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Sandia National Laboratories

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Towards Understanding the Controlling Nature of Crack Tip Chemistry on the Stress Corrosion Cracking of Austenitic Stainless Steels

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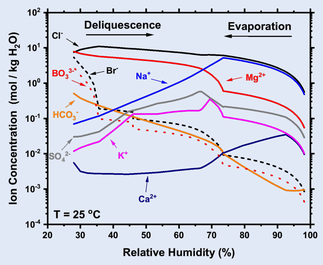
$MgCl_2$ Brine Dominant at Low Relative Humidities

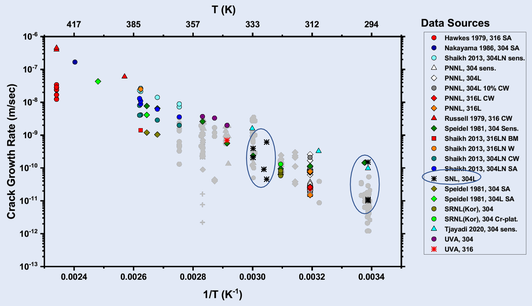


- For Spent Nuclear Fuel canisters, as radioactive materials decay, a decrease in temperature and increase in relative humidity occurs
- In a sea salt environment, concentrated chlorides ($MgCl_2$ dominant < 75 % RH) will be the first deliquesced salts on the canister surface [1]

- Goal: Explore the similitude of stress corrosion cracking of SS304 in concentrated chloride environments

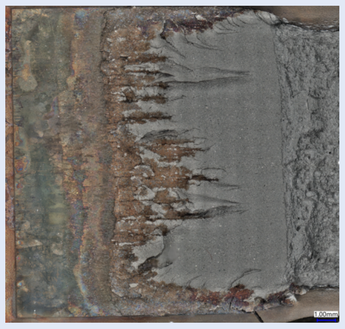
Austenitic SS304L Exhibits Solution-Dependent Fracture Morphology

- SS304L, under the same loading protocol and maximum stress intensity, exposed to saturated $MgCl_2$ and NaCl
- SNL measured crack growth rates within literature scatter [2]



- Solution composition, material lot, direction, and temperature influence fracture morphology

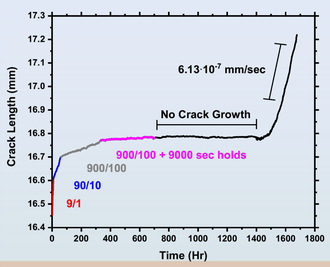
5 M $MgCl_2$ 25 ˚C

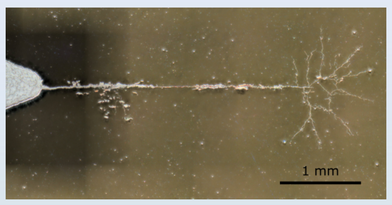


5 M $MgCl_2$ 55 ˚C

5 M NaCl 60 ˚C

- Significant crack branching in $MgCl_2$ solutions at 55 ˚C may influence mechanical driving force and cracking kinetics

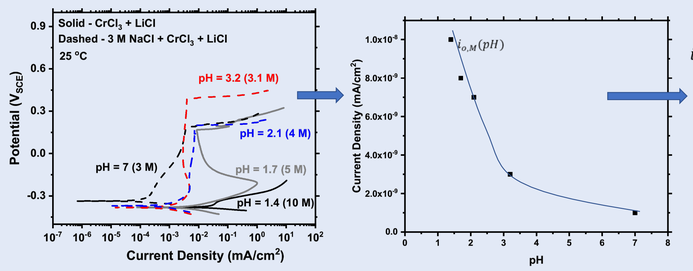




Could differences in crack tip electrochemistry be causing the differences in cracking morphology?

Creation of Reactive Transport Model to Predict Crack Tip Electrochemistry

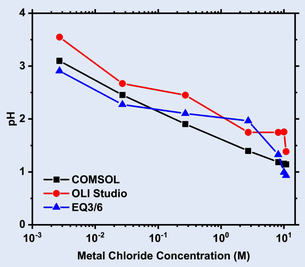
Measurement of crack tip boundary conditions in deaerated solutions as a function of pH



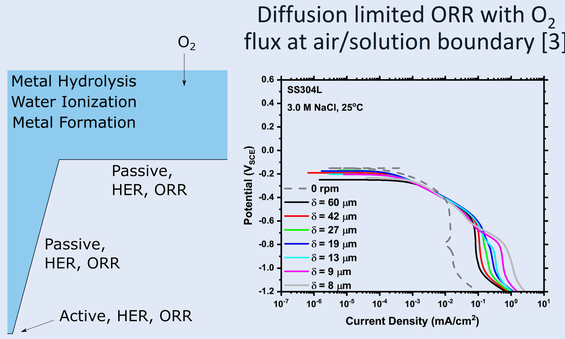
$$i_{act,M}(pH) = i_{o,M}(\mathrm{pH}) \cdot 10^{\frac{\eta_M}{A_M}}$$

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

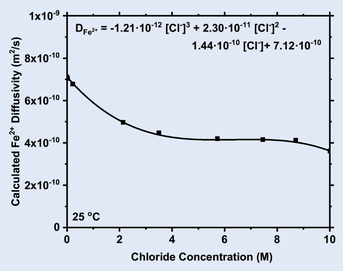
COMSOL pH calculated with $[H^+]$ agrees with activity-based pH



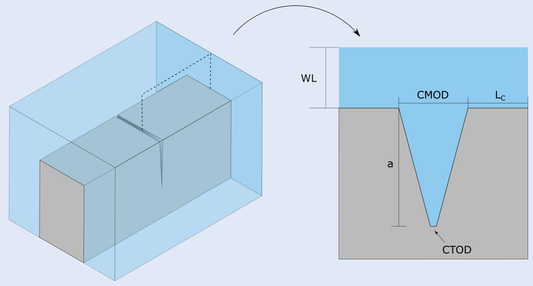
Diffusion limited ORR with O_2 flux at air/solution boundary [3]



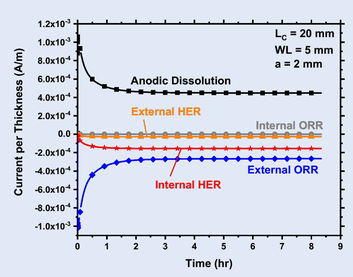
Incorporation of concentration dependent diffusivities



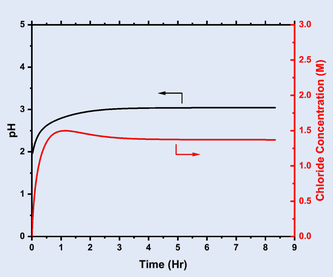
2D crack tip geometries based on stress intensity (load) [4]



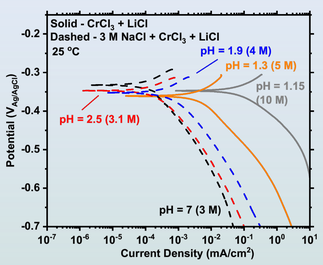
Local Cathodic Reactions Play Significant Role in Determining Modeled Crack Tip Electrochemistry

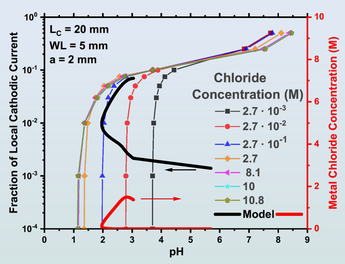


Parameters
- WL = 5 mm
- a = 2 mm
- L_c = 20 mm
- [NaCl] = 3 M
- T = 25 ˚C

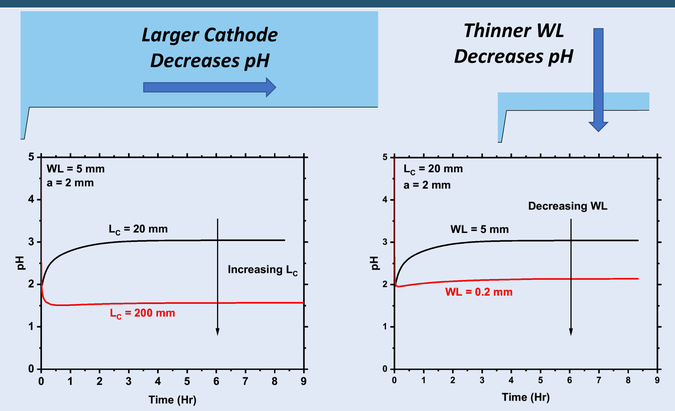


- Majority of cathodic current is external ORR (strong coupling to ext. surface)
- ~10% of total cathodic current is HER local to inside the crack which causes a significant pH rise



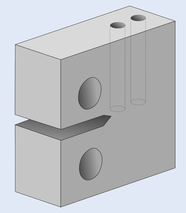


Model Indicates Electrochemical Similitude is Often not Up-held

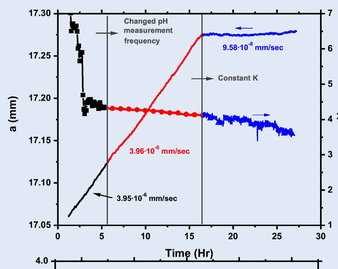


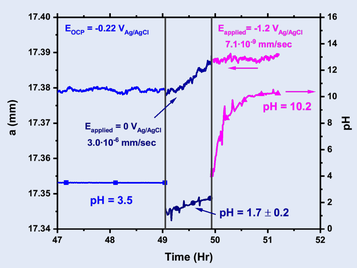
- Increasing cathode length and decreasing WL thickness decrease pH at the crack tip
- Electrochemical similitude not maintained
- Extrapolating crack growth from lab-scale specimens to field-relevant conditions could be problematic

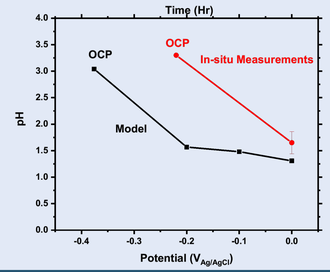
In-situ Measurements Confirm Polarizations Highly Influences Crack Tip Chemistry



- Holes do not significantly change mechanical driving force
- Confined dimensions do not significantly impact ohmic drop
- Measurement of in-situ crack tip pH and cracking kinetics with DCPD







- pH in SS304L exposed to 3M NaCl ~ 3.5 during constant K
- Anodic polarizations increase CGR and decrease pH
- Same trend present between model and experiments

Conclusions and Future Exploration of Electrochemical Similitude of SCC

- SS304L exhibits CGR within literature scatter however displays non-uniform crack front
- Newly created model to predict crack tip electrochemical conditions shows significant influence of internal HER
- Model indicates external environment (sample size and WL thickness) highly influence crack tip conditions
- *In-situ* crack tip measurements show same trend as model
- Future exploration of influence of sample geometry and exploration of NaCl vs. $MgCl_2$ with model and *in-situ* crack tip measurements

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[1] C.R. Bryan, et al., Physical and chemical properties of sea salt deliquescent brines as a function of temperature and relative humidity, Science of The Total Environment, (2022).
[2] C.R. Bryan, et al., FY21 Status Report: SNF Interim Storage Canister Corrosion and Surface Environment Investigations, in, Albuquerque, NM, (United States), 2021.
[3] R.M. Katona et al., Editors' Choice—Natural Convection Boundary Layer Thickness at Elevated Chloride Concentrations and Temperatures and the Effects on a Galvanic Couple, Journal of The Electrochemical Society, 168 (2021) 031512.
[4] H. Tada, P.C. Paris, G.R. Irwin, The Stress Analysis of Cracks Handbook, Third Edition, ASME Press, St. Louis, Missouri, 2000.

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