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A Search for Electrochemical Similitude in SCC Testing

R.G. Kelly[1], R. M. Katona[2], J.T. Burns[1], R. Schaller[2]

[1]Department of Materials Science and Engineering, University of Virginia
[2]Sandia National Laboratories, Albuquerque, NM 87123, USA

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Similitude

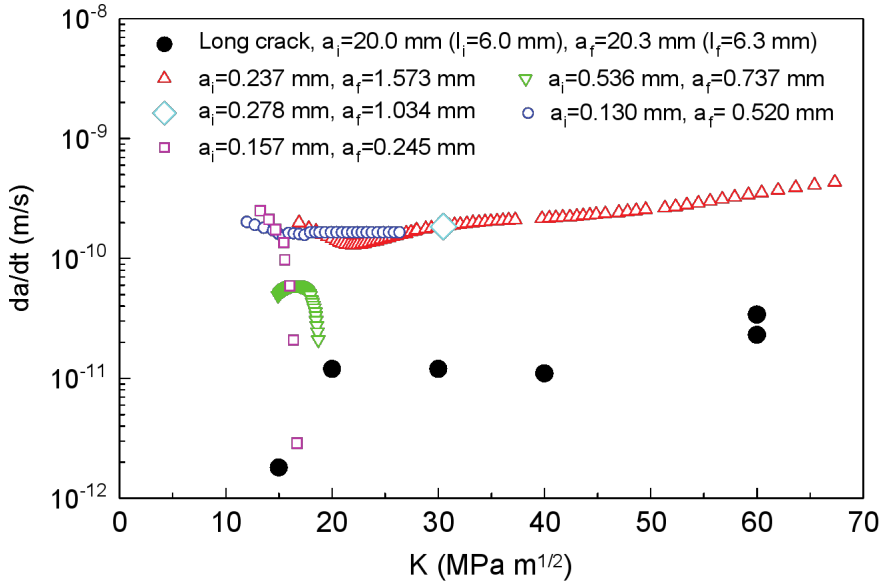
- Fracture mechanics has the power of similitude through the stress intensity factor, *K*

$$K = Y\sigma\sqrt{\pi a}$$

- Captures all of the mechanical driving force, allowing application of laboratory crack growth to engineered structures of different geometries for fatigue, fast fracture
- We do not have an equivalent in corrosion

Challenges to Corrosion Similitude in SCC

- Short-crack effect
  - Turnbull and Zhou
    - Small SCC cracks grow >10x faster than long cracks
  - Turnbull and Gangloff:
    - small corrosion fatigue cracks in 4130 (0.1–2 mm) grow up to 500 times faster than long cracks (15–40 mm)
- Natural exposures generally are thin electrolytes on the surface, adding more variables



Turnbull and Zhou (2011)

Past Models of SCC Chemistry

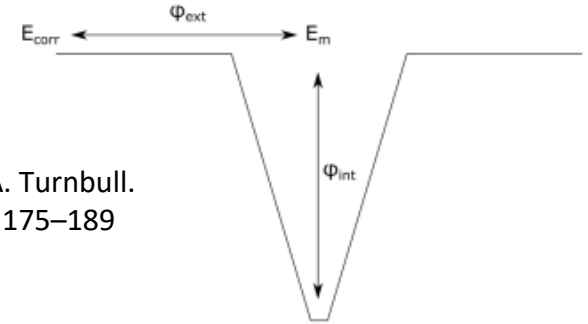


Figure adapted from A. Turnbull. Corrosion. 57 (2001) 175–189

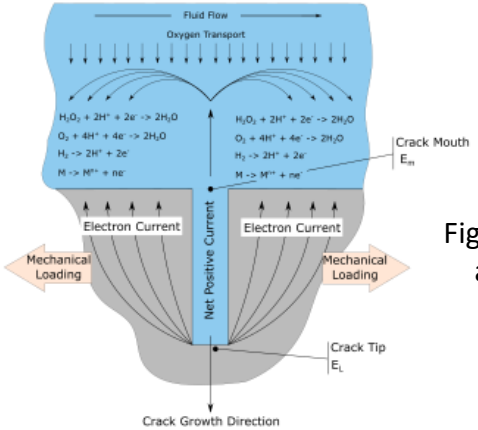
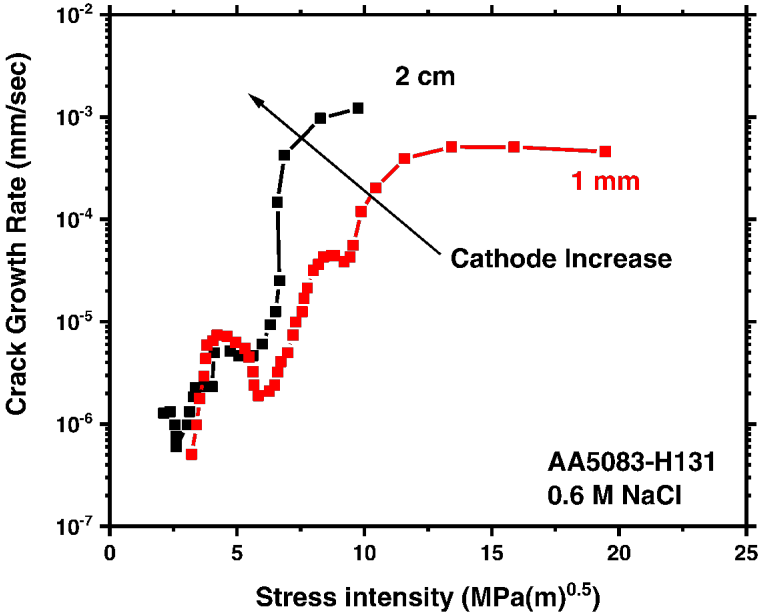
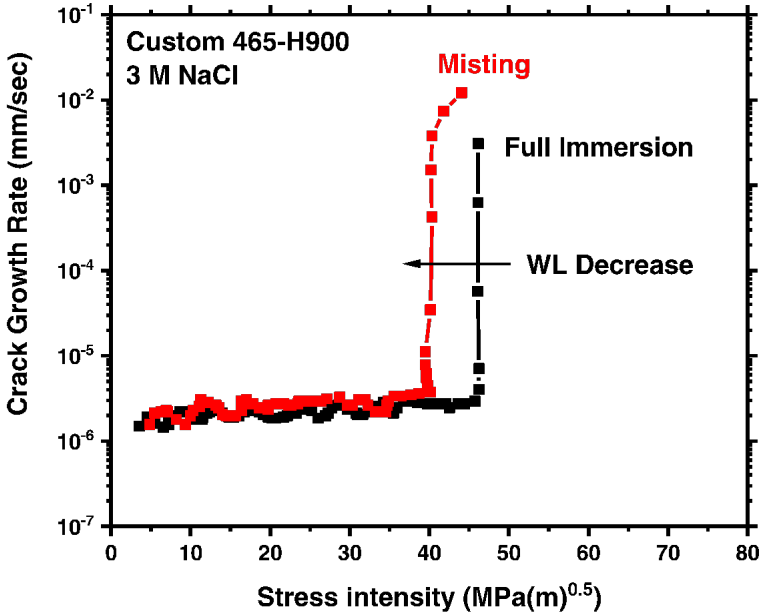


Figure adapted from M.P. Manahan, et al., Corros. Sci. 37 (1995) 189–208

- 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)**

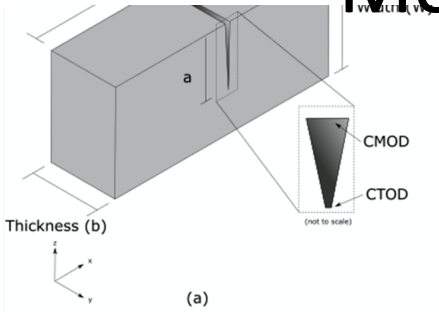
External area available can control cracking

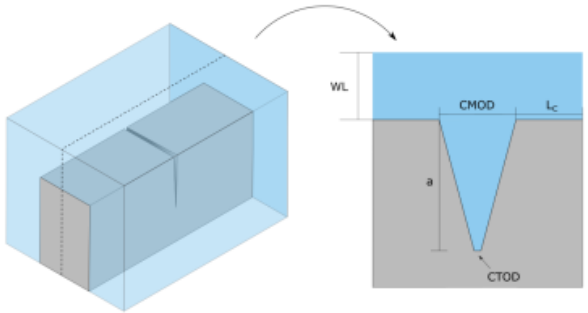


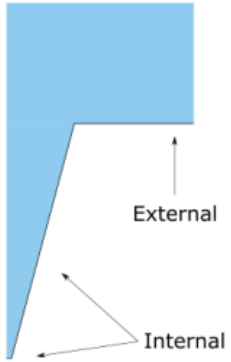


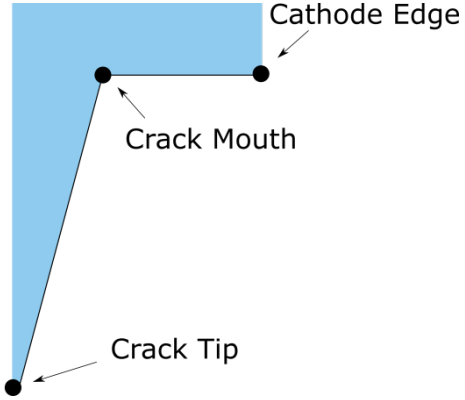
J. T. Burns, UVA

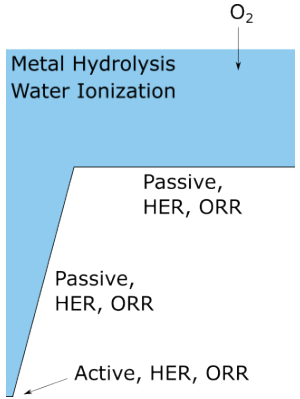
Modeled System: SENT samples









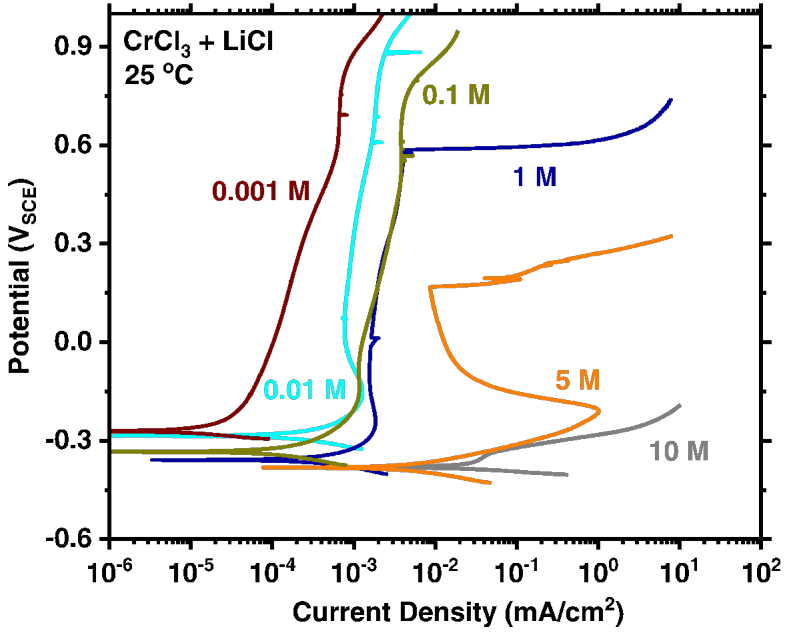


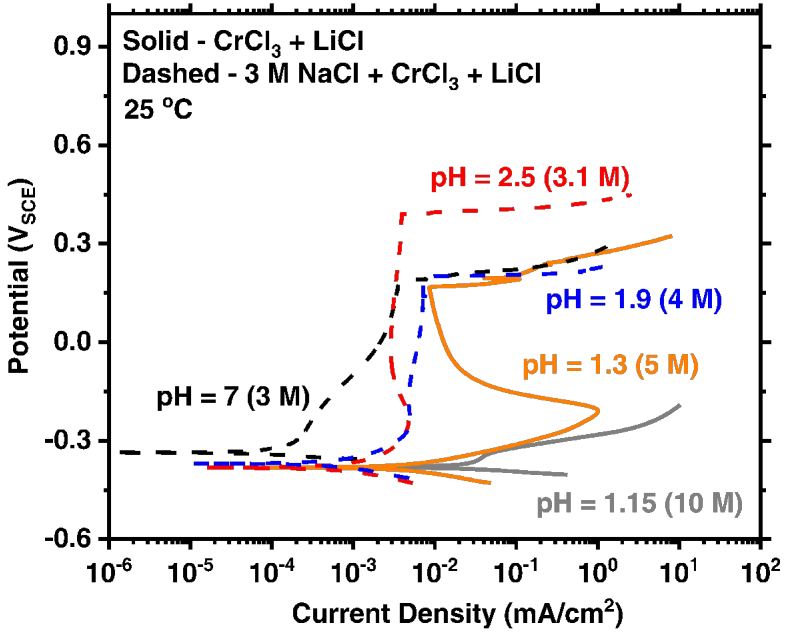
- Finite Element Model (FEM) utilized to predict crack tip conditions
- 2-D geometry, based on single edge notch tension (SENT) specimen of 316L
- Reactive transport model with chemistry dependent electrochemical boundary conditions

FEM Boundary Condictions:

Anodic kinetics as f([MCl_x])

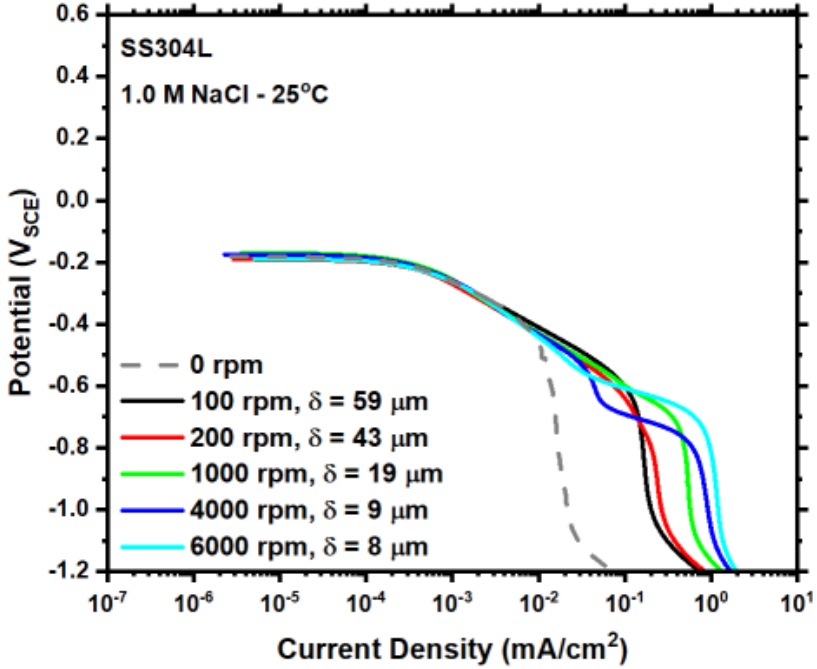
316L



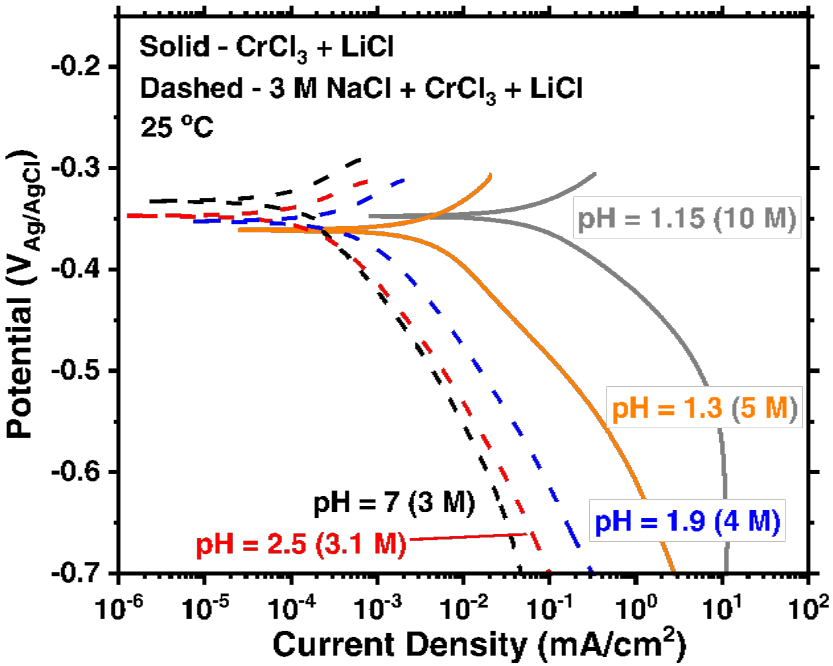


FEM Boundary Condictions:

Cathodic kinetics as f(location, WL, [MCl_x])

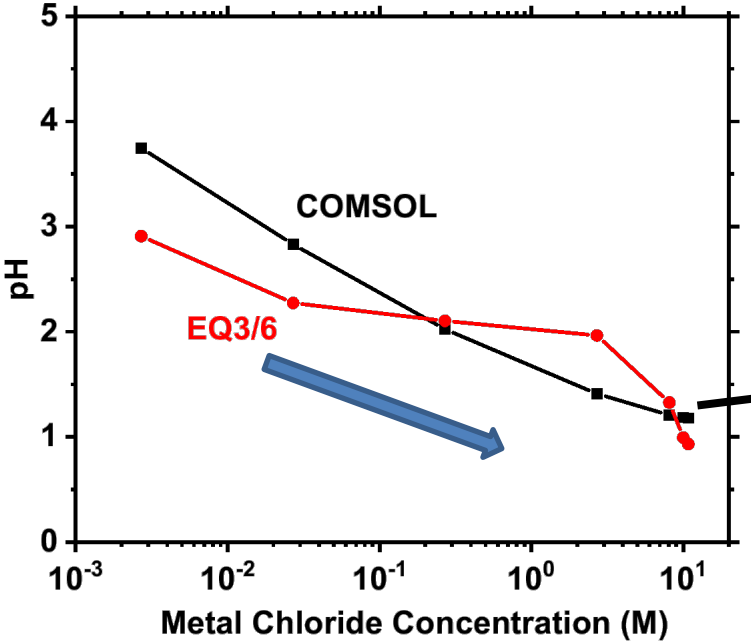


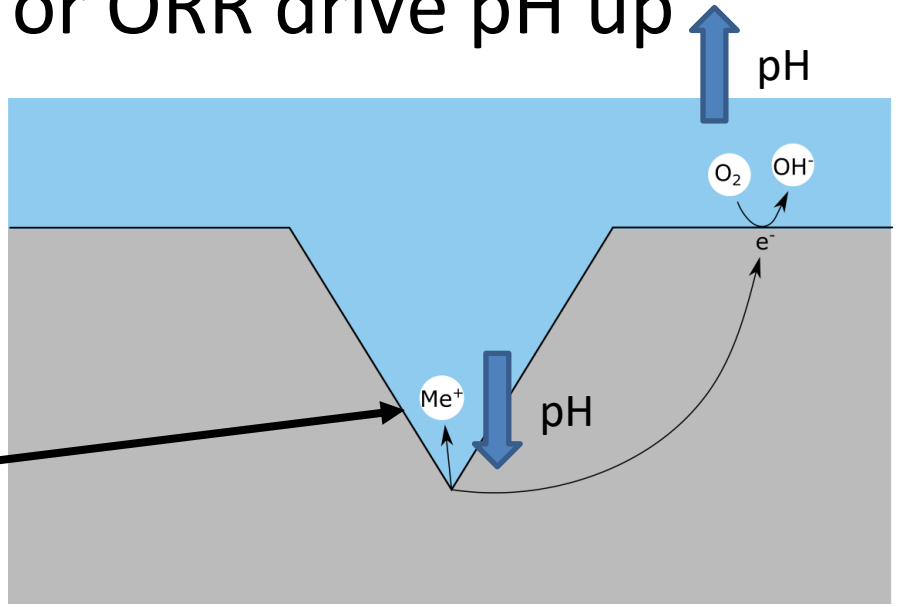
External surfaces



Internal surfaces

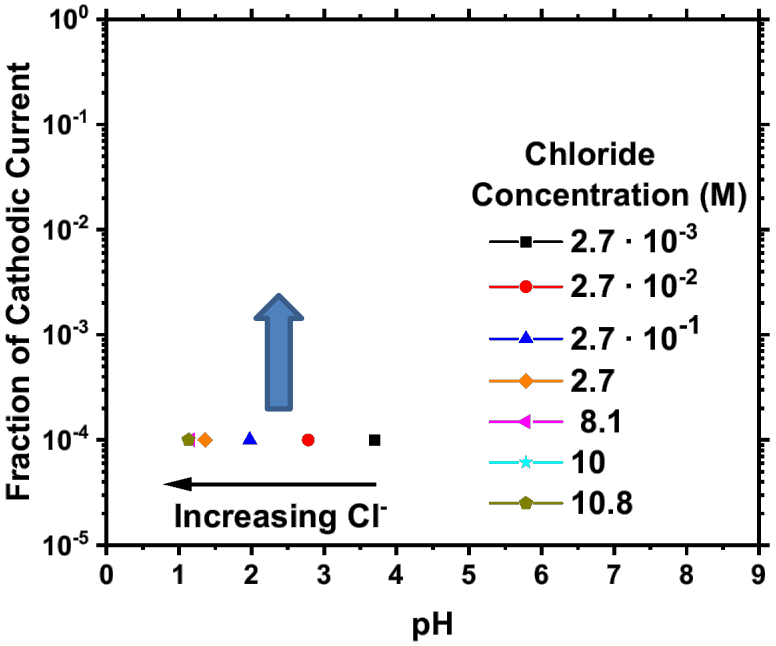
Inside crack, hydrolysis drives pH down
Outside crack, HER or ORR drive pH up

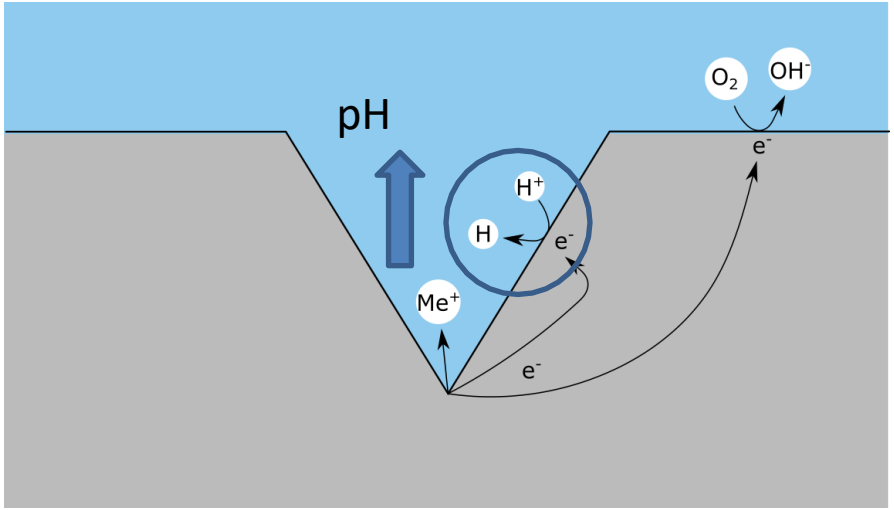




- Similar pH's when comparing concentration (COMSOL) and activity based calculations (EQ3/6)
- Can consider just metal chloride concentration (*i.e.,* $FeCl_2$+ $CrCl_3$ +$NiCl_2$)

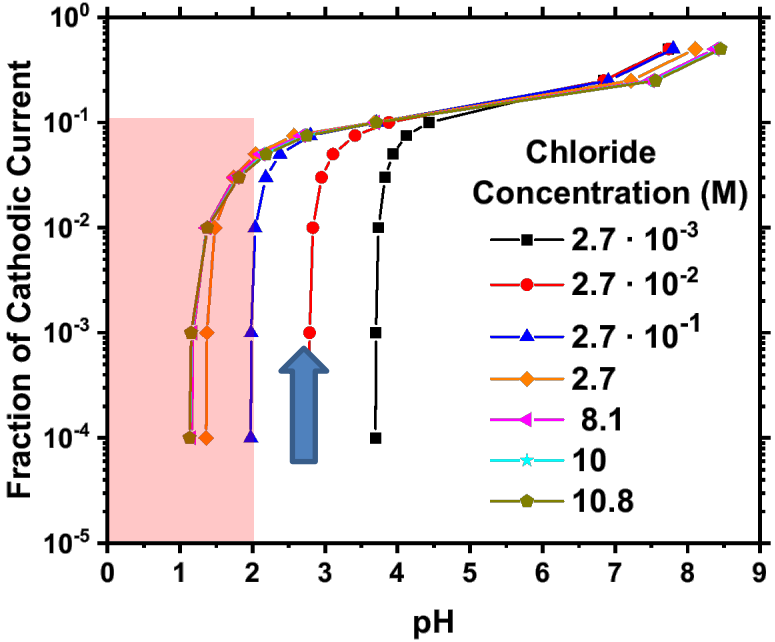
But, *local* cathodic current affects *crack* pH

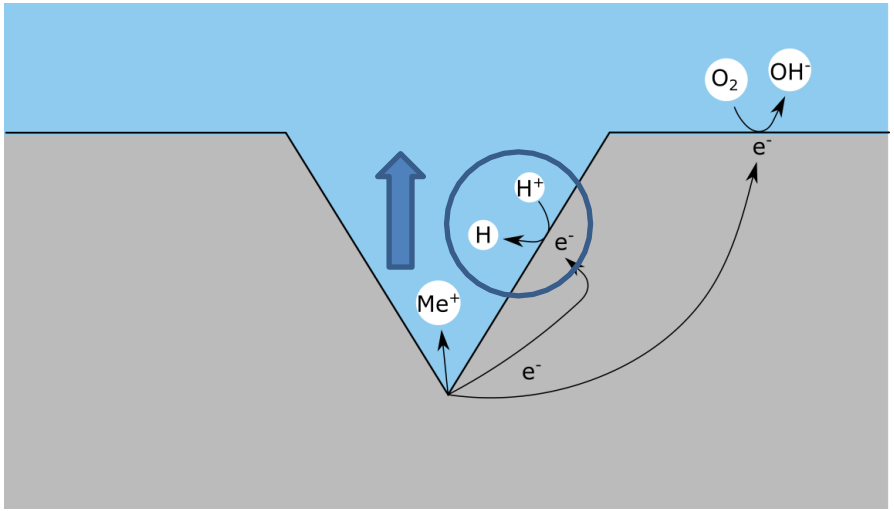




Fraction of Local Cathodic Current = $\frac{i_{cathodic}}{i_{anodic}}$

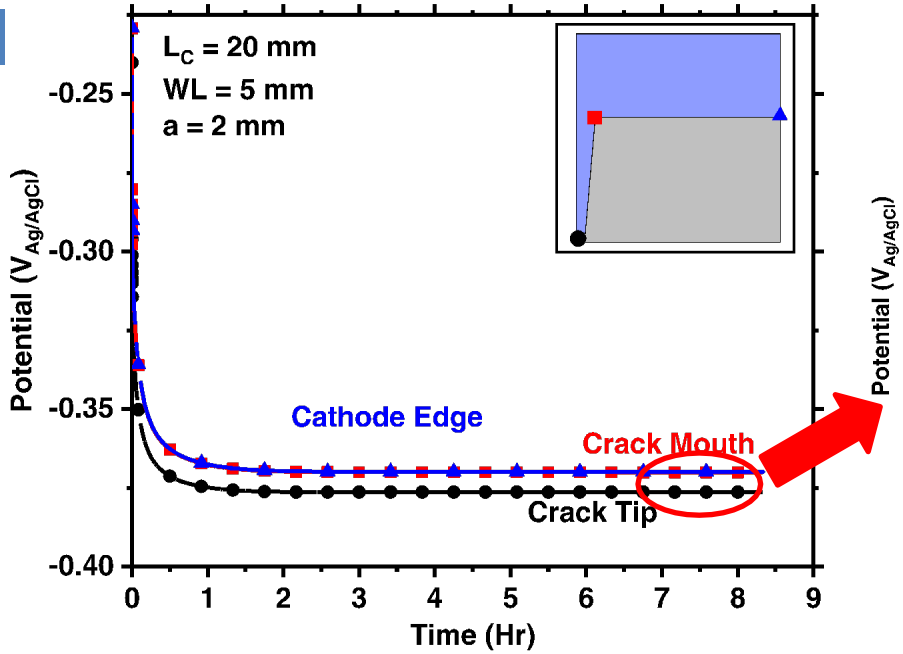
pH is a function of both anodic dissolution and local cathodic reactions which are both a function of time

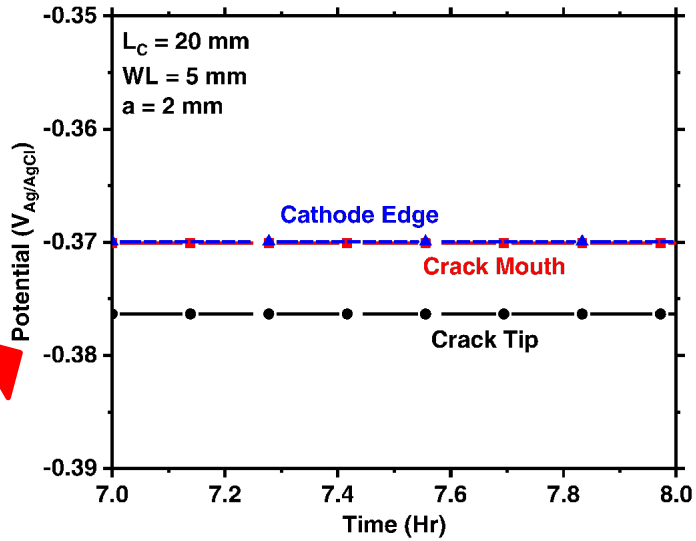




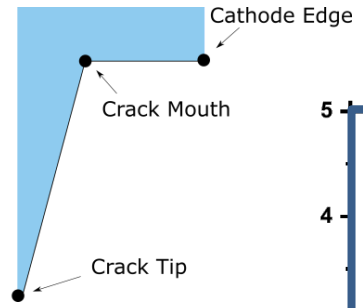
$$\text{Fraction of Cathodic Current} = \frac{i_{cathodic}}{i_{anodic}}$$

Limited IR drop along surface and in crack under these conditions

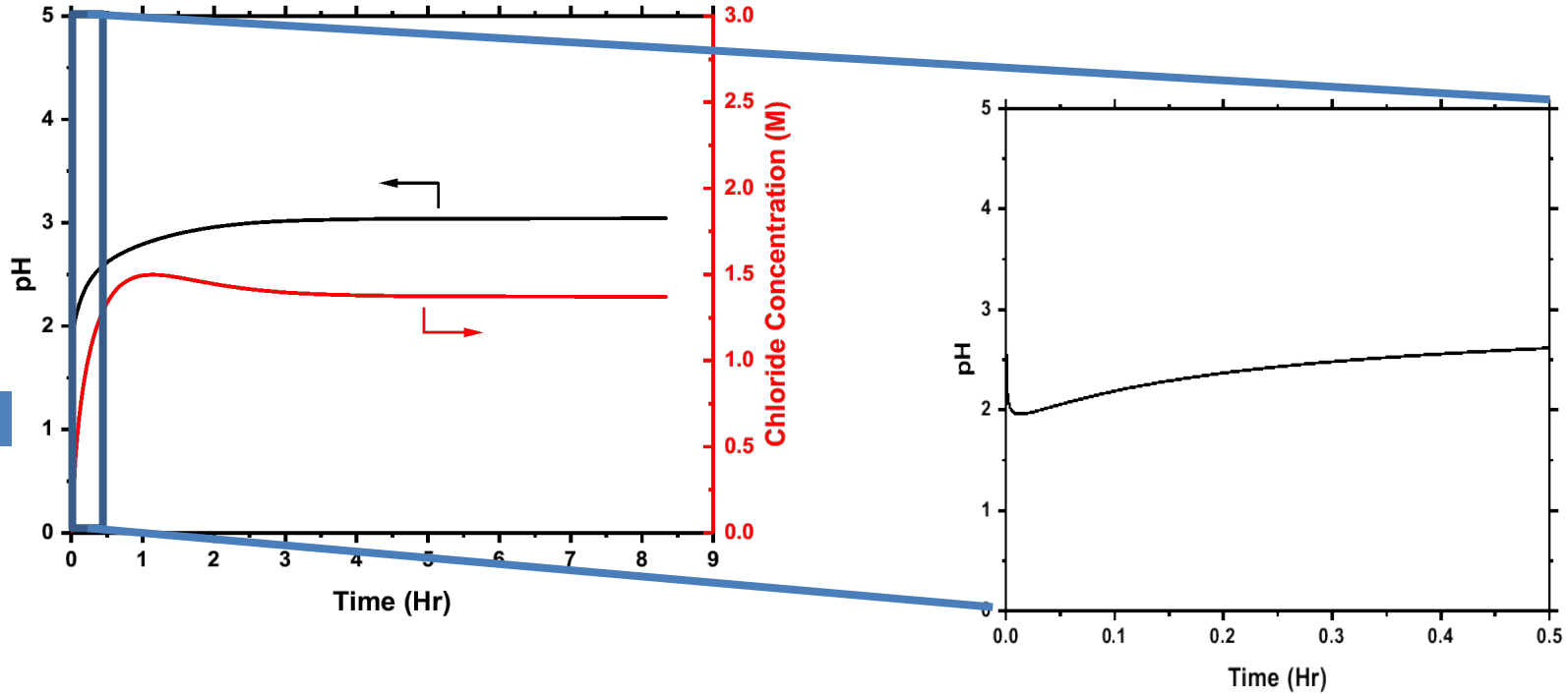




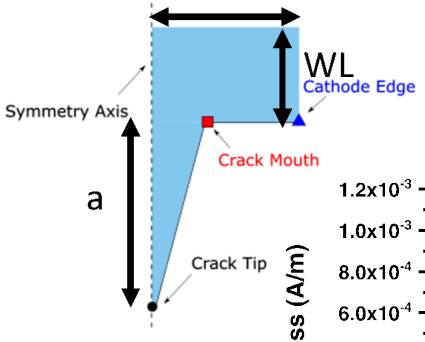
Crack tip pH initially decreases, but increases to a steady state

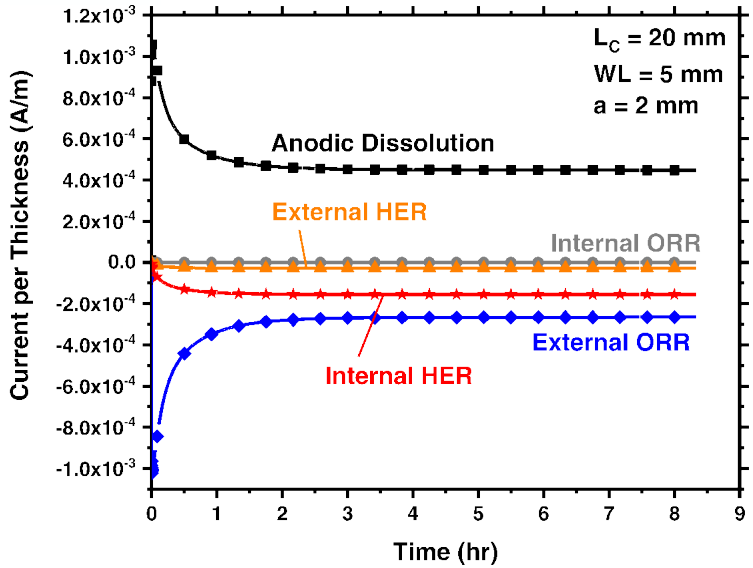


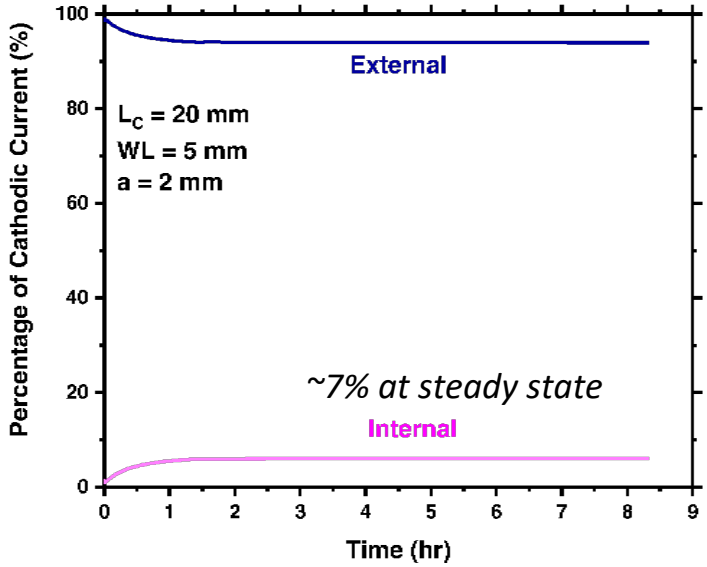
L_c = 20 mm
WL = 5 mm
a = 2 mm



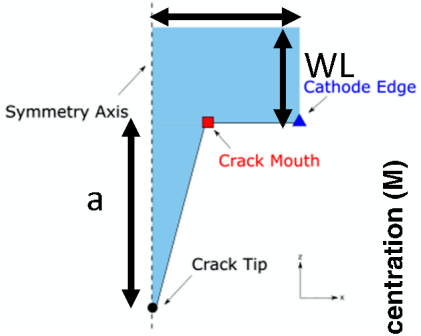
Vast majority of cathodic current on external surface

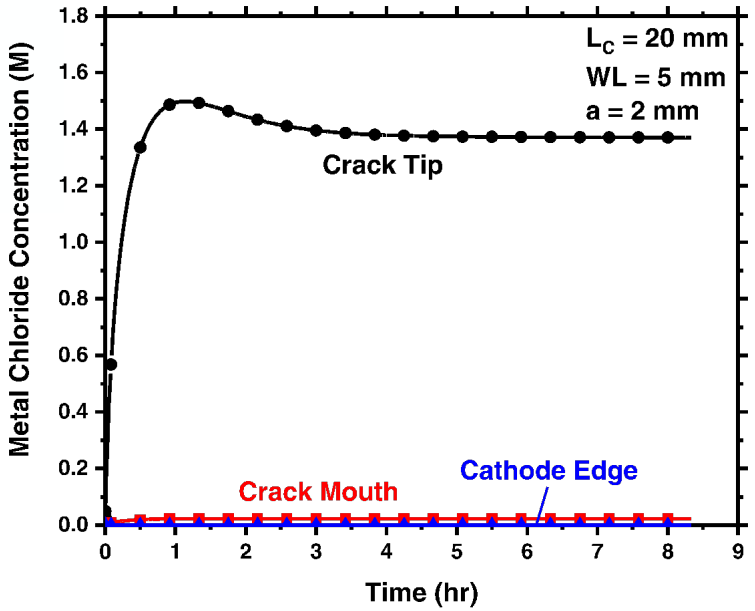


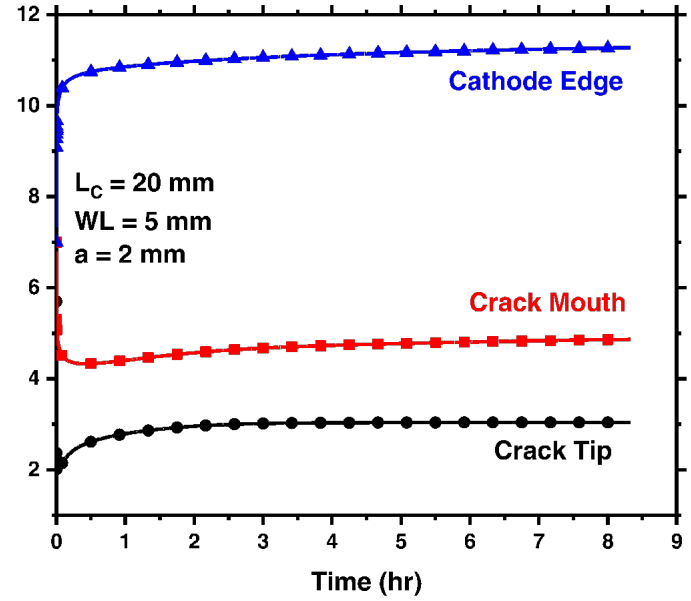




pH at crack tip ~3, pH cathode ~11



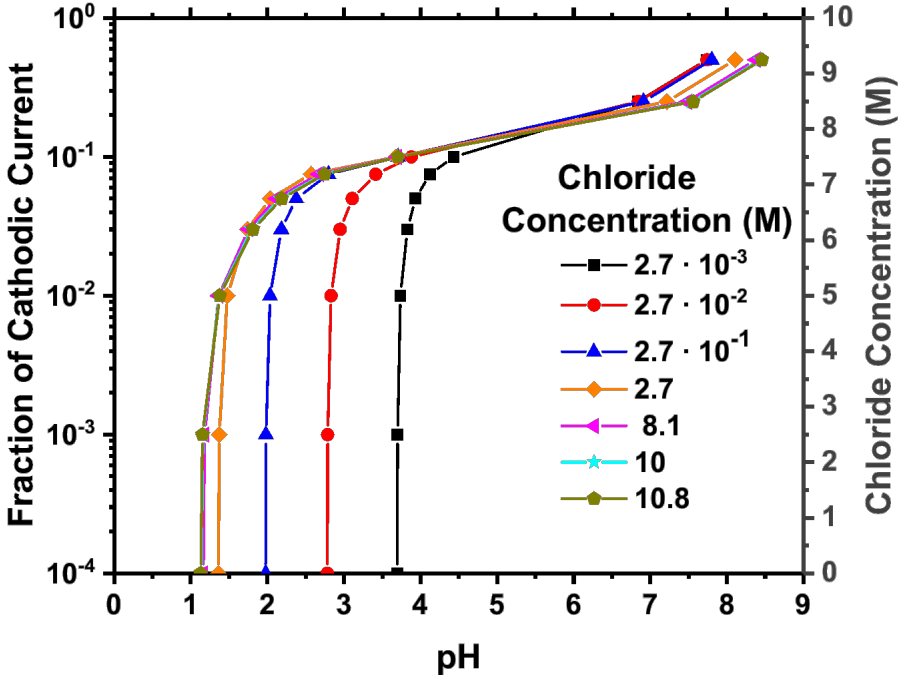




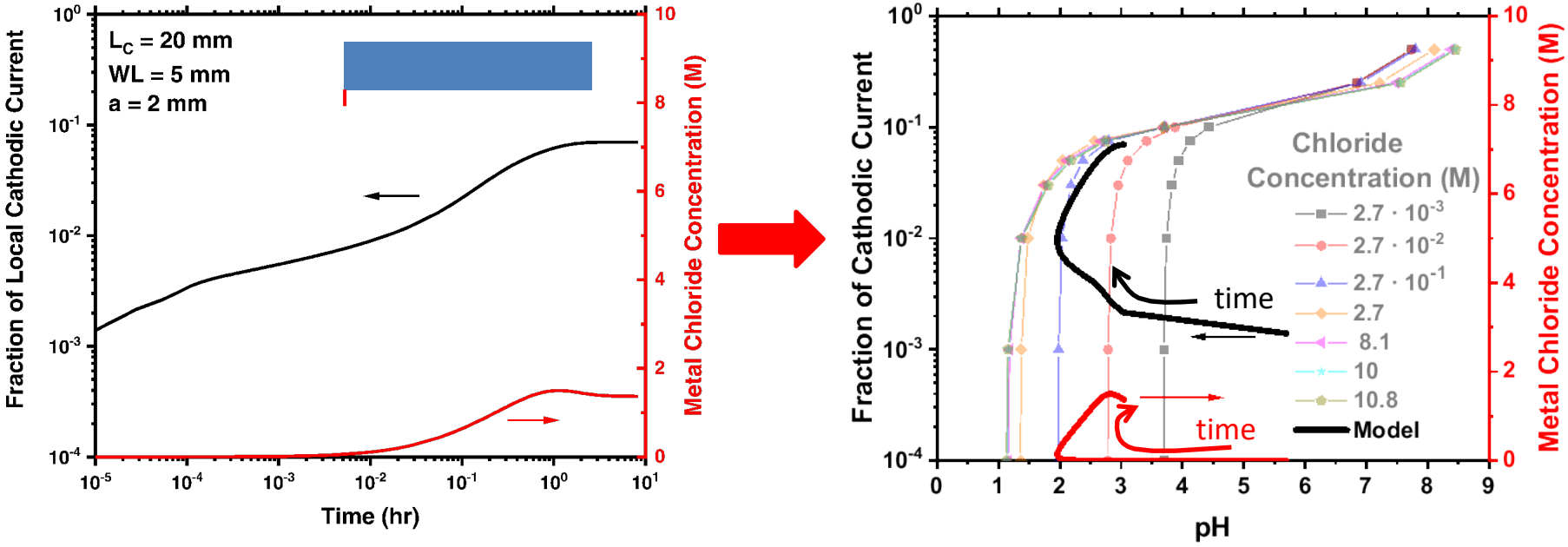
$\frac{1}{3}$ h

Revisit relation between [MCl_x], pH, and $i_{c,loc}$

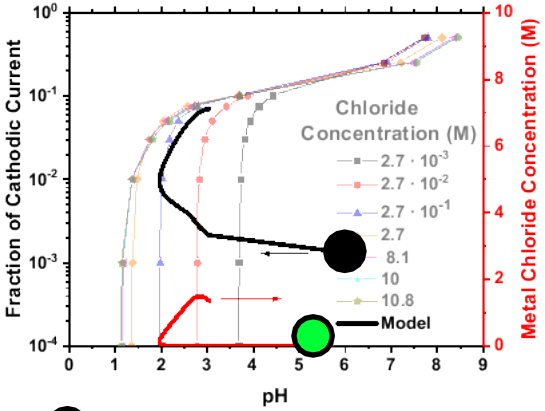
- Metal dissolution + hydrolysis decreases pH
- Local cathodic reactions increase pH
- Must remain < pH 2 for active crack tip

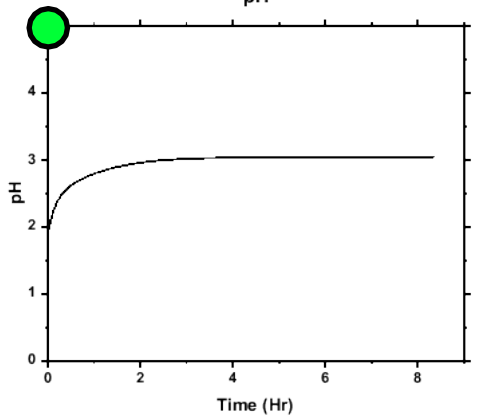


Cathodic current in crack increases with time



Crack tip pH evolution





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WL = 5 mm
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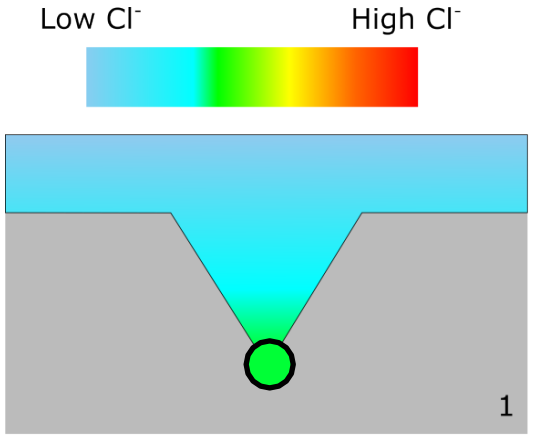
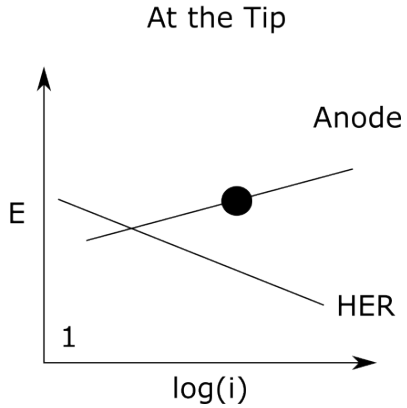
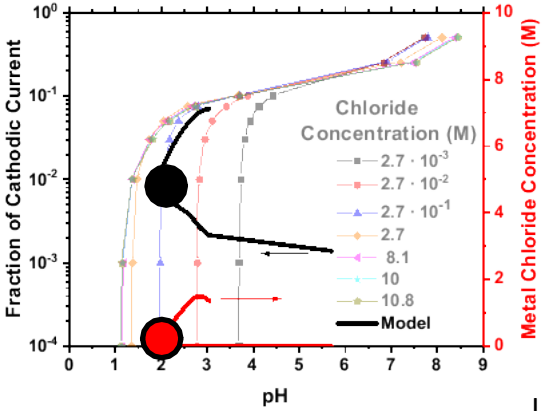
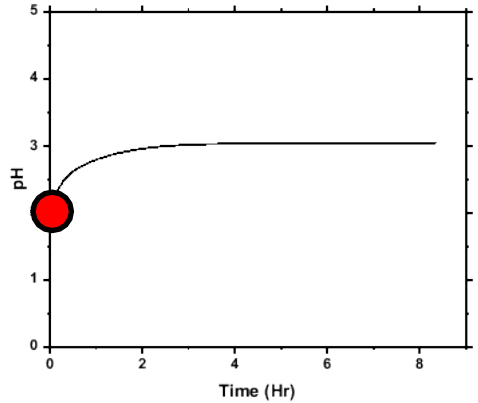




Crack tip pH evolution





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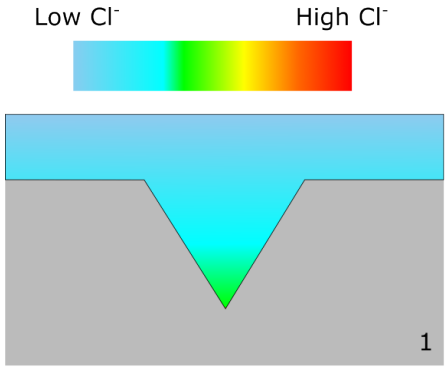
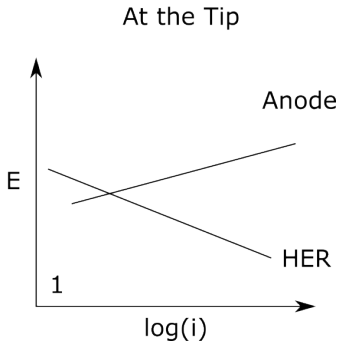
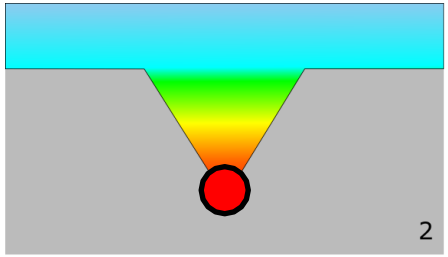
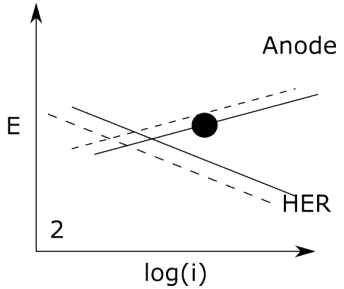
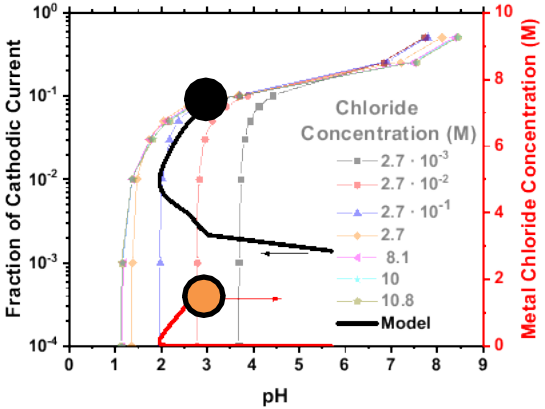


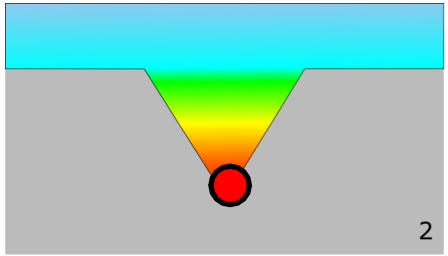


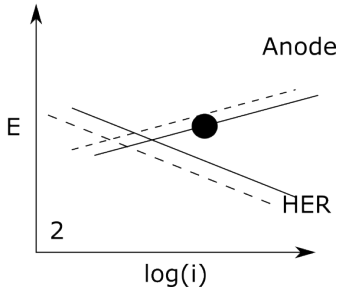


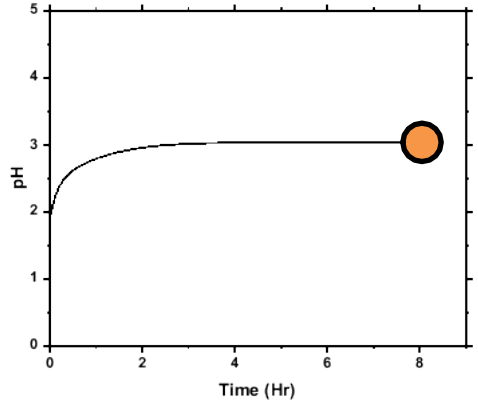


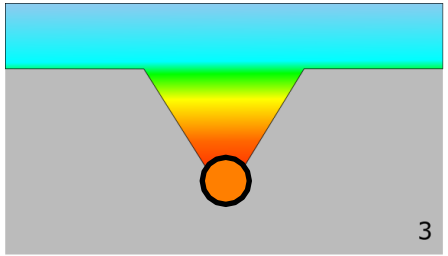
Crack tip pH evolution indicates crack will die

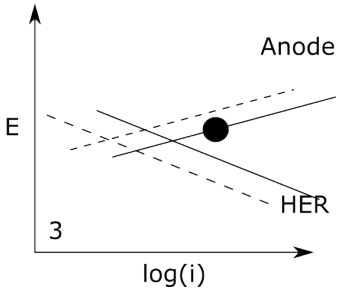




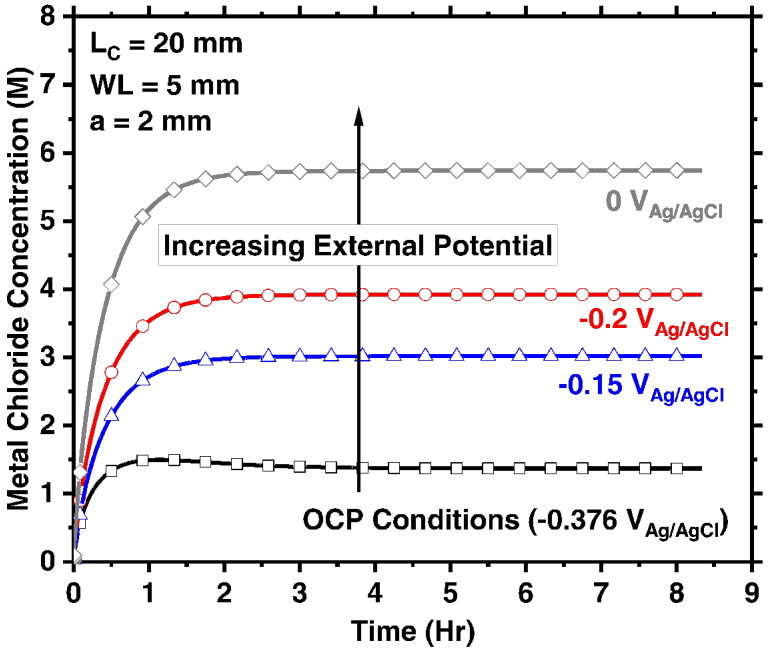


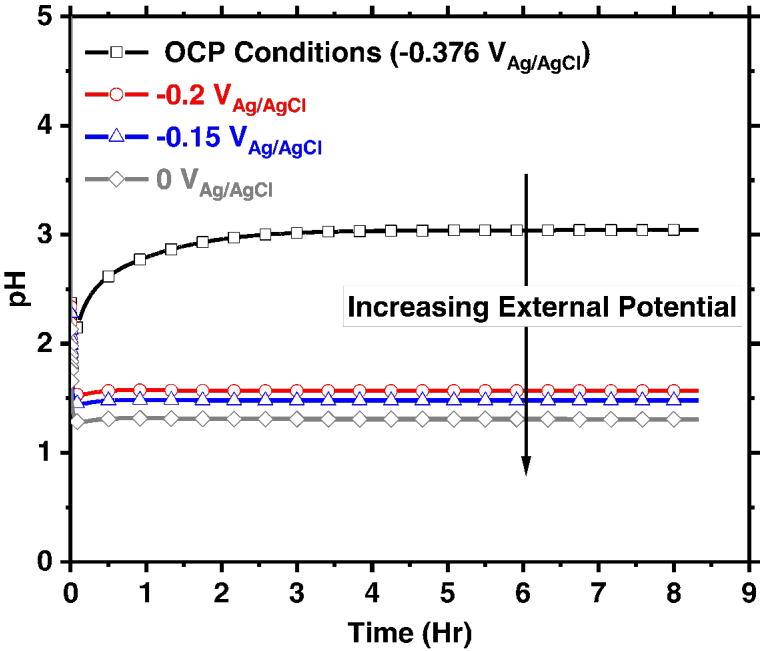




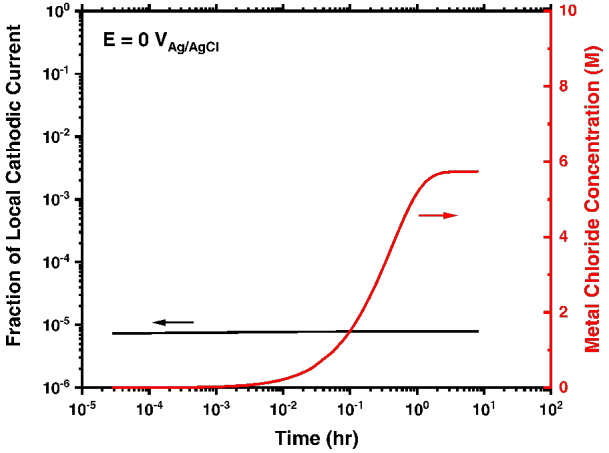


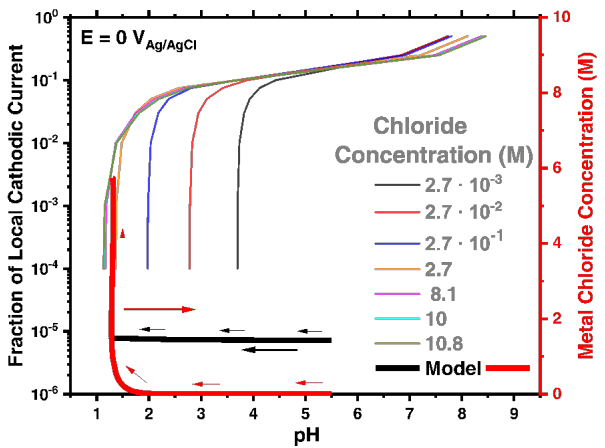
Can stabilize crack with external polarization

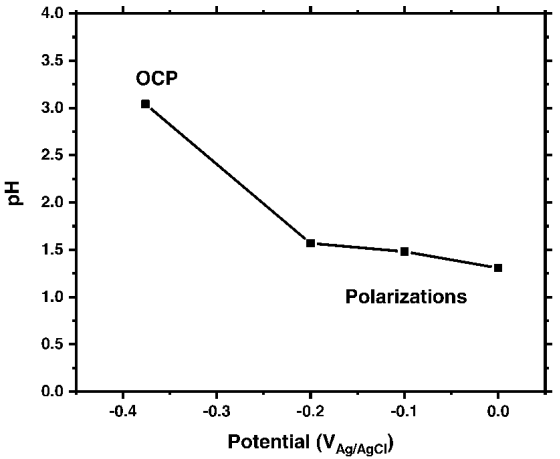




Anodic polarization drives crack tip dissolution and decreases crack tip cathodic reaction

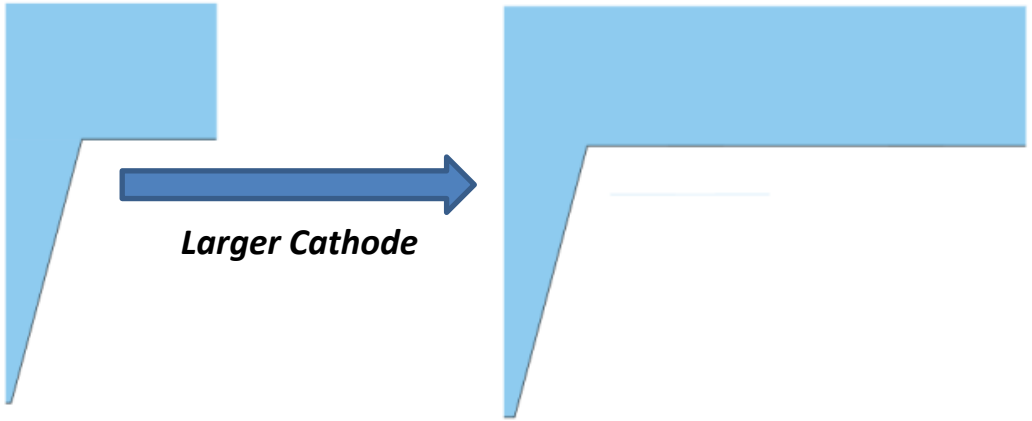


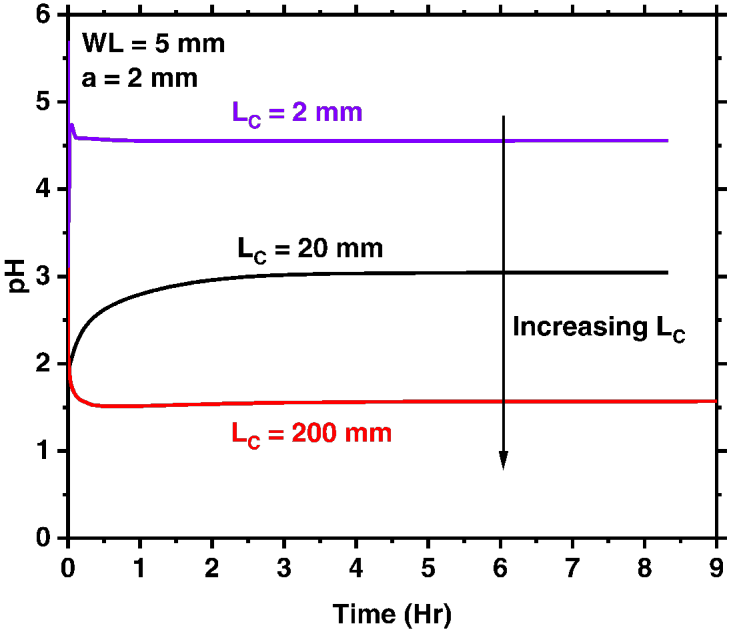




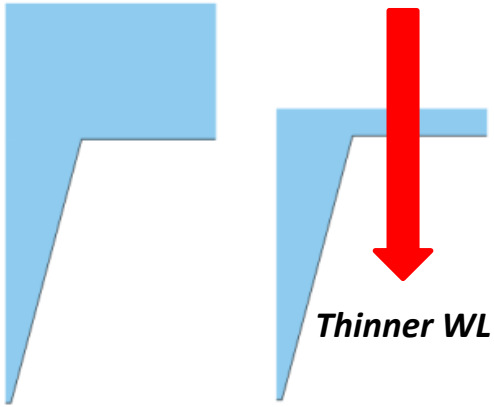
Metal chloride concentration rises with local cathodic current staying small

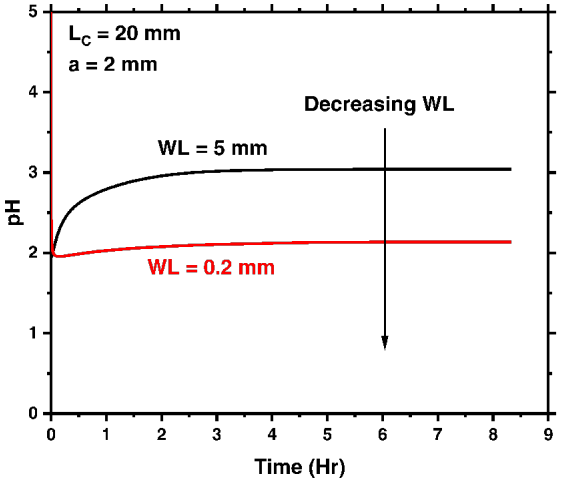
Can achieve with external cathode if large enough

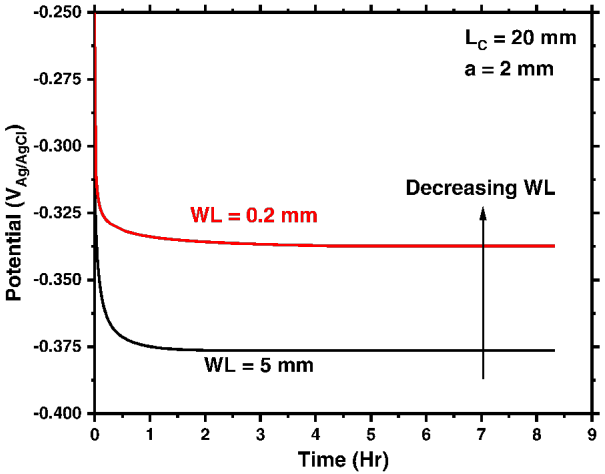


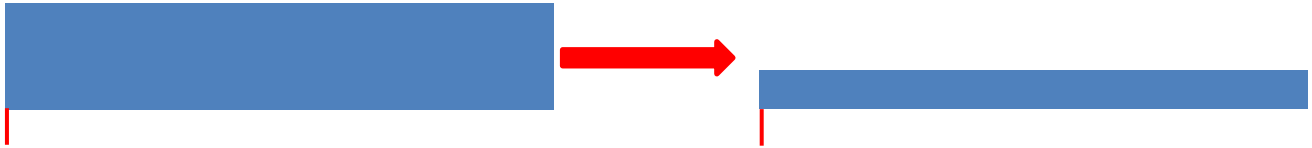


Or if WL is thin enough to increase ORR

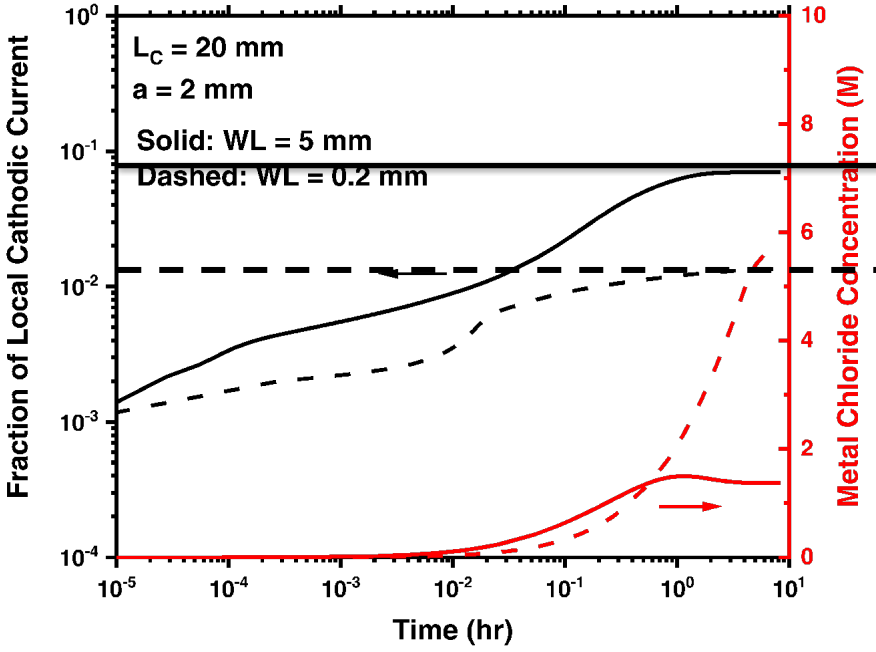


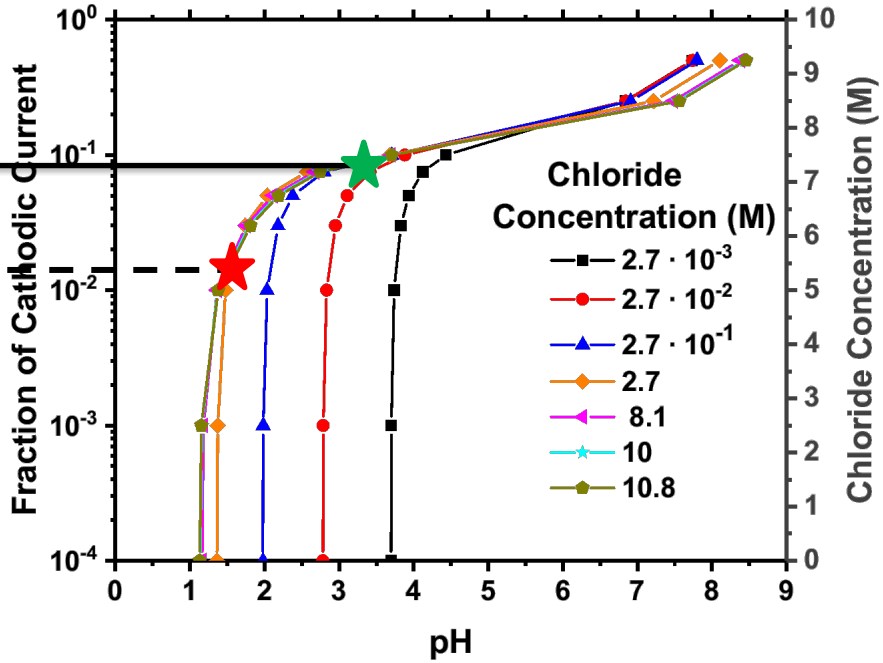






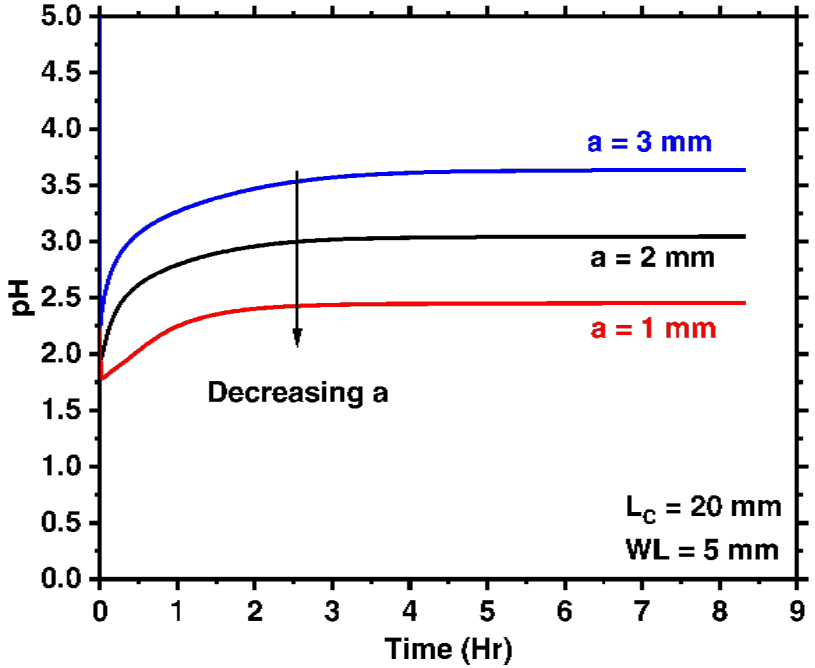
Thinner WL decreases $i_{c,loc}$, and increases $[MCl_x]$



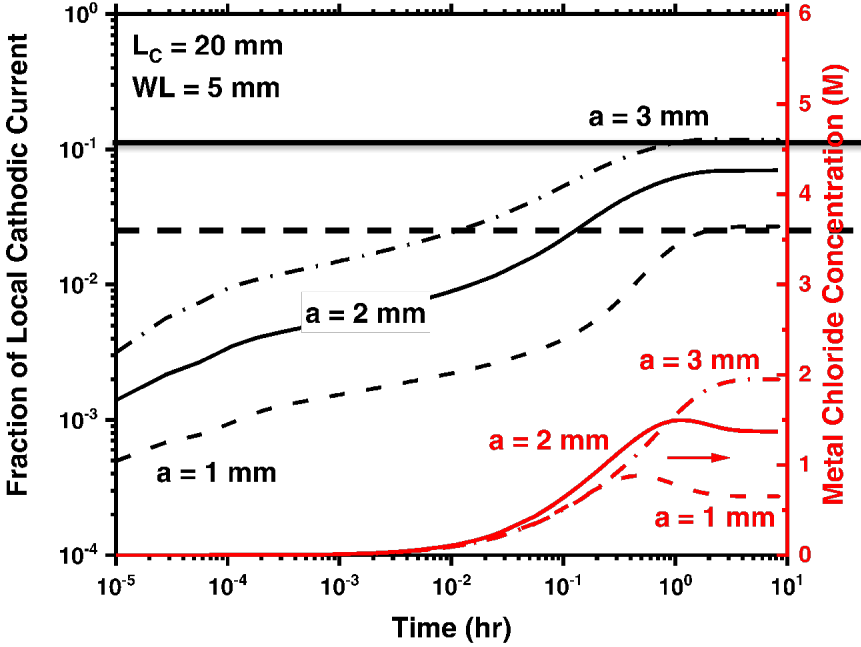


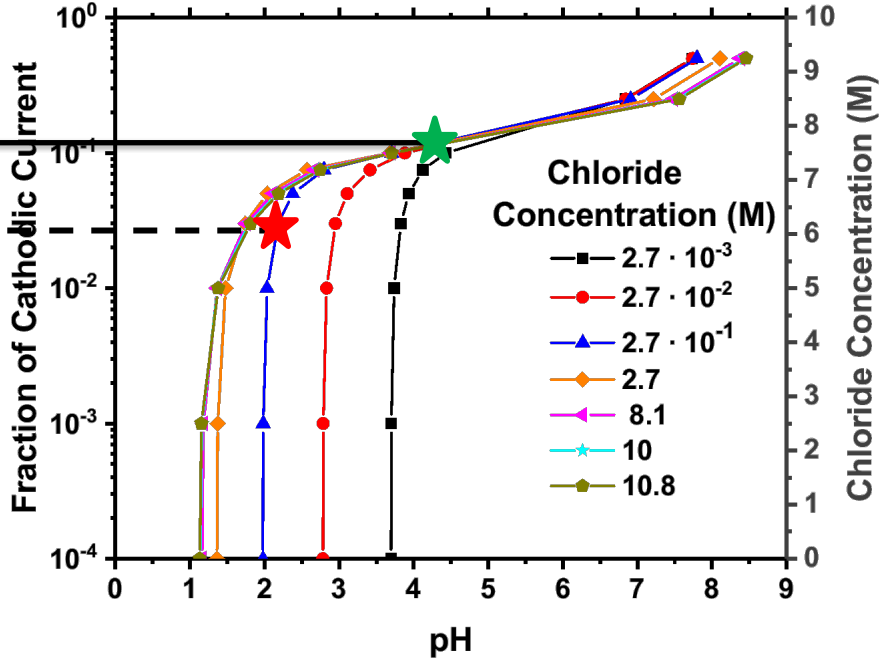
Model implies a maximum crack length for atmospheric conditions

- For a **given cathode size and WL,**
  - Only a certain amount of current is available outside crack
  - So internal cathodic current increases for longer cracks
  - $\frac{i_{c,loc}}{i_a}$ increases
  - Crack tip pH increases



For atmospheric exposures, larger a increases $i_{c,loc}$, limits [MCl_x], and allows high pH





Conclusions and Implications

- Created model to accommodate changes in sample size, external environment (WL thickness and solution) and sample geometry
- 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
  - Leads to the prediction of a maximum crack size under atmospheric conditions
- ***Important to understand internal and external cathodic kinetics to approach similitude***

Acknowledgements

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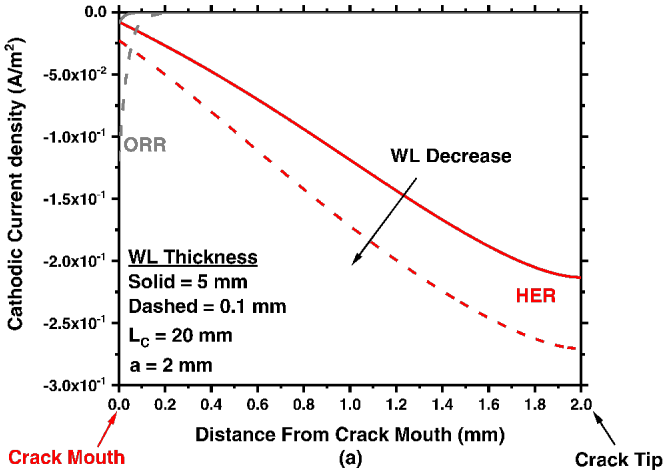
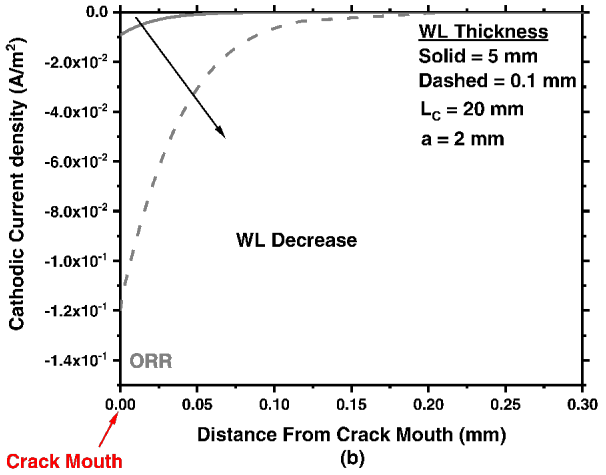
- This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.


Cathodic Current density (A/m^2)
0.0
-5.0x10^{-2}
-1.0x10^{-1}
-1.5x10^{-1}
-2.0x10^{-1}
-2.5x10^{-1}
-3.0x10^{-1}
ORR
WL Decrease
HER
WL Thickness
Solid = 5 mm
Dashed = 0.1 mm
L_C = 20 mm
a = 2 mm
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
Distance From Crack Mouth (mm)
(a)
Crack Mouth
Crack Tip


Cathodic Current density (A/m^2)
0.0
-2.0x10^{-2}
-4.0x10^{-2}
-6.0x10^{-2}
-8.0x10^{-2}
-1.0x10^{-1}
-1.2x10^{-1}
-1.4x10^{-1}
WL Thickness
Solid = 5 mm
Dashed = 0.1 mm
L_C = 20 mm
a = 2 mm
WL Decrease
ORR
0.00 0.05 0.10 0.15 0.20 0.25 0.30
Distance From Crack Mouth (mm)
(b)
Crack Mouth

Time course of [MCl_x], $i_{c,loc}$, and pH

L_c = 20 mm
WL = 5 mm
a = 2 mm