SAND2021-12101C

Fontana Corrosion Center AT THE OHIO STATE UNIVERSITY

THE OHIO STATE UNIVERSITY

Sandia National Laboratories

Chemical Factors Affecting RH-dependent Pit Morphology in Stainless Steels

J. Srinivasan, A. M. Parey, A. W. Knight, R. F. Schaller, J. S. Locke, E. J. Schindelholz

Fontana Corrosion Center, The Ohio State University

Materials Science and Engineering, Sandia National Laboratories

240th Electrochemical Society Meeting

October 10-14 2021

C02-0548 – Critical Factors in Localized Corrosion 9

This work is supported at the Ohio State University by Sandia National Laboratories (SNL). SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This document

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

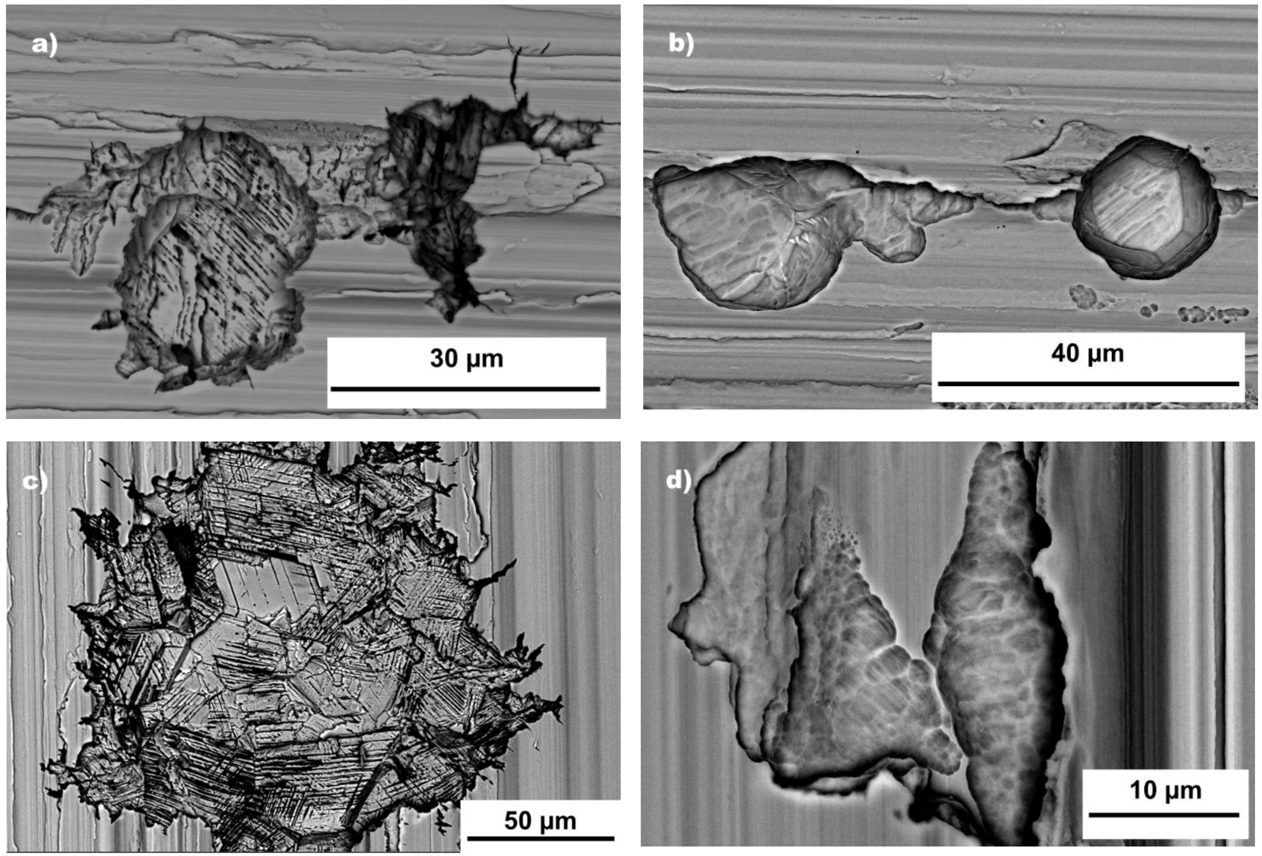
Pit morphology differences are RH-dependent

40% RH

76% RH

Atmospheric exposures

Full immersion exposures in eq. brines



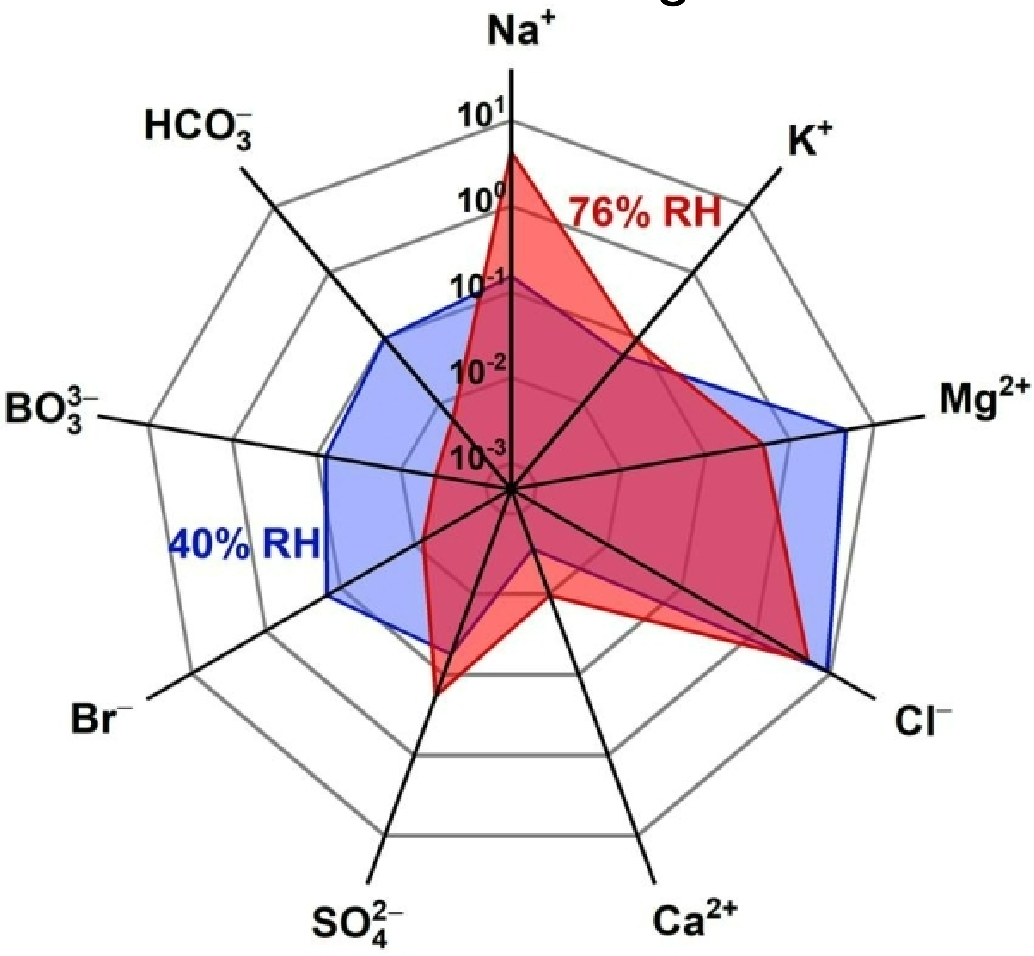
cross-hatched pits, microcracks, fissures

Ellipsoidal, faceted pits

[1]Weirich et al., J. Electrochem. Soc. 166 (2019).
[2]Srinivasan et al., J. Electrochem. Soc. 168 (2021).

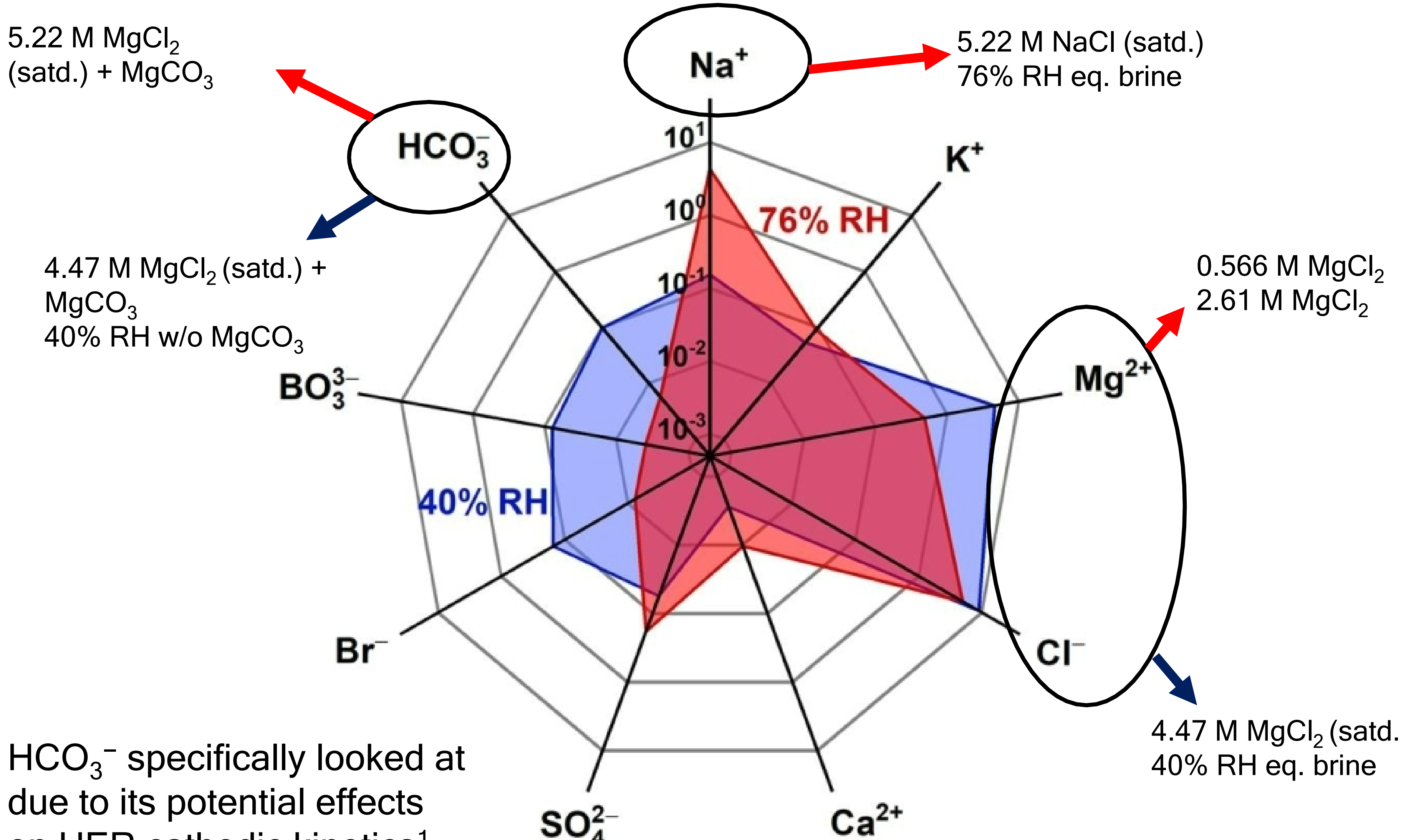
Differences in electrolyte chemistry may be responsible for morphology differences

High-RH – Na-Cl-rich



Low-RH – Mg-Cl-rich

Full immersion in relevant electrolytes to evaluate chemical causes



HCO_3^- specifically looked at due to its potential effects on HER cathodic kinetics[1]

[1]Katona et al., Corr. Sci. 177 (2020).

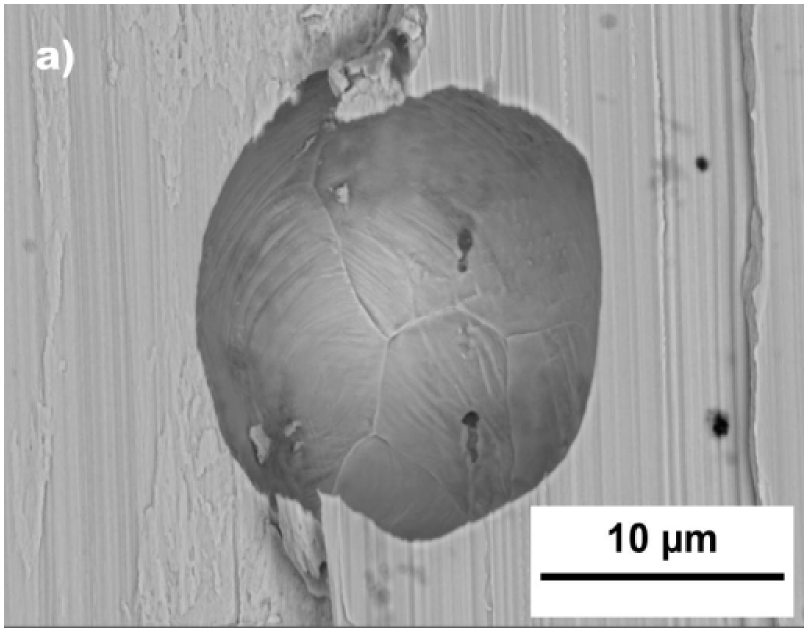
Full immersion experiments to evaluate specific chemical causes

Solution	pH	$[Cl^-]$/M	$[HCO_3^-]$/M
76% RH equivalent sea salt brine	7.61	5.009	5.73×10^{-3}
5.22 M NaCl	5.187	5.22	5.09×10^{-6}
5.22 M NaCl + added $MgCO_3$	8.61	5.22	7.29×10^{-3}

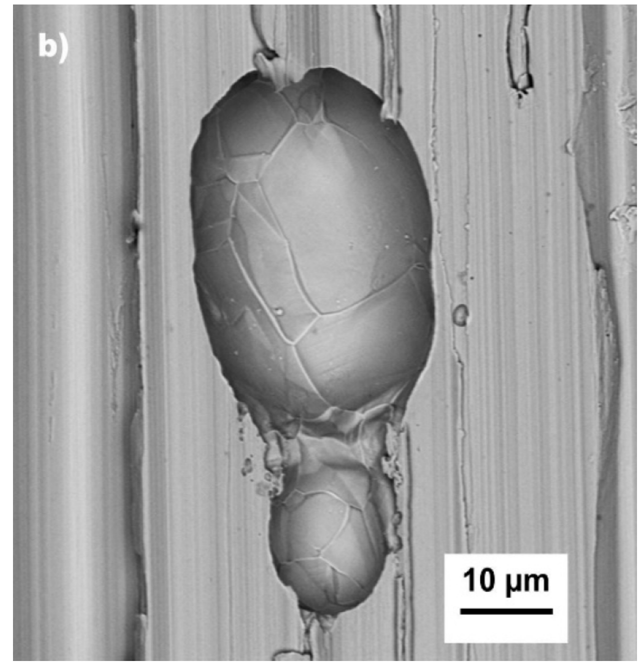
Solution	pH	$[Cl^-]$/M	$[HCO_3^-]$/M
40% RH equivalent sea salt brine	6.85	9.003	9.79×10^{-2}
40% RH sea salt brine without $MgCO_3$ addition	3.39	9.003	2.82×10^{-5}
0.566 M $MgCl_2$	5.42	1.132	1.37×10^{-5}
2.61 M $MgCl_2$	4.90	5.22	1.60×10^{-5}
4.47 M $MgCl_2$	3.51	8.94	3.08×10^{-5}
4.47 M $MgCl_2$ + added $MgCO_3$	7.07	8.94	4.55×10^{-2}

Na-Cl-rich brines show ellipsoidal pits

76% RH-eq. brine

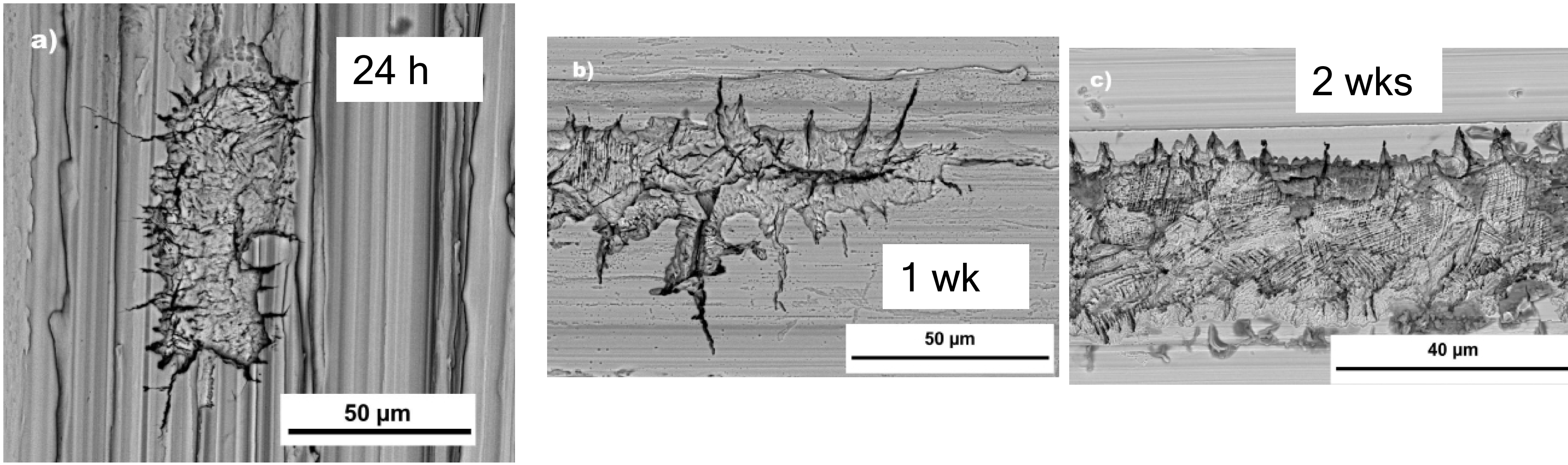


5.22 M NaCl



Ellipsoidal pits, faceting on base

40% RH eq. brines show cross-hatching, micro-crack-like features

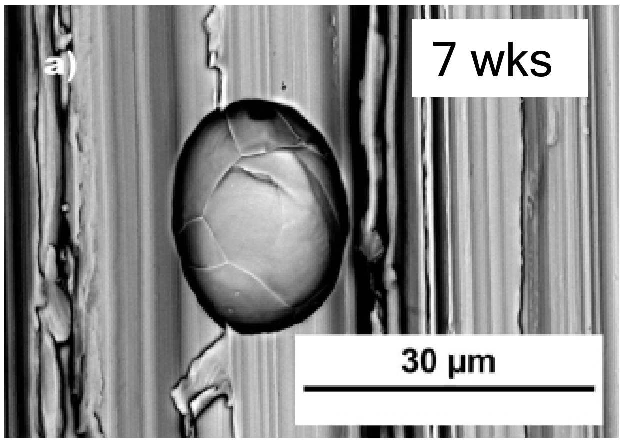


Cross-hatching consistent across different exposure times

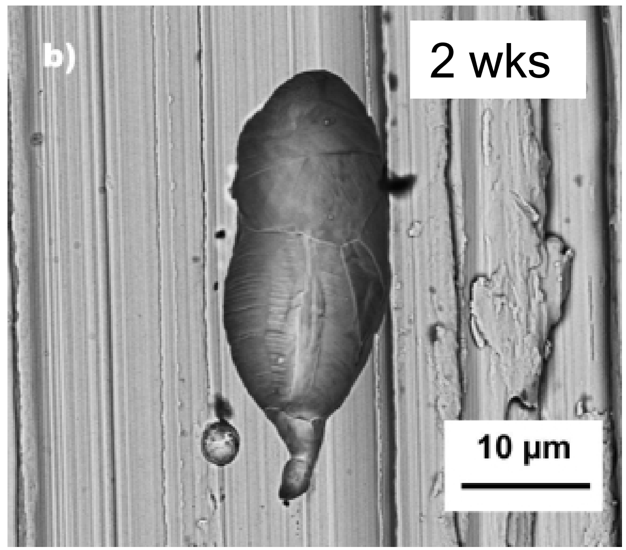
Microcrack-like features may be consumed by pit growth for longer exposures

$[MgCl_2]$ influences pit morphology

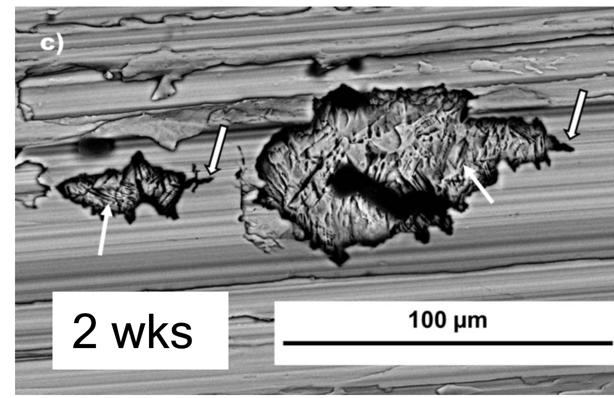
0.566 M $MgCl_2$



2.61 M $MgCl_2$



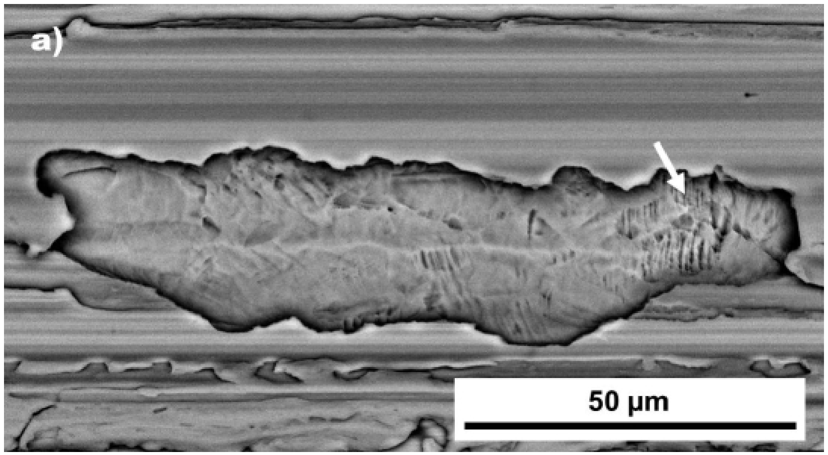
4.47 M $MgCl_2$ (satd.)



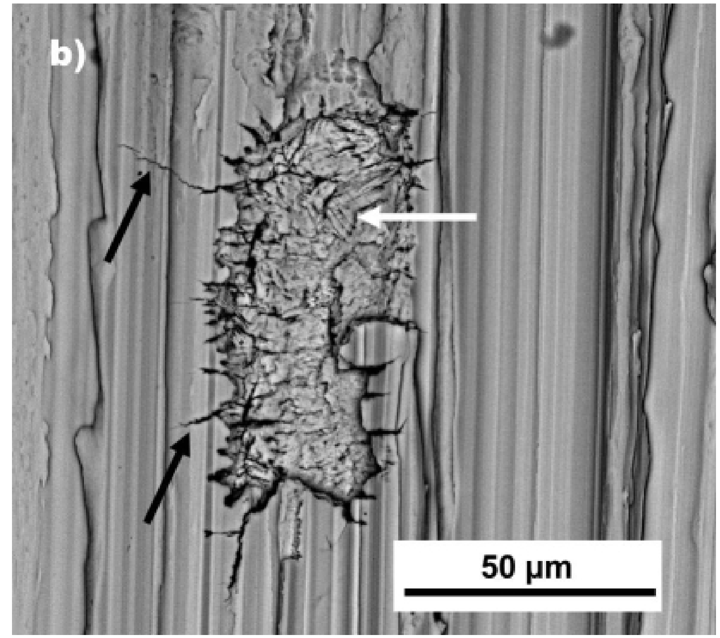
Concentrations < saturation show ellipsoidal pits

Saturated $MgCl_2$ shows cross-hatching, no clearly discernible microcrack-like features

Microcracking seen very early in 40% RH-eq. brine



4.47 M $MgCl_2$



40% RH

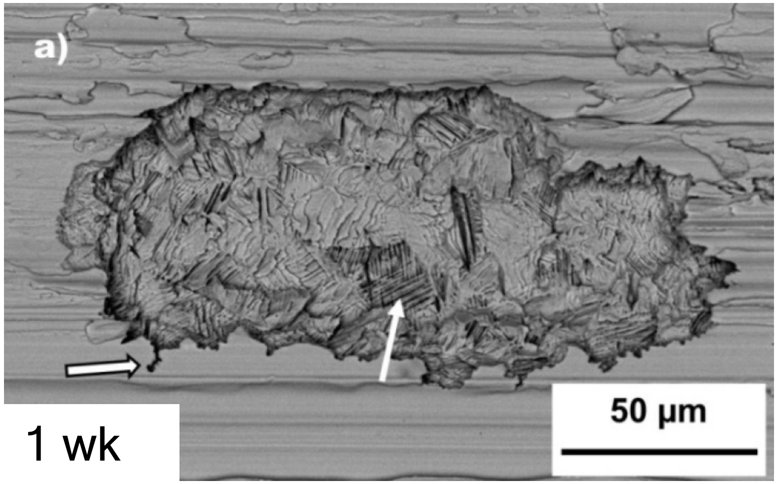
a) Cross-hatching observed in unary sat. $MgCl_2$ solutions, no micro-cracks however

b) Micro-cracks originate even at very short exposure times in 40% RH-eq. brine

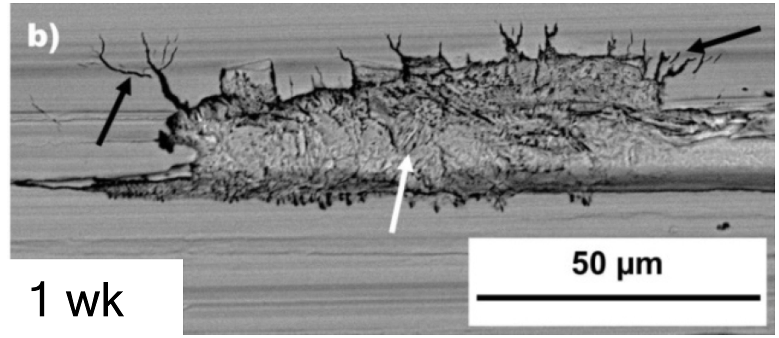
Presence of sat. $MgCl_2$ related to cross-hatching but what leads to micro-cracking?

Solution	$[Cl^-]$/M	**$[HCO_3^-]$ /M**
40% RH equivalent sea salt brine	9.003	**9.79×10^{-2}**
40% RH sea salt brine without $MgCO_3$ addition	9.003	**2.82×10^{-5}**
4.47 M $MgCl_2$	8.94	**3.08×10^{-5}**
4.47 M $MgCl_2$ + added $MgCO_3$	8.94	**4.55×10^{-2}**

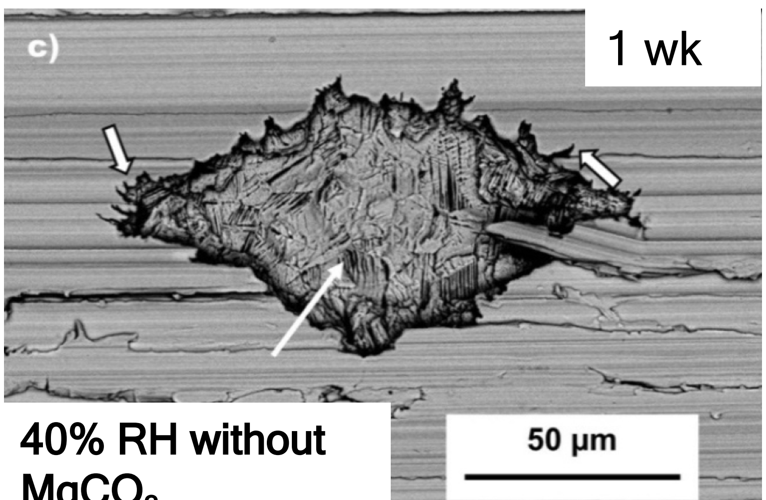
Microcracking may occur due to [HCO_3^-]



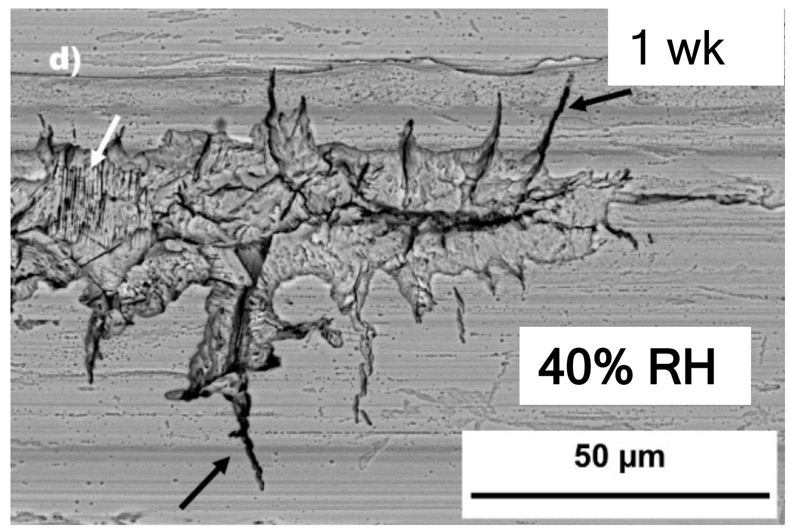
4.47 M $MgCl_2$



4.47 M $MgCl_2$ + added $MgCO_3$

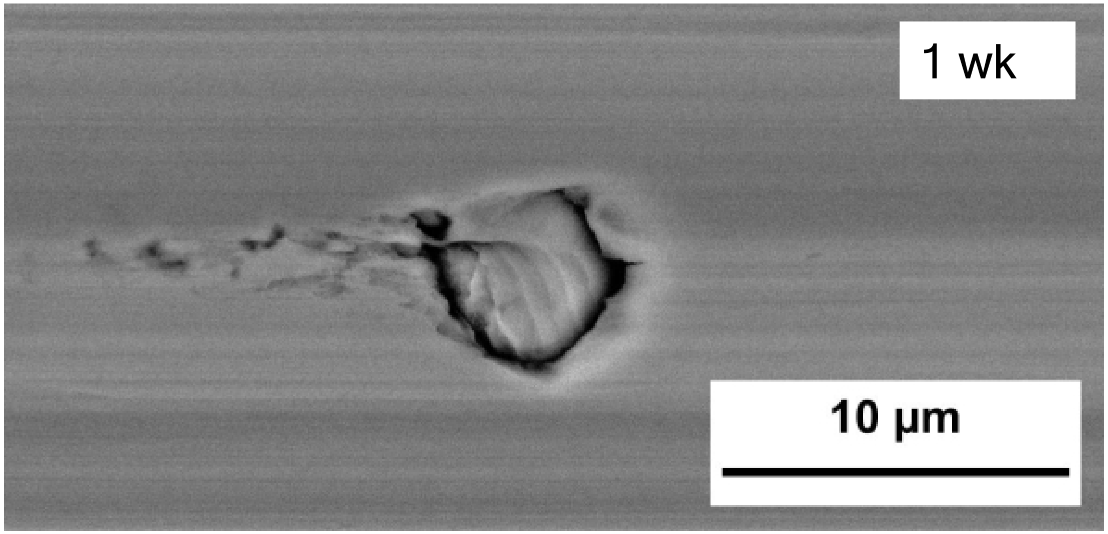


40% RH without $MgCO_3$

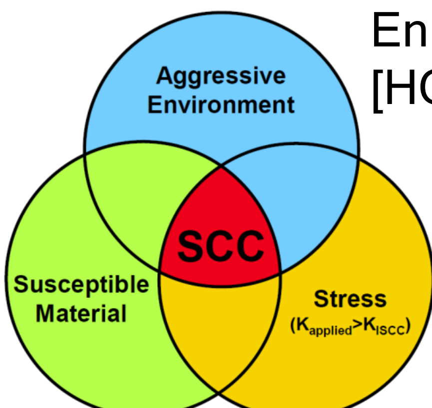


While cross-hatching may be due to sat. $MgCl_2$, HCO_3^- may affect micro-crack occurence

But HCO_3^- on its own does not produce microcracks, may need cross-hatching



Saturated NaCl + $MgCO_3$ produces no microcracks



Enhanced HER due to higher [HCO_3^-]

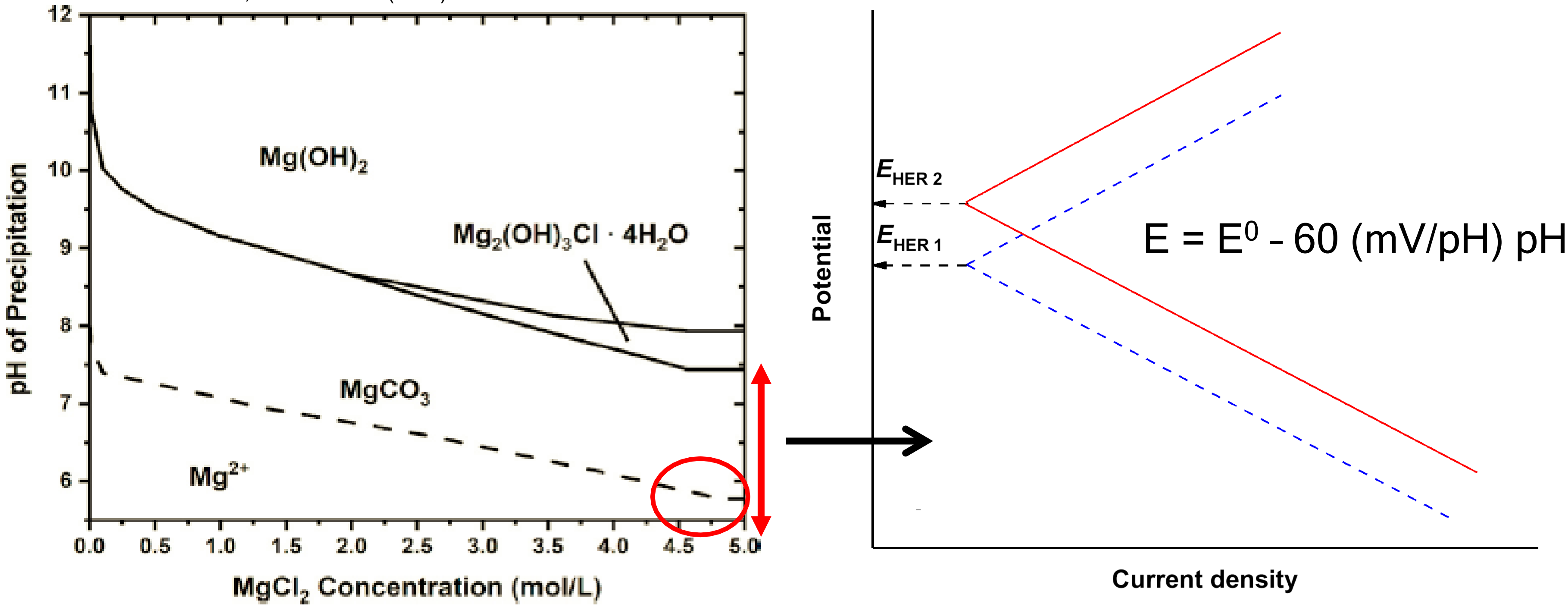
Residual stress, cross-hatching stress concentrator

Strain-induced martensite from surface grinding

Weirich et al. JECS (2019).

Higher [HCO_3^-] may accelerate HER kinetics by precipitate buffering

[1]Katona et al., Corr. Sci. 177 (2020).



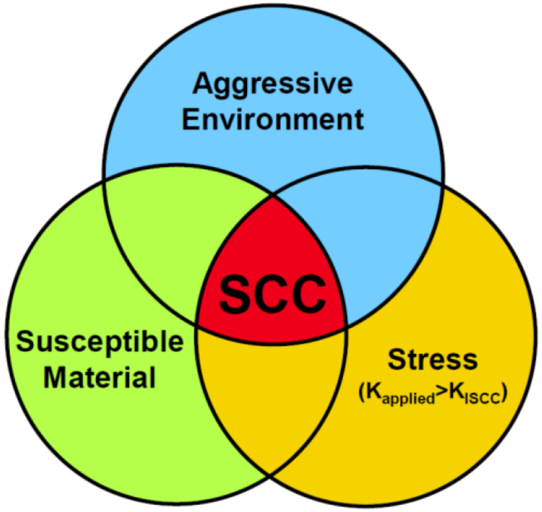
Higher [HCO_3^-] may cause carbonate species to precipitate (ppt), buffering surface to lower pH

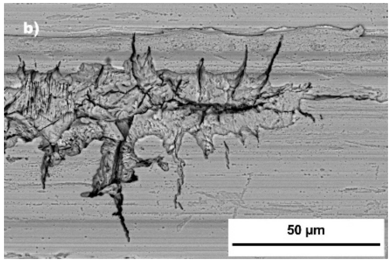
Lower near-surface pH raises HER Nernst potential, enhances kinetics

Exact Mg-species that precipitates is kinetics-dependent – $MgCO_3$ precipitation kinetically hindered[2,3]

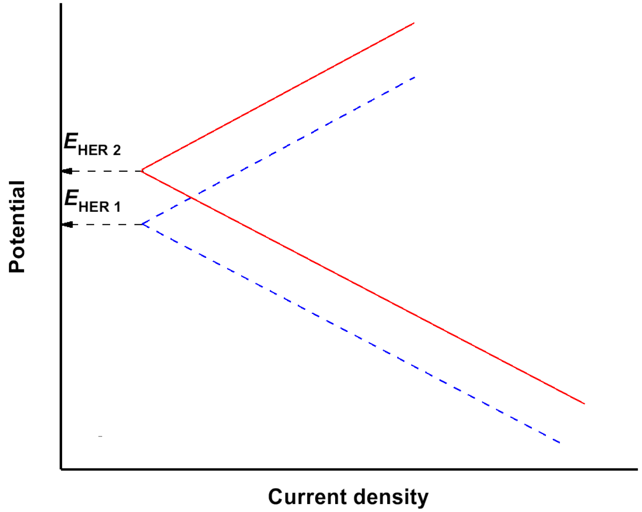
[2]Katona et al., Echem. Comm. 118 (2020).
[3]Swanson et al., PCCP 16(42) (2014).

Microcracking may occur via HEAC at low RH

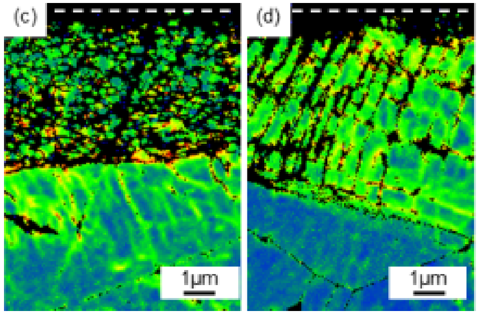




Stress concentration



Accelerated HER



Weirich et al. JECS (2019).

Sufficient residual stress, SI martensite

Key takeaway points from current work

- Ellipsoidal pits observed in NaCl-rich brines and $MgCl_2$ brines at concentrations less than saturation
- Cross-hatching observed in $MgCl_2$ brines at saturation
- Microcracking observed in saturated $MgCl_2$ brines with high $[HCO_3^-]$
- Micro-cracking may occur via HEAC due to enhanced HER as Mg-species ppt buffer near-surface pH to lower values

Currently open questions and future work

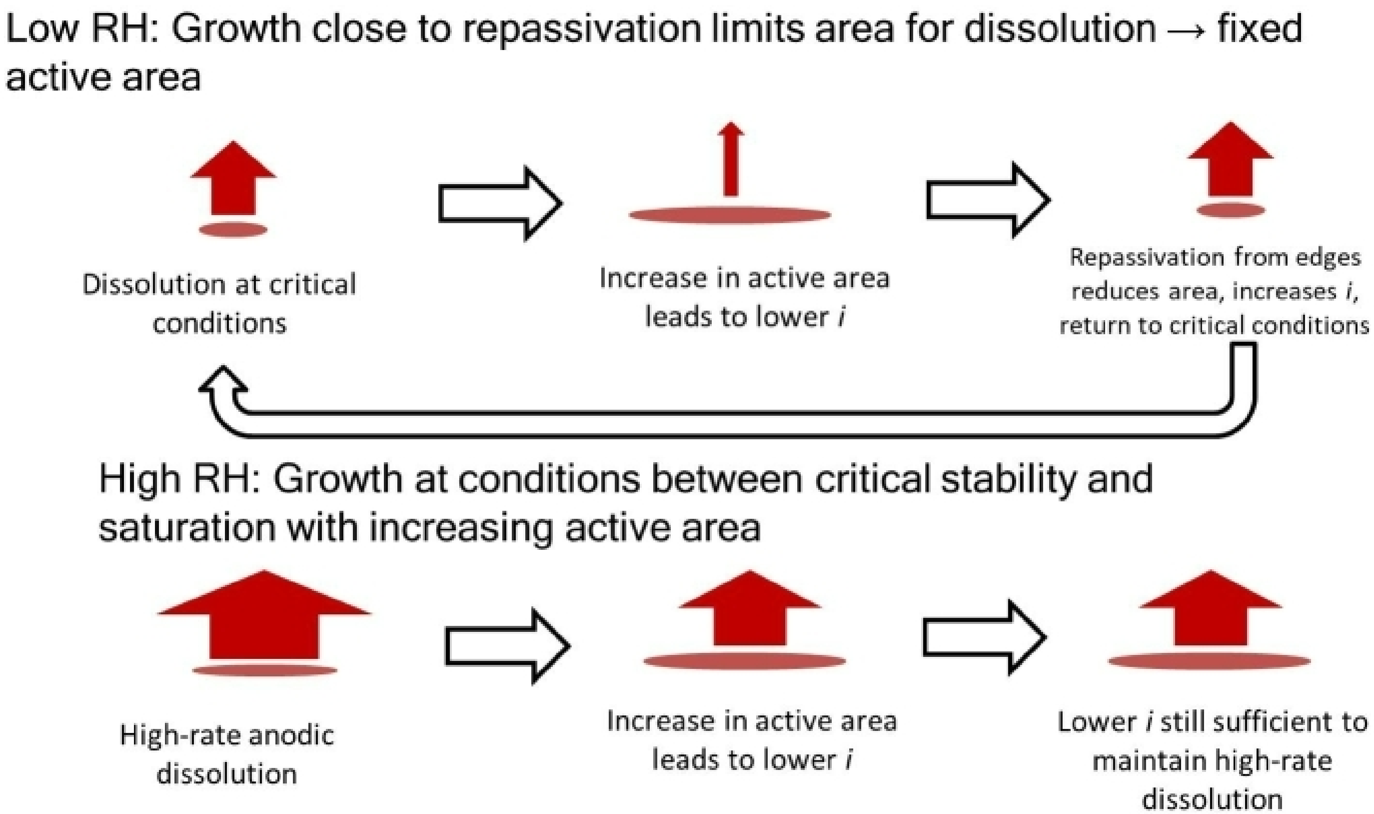
- *In situ* HER quantification to determine role of H_2 in determining morphology
  - Combined corrosion-permeation tests
- Removal of residual stress by annealing to evaluate effects on morphology
- Identity of precipitating Mg-species to better understand near-surface pH buffering effects

Acknowledgments

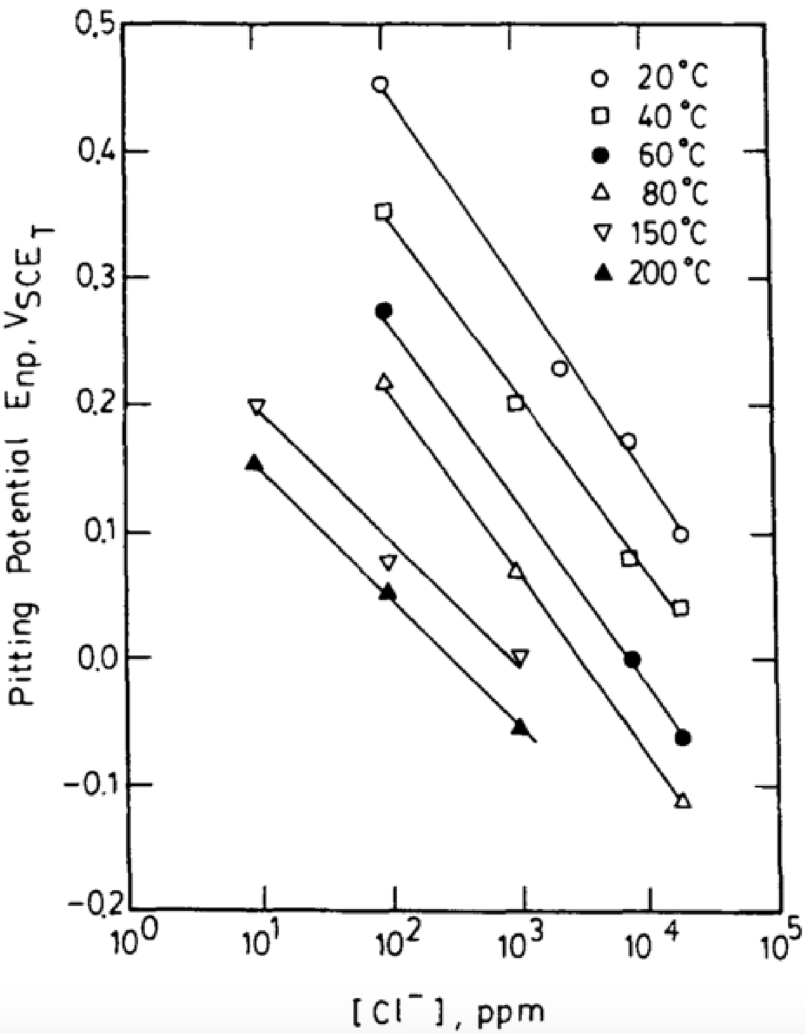
- This work is supported at the Ohio State University by Sandia National Laboratories (SNL). SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.
- The support of the Momental Foundation through the Mistletoe Research Fellowship 2020-2021 in purchasing equipment used in the study is acknowledged.

SUPPLEMENTAL

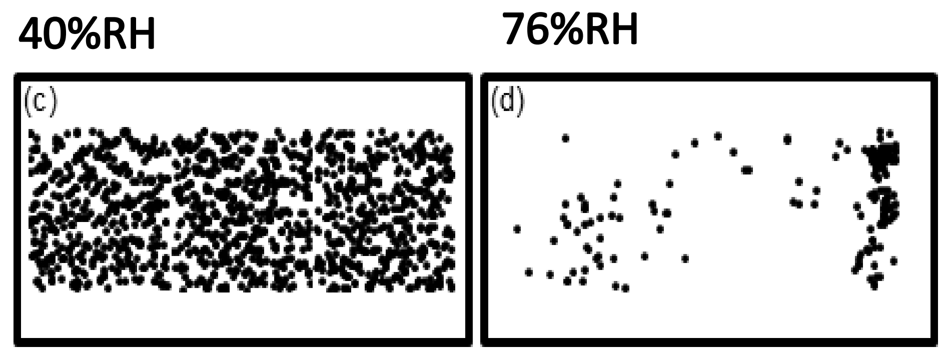
Cathodic current availability determines polarization levels, morphology



Easier to initiate pits at low RH due to high [Cl^-]



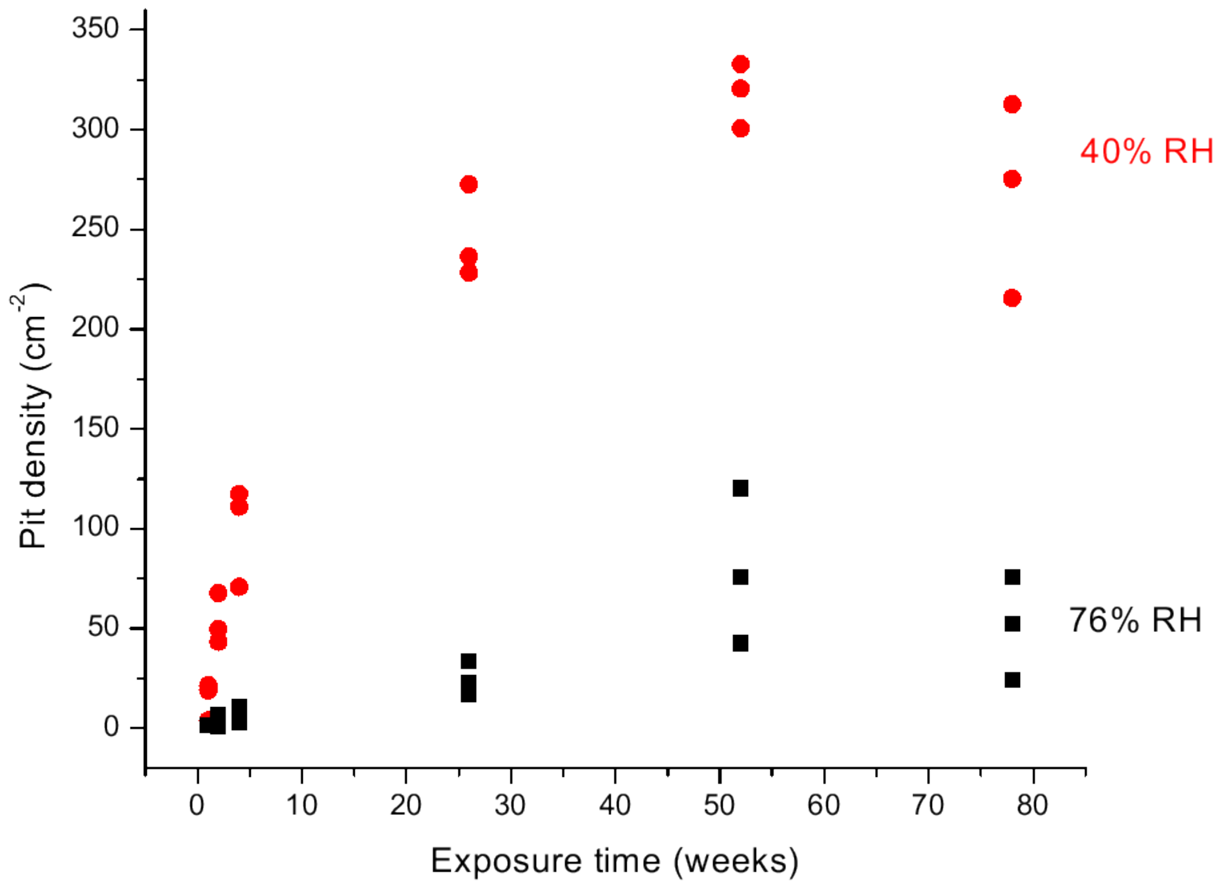
Wang et al., Corrosion (1988).



Low RH → High [Cl^-] multiple pits initiate

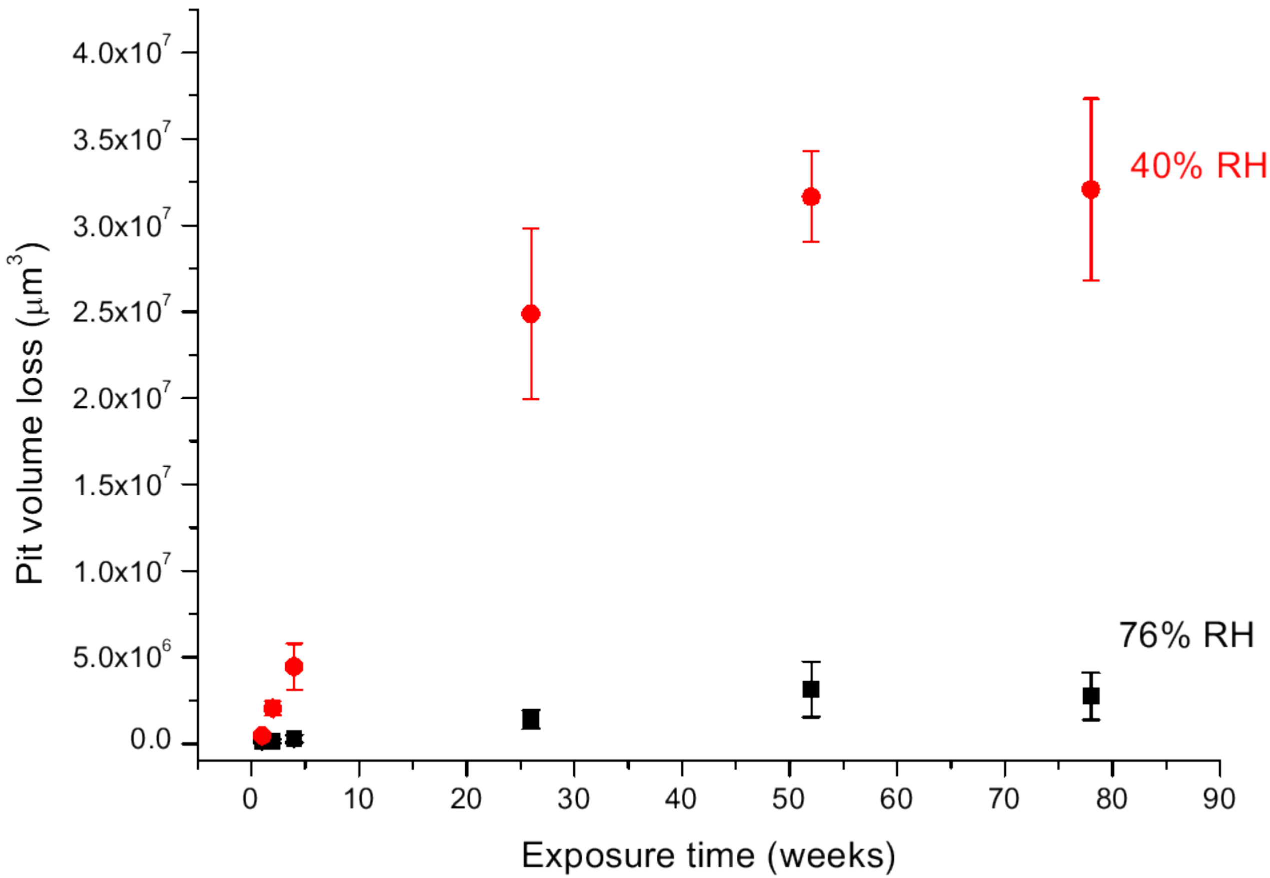
High RH → fewer pits initiate due to high E_{pit} required

RH shows differences in pit density



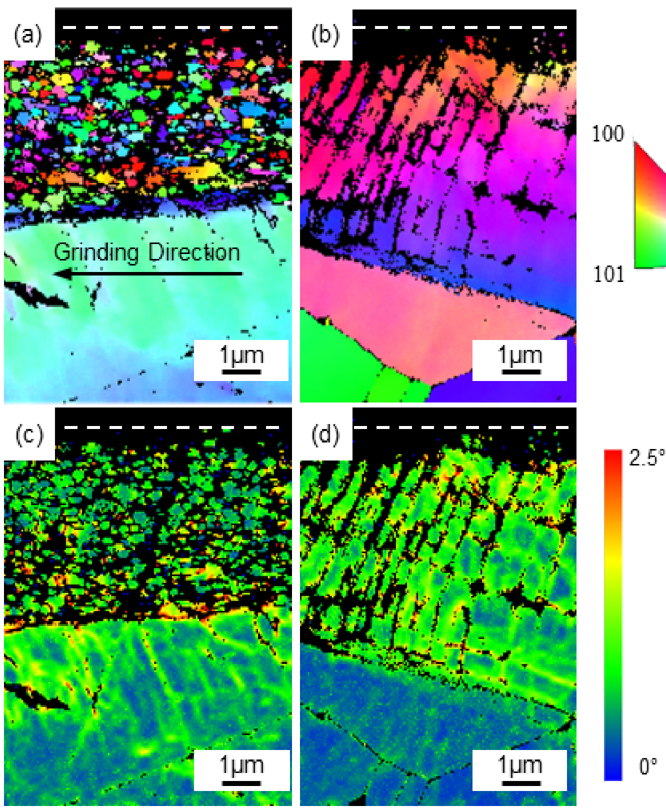
Pit density appears to plateau at long exposure time (>26 weeks)
Higher pit density (4-6x) at low RH than high RH

RH shows differences in corrosion damage volume



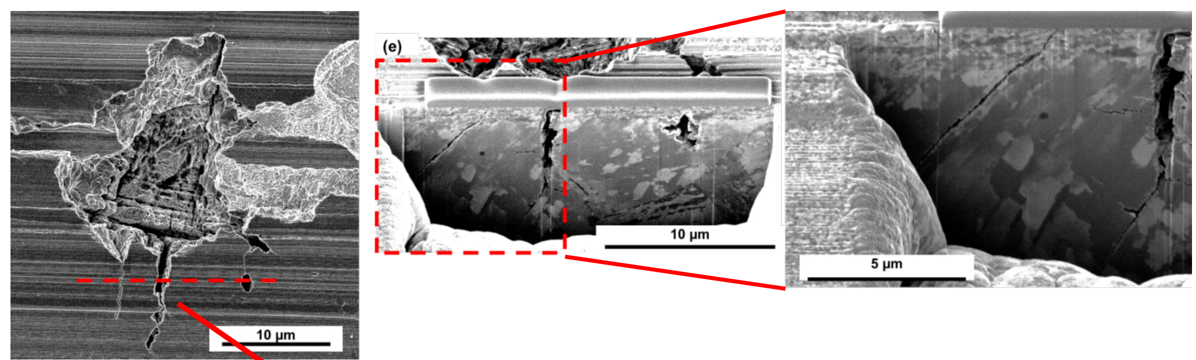
Pit volume loss appear to plateau at long exposure time (>26 weeks)
Corrosion damage at low RH much greater (≈10x) than at high RH

Deformation substructure may contribute to susceptible morphology



Deformation from grinding may create susceptible microstructure

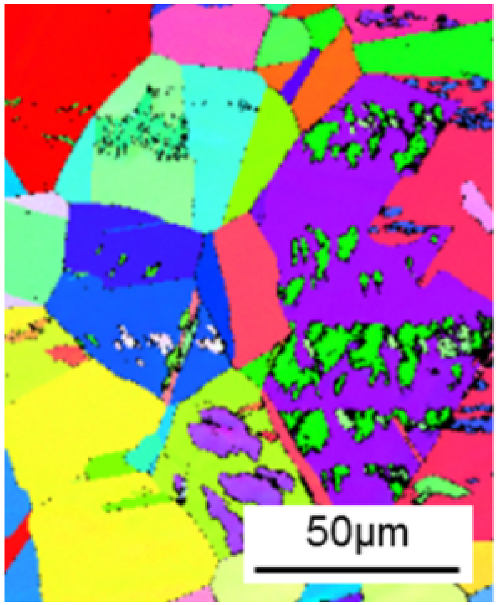
FIB-SEM of small pits show long cracks



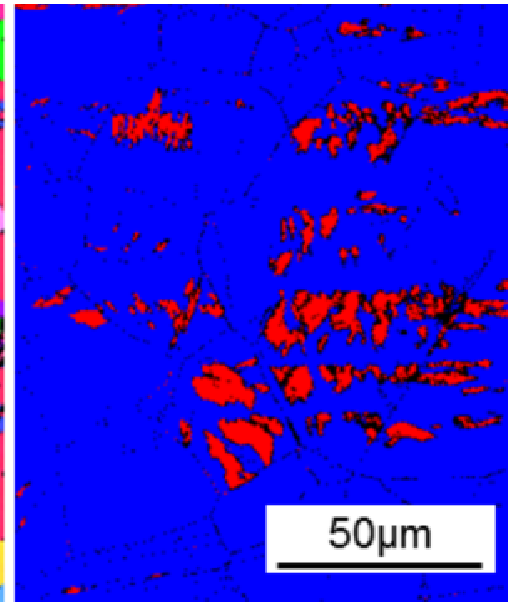
SCC initiator?

Weirich et al. JECS (2019).

Susceptible morphology does not match ferrite distribution



Grain structure map



Phase distribution map – red indicates ferrite/martensite