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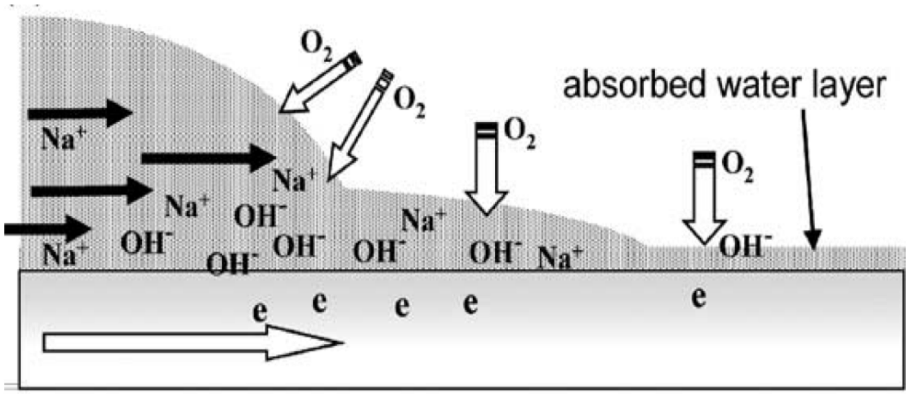

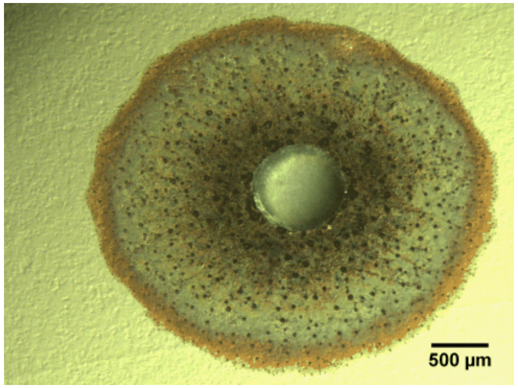

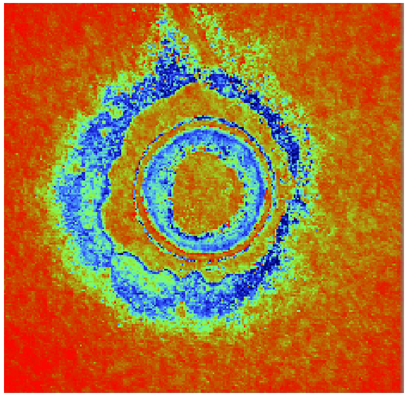

Beyond Evans Drop:

Electrolyte Evolution during Atmospheric Corrosion

Eric Schindelholz, Harry Moffat, Kevin Zavadil, Rob Sorensen

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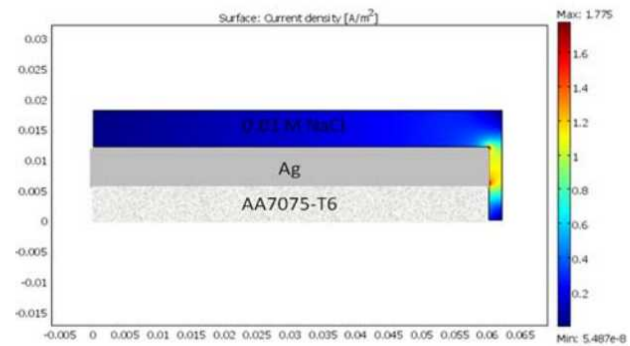
Electrochemical Modeling of Atmospheric Corrosion

- Electrolyte geometry can govern corrosion damage distributions and kinetics

- Limited experimental options for directly probing corrosion reactions hinders mechanistic insight

- Rich opportunity space for integrated computational and experimental approach



Shi, Kelly, 2013

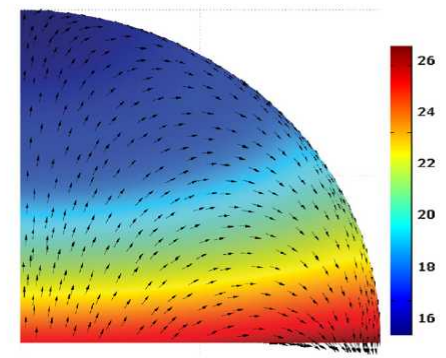


Fig. 10. ($C_{Zn^{2+}}/C^0_{Zn^{2+}}$) of zinc ions and arrow plot of current density vectors showing separation of metal surface into anodic and cathodic regions over time.

Cole et al., 2011

Evans Drop

Differential Aeration Cell

Diffusion limited O_2 reduction kinetics control attack rate and damage distribution

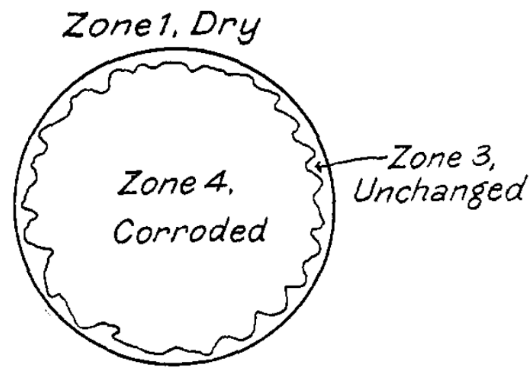
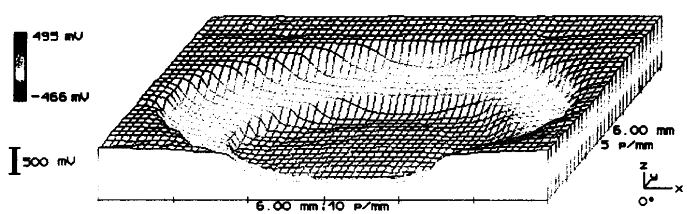
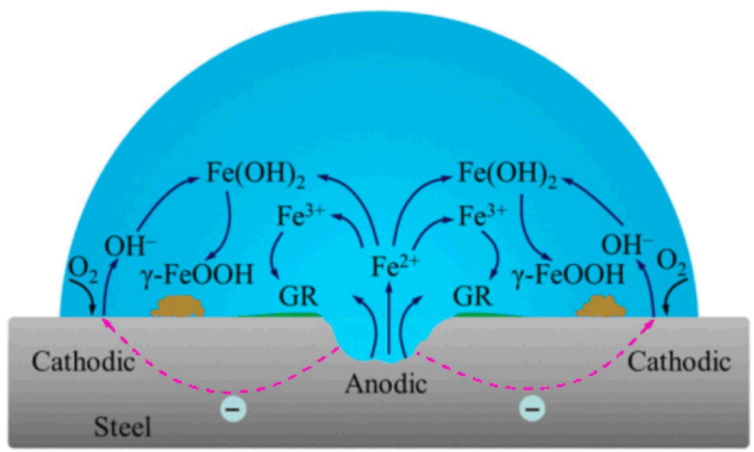


Figure 2—Effect of Drop of Distilled Water on Zinc

Evans, 1926



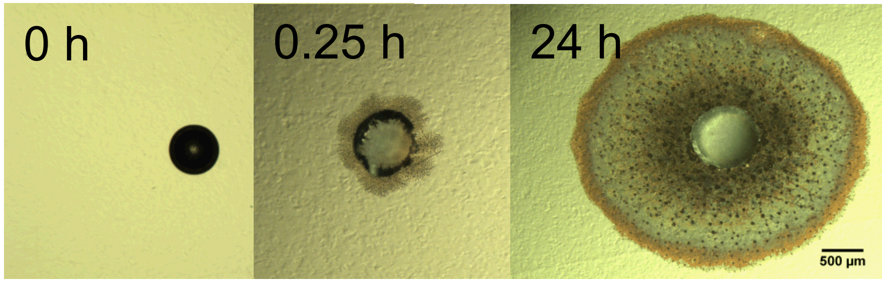
Chen and Mansfeld, 1997



Li and Hihara, 2012

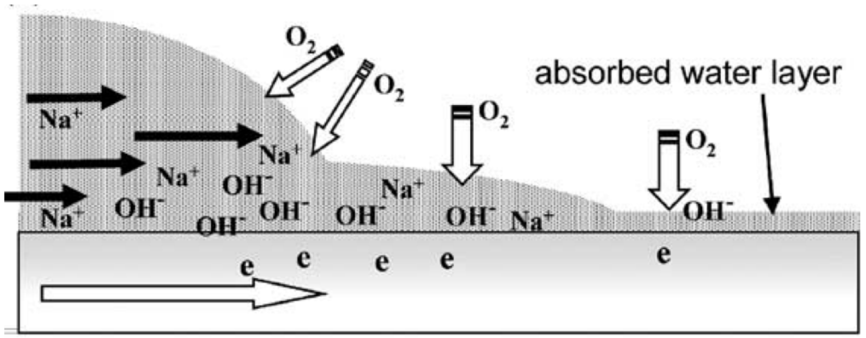
Divergence from Evans Drop

Secondary Spreading



<u>rate and extent</u>

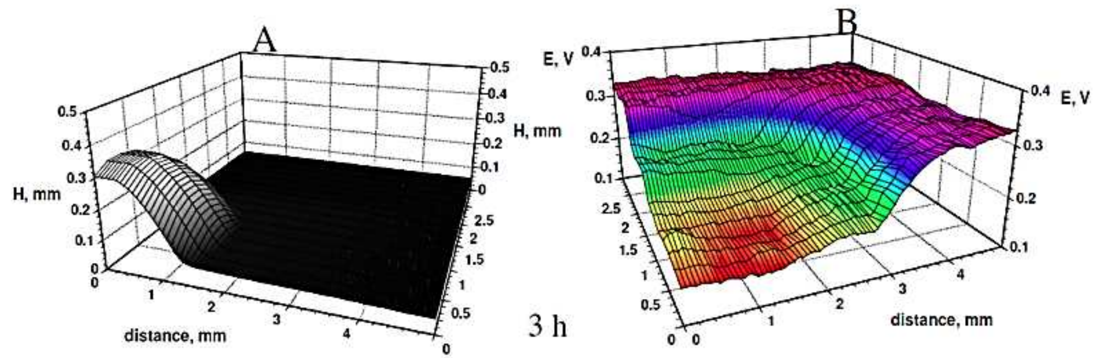
- initial drop size and chemistry
- substrate alloy
- environment (P_{CO2}, RH)



Tsuru et al, 2004

Impact of Secondary Spreading

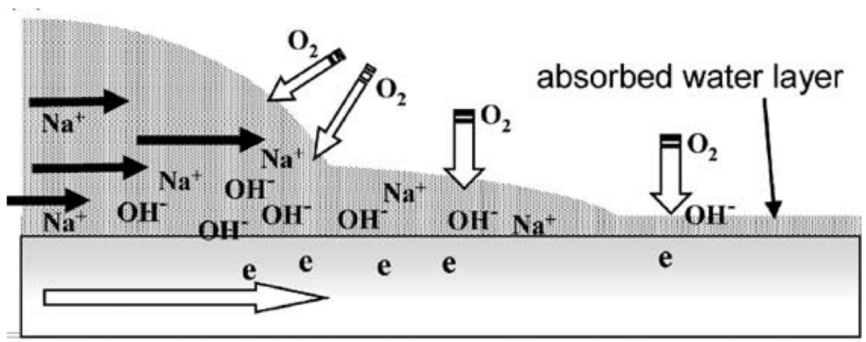
High potential areas in secondary spreading regions



Chen, 2005

$$I_{m,drop} = I_{O_2,drop} + I_{O_2,film}$$

To what extent do films contribute to cathodic current?



Study Framework

Driving Question

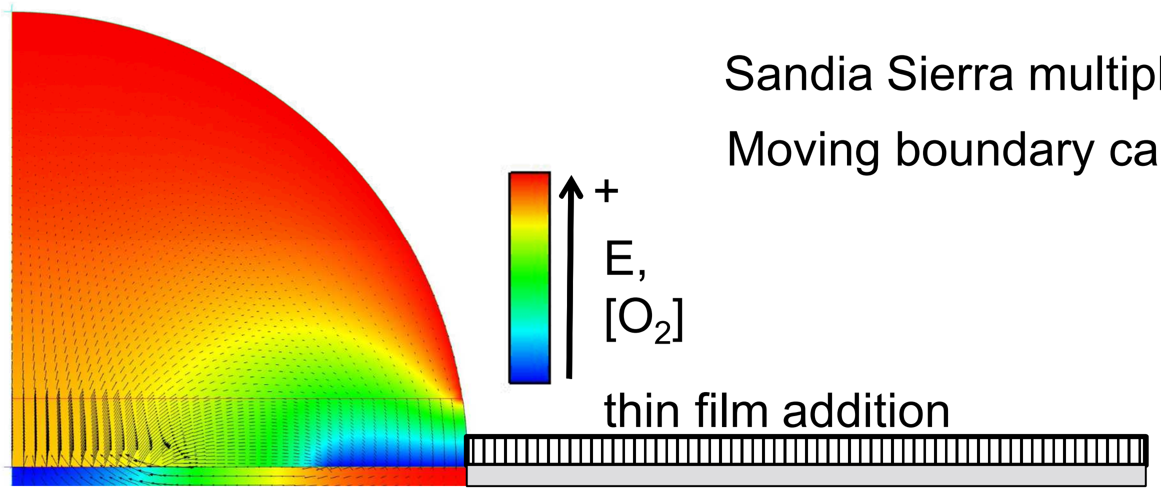
How do secondary films impact corrosion kinetics and damage distributions?

Approach

- Electrochemical continuum model of droplet-film system to predict influence of electrolyte geometry and physicochemical attributes on anode-cathode distributions

- Define physiochemical properties of film and realize influence of film and drop size on corrosion rates and damage distributions to inform model – Cu, NaCl

Droplet-Film Model: Construct



Sandia Sierra multiphysics architecture

Moving boundary capability – electrolyte evolution

Governing Equation- Nernst Planck

$$\frac{\partial c_i}{\partial t} = \nabla\left(-D_i \nabla c_i - z_i \frac{D_i F}{RT} \nabla \emptyset\right)$$

Boundary Conditions: Butler-Volmer

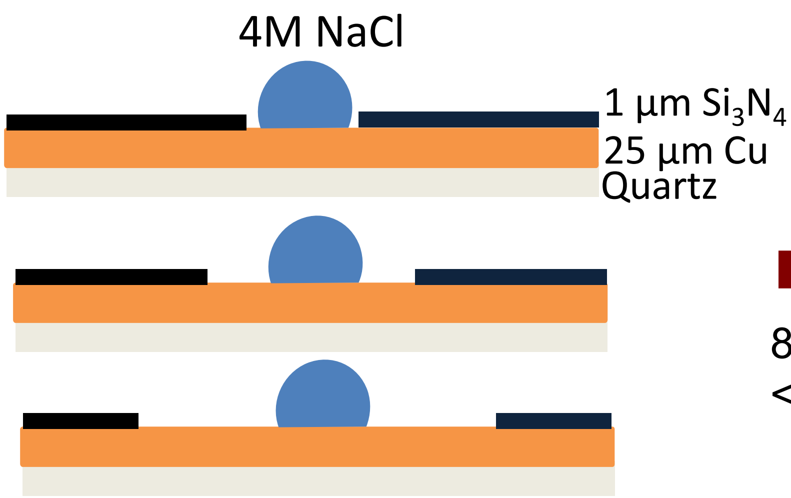
$O_2 + 2H_2O + 4e- \longrightarrow 4OH-$

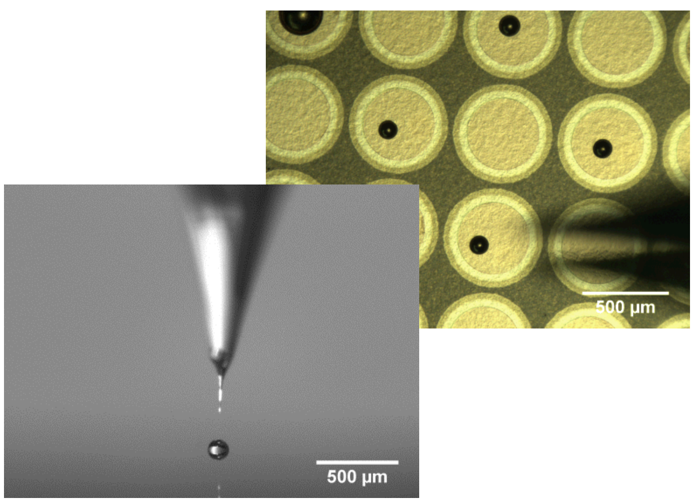
$$i_{O_2/OH} = -i_{\,o_{O_2/OH}} exp\left(\frac{-2\left(1+\alpha_{\frac{O2}{OH}}\right)F}{RT}\left(\Delta\emptyset_{O2/OH}\right)\right)$$

$M \longrightarrow M^{x+}$

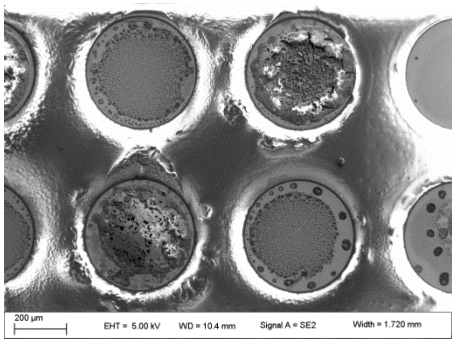
$$i_{M/M^{X+}} = -i_{\,oM/M^{X+}} exp\left(\frac{-x\left(1+\alpha_{\frac{M}{M^{X+}}}\right)F}{RT}\left(\Delta\emptyset_{M/M^{X+}}\right)\right)$$

Experimental: Restricted Cu Substrate

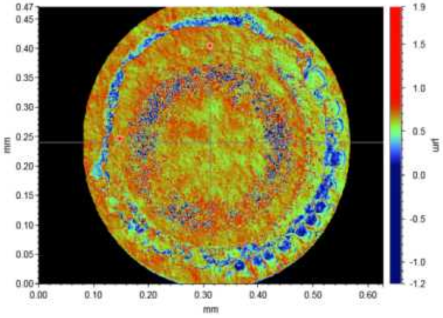




85% RH, 25 °C,
< 1 ppm CO_2



spreading chemistry and distribution

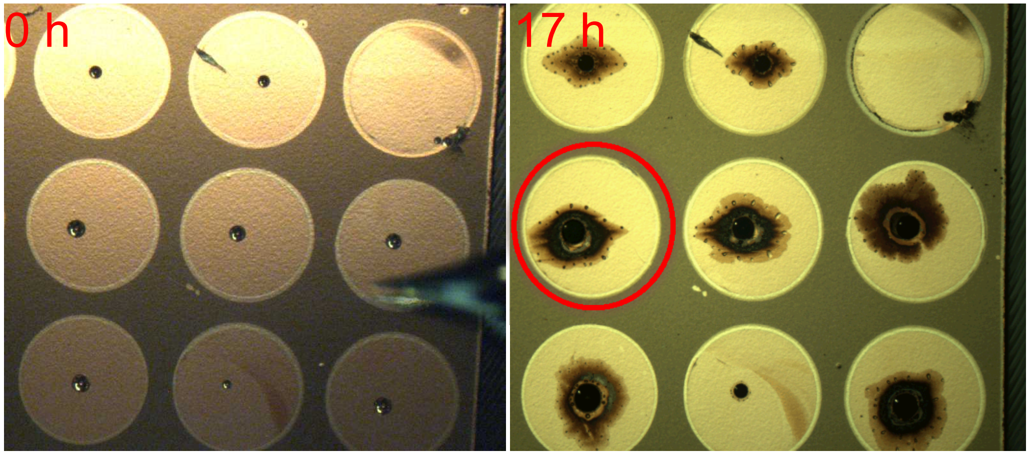


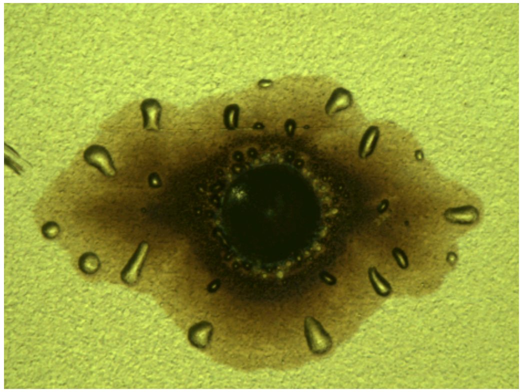
damage profiles

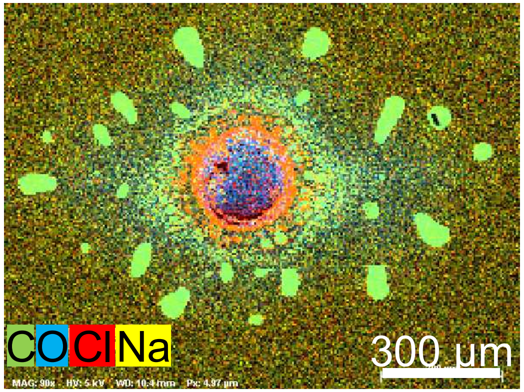
Unrestricted Spreading: Chemistry

2mm Windows

85% RH, 25 °C,
< 1 ppm CO_2

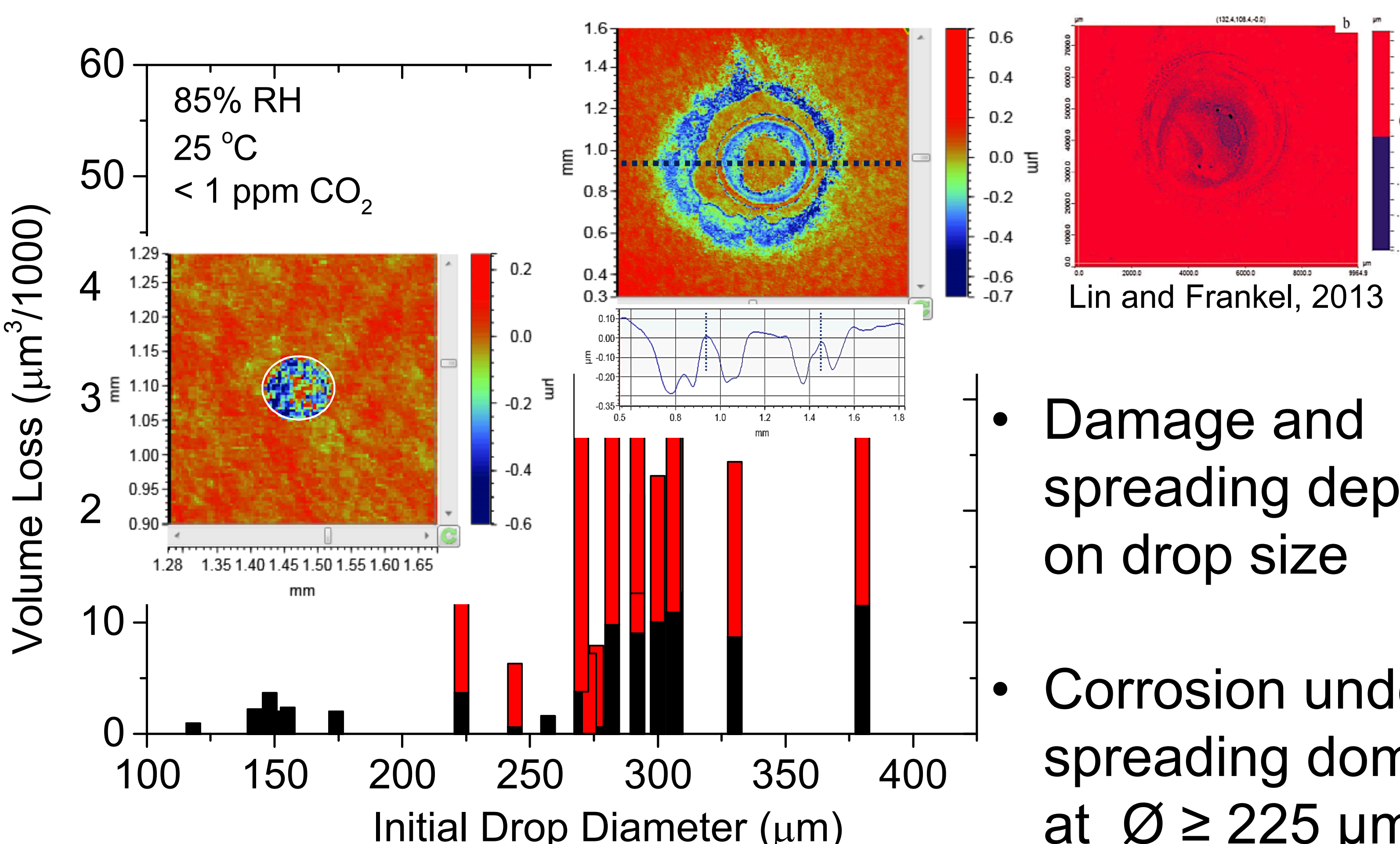






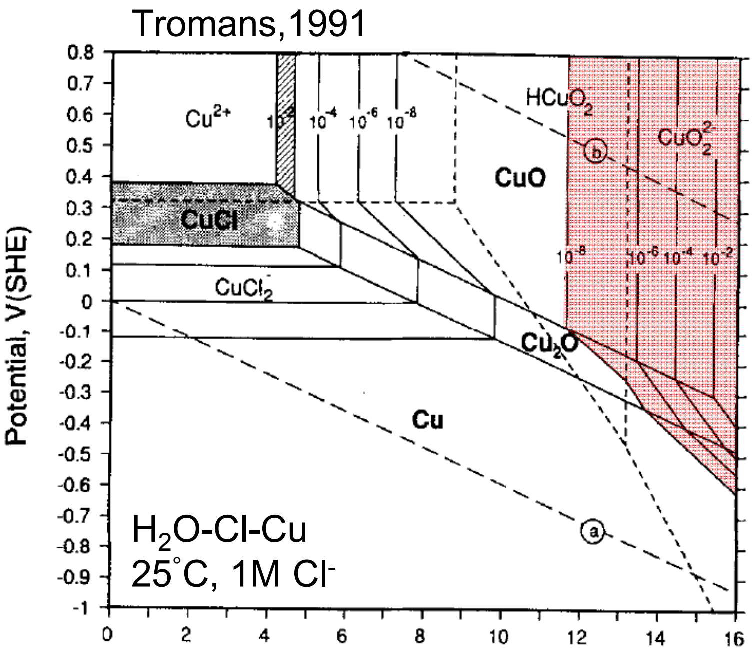
- Spreading chemistry in accordance with previous studies
- After 17 hours, can spread > 2x original drop radius

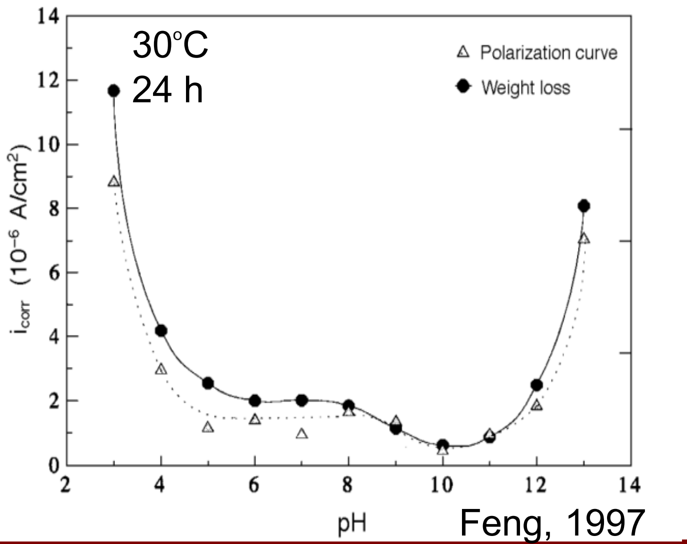
Unrestricted Spreading: Damage

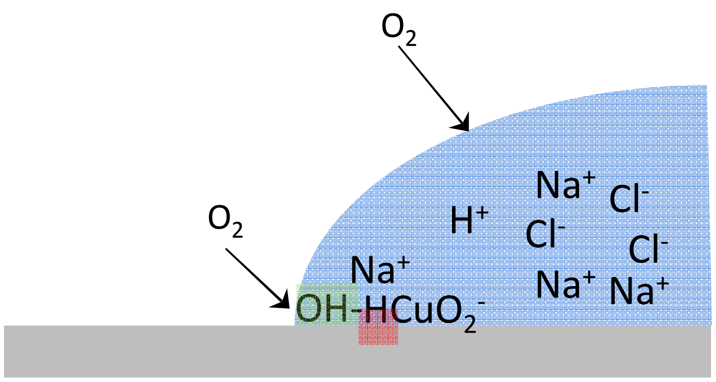


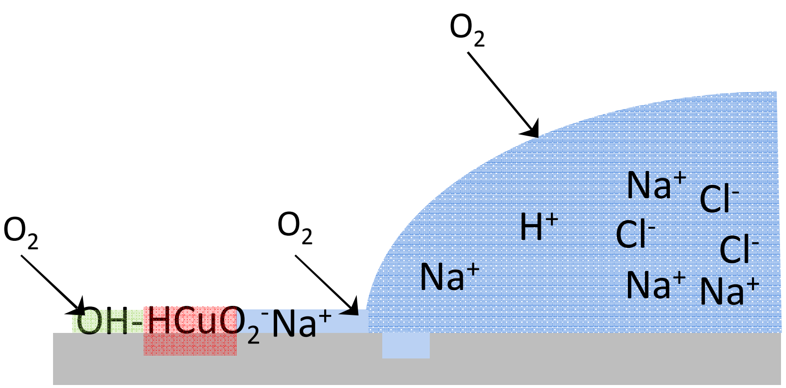
- Damage and spreading dependent on drop size
- Corrosion under spreading dominates at Ø ≥ 225 µm, inverse Evans

Inverse, Spreading Evans Drop

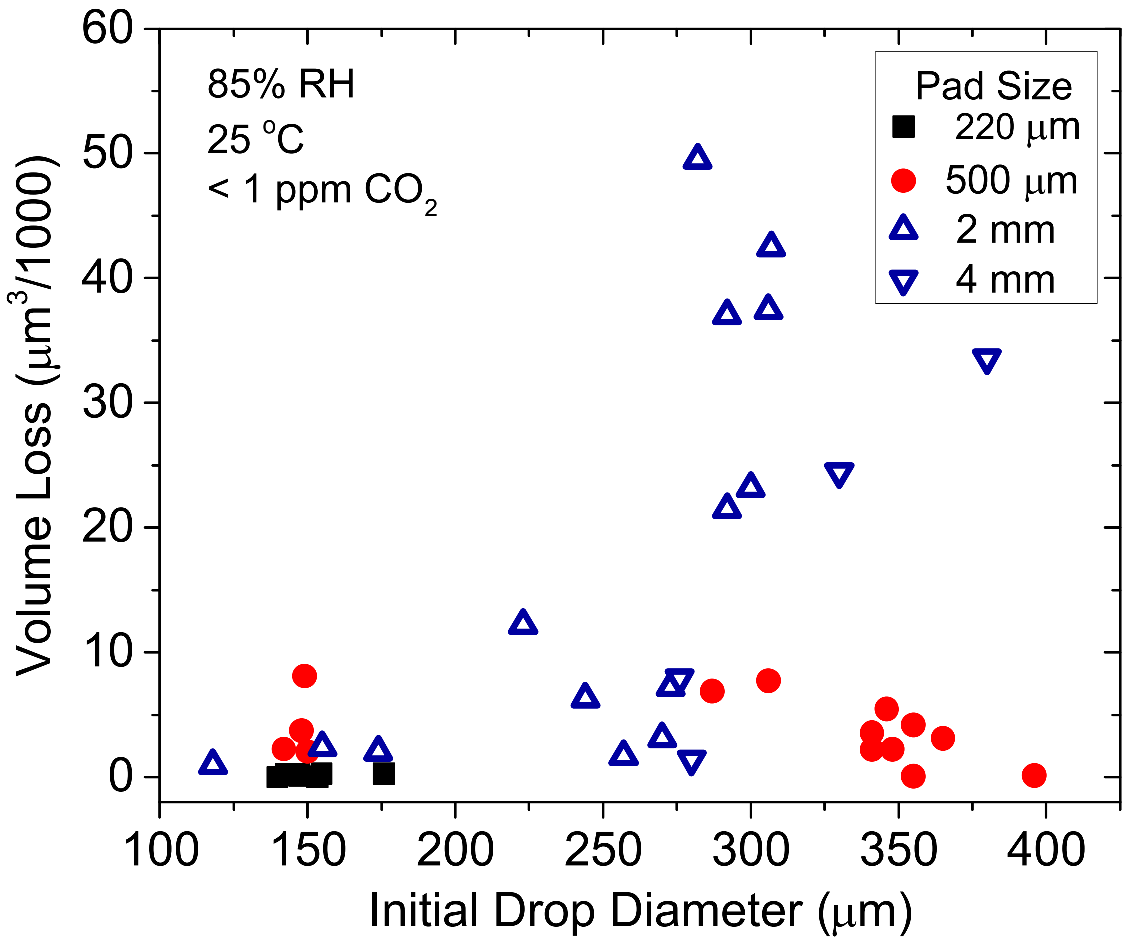








Restricted Substrates: Damage



- Corrosion loss strongly dependent on spreading S.S. at Ø ≥ 225 µm

Conclusions

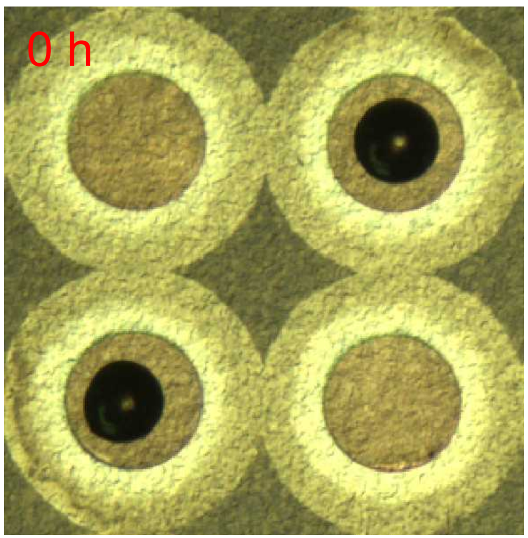
- Damage distribution and rate highly dependent on drop size/secondary spreading
- Larger drops exhibit inverse Evans drop behavior due to anodic dissolution in high pH regions near triple phase boundaries
- Efforts under way to develop droplet-film model to understand how film and droplet geometry and chemistry impact anode-cathode distributions and corrosion kinetics
- Future work will focus on acquiring physicochemical properties of secondary spreading region and electrochemical measures of system to inform model

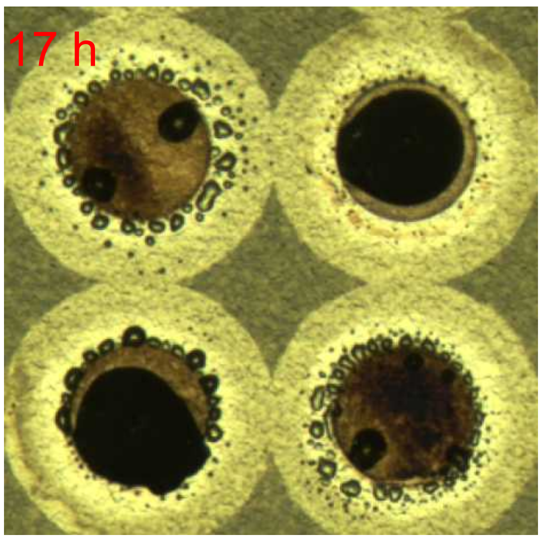
EXTRAS

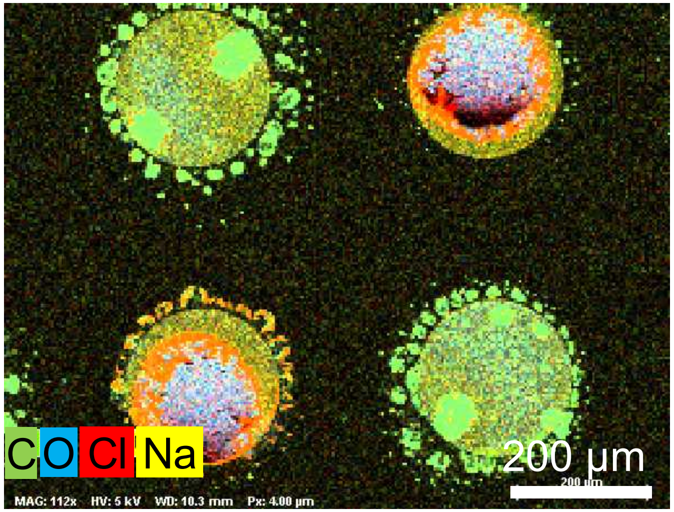
Restricted Substrates

220 µm Windows

85% RH, 25 °C,
< 1 ppm CO_2



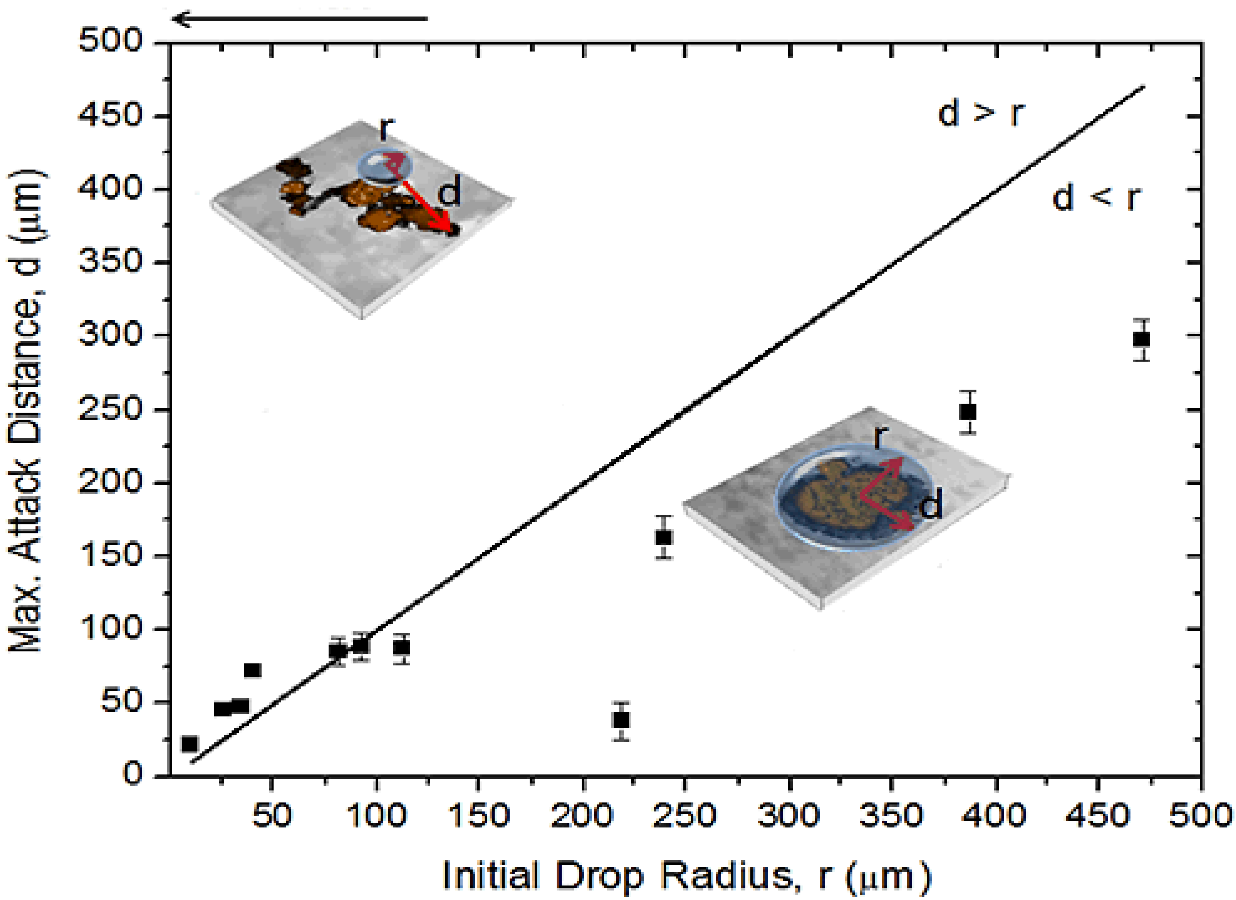




- Development of S.S. chemistry over Si_3N_4 with highest concentrations on non-deposited pads

Divergence from Evans Drop

Atmospheric Particles
Contaminants



Risteen, Schindelholz, Kelly 2014