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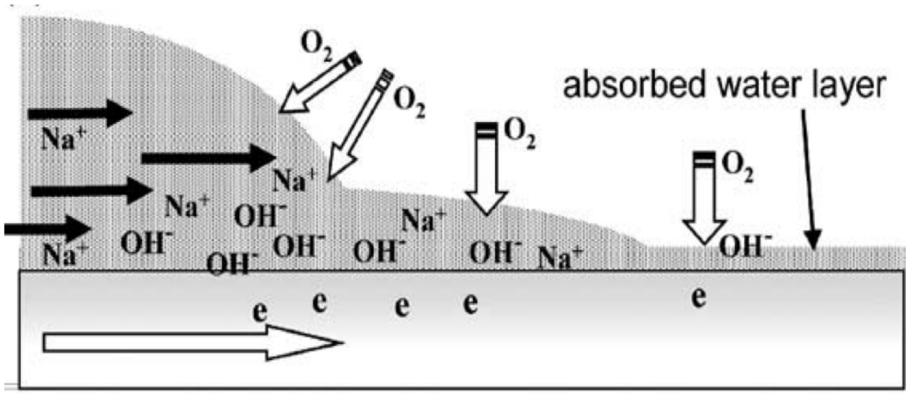

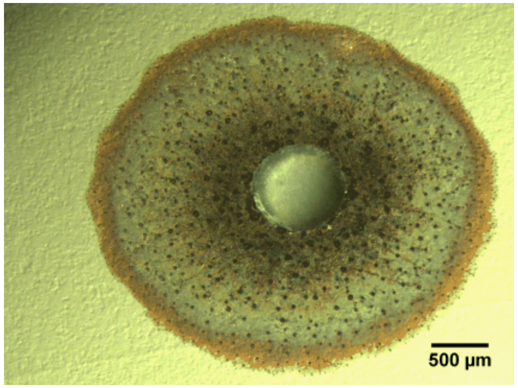

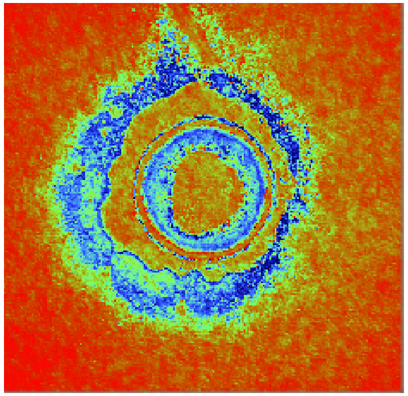

Role of Electrolyte Evolution on Damage Distributions and Rates Under NaCl Drops

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U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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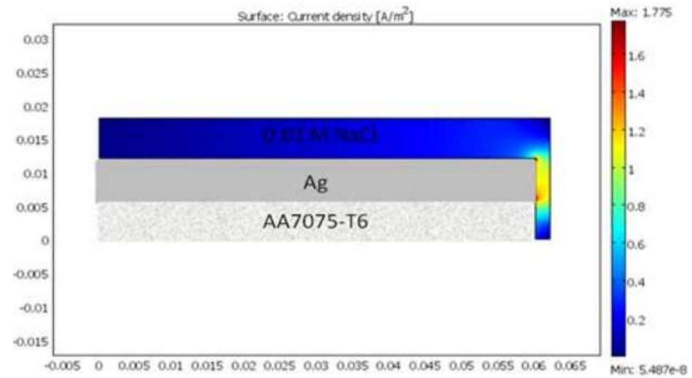
Electrochemical Modeling of Atmospheric Corrosion

- Electrolyte geometry can govern corrosion damage distributions and kinetics



Shi, Kelly, 2013

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

- Rich opportunity space for integrated computational and experimental approach

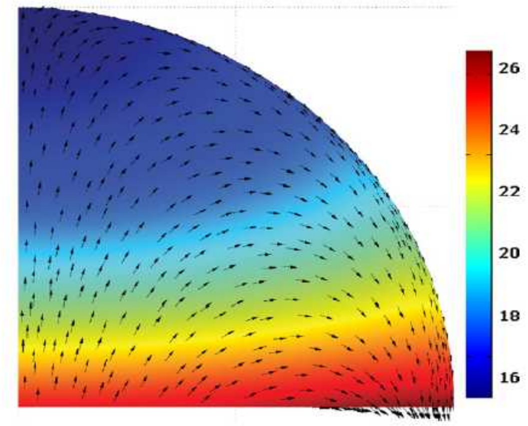


Fig. 10. $(C_{Zn^{2+}}/C^0_{Zn^{2+}})$ of zinc ions and arrow plot of current density vectors showing separation of metal surface into anodic and cathodic regions over time.

Cole et al., 2011

Classic Understanding: Evans Drop

Differential Aeration Cell

Diffusion limited O_2 reduction kinetics control attack rate and damage distribution

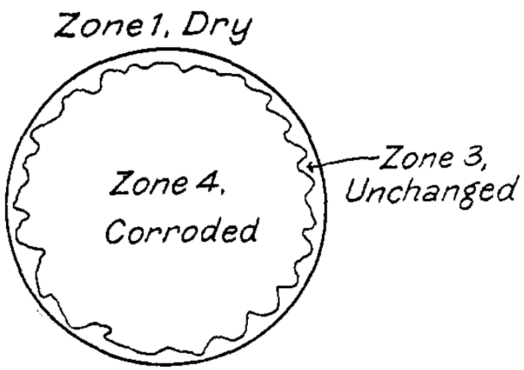
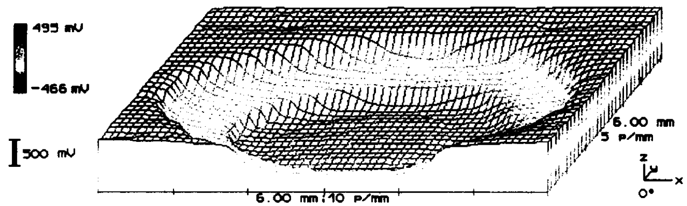
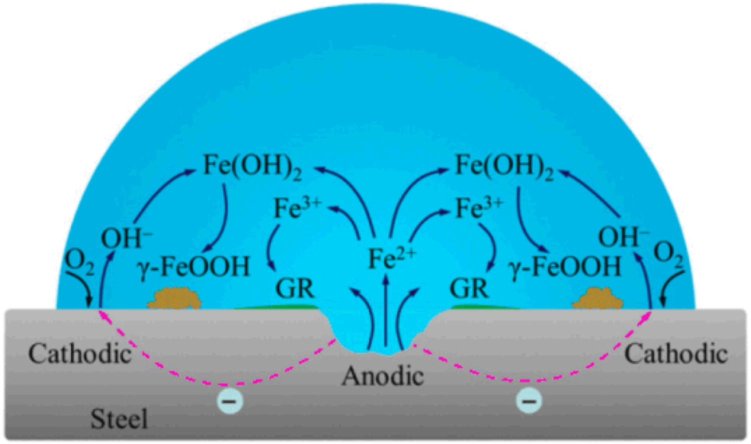


Figure 2—Effect of Drop of Distilled Water on Zinc

Evans, 1926



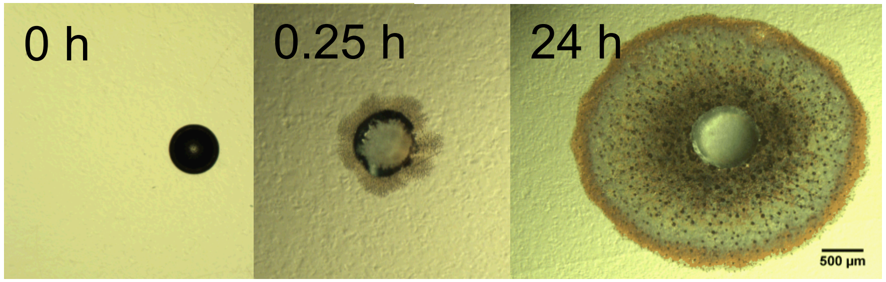
Chen and Mansfeld, 1997



Li and Hihara, 2012

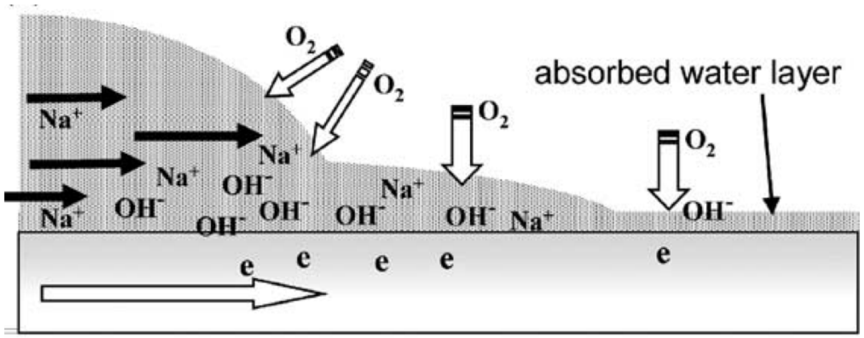
Divergence from Evans Drop

Secondary Spreading



<u>rate and extent</u>

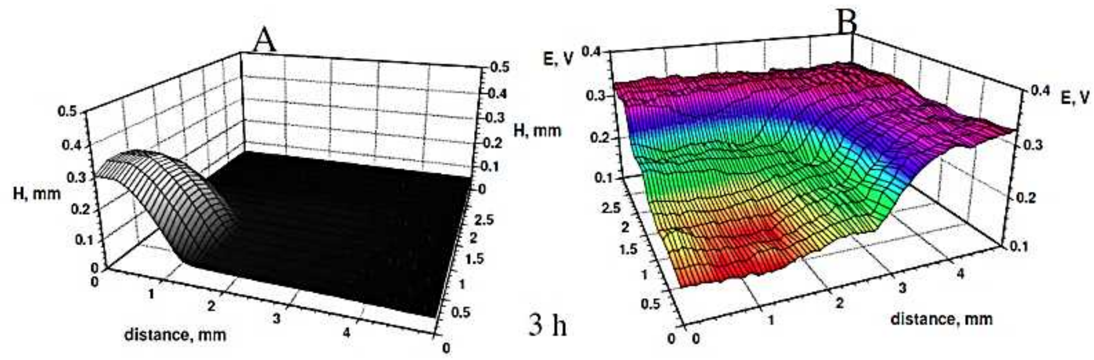
- initial drop size and chemistry
- substrate alloy
- environment (P_{CO2}, RH)



Tsuru et al, 2004

Impact of Secondary Spreading

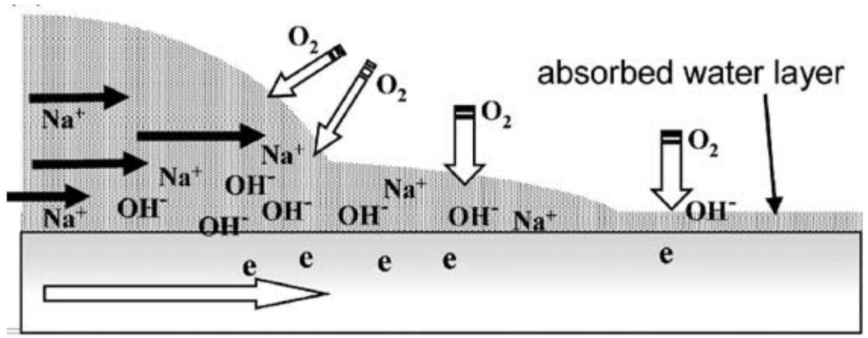
High potential areas in secondary spreading regions



Chen, 2005

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

To what extent do films contribute to cathodic current?



Study Framework

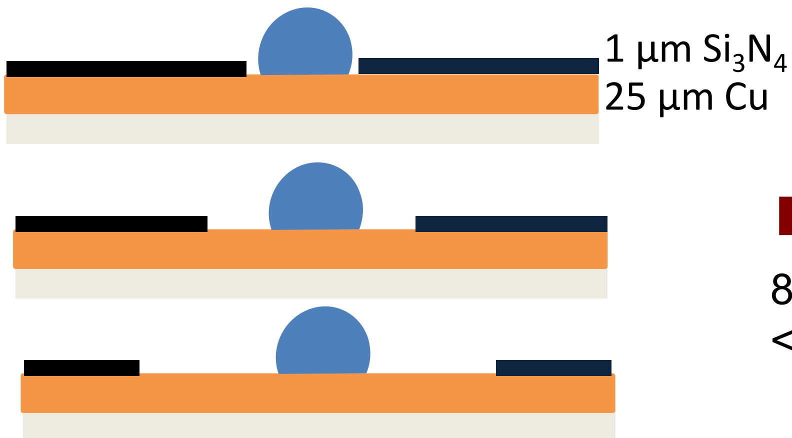
Driving Question

How do secondary films impact corrosion kinetics and damage distributions?

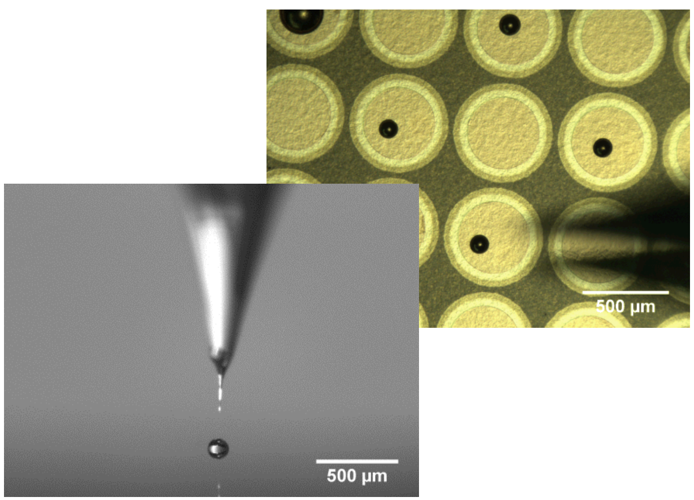
Approach

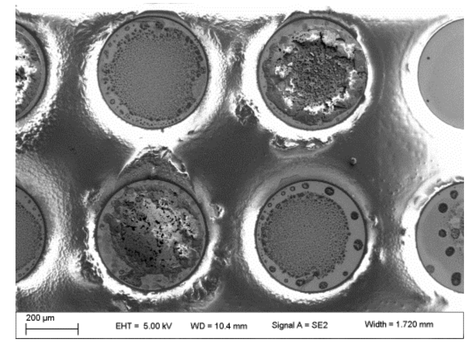
- Define physiochemical properties of film and realize influence of film and drop size on corrosion rates and damage distributions – Cu, NaCl
- Multiphysics continuum model of droplet-film system-physical-chemical evolution of system for experiment interpretation, predict damage distribution and rates

Experimental: NaCl Drops on Cu Pads

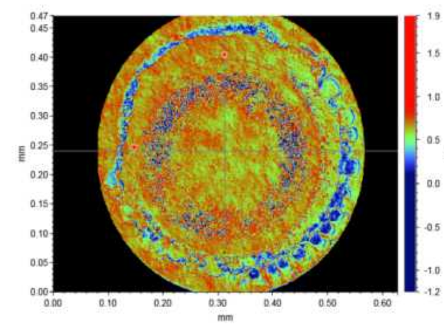


85% RH, 25 °C,
< 1 ppm CO_2





spreading chemistry and distribution

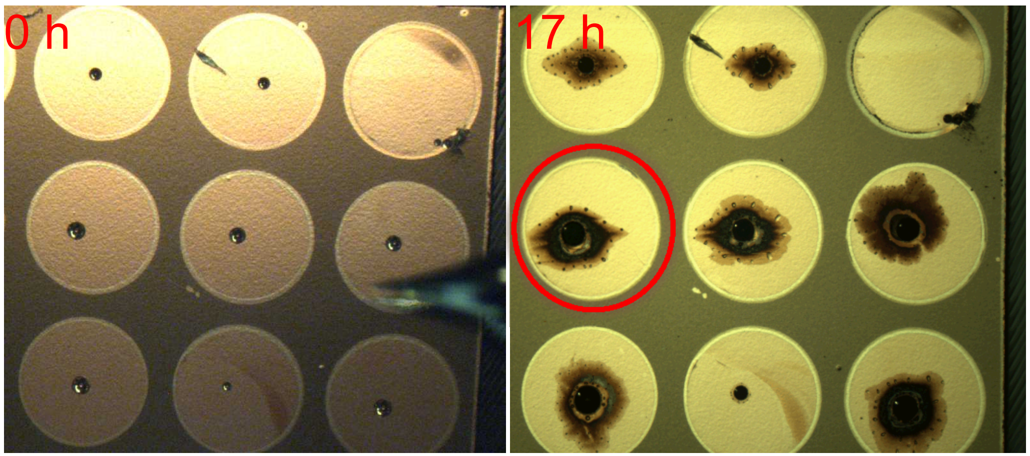


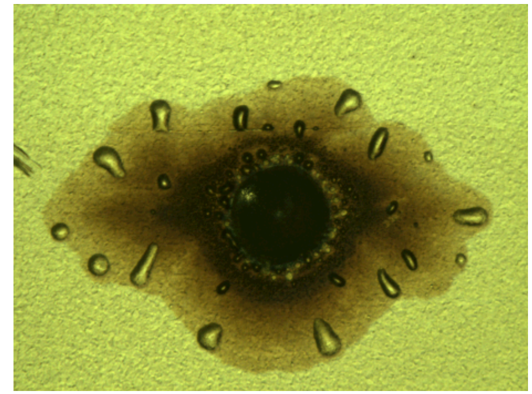
damage profiles

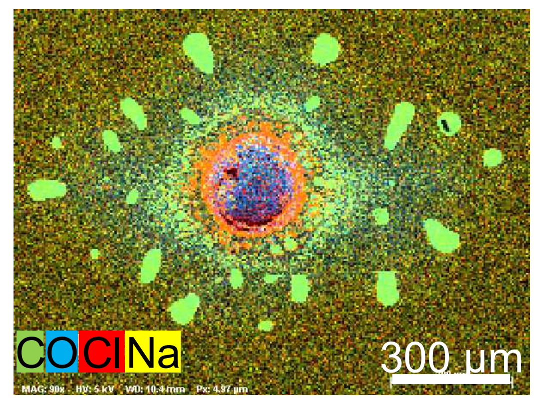
Unrestricted Spreading: Chemistry

2mm Windows

85% RH, 25 °C,
< 1 ppm CO_2

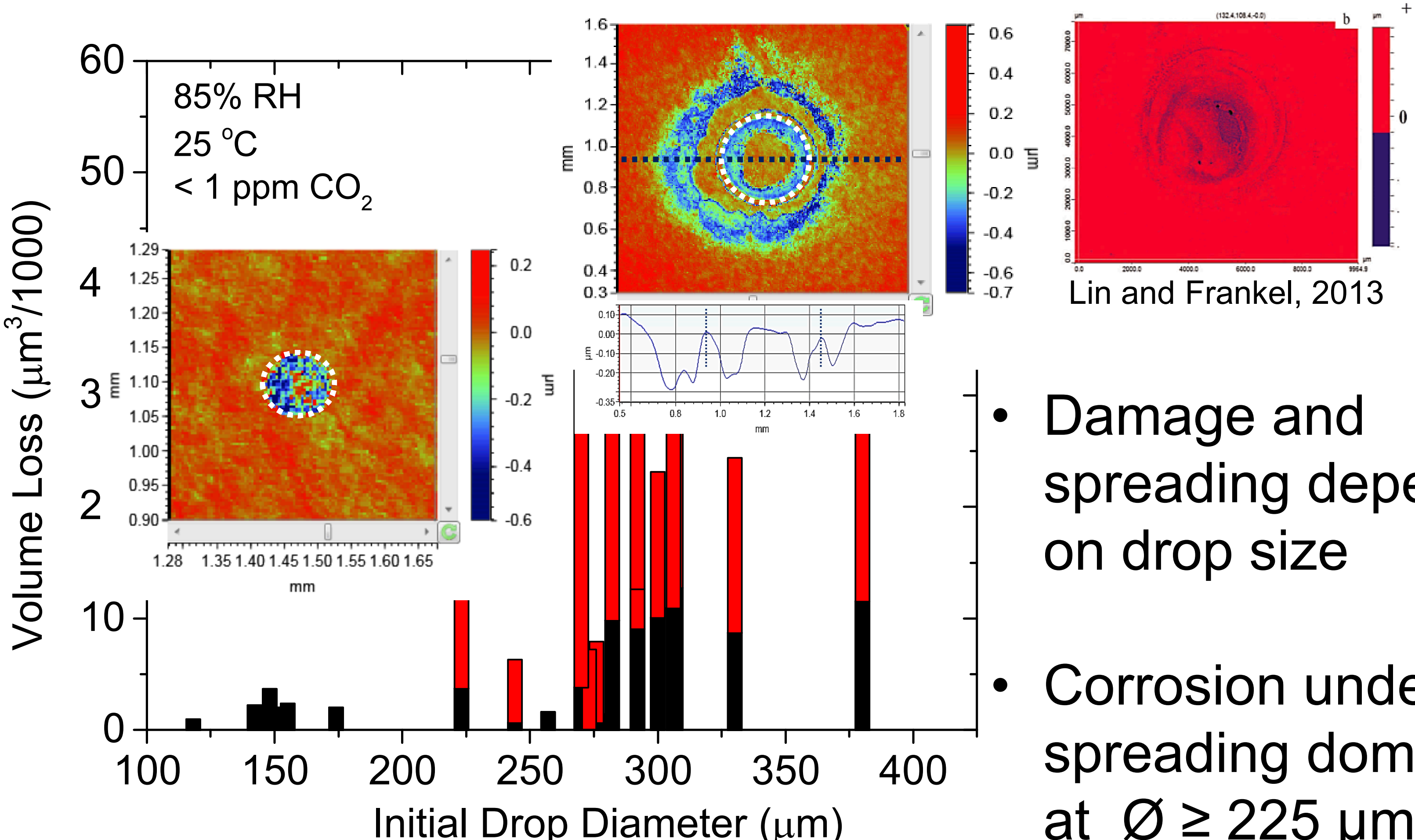






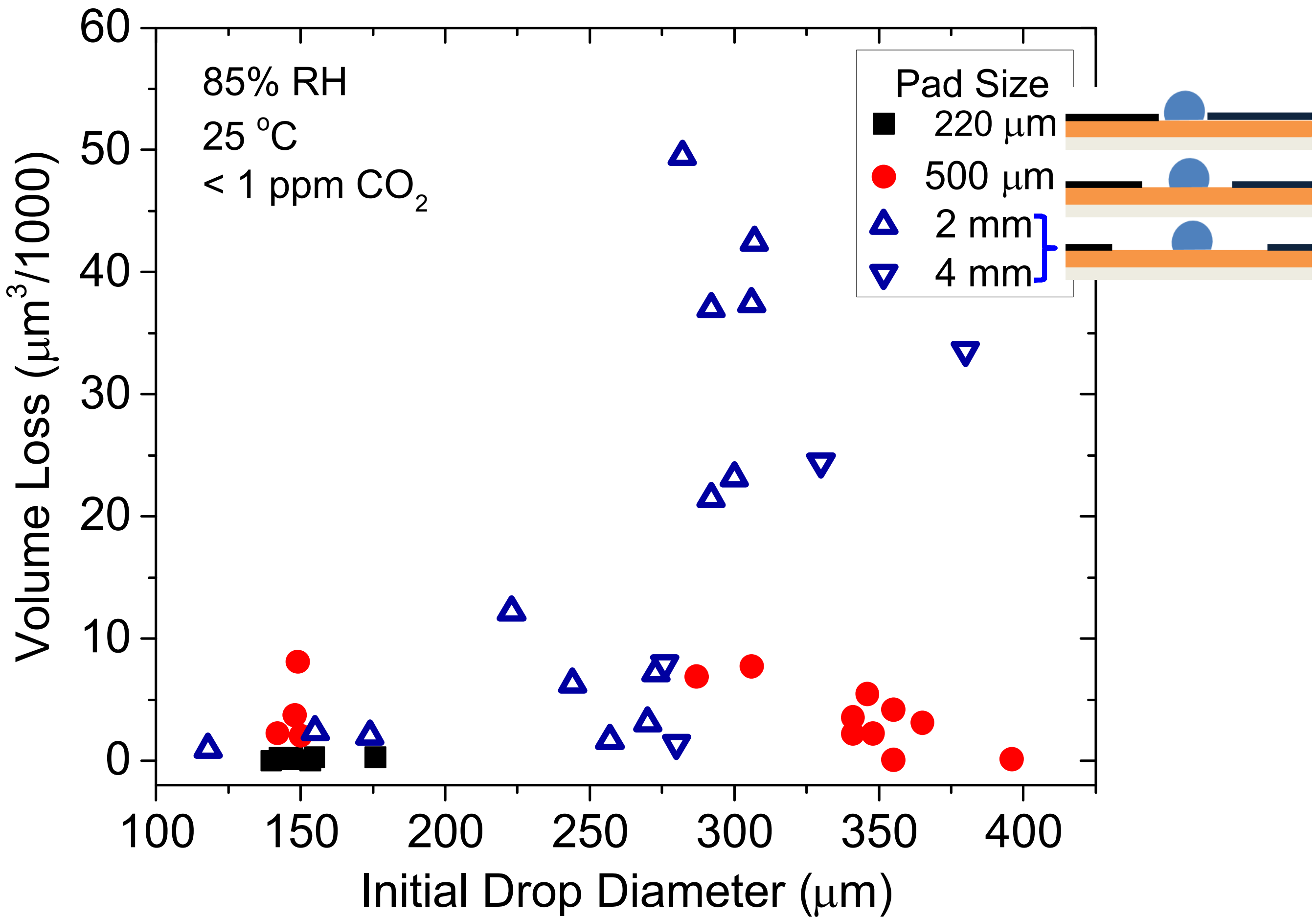
- Spreading chemistry in accordance with previous studies
- After 17 hours, can spread > 2x original drop radius

Unrestricted Spreading: Damage



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

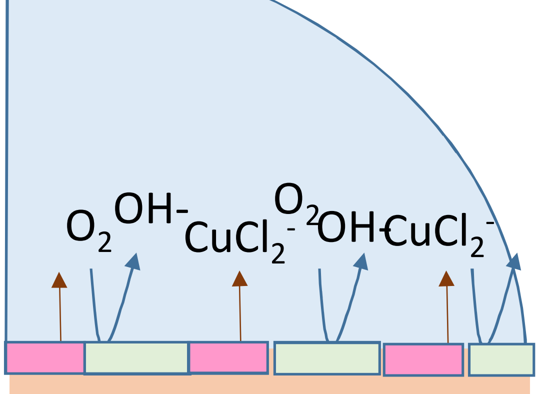
Restricted Substrates: Damage



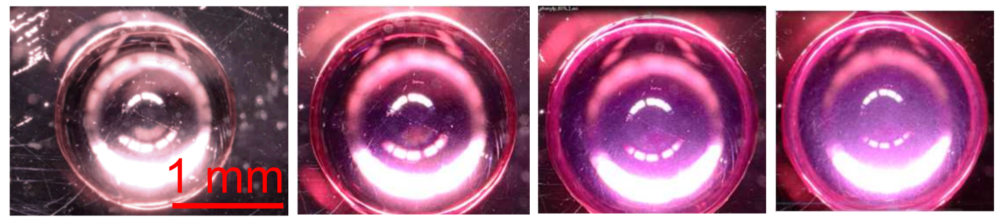
Corrosion loss strongly dependent on spreading S.S. at Ø ≥ 225 μm

Electrolyte and Damage Evolution

Initiation



pH 6 | pH > 8 | pH ≥ 10



20s | 2 min | 7 min | ≥ 30 min

pH 2-10

$O_2 + 2H_2O + 4Cu + 8Cl^- = 4CuCl_2^- + 4OH^-$

$4Cu + 8Cl^- = 4CuCl_2^- + 4e^-$ *Tromans, 1991,1992

$O_2 + 2H_2O + 4e^- = 4OH^-$

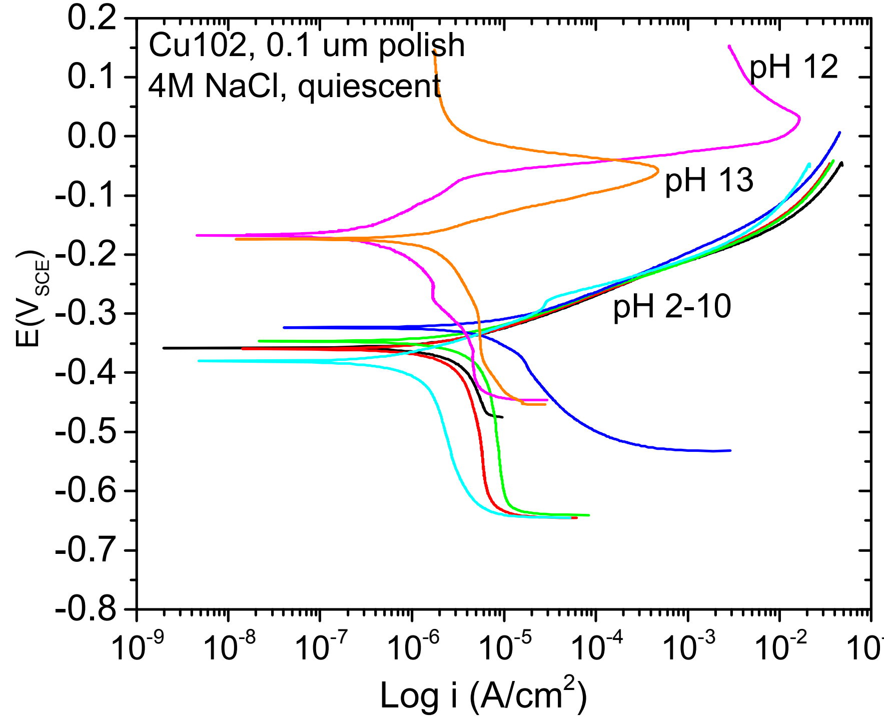
pH 12,13

$4CuCl_2^- + 6H_2O + O_2 + 4OH^- = 4Cu(OH)_2 + 8Cl^-$

$4CuCl_2^- + 2H_2O = 2Cu_2O + 4H^+ + 8Cl^-$

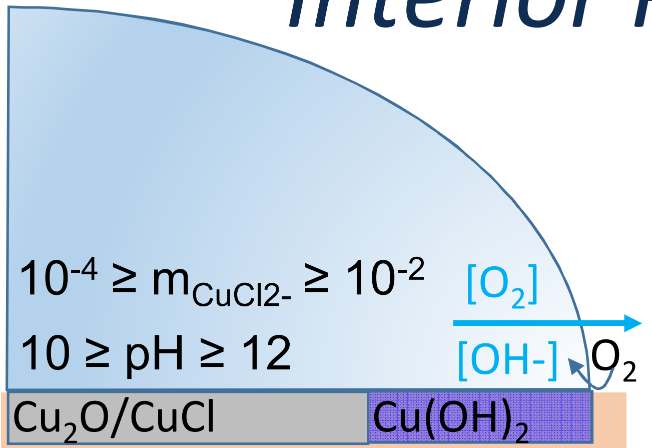
$2Cu_2O + 4OH^- + 2H_2O = 4Cu(OH)_2 + 4e^-$

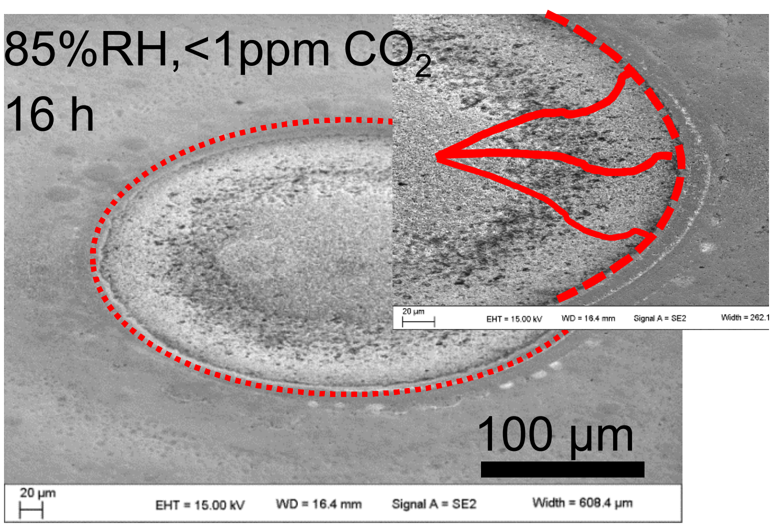
$O_2 + 2H_2O + 4e^- = 4OH^-$

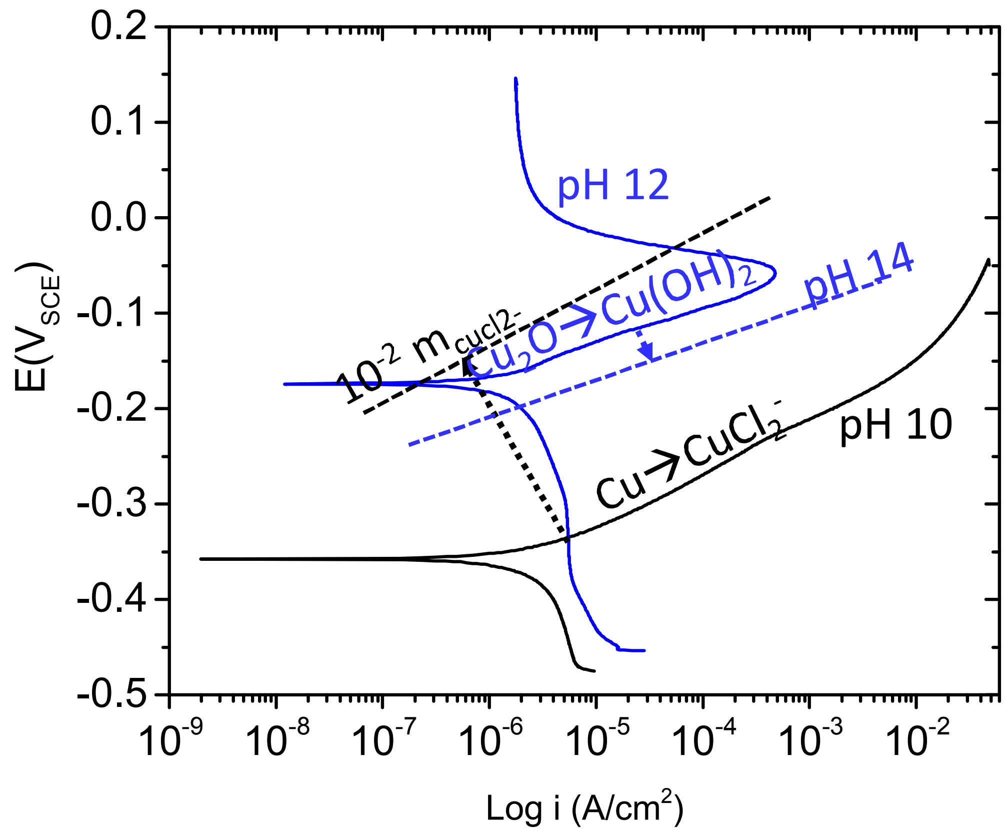


pH likely buffered by $CuCl_2^- \leftrightarrow Cu_2O \leftrightarrow Cu(OH)_2$

Electrolyte and Damage Evolution
Interior Perimeter Trenching

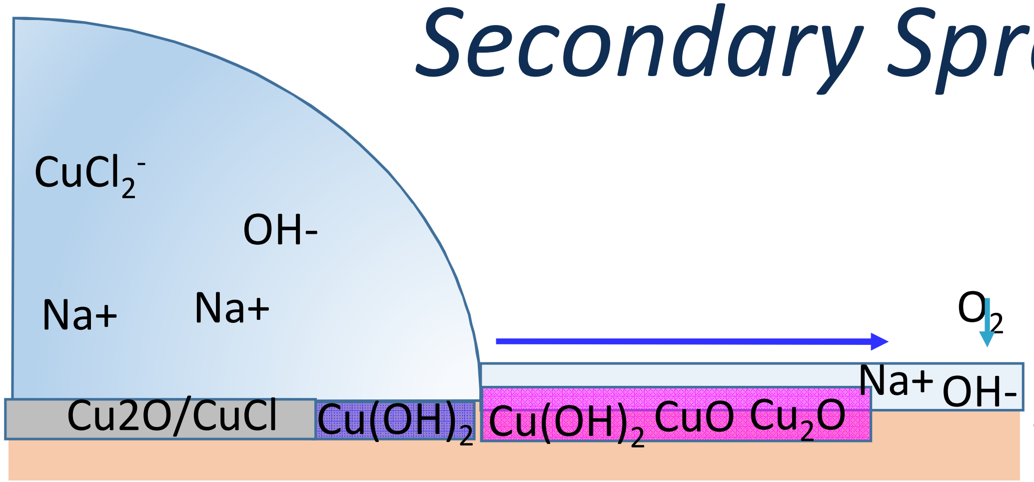


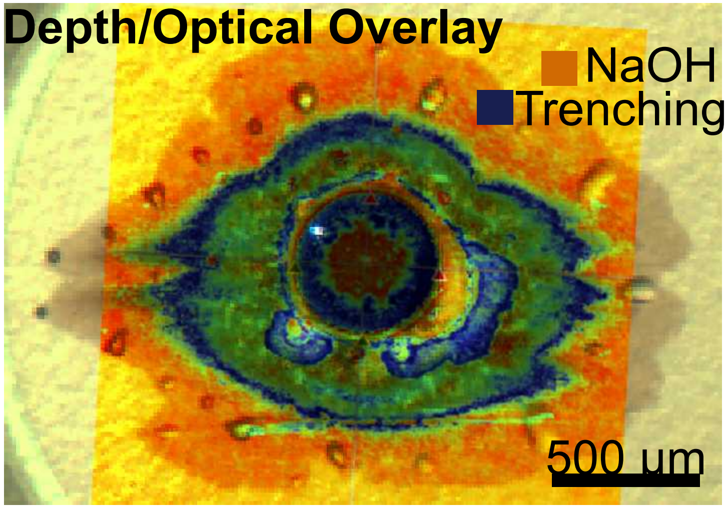


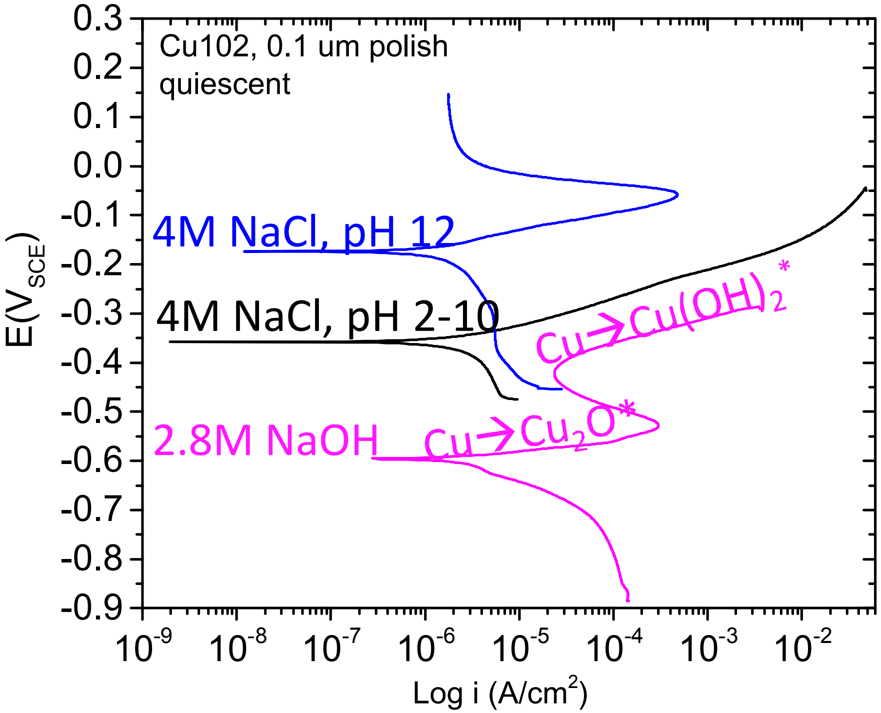


$[O_2]$ gradient may cause trenching near drop edge

Electrolyte and Damage Evolution
Secondary Spreading







*Biton *et al.*, 2006

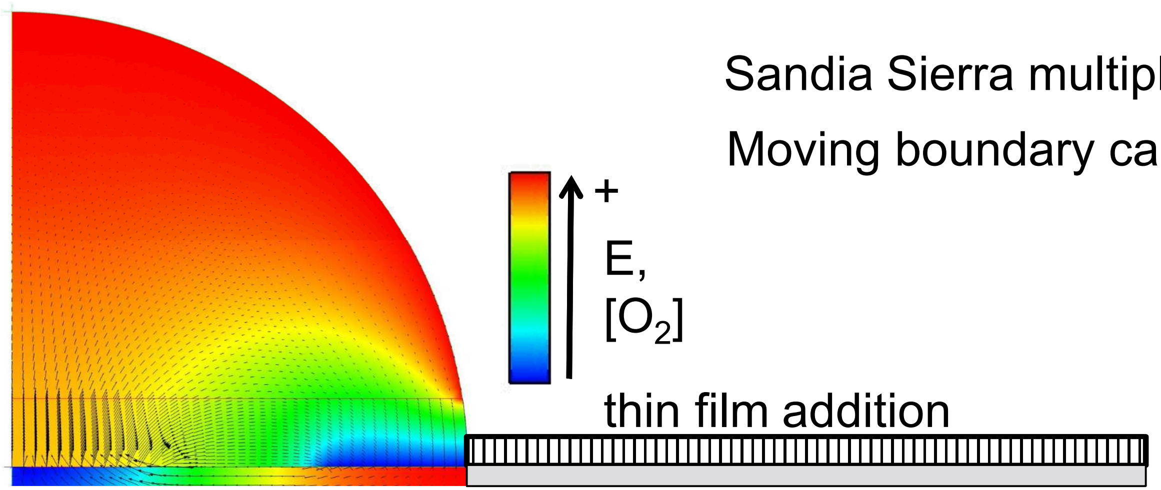
Trenching in spreading film region due to $Cu \rightarrow Cu_2O$, $Cu(OH)_2$

Conclusions

- Damage distribution and rate highly dependent on drop size/secondary spreading
- Larger drops exhibit damage pattern inverse of classic Evans drop, with greatest corrosion loss in secondary spreading zone- not strictly a cathode
- Damage evolution rationalized via mixed potential theory in analogous bulk electrolyte solution- preferential, high pH anodic dissolution
- Exemplifies need to account for electrolyte evolution in electrochemical atmospheric corrosion models predicting damage distributions and rates

EXTRAS

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

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

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

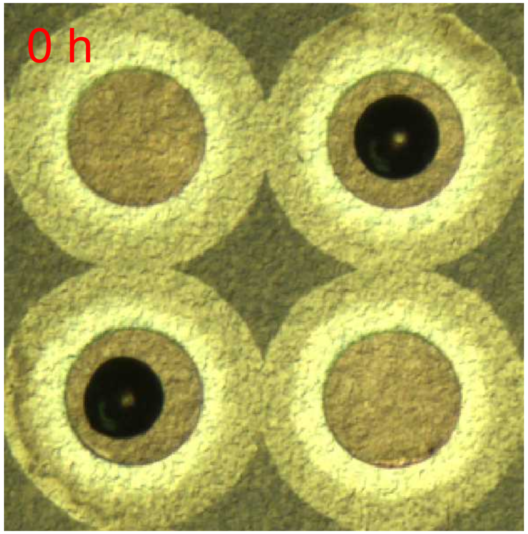
$M \longrightarrow M^{x+}$

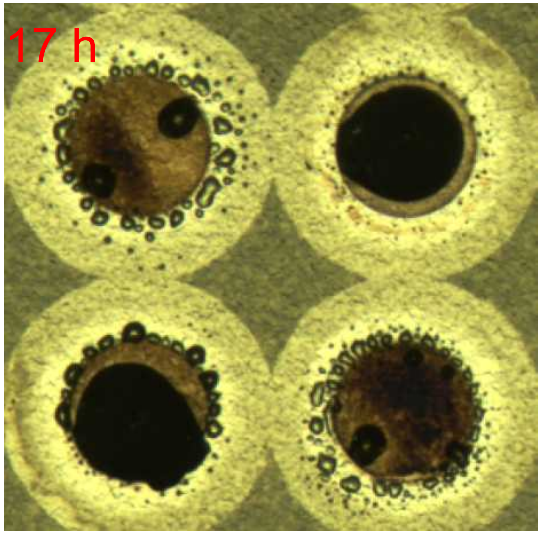
$$i_{M/M^{X+}} = -i_{\ oM/M^{X+}} exp\left(\frac{-x\left(1+\alpha_{\frac{M}{M^{X+}}}\right)F}{RT}\left(\Delta\emptyset_{M/M^{X+}}\right)\right)$$

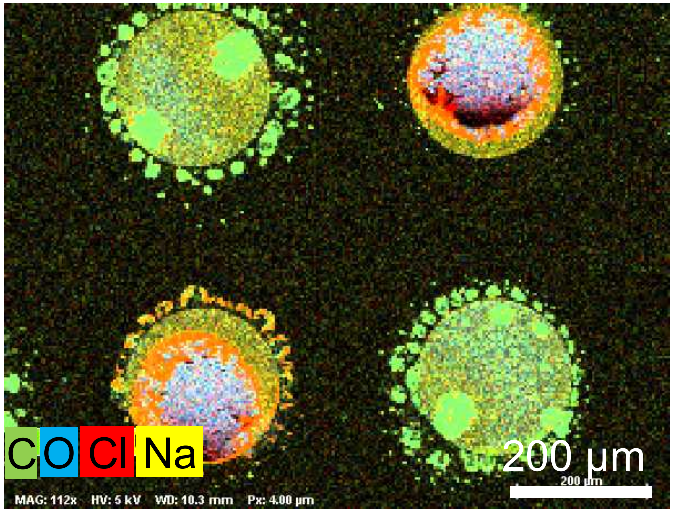
Restricted Substrates

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