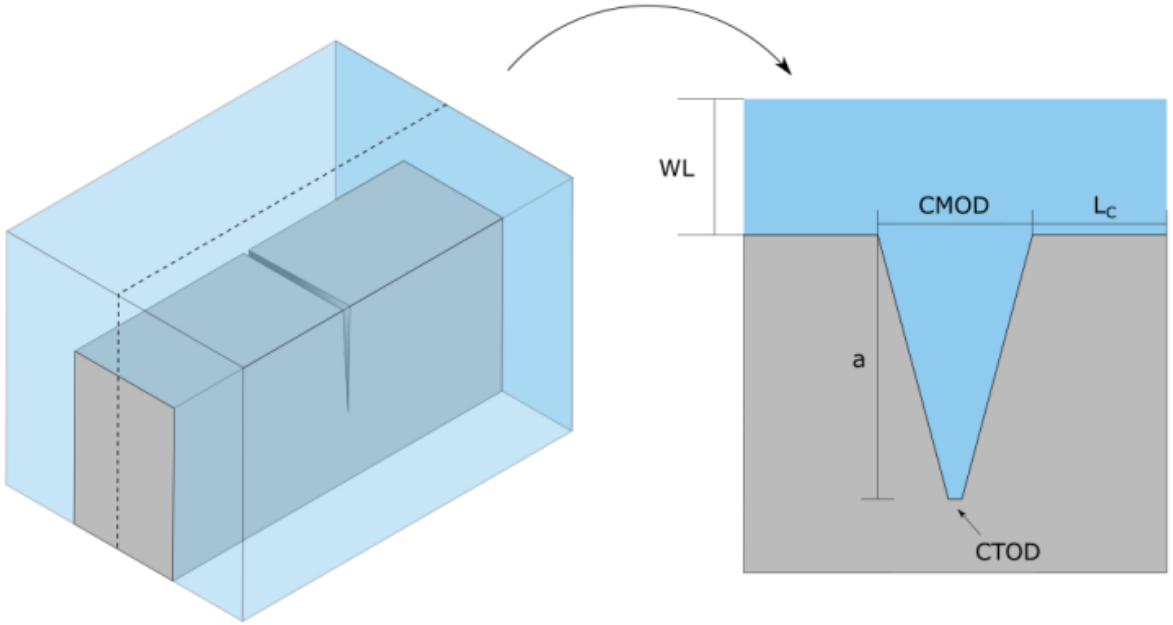
Figure adapted from Manahan

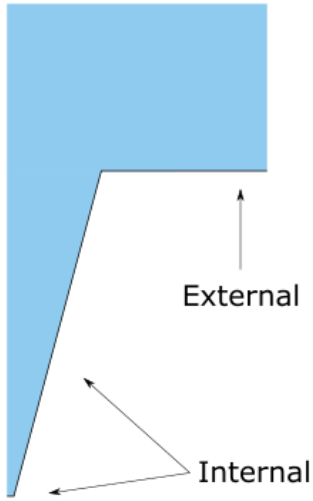
- Current models assume crack tip current density and external potentials to determine electrochemical conditions in the crack
  - Originally built for high temperature boiling water reactors
  - ***Static boundary conditions***
  - **Size of external cathode and WL** not explicitly considered
  - **No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

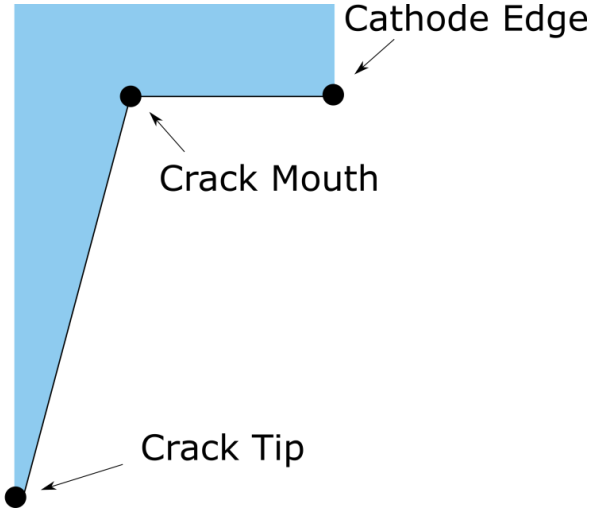
A. Turnbull. Corrosion. 57 (2001) 175–189.

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

Finite Element Model Allows for Incorporation of New Phenomena

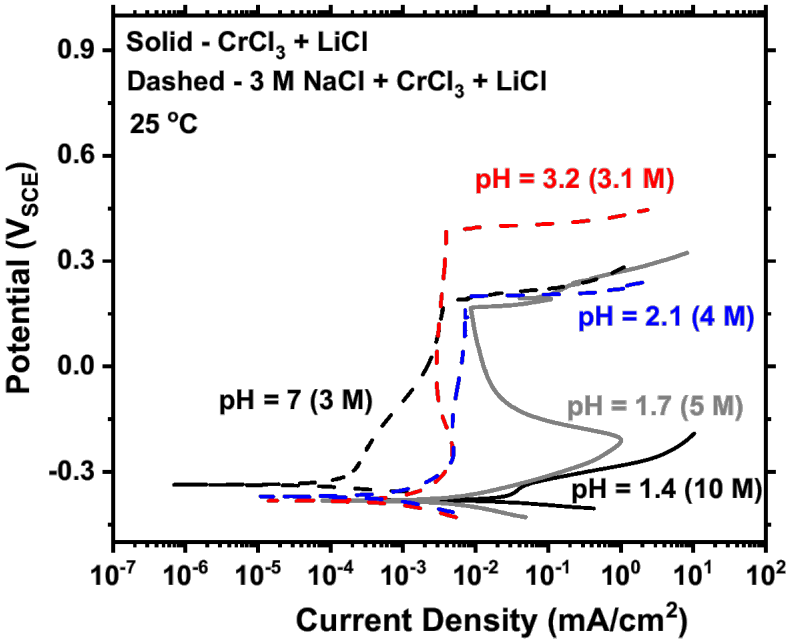




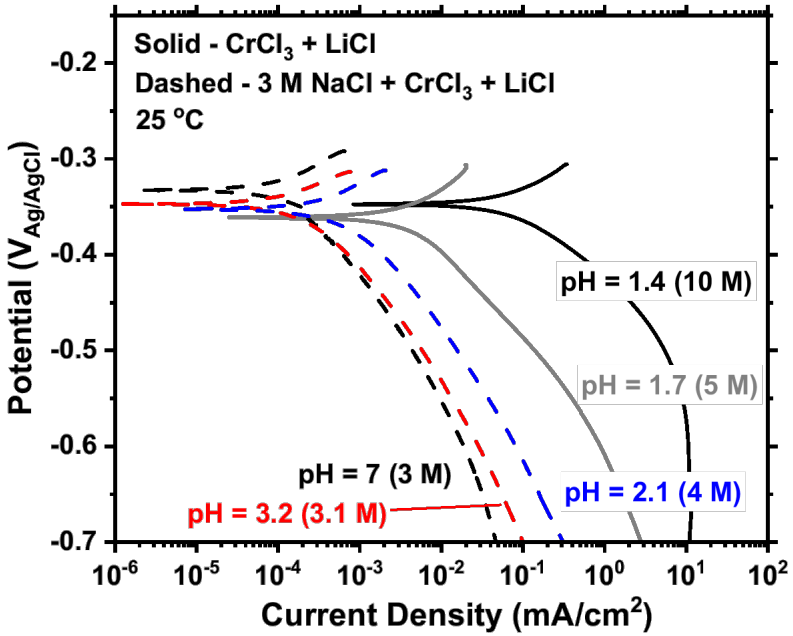


- Finite Element Model (FEM) utilized to predict crack tip conditions
- 2-D geometry, based on single edge notch tension (SENT) specimen
- Reactive transport model with chemistry dependent electrochemical boundary conditions

Current Model Accounts for Changing Electrochemistry



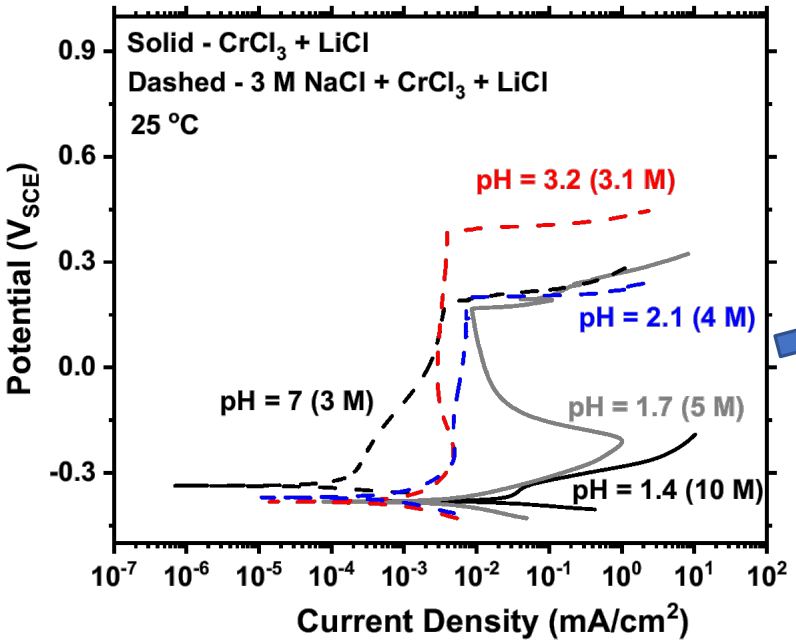
Anodic $(Me \rightarrow Me^{n+} + ne^-)$

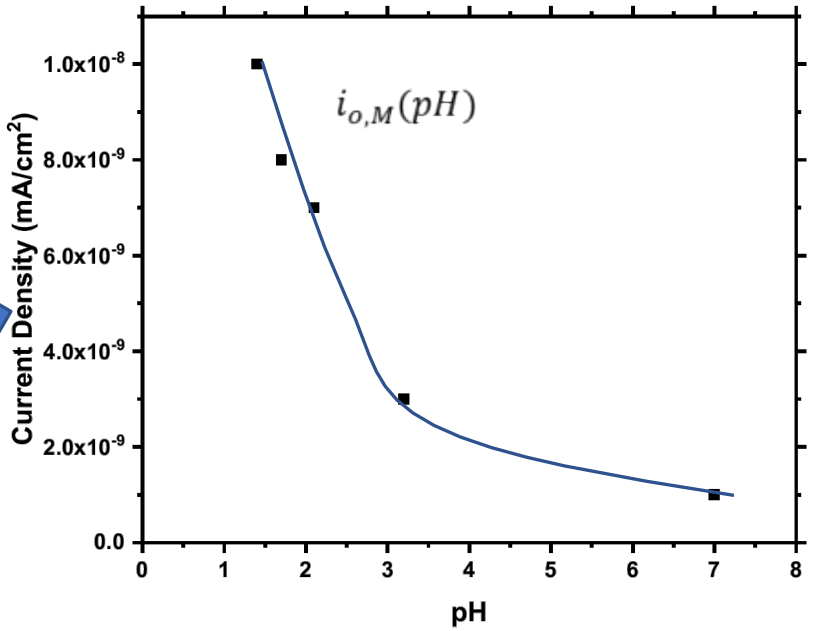


Cathodic $(H^+ + e^- \rightarrow H)$

- Measured electrochemical parameters as a function of pH

Current Model Accounts for Changing Electrochemistry



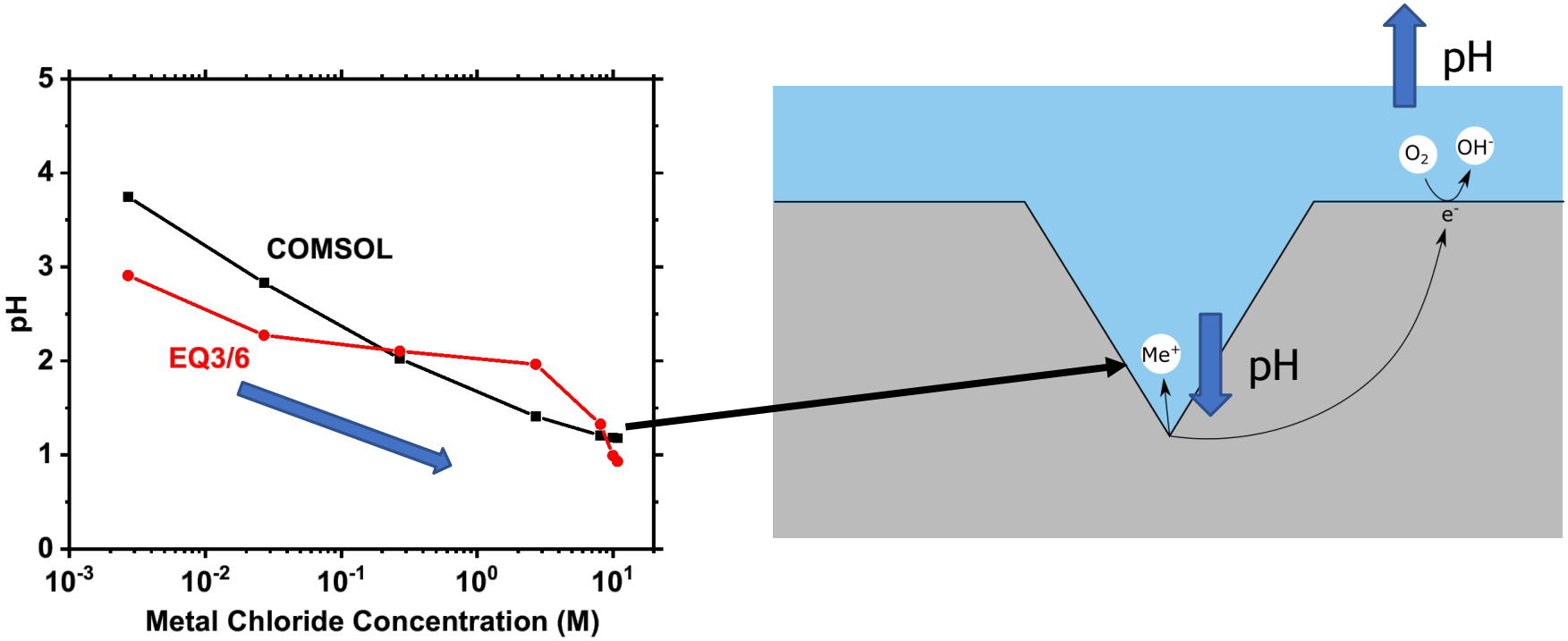


$$i_{act,M}(pH) = i_{o,M}(\mathrm{pH}) \cdot 10^{\frac{\eta_M}{A_M}}$$

- Measured electrochemical parameters as a function of pH

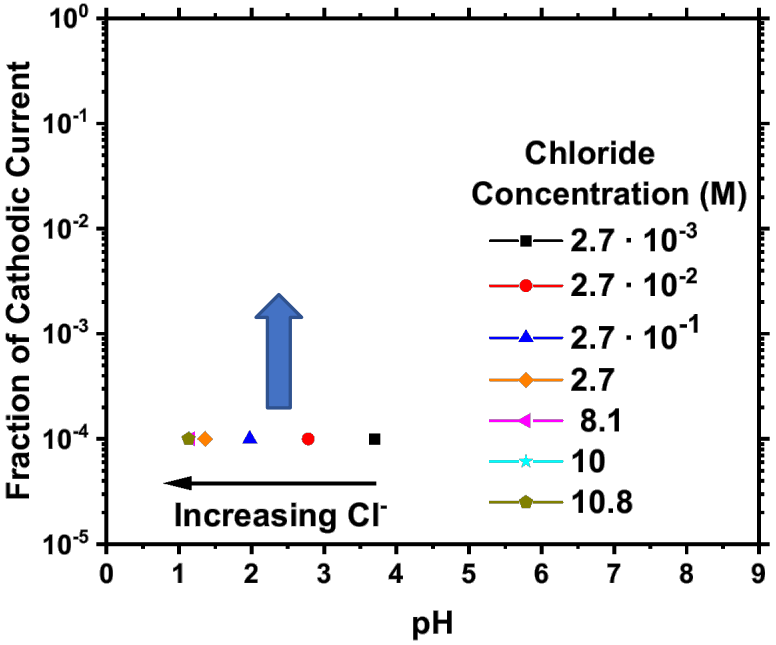
$$i_M(pH) = \frac{i_{act,M}(pH)}{1 + \frac{i_{act,M}(pH)}{i_{pass,M}(pH)}}$$

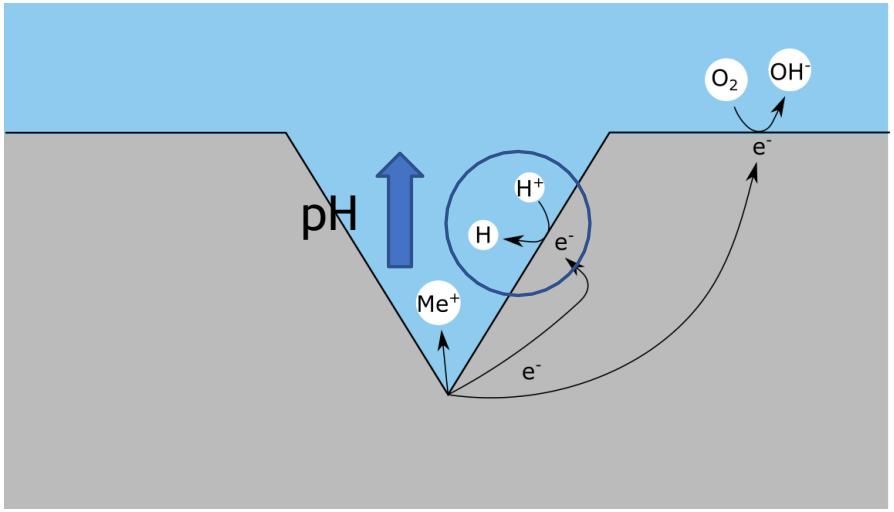
Local Cathodic Current Influences Solution pH



- Similar pH's when comparing concentration and activity based calculations
- Just metal chloride concentration (*i.e.,* $FeCl_2$, $CrCl_3$, $NiCl_2$)

Local Cathodic Current Influences Solution pH

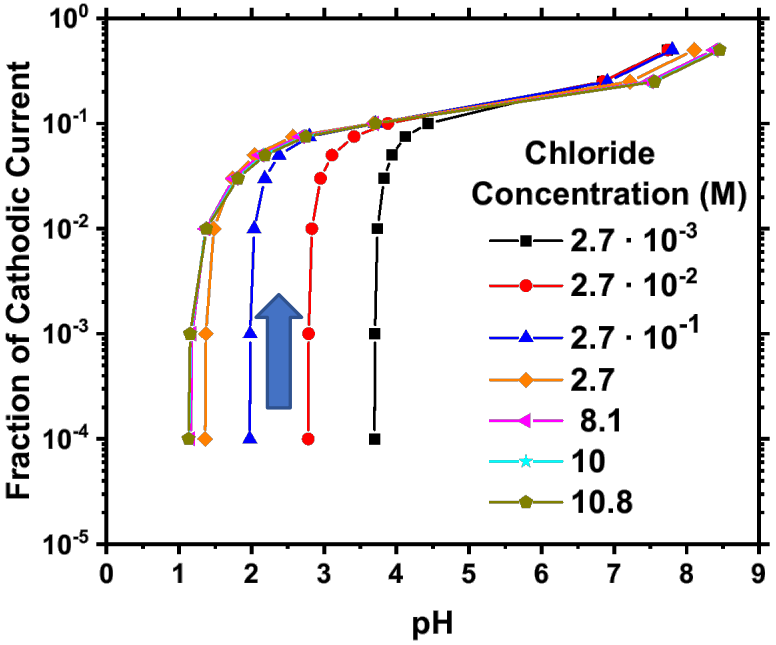


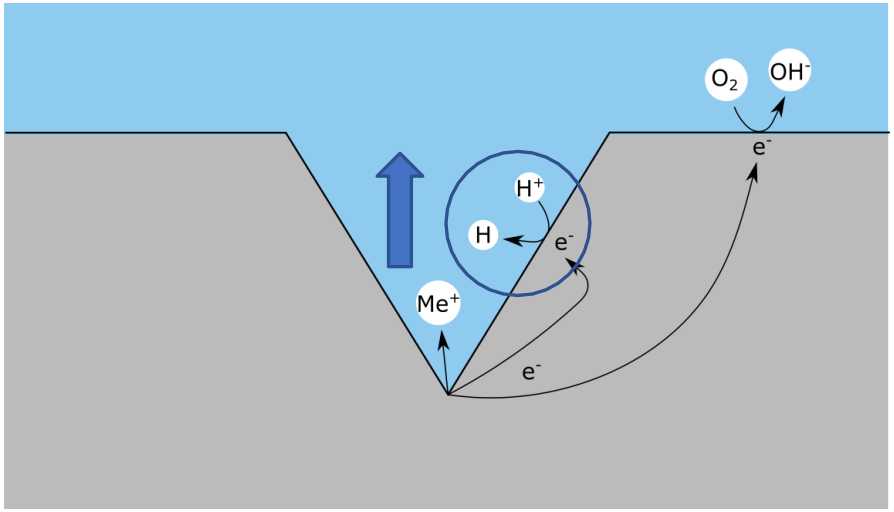


Fraction of Local Cathodic Current = $\frac{i_{cathodic}}{i_{anodic}}$

- Similar pH's when comparing concentration and activity based calculations

Local Cathodic Current Influences Solution pH

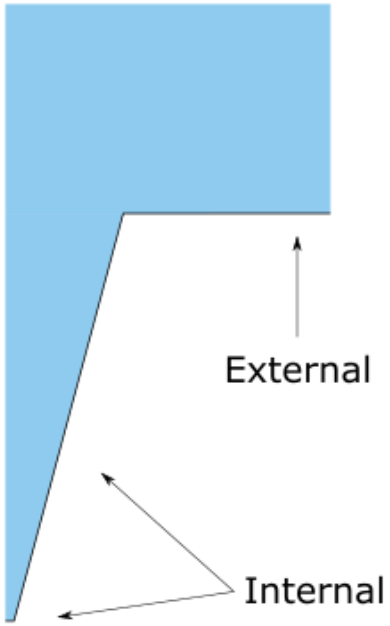


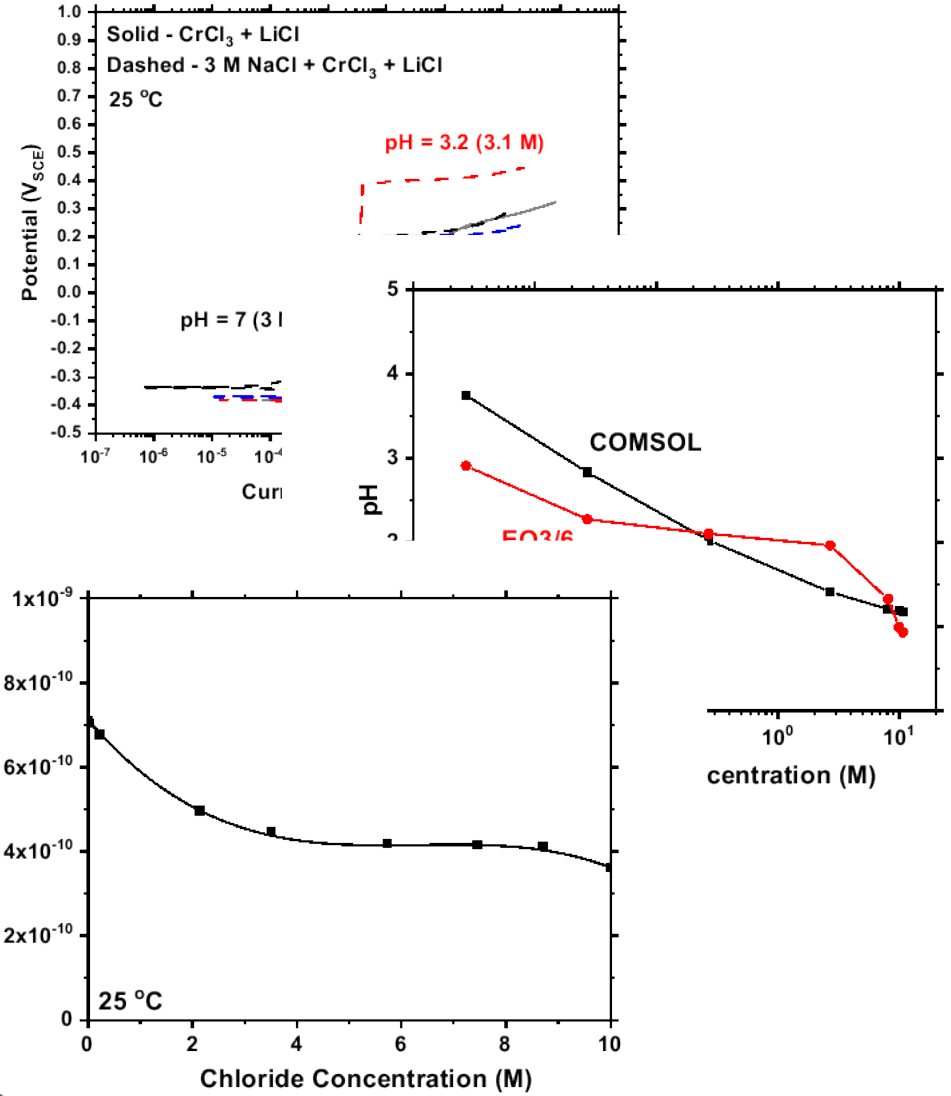


$$\text{Fraction of Cathodic Current} = \frac{i_{cathodic}}{i_{anodic}}$$

- Similar pH's when comparing concentration and activity based calculations
- pH is a function of both anodic dissolution and local cathodic reactions which are both a function of time

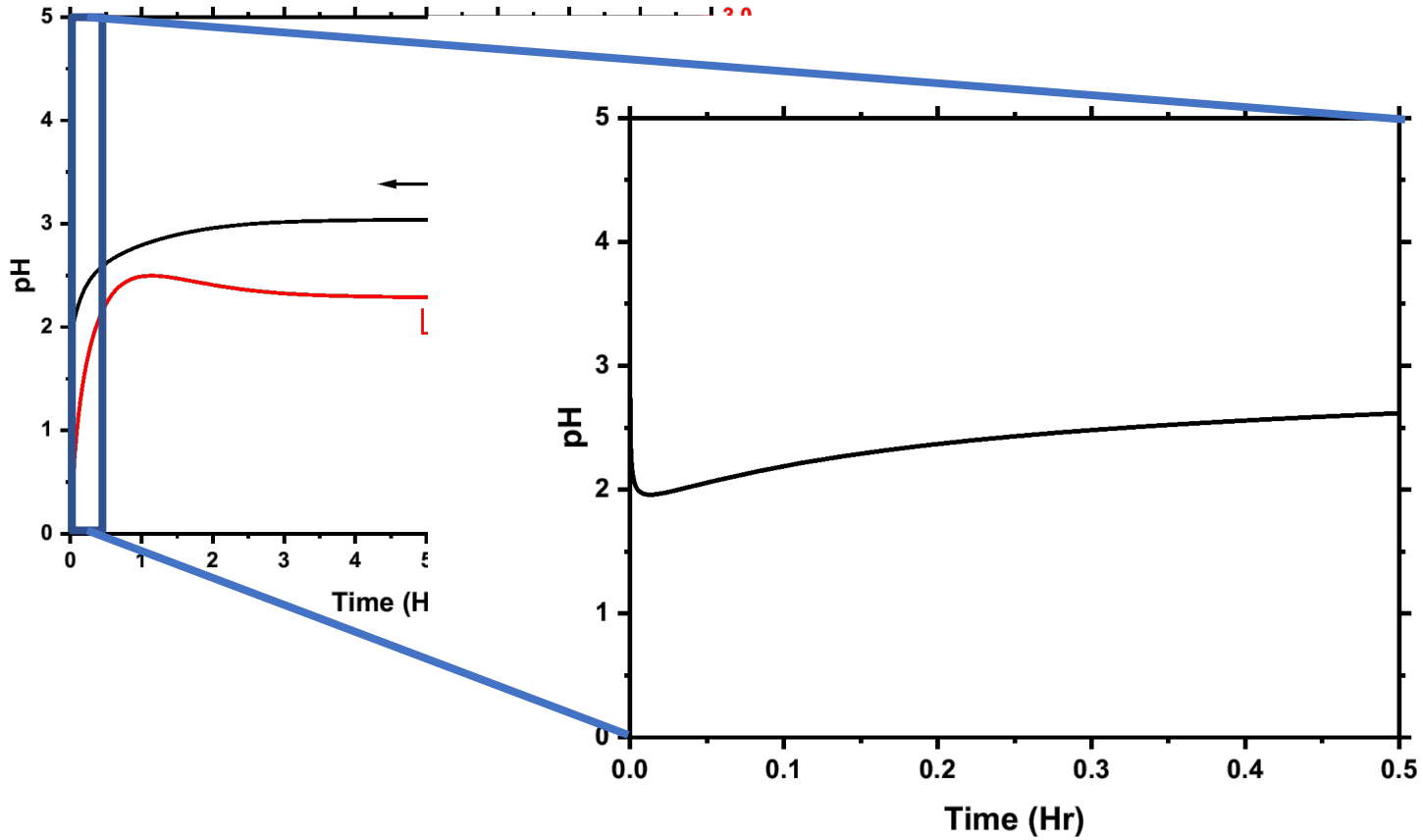
Model Summary





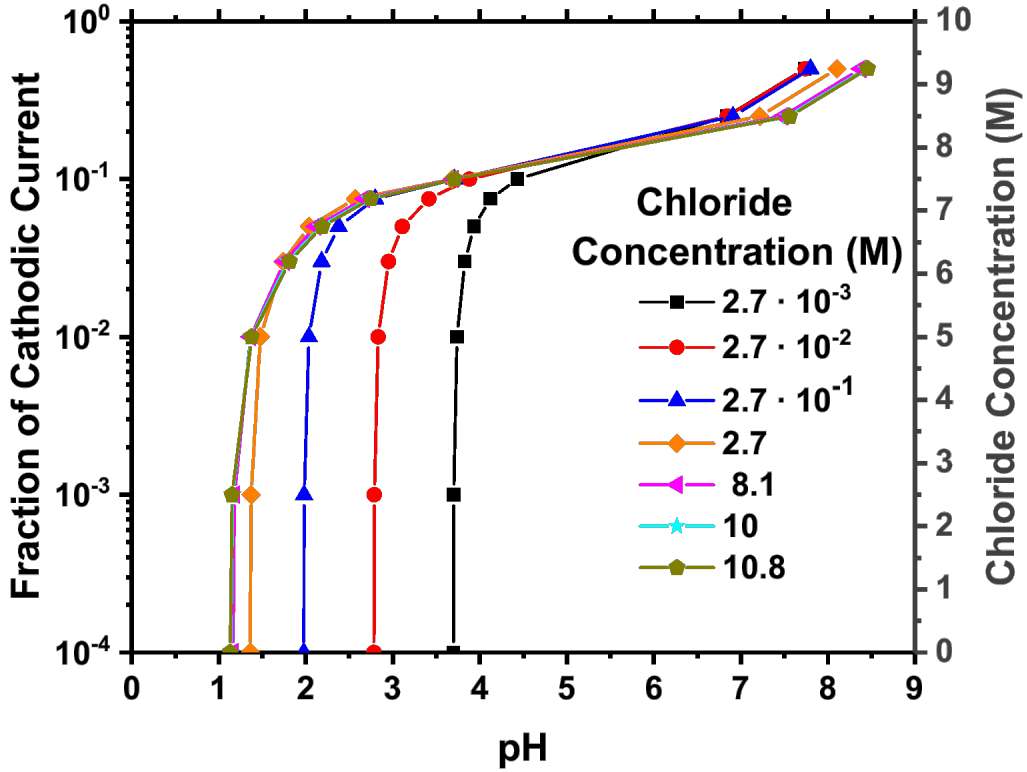
- 3 M NaCl, 25 ˚C
  $K = 10\ MPa\sqrt{m}$
- WL = 5 mm, L_C = 20 mm, a = 2 mm

Crack tip pH Initially Decreases but Increases to Reach a Steady State

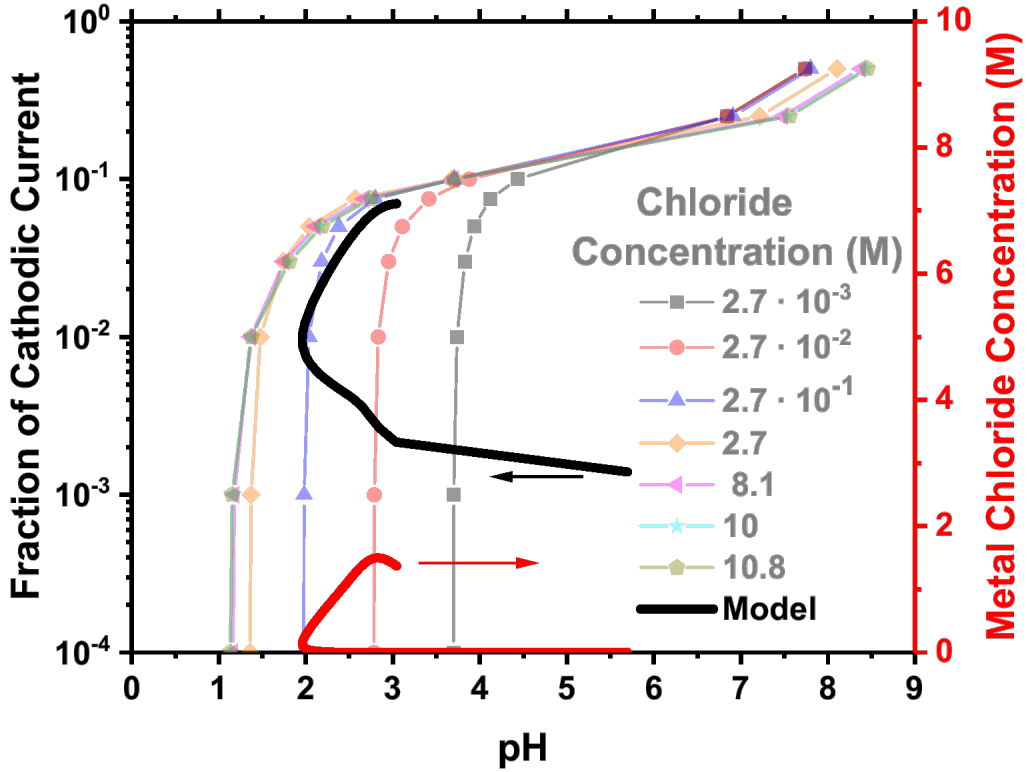


- Increase in chloride concentration to steady state value
- Initial decrease in pH then subsequent increase

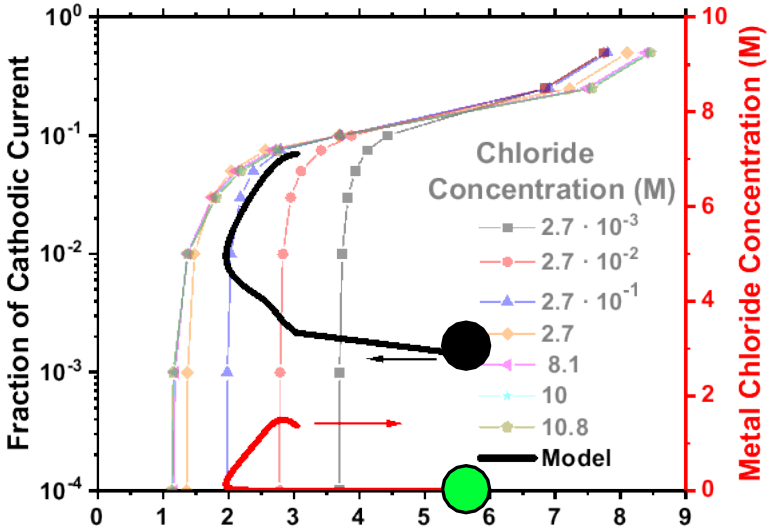
Crack tip pH Initially Decreases but Increases to Reach a Steady State

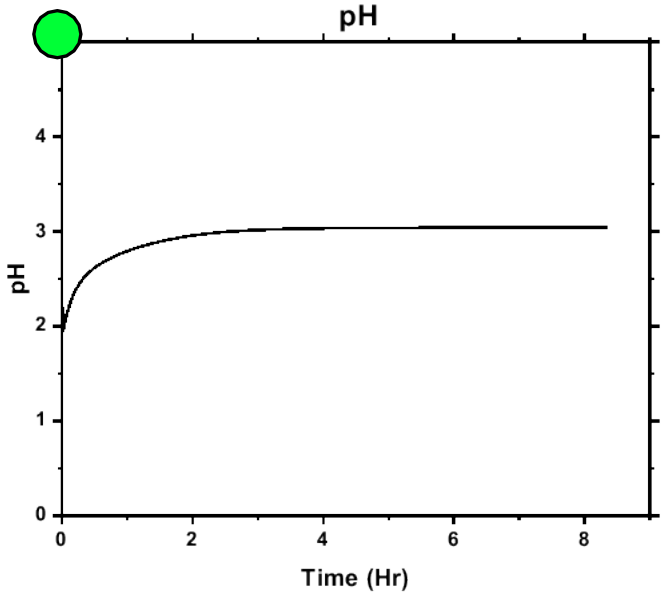


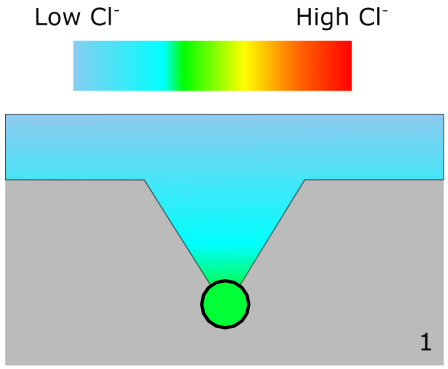
Crack tip pH Initially Decreases but Increases to Reach a Steady State

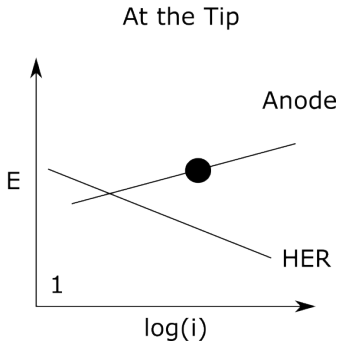


Crack tip pH Initially Decreases but Increases to Reach a Steady State









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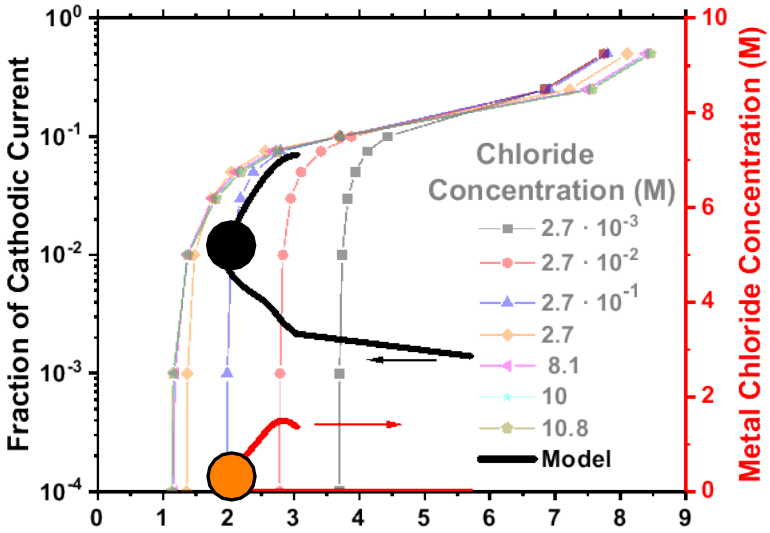

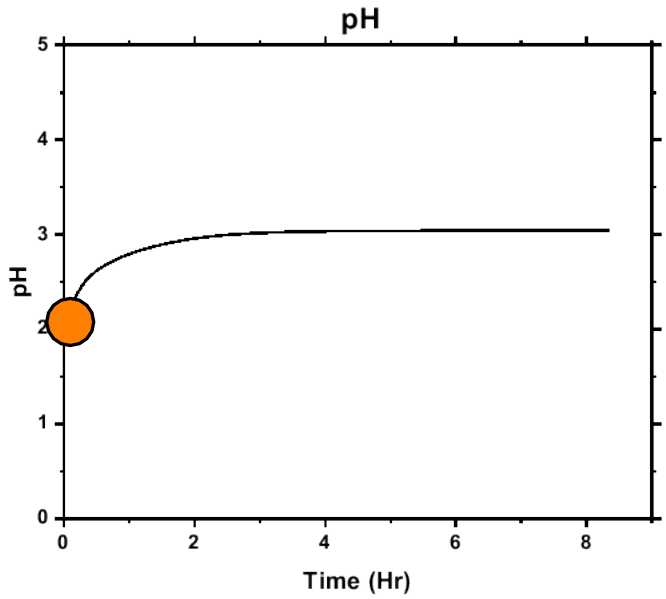

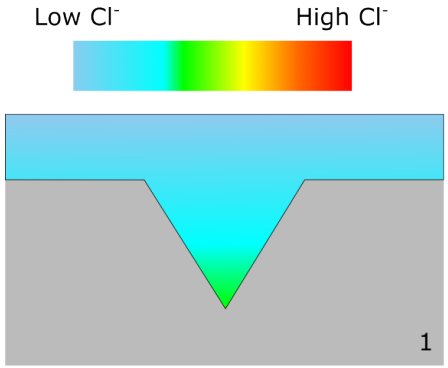

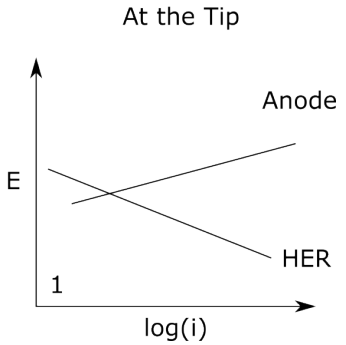

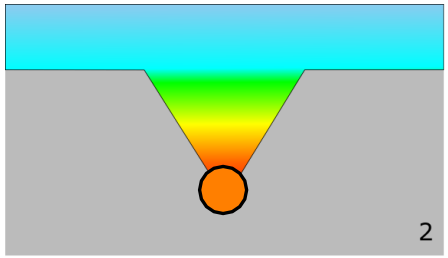

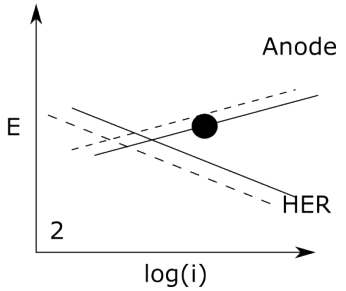

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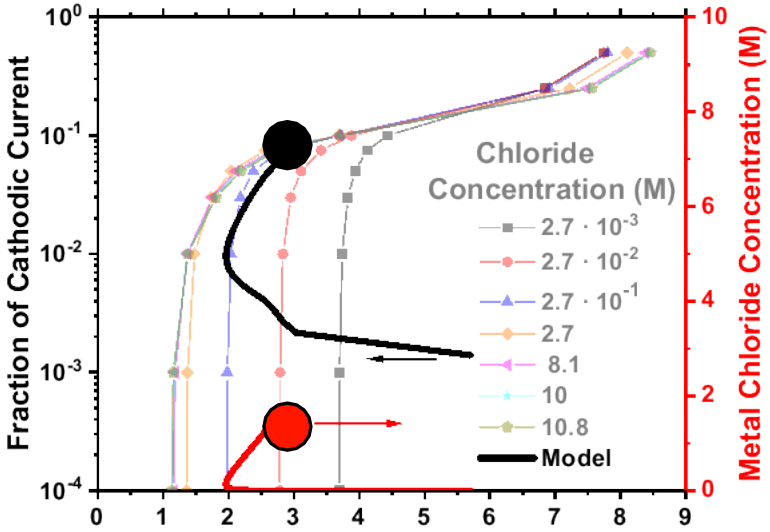
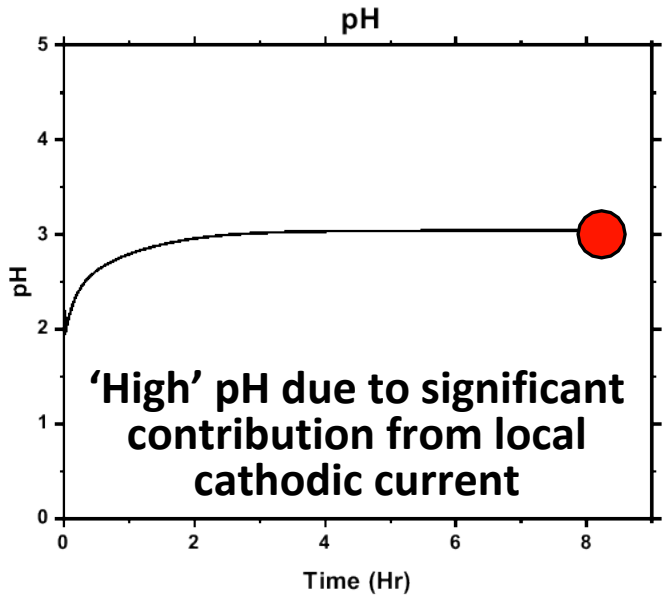
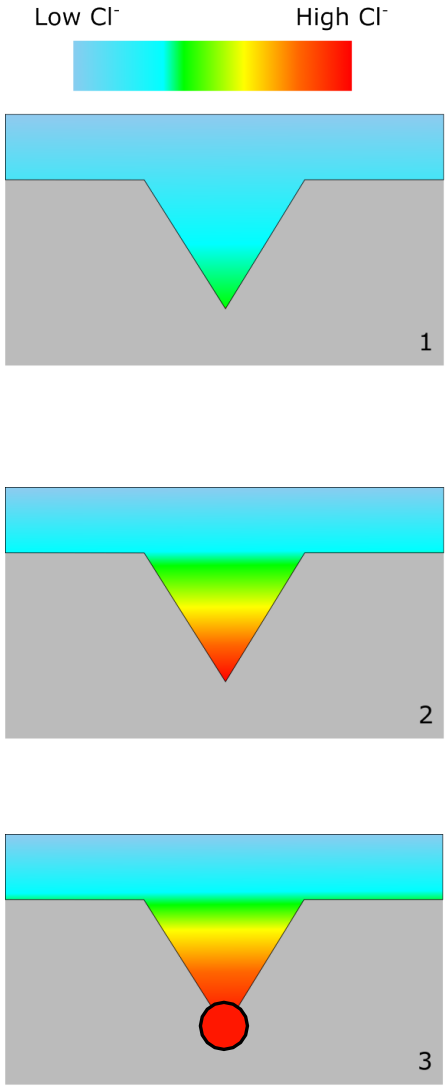
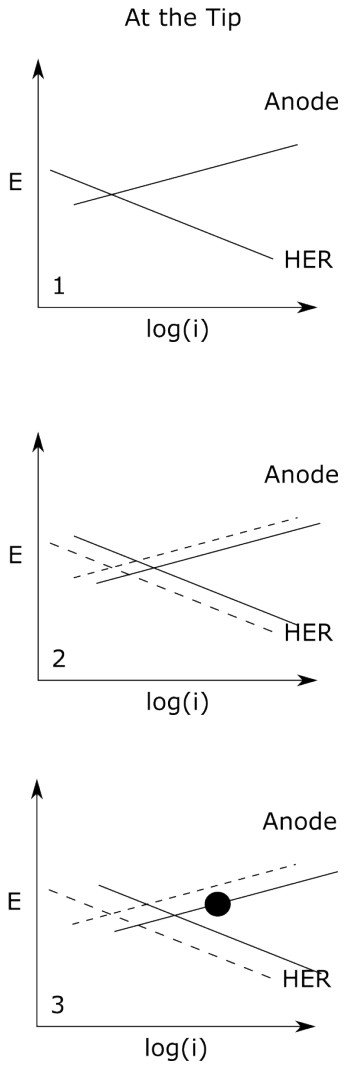
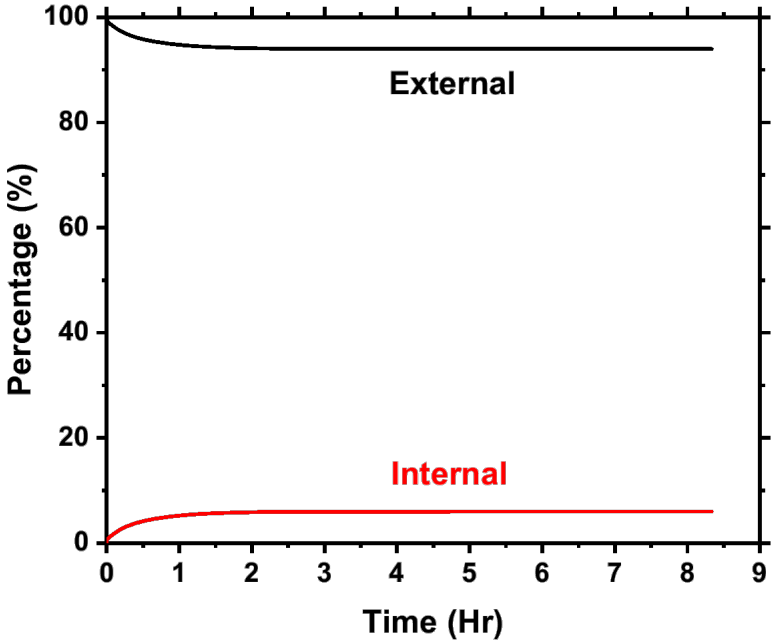


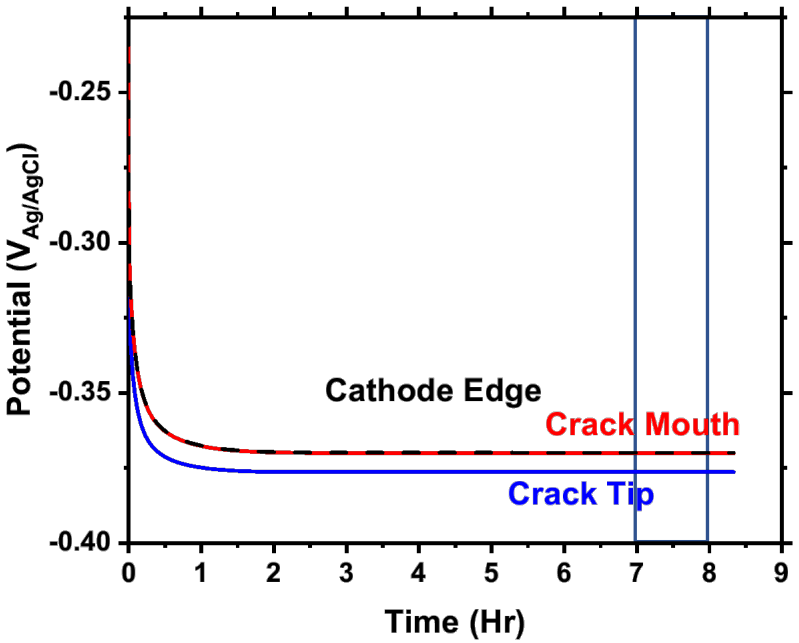






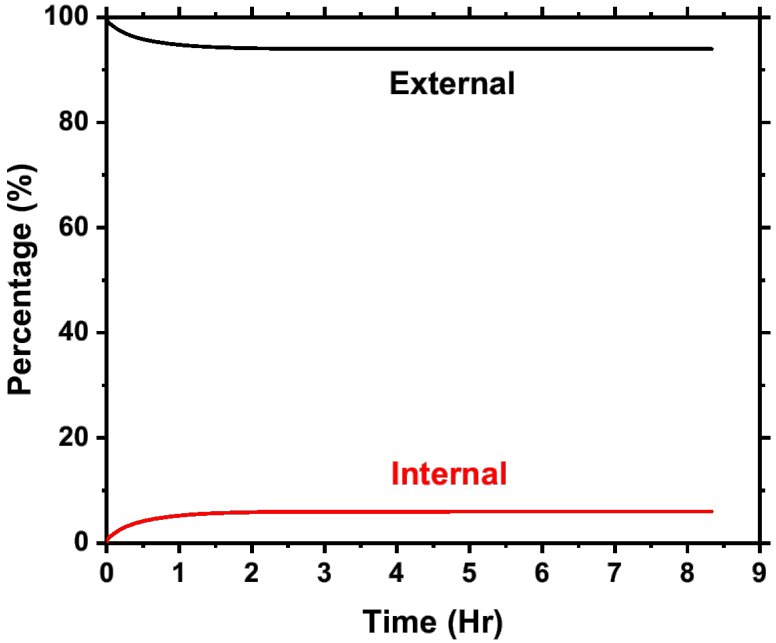
Cathodic Current External to Crack and Crack Tip Polarized Negatively compared to Cathode

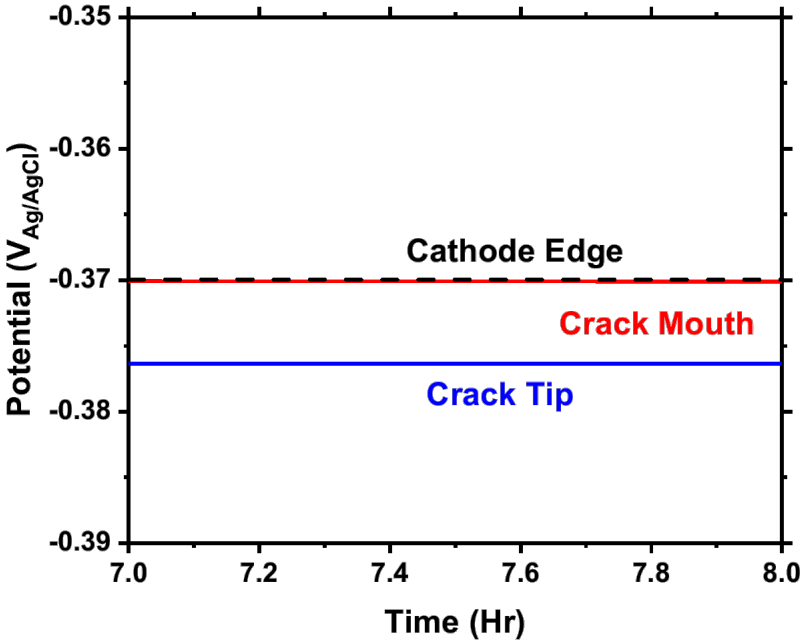




- Majority of cathodic current on external surface due to oxygen reduction reaction (ORR)
- Crack tip polarized negatively with respect to cathode edge

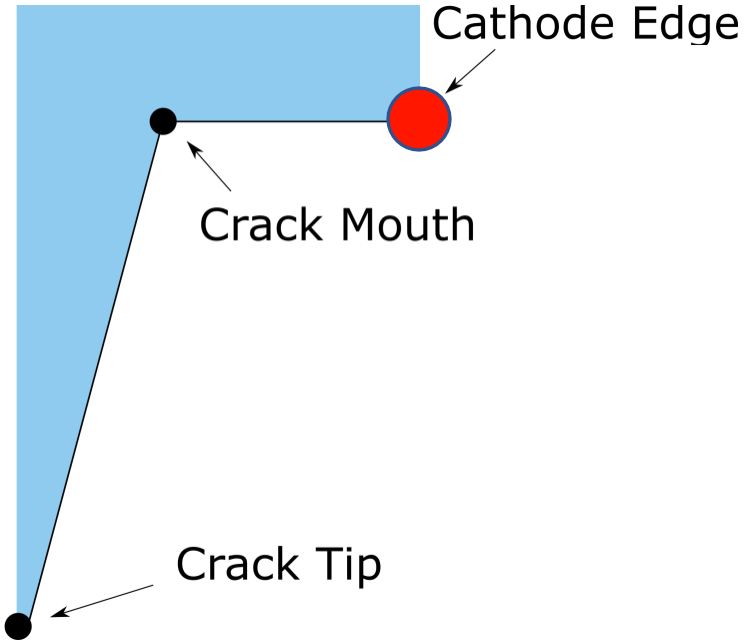
Cathodic Current External to Crack and Crack Tip Polarized Negatively compared to Cathode

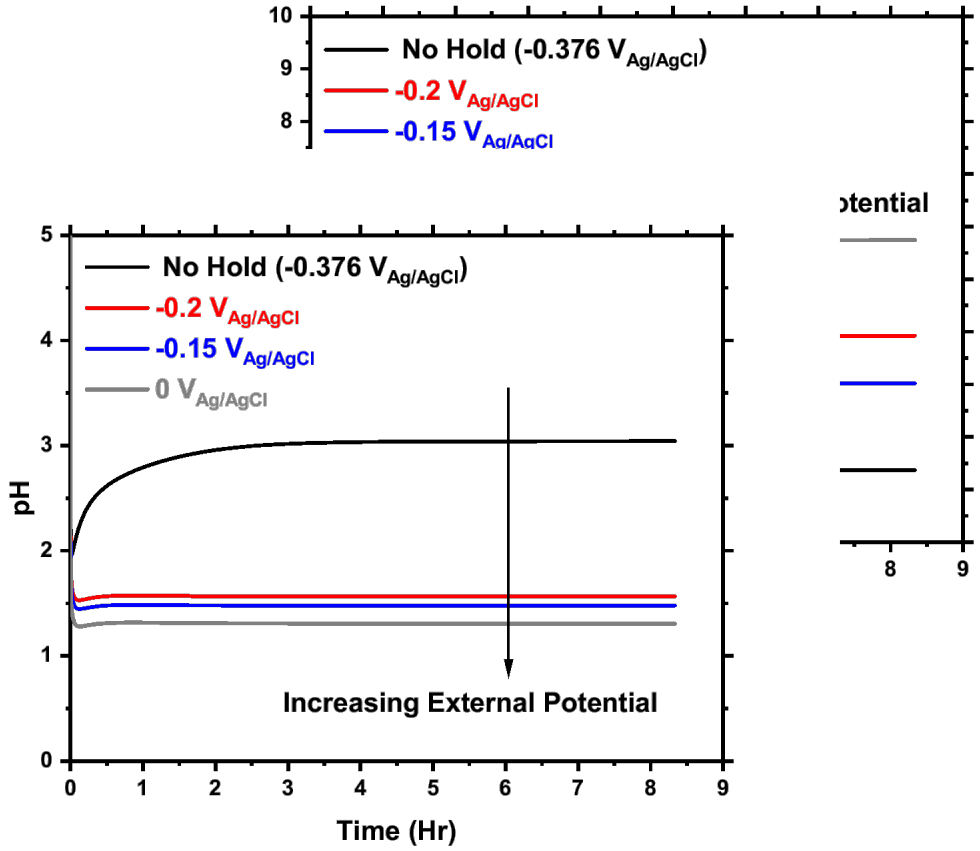




- Majority of cathodic current on external surface due to oxygen reduction reaction (ORR)
- Crack tip polarized negatively with respect to cathode edge
- Cathode edge and crack mouth near same potential
  - ***Limited potential drop on the external surface***

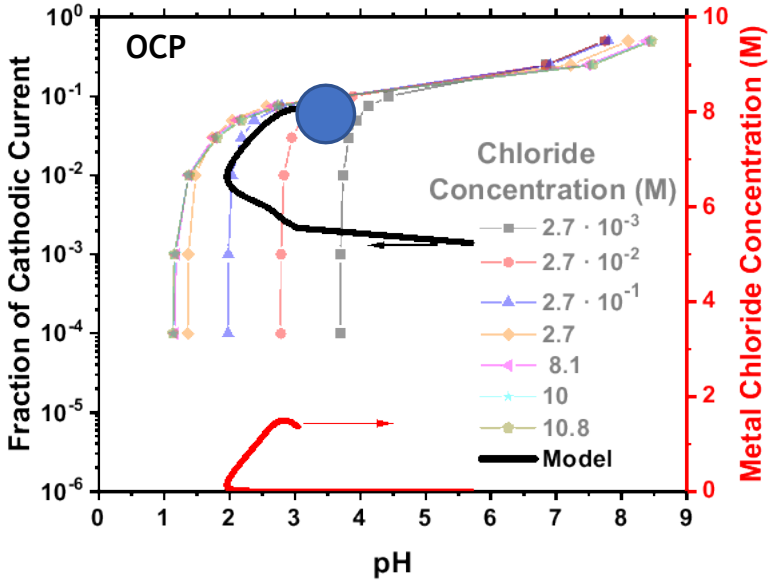
Increasing External Potential Increases Chloride Concentration and Decrease pH at Tip

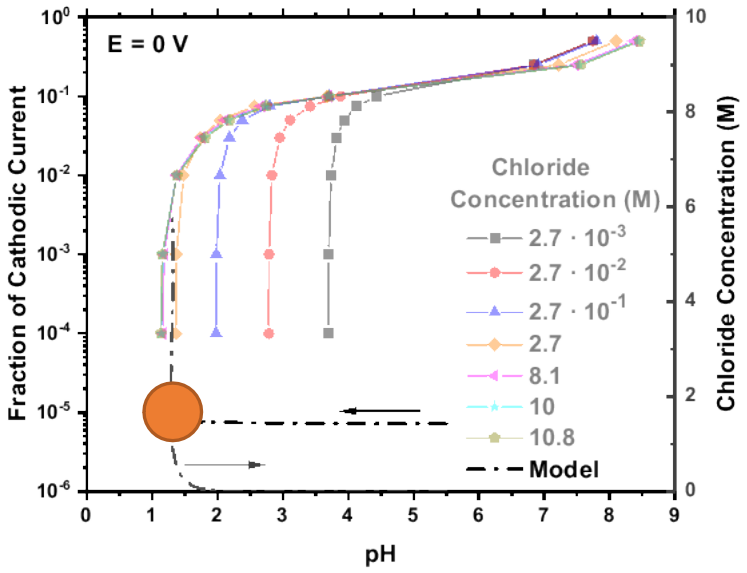




- Increasing external potential increases chloride concentration
- Increasing external potential decreases pH
- ***Modest polarization of external surface can greatly change crack tip conditions***

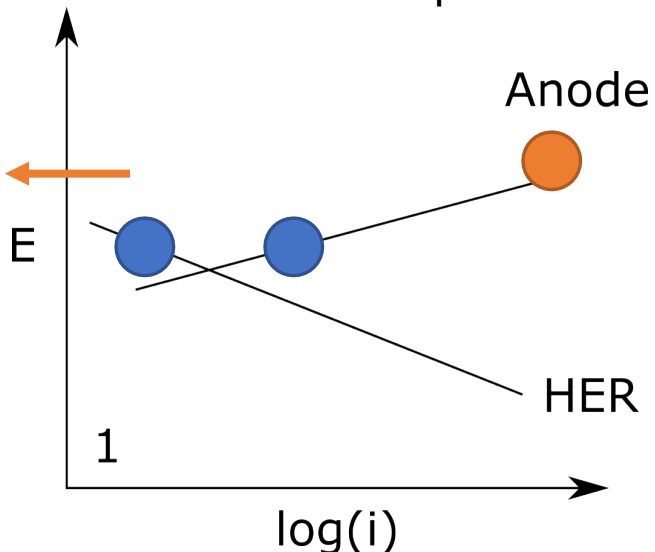
Increasing External Potential Decreases Local Cathodic Reactions





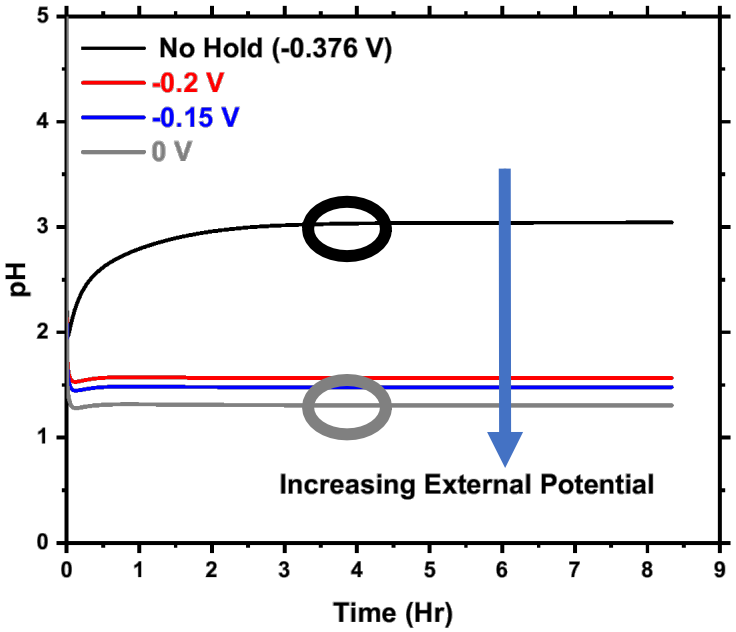
- Increasing external potential increases crack tip potential
- Decrease in local cathodic current
- ***Overall increase in crack tip severity***

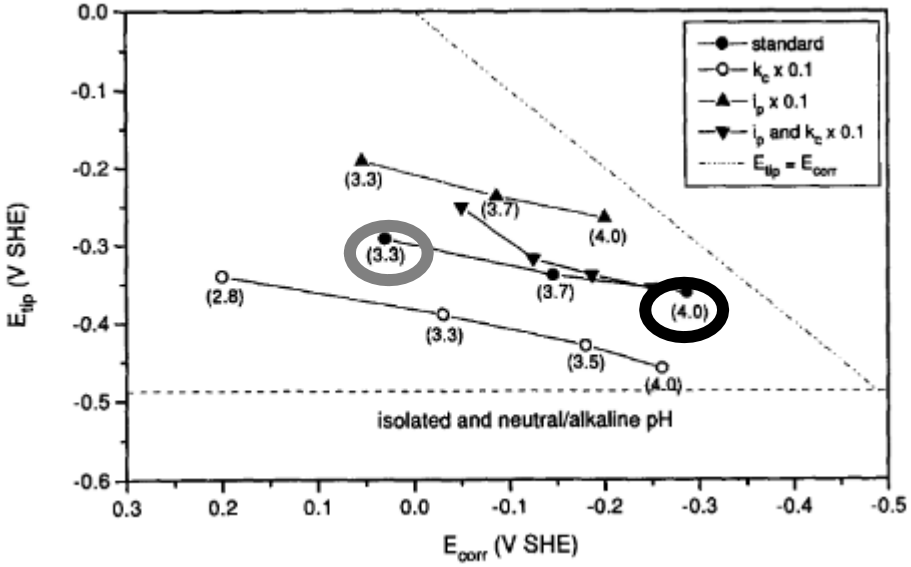
At the Tip



Comparison to Other Models

- Increasing external potential decreases pH
- Anodically polarizes crack tip

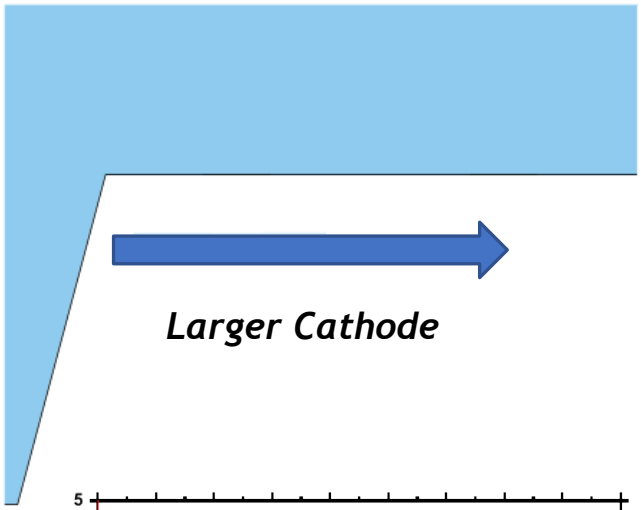


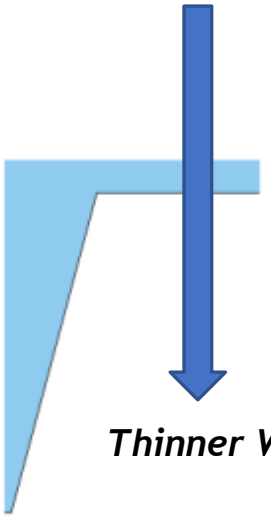


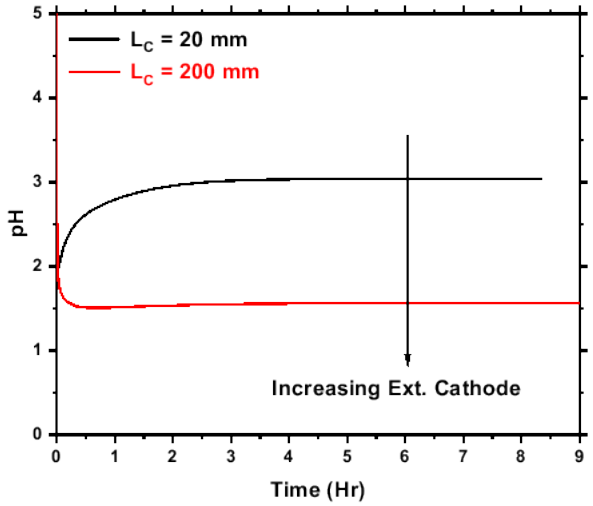
Increasing external potential

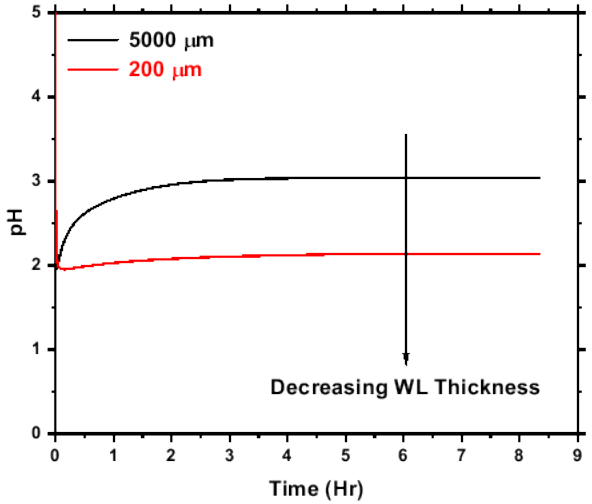
A. Turnbull, Corrosion Science, 39 (1997) 789-805.

Increasing Cathode Length and Decreasing WL Increases Decreases pH







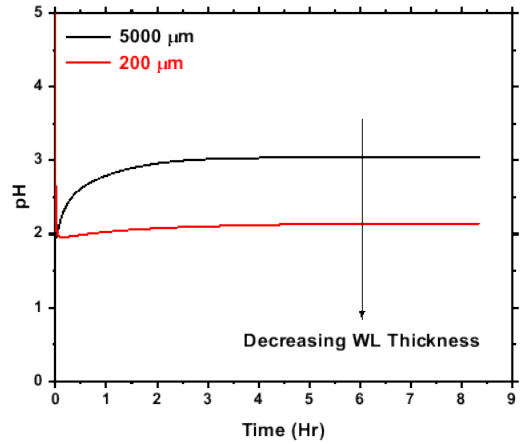


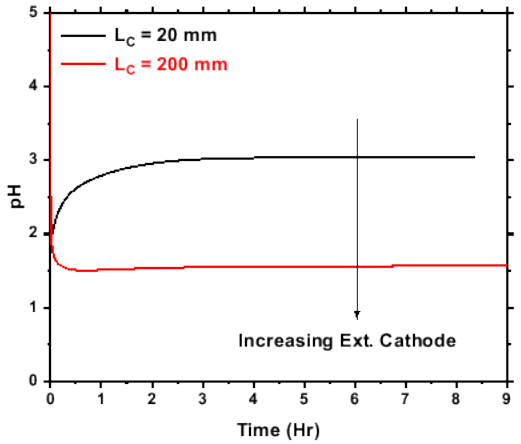
Driven by increase in external cathodic current

Can we represent atmospheric SCC with full immersion?

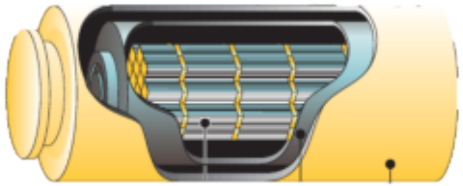
Conclusions and Implications

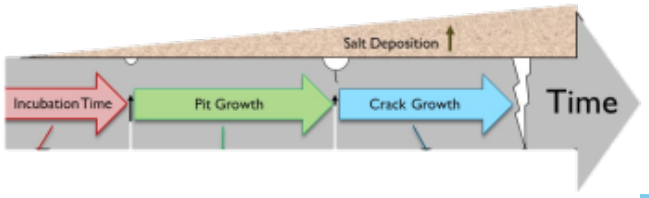
- Created model to accommodate changes in sample size, external environment (WL thickness and solution) and sample geometry
  - Results follows trends in literature
- Modest anodic polarization of samples can increase electrochemical severity at the crack tip
  - Are polarizations representative of real life scenarios?
  - Are laboratory scale specimens representative of field conditions?
- Strong influence of external surface on crack tip electrochemistry
  - Will this change in 3D?
- ***Important to understand internal and external cathodic kinetics***

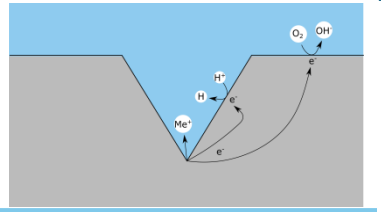




Predicting Electrochemical Conditions in a Stress Corrosion Crack Tip and the Influence of Exposure Environment







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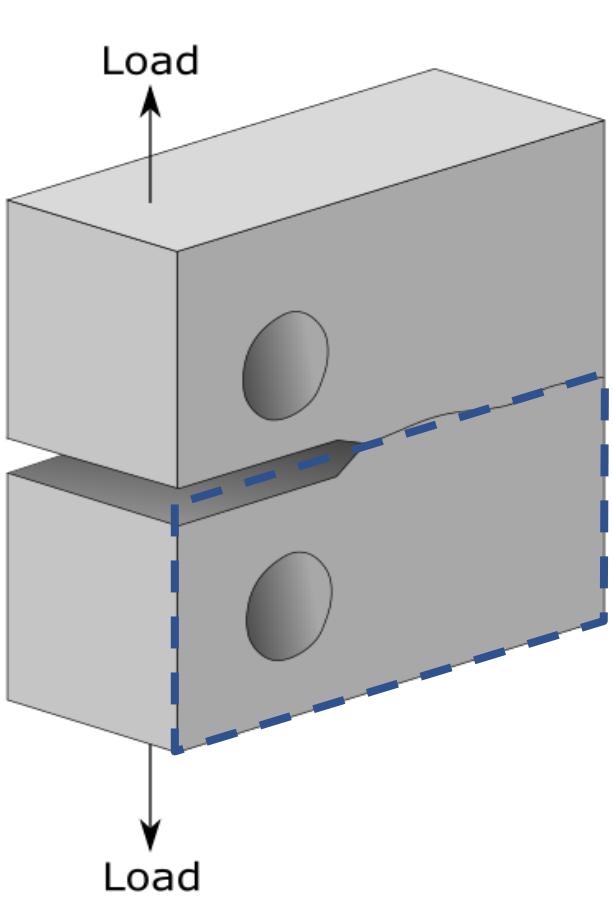
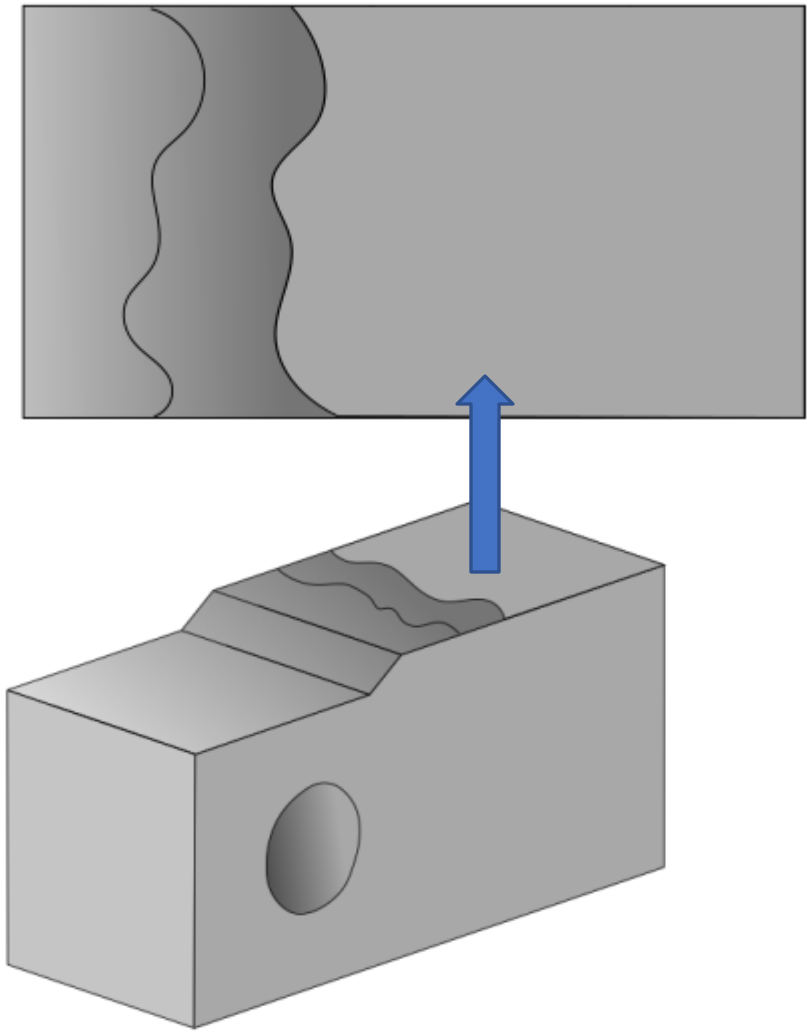
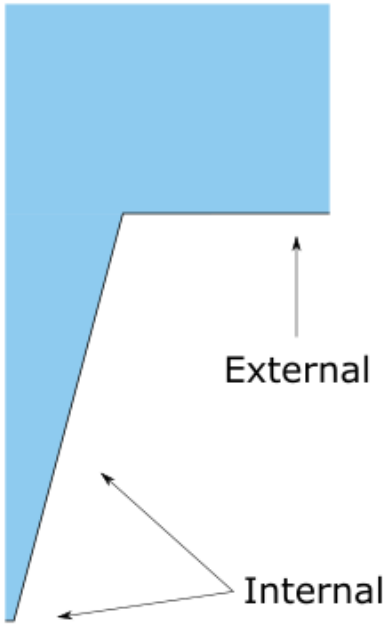
Need to understand crack chemistry and trends with changes in environment and sample

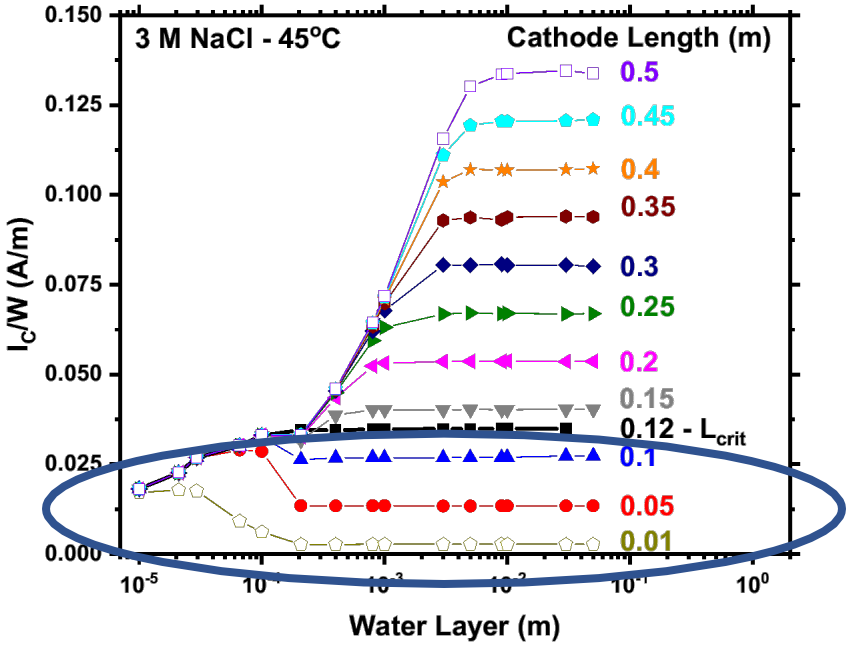




How large of a sample/cathode do you need to represent a limiting condition?

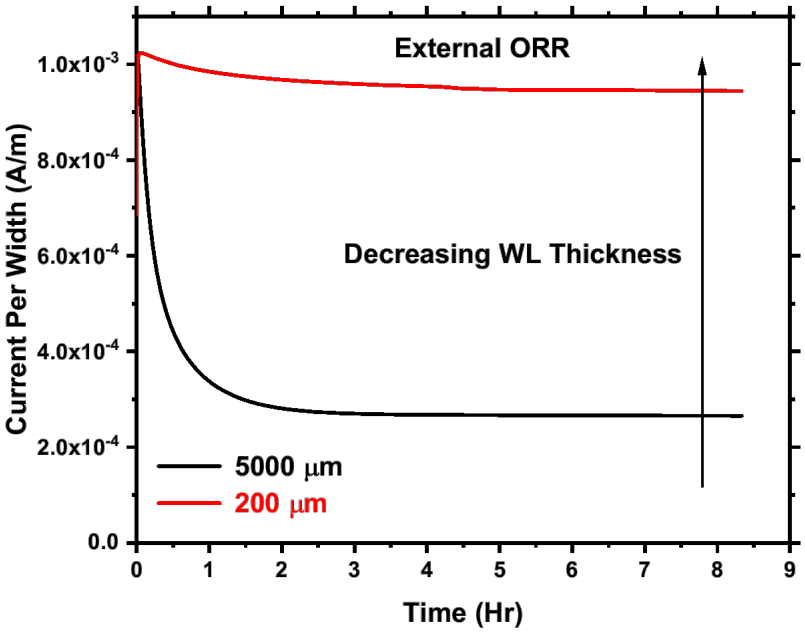
- Investigated for a galvanic coupling
- Strong coupling of water layer thickness and cathode length

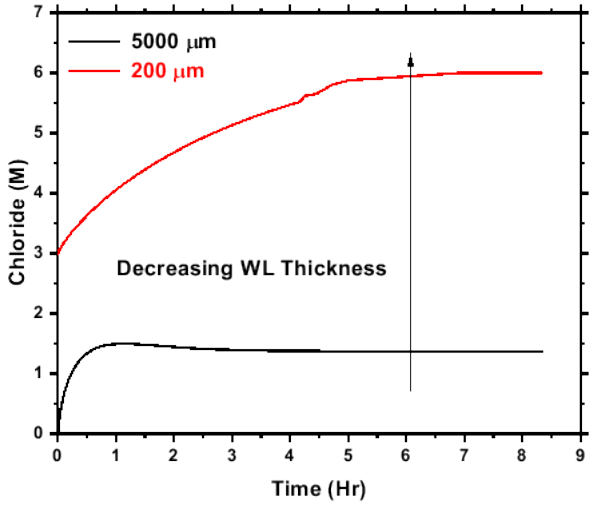


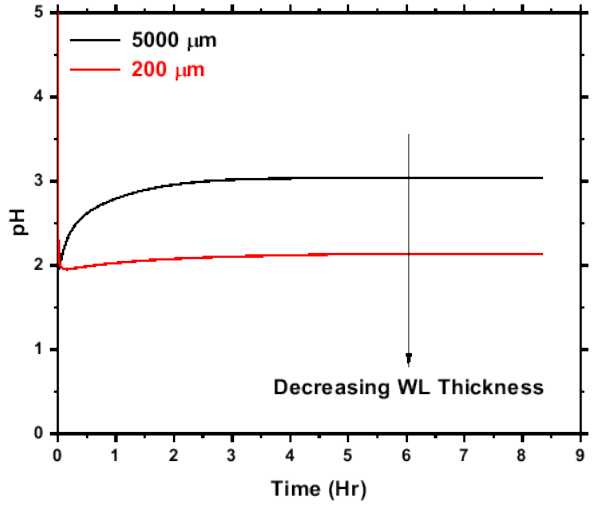


Decreasing WL Thickness Increases Cl and Decreases pH

- Roughly 4 times as much chloride at the crack tip with increasing chloride concentration
- Increase in chloride and decrease in pH driven by increase in external ORR







Increasing Cathode Length Increases Chloride Concentration and Decreases pH

- Roughly 3 times as much chloride at the crack tip with increasing chloride concentration
- Increase in chloride and decrease in pH driven by increase in external ORR