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Atmospheric Corrosion Through a Multiphysics Lens

The Linkage between Surface Environment and Electrochemical Processes

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*Exceptional
service
in the
national
interest*

Acknowledgements: Rebecca Schaller, Harry Moffat, Carlos Jove-Colon, Rob Sorensen, Doug Wall



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Aging of High Reliability, Long Life Systems

At what rate and to what extent will corrosion damage propagate?

What frequency and where should we inspect?

How can we change environment to minimize corrosion?

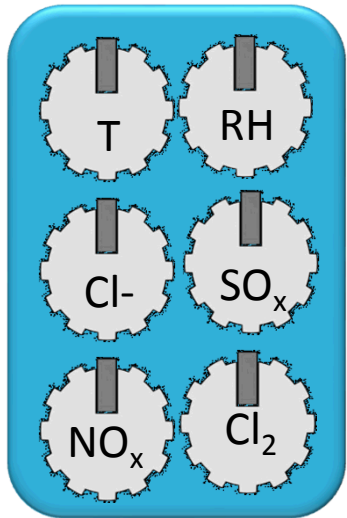
How robust is this design against corrosion in expected environment?

Where are corrosion weak points?



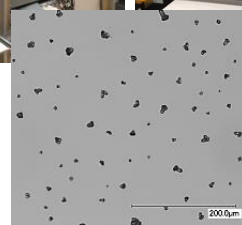
Current Engineering Approaches are Limited to Correlative Observations

Answering these questions.....

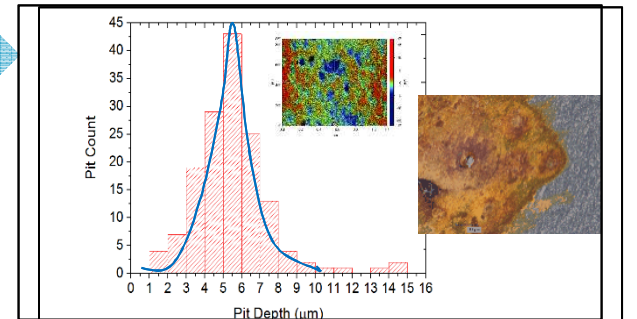
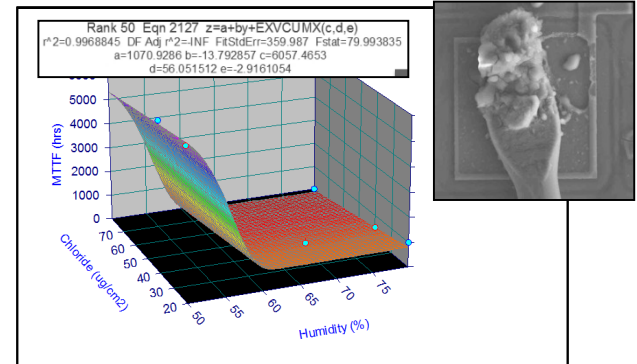


Environmental Parameters

Gas Exposure



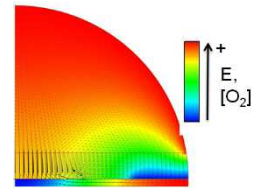
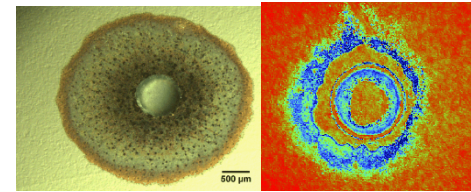
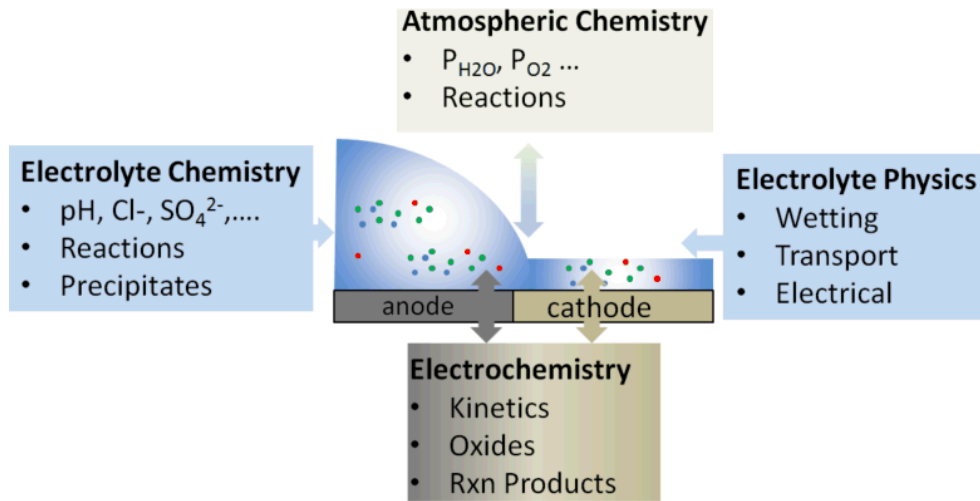
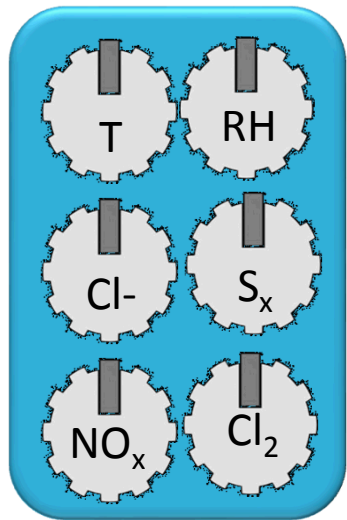
Contaminant Loading



Corrosion Response

Limited prediction of extent or rate, Limited mechanistic insight ₃

Linking Surface Environment to Corrosion Response



damage distributions and rates

Environmental Parameters



Corrosion Response

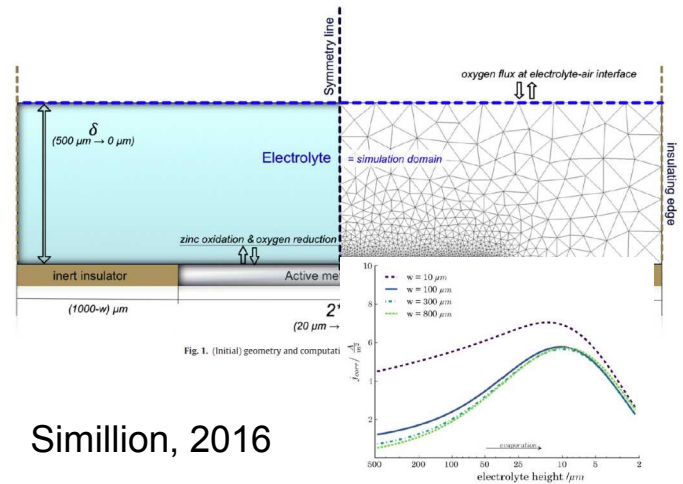
Foundational challenge inhibiting fundamental understanding is the limited ability to directly probe surface environment and corrosion processes

Quantitatively Linking Surface Environment to Corrosion Behavior

Analytical/computational approaches

Variety of Assumptions

- fixed geometry – films or droplets
- Limited homogenous reactions- fixed chemistry
- no heterogeneous reactions
- bulk electrolyte- electrochemical kinetics



Simillion, 2016

Fig. 15. Corrosion current density for different electrode widths during evaporation ($\delta = 500 \mu\text{m}$, $[\text{NaCl}]_{\text{sat}} = 0.1 \text{ wt}\%$, $h_{\text{sat}} = 500 \mu\text{m}$).

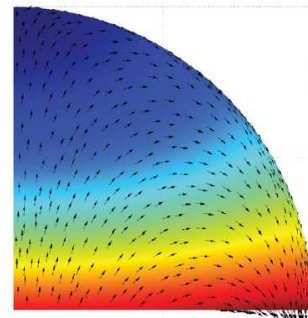
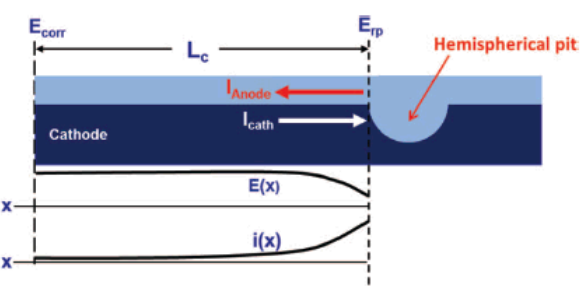


Fig. 10. $(C_{\text{Zn}^{2+}}/C_{\text{Zn}^{2+}}^0)$ of zinc ions and arrow plot of current density vectors showing separation of metal surface into anodic and cathodic regions over time.

Cole, 2011



Kelly group, 2009, 2014

Corrosion Processes and a *Dynamic* Surface Environment

How do saline electrolytes evolve once corrosion initiates in humid environments?

What is the interplay between electrolyte dynamics and corrosion damage distributions and rates?

Studies under highly simplified conditions:

(1) NaCl droplets on Cu: role of alkaline films and computationally capturing the evolving system

(2) NaCl droplets on 1100 Al: relationship between salt loading and damage extent

Cu-NaCl-H2O: Beyond Evans Drop

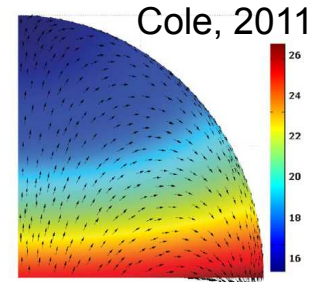
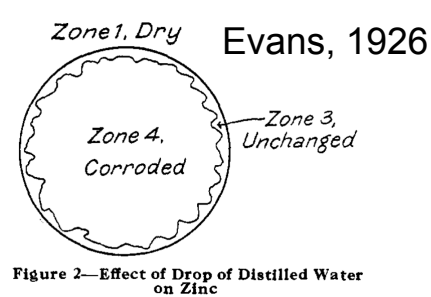
How does electrolyte evolution impact electrochemical processes?

rate and extent of spreading

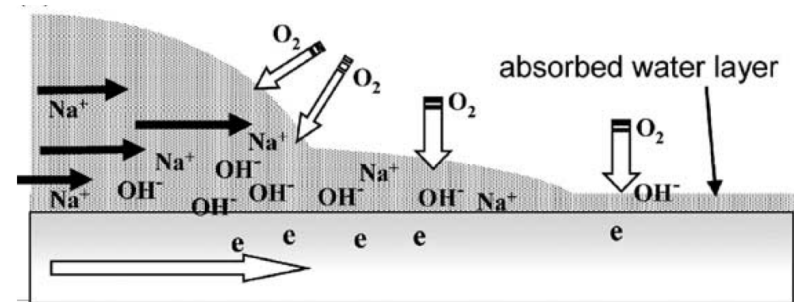
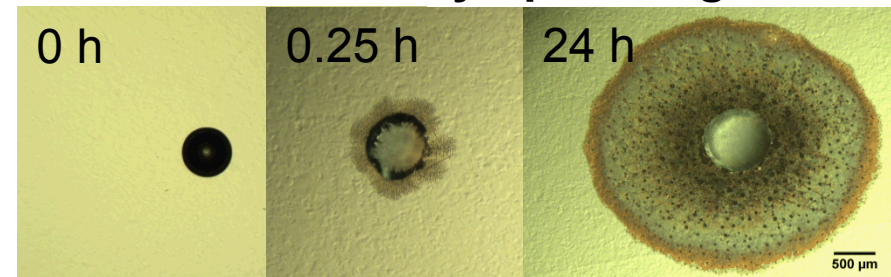
- initial drop size and chemistry
- substrate alloy
- environment (P_{CO_2} , RH)

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

Chen, 2005

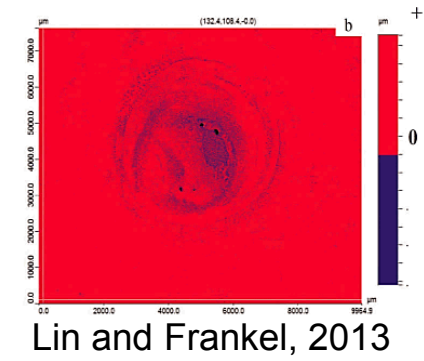
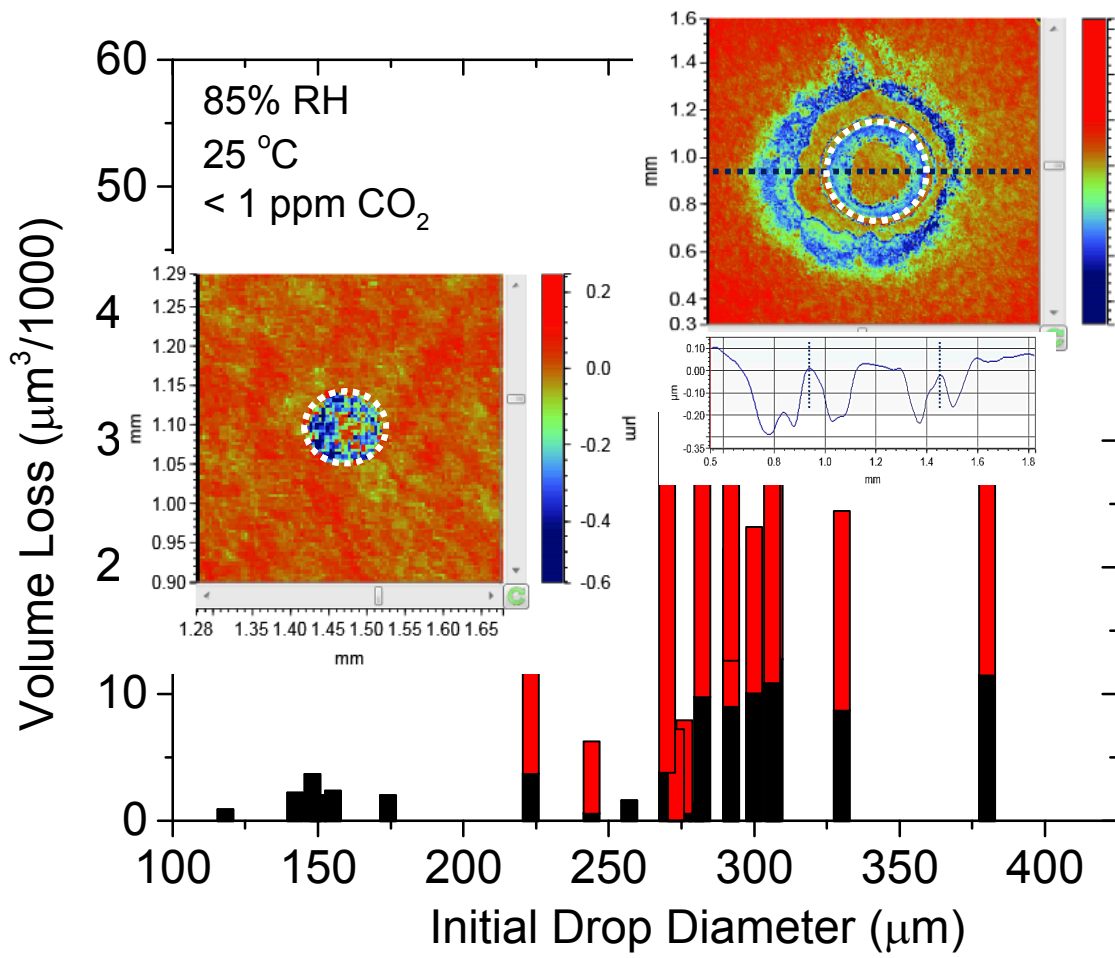


Secondary Spreading



Tsuru et al, 2004

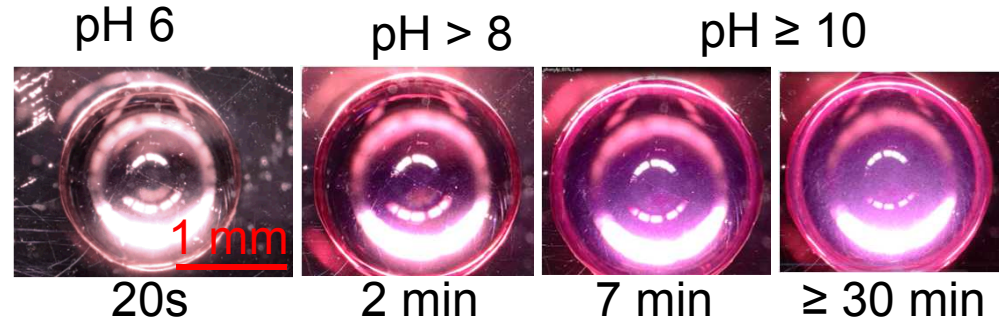
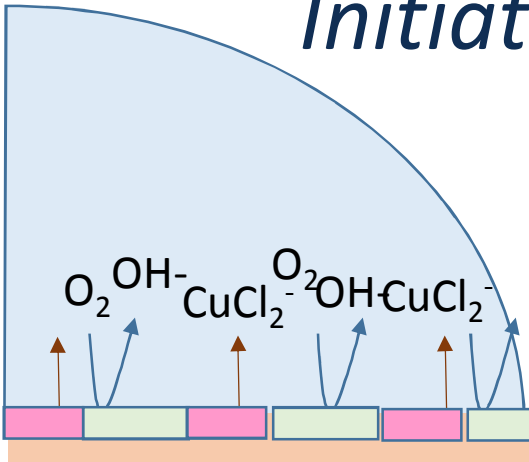
Damage Relation to Initial Drop Size and Spreading



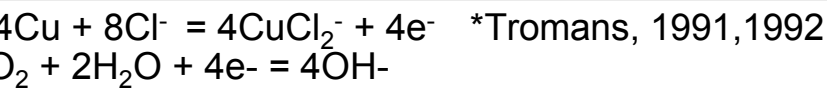
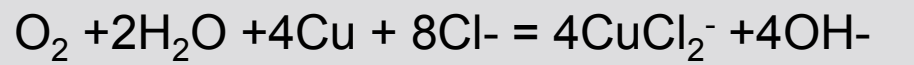
- Corrosion under spreading dominates at $\varnothing \geq 225 \mu\text{m}$, inverse Evans

Electrolyte and Damage Evolution

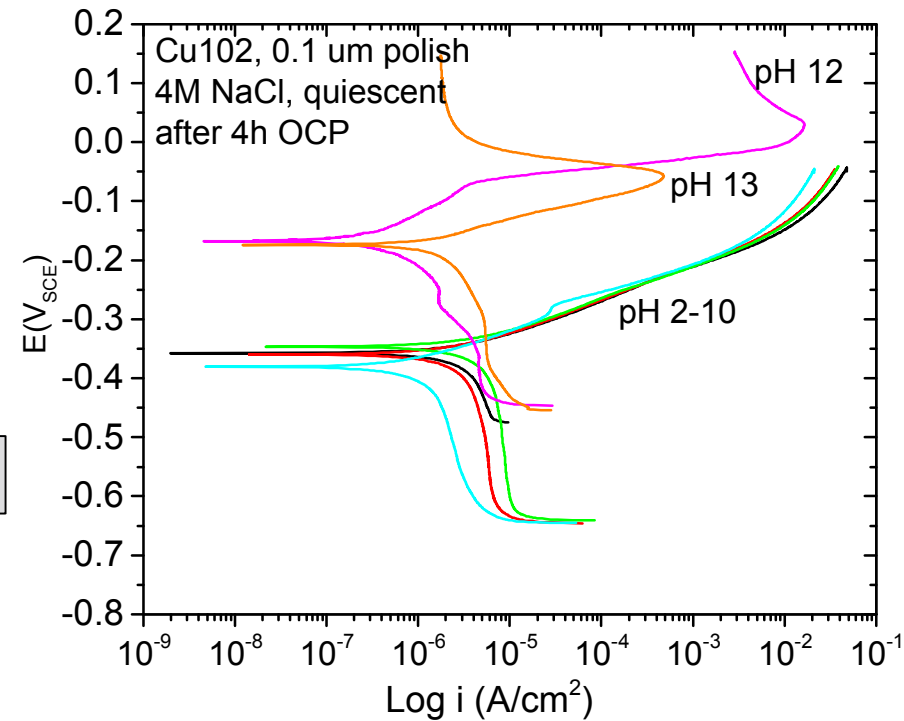
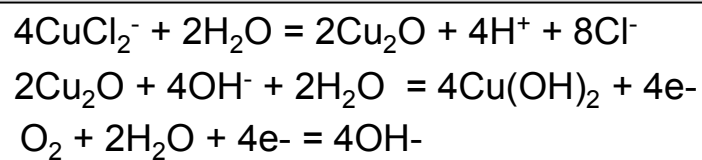
Initiation



pH 2-10



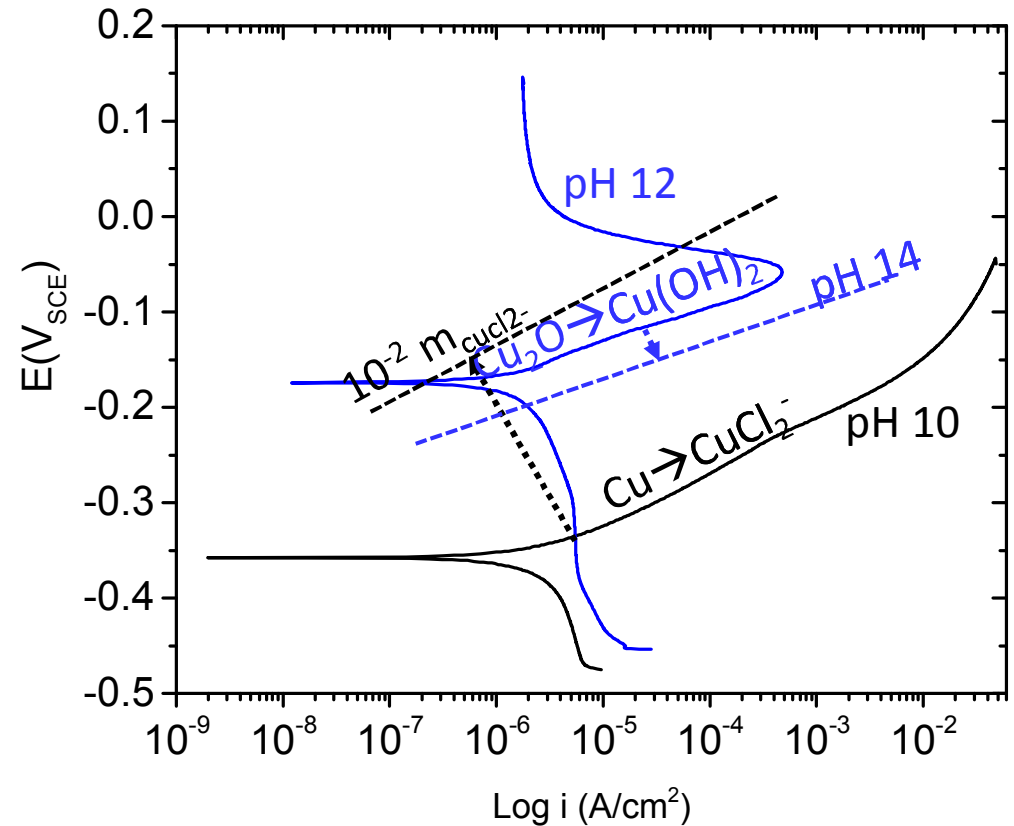
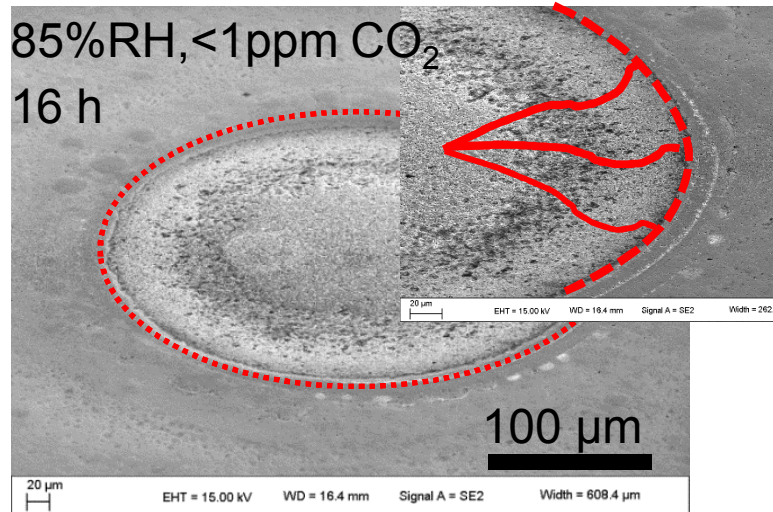
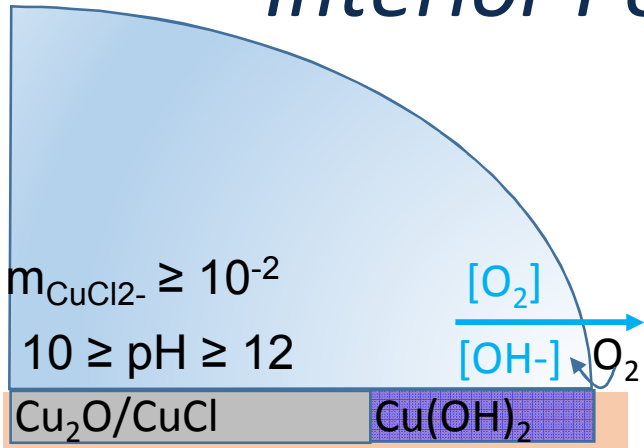
pH 12,13



pH likely buffered by $\text{CuCl}_2^- \leftrightarrow \text{Cu}_2\text{O} \leftrightarrow \text{Cu}(\text{OH})_2$

Electrolyte and Damage Evolution

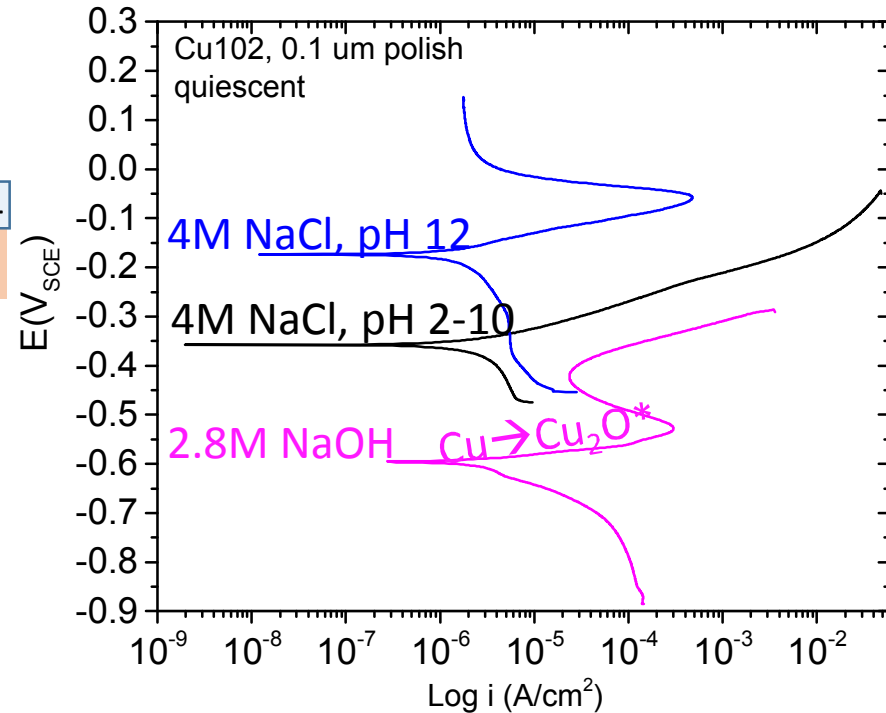
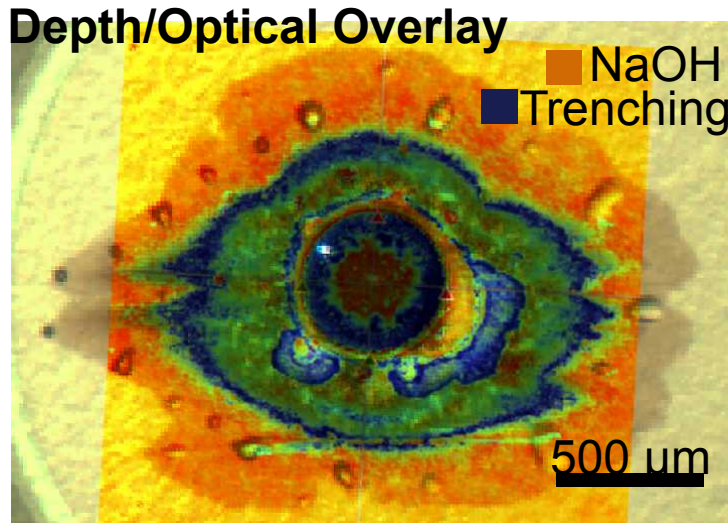
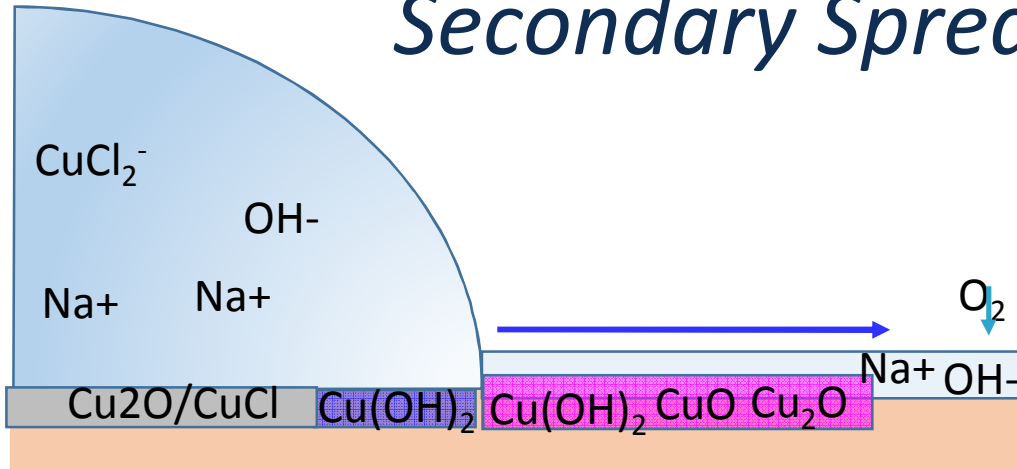
Interior Perimeter Trenching



$[\text{O}_2]$ gradient may cause trenching near drop edge

Electrolyte and Damage Evolution

Secondary Spreading



*Biton *et al.*, 2006

Trenching in spreading film region due to $\text{Cu} \rightarrow \text{Cu}_2\text{O}$, $\text{Cu}(\text{OH})_2$ 11

0D Reactor Network Model for Evolving Electrolyte

Cantera/Zuzax

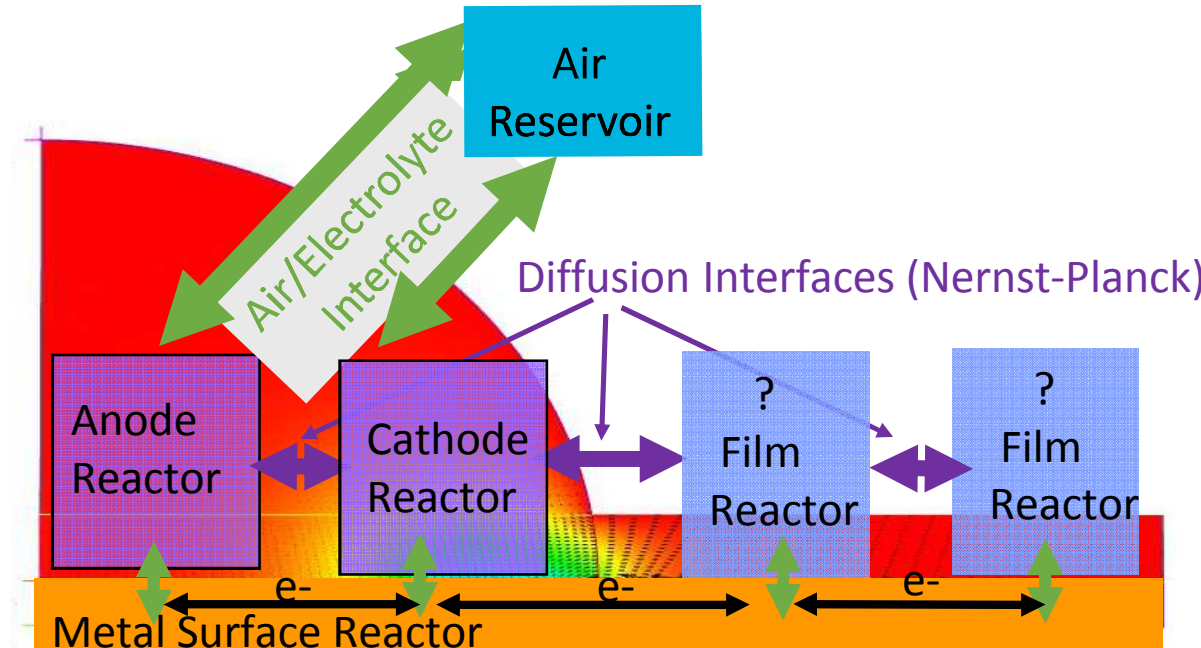
Non-Ideal Solution Thermodynamics, Electro/Chemical Kinetics, Transport

Reactors

- Pitzer non-ideal thermo.
- Mass balances: homogenous and interfacial chemistry, and diffusion interfaces
- Precipitation of salts, oxides
- Potential

Interfaces

- Air-Brine Equilibrium
- Diffusion between reactors
- Redox Reactions-charge trans:



0D Reactor Network Model

$$\frac{d(\Xi_{R,k})}{dt} = V_R \dot{W}_k + \sum_I A_{R,I} \dot{S}_{R,I,k} + \sum_D A_{R,D} \dot{N}_{R,D,k}$$

$\Xi_{R,k}$ = Total moles of species k in Reactor R (multiple phases allowed)

$\dot{S}_{R,I,k}$ = Source term for species k in Reactor R due to Interface I

$\dot{W}_{R,k}$ = Source term for species k in Reactor R due to homogeneous and heterogeneous Rxns

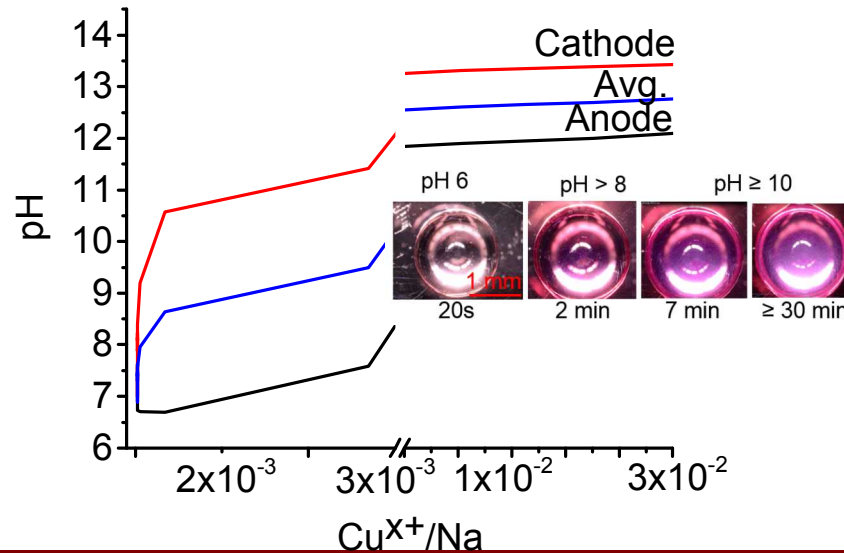
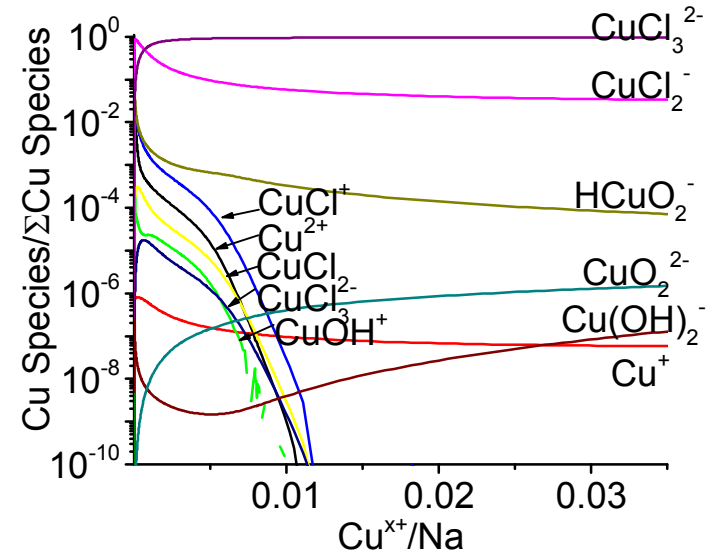
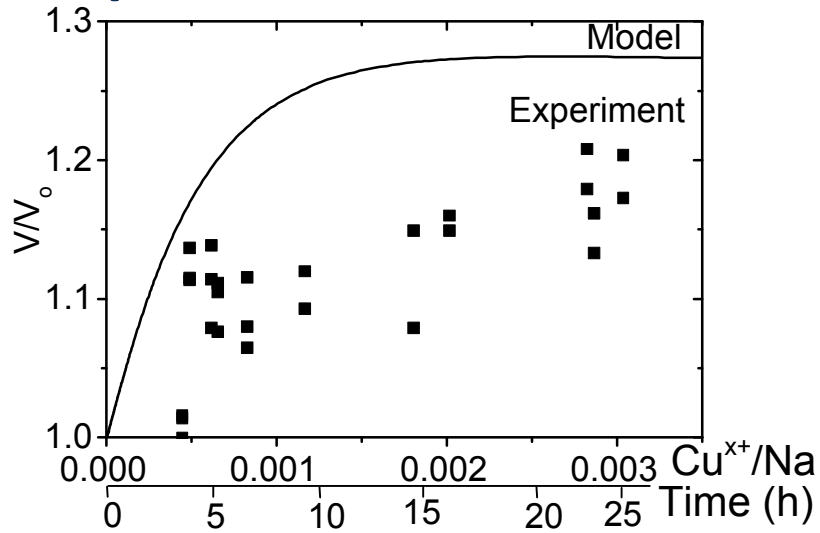
$\dot{N}_{R,D,k}$ = Source term for species k in Reactor R due to diffusional interface R

$$\dot{N}_{R,D,k}(L) = -D_k C_T \frac{\Delta X_k}{L} + D_k C_k z_k \frac{F}{RT} \frac{\Delta \phi_R}{L}$$

Electric Potential for brine in each Reactor solved via an Algebraic Constraint:

$$0 = \sum_k z_k \left(\sum_I A_{R,I} \dot{S}_{R,I,k} + \sum_D A_{R,D} \dot{N}_{R,D,k} \right)$$

0D Reactor Network Model of Droplet: Proof of Concept



Summary: Cu-NaCl in humid zero air Sandia National Laboratories

- Greatest damage occurred external to original droplet geometry – secondary spreading zones not strictly a cathode
- Hypothetical process presented via mixed potential theory in analogous bulk electrolyte solution- preferential, high pH anodic dissolution
- Computational approach/tool being developed to capture physical and chemical evolution of electrolyte and provide insight on impact on electrochemical processes.

Corrosion Processes and a *Dynamic* Surface Environment

How do saline electrolytes evolve once corrosion initiates in humid environments?

What is the interplay between electrolyte dynamics and corrosion damage distributions and rates?

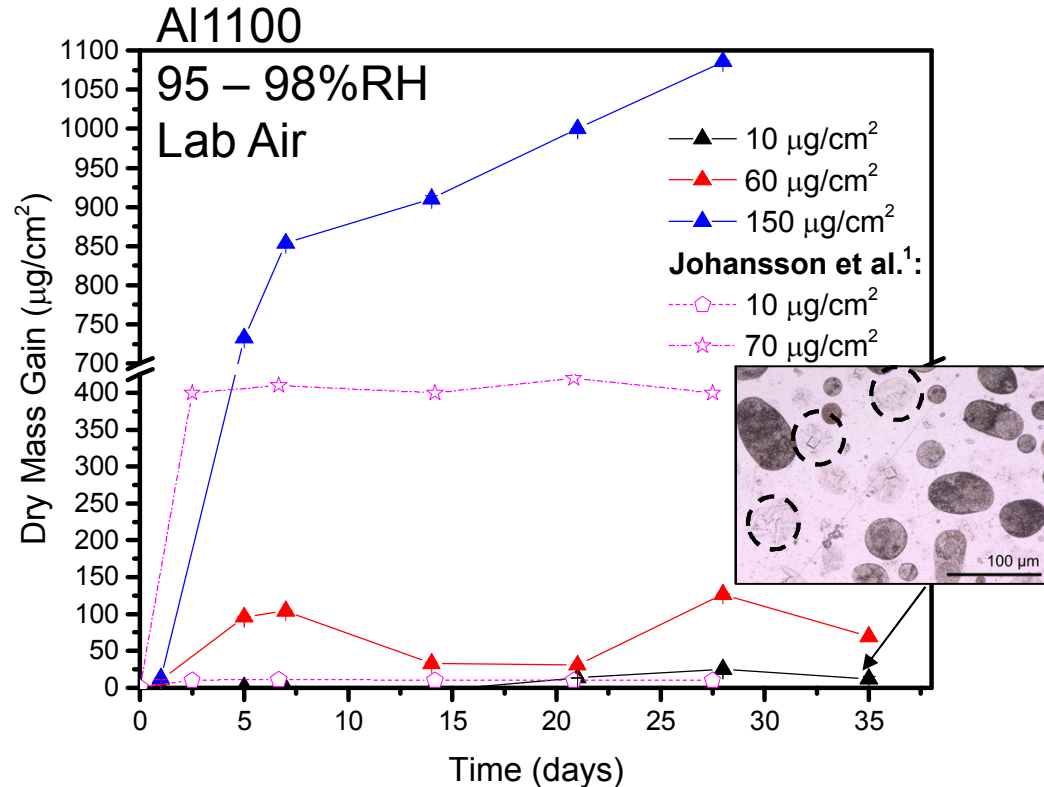
Studies under highly simplified conditions:

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(2) NaCl droplets on 1100 Al: relationship between salt loading and damage extent

Influence of NaCl Loading Amounts on Aluminum

- Laboratory exposures:
 - Extent of corrosion increases with increasing NaCl loading
 - “Stifling” or bendover in rate occurs at lower loadings
 - Johansson et. al (2005) attribute to CO₂
 - pH buffering of electrolyte



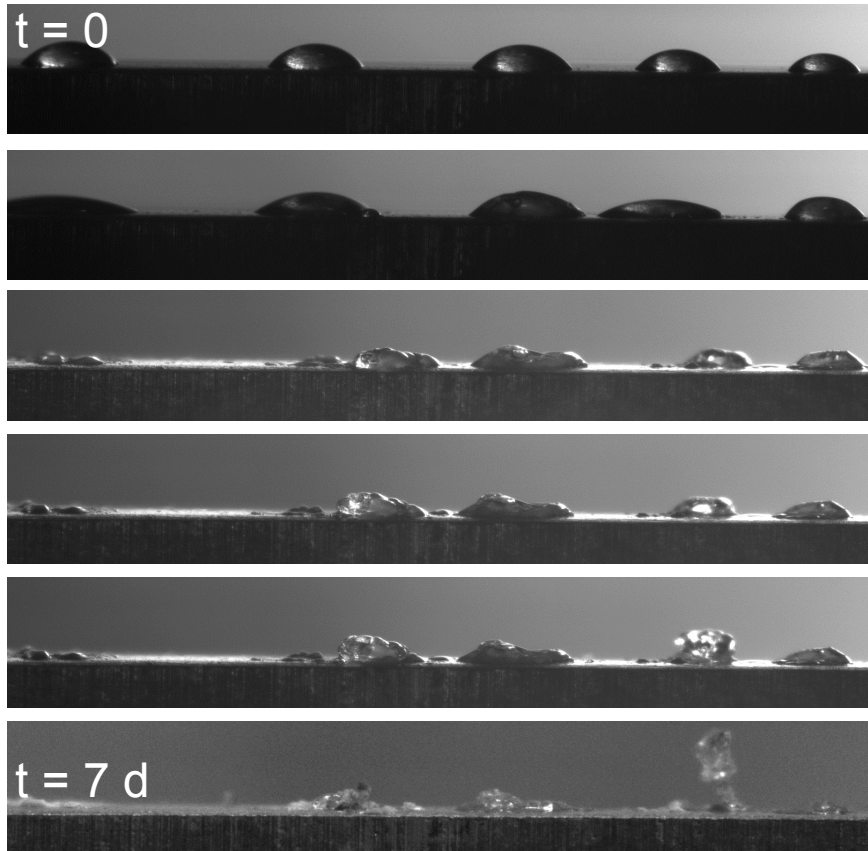
What is causing apparent “stifling” at relatively short times?

Hypothesis: gettering of NaCl by corrosion product

Can we predict a maximum effective extent of corrosion based on initial salt loading?

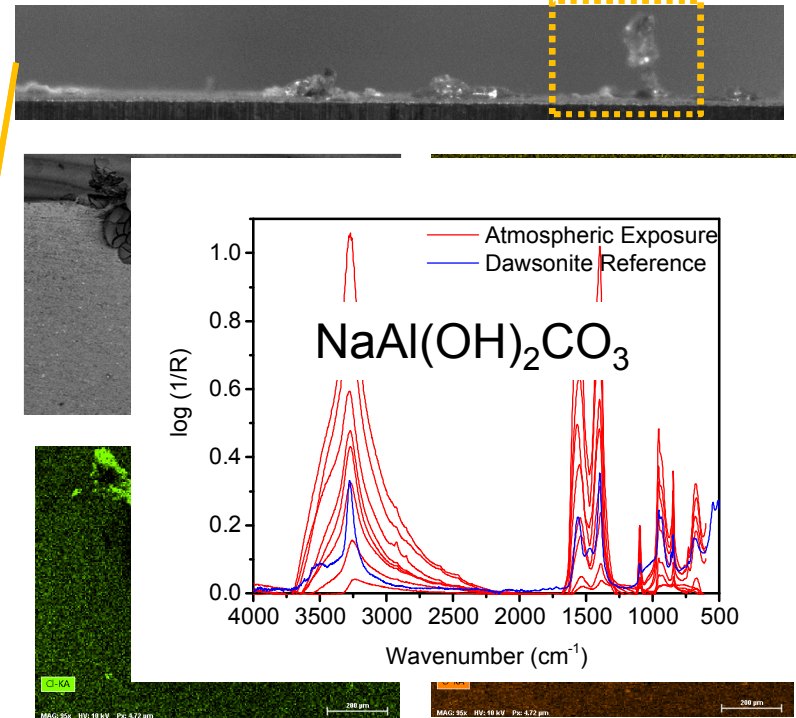
Bend over in corrosion rate \sim drying

98 %RH, 298K, Lab Air



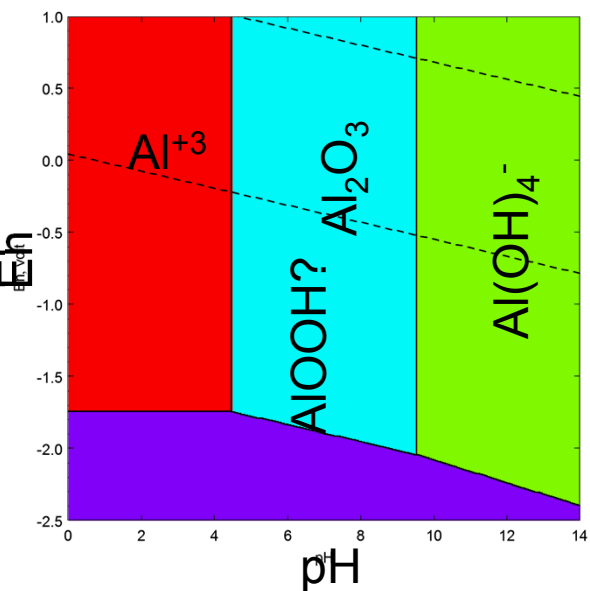
Electrolyte volume dramatically shrinks and replaced by gel-like solid within days

Ex-situ surface analysis

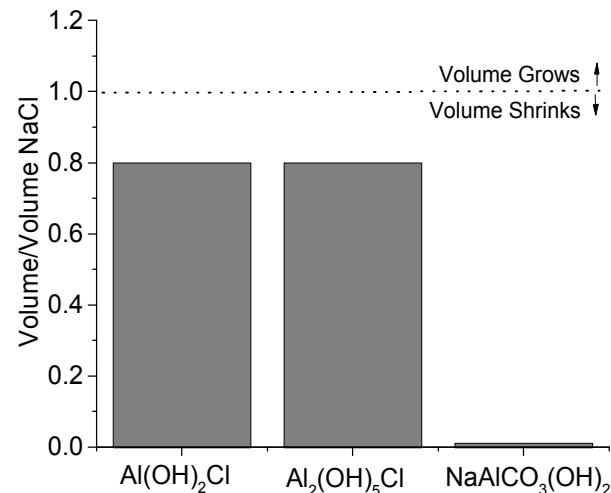
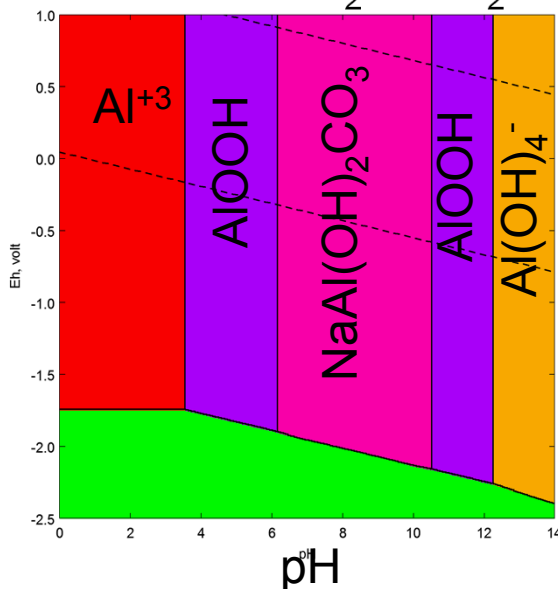


Considering the Role of CO₂

Al-H₂O



Na-Al-H₂O-CO₂



Total [carbonate] = 5.6×10^{-3} M
 Total [Na⁺] & [Cl⁻] = 0.2 M
 H₂O activity = 0.98
 T = 298K

*Thermodynamic data
 NaAl(OH)₂CO₃ - Benezeth, 2007
 AlOOH - Tutolo, 2014

Summary: Al-NaCl in humid air

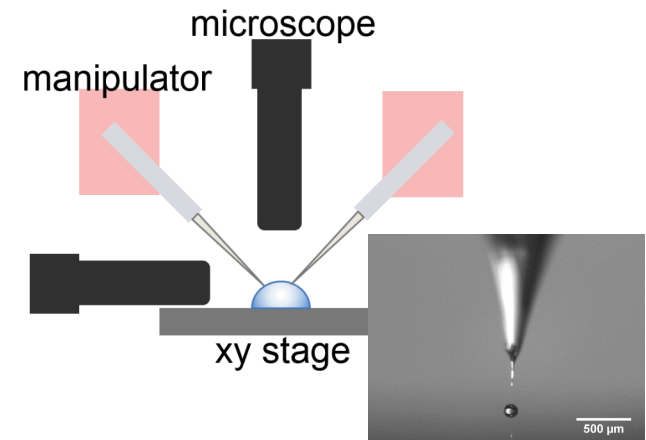
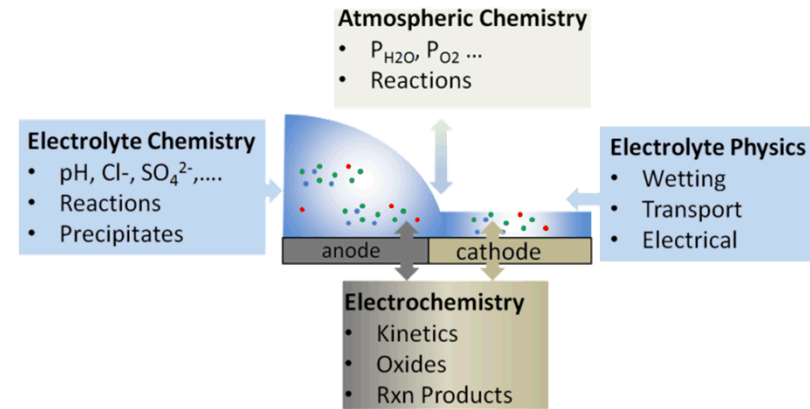
- “Stifling of corrosion correlated with considerable electrolyte volume loss and growth of corrosion products
- Only detectable corrosion product was $\text{NaAlCO}_3(\text{OH})_2$, a low solubility compound able to getter Na
- The presence of NaCl crystals, to varying degrees, after all exposures suggests that either exposure times were insufficient to consume all Na or that it is mobile to some extent
- The state of Cl in the system – free versus bound has not been established
- Phase field thermodynamic modeling and in-situ correlation of corrosion rate to electrolyte chemistry and corrosion products under way.

Summary and Conclusions

Electrolyte can rapidly evolve in finite volumes, with considerable impact on damage distributions and rates

Need for more detailed definition of evolving surface environments and relationship to electrochemical processes- inform and benchmark current models

Developing computational and experimental tools aimed at surface environment-electrochemical linkage



micro-electrochemical
atmospheric platform

Extras

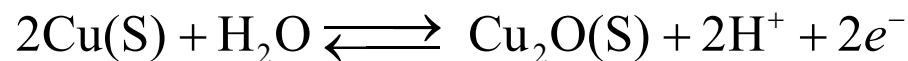
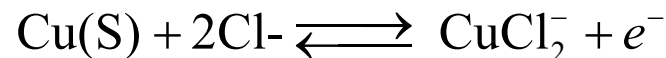
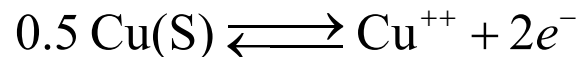
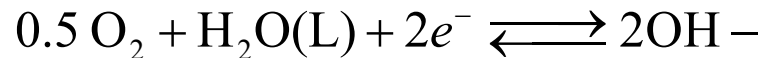
Homogenous Species included in Brine (Moffat, Jove-Colon 2009)

H₂O(L), Cl⁻, H⁺, Na⁺, OH⁻, Cu⁺⁺, ClO₄⁻,
Cu⁺, CuOH⁺, CuCl⁺, CuO(aq), CuCl(aq),
CuCl₂⁻, CuCl₂(aq), HCuO₂⁻, CuCl₃, CuCl₃⁻⁻,
Cu(OH)₂⁻, Cu(OH)(aq), CuO₂⁻⁻, O₂(aq)

Solid Species included in Precipitation Mechanism

Cu₂O(S) Cu(OH)₂ (s)

Charge Transfer Reactions (B-V kinetics)



Description of Nucleation Modeling of Phases:

$A + B \rightleftharpoons [S] + C$ For nucleation of a solid, from the liquid phase, the following form leads to abrupt transitions in source terms

$$ROP = k_f a_f [\gamma_A c_A][\gamma_B c_B] - k_r a_r [a_s = 1][\gamma_c c_c]$$

We avoid the abrupt transitions by changing the effective area of the reverse reaction to linear in the total area

$$a_f \neq a_r \quad a_r = a_f \min\left(\frac{\Xi_k^S}{\Xi_{cutoff}^S}, 1\right) \quad \text{where } \Xi_{cutoff}^S \text{ is small}$$

Description of Morphology of solid oxides and connectedness to Cu coupon

Short answer is that we cheat, because we have no idea. Passive layer models to be implemented later

Pourbaix Diagrams for system demonstrate the complexity of the phenomena

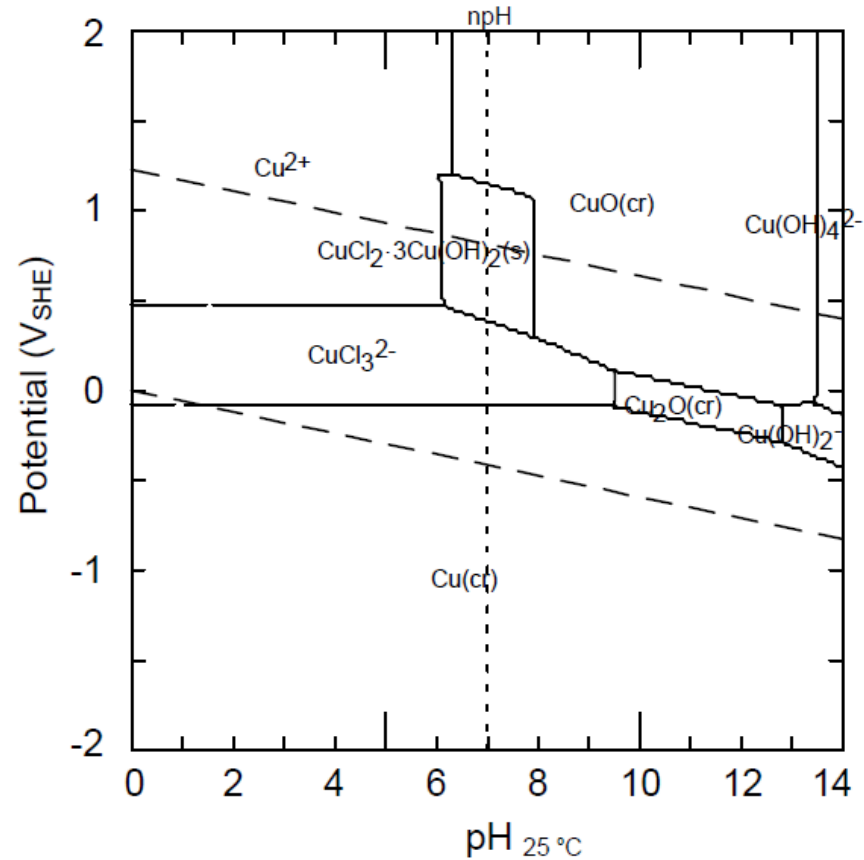


Figure 7B

Pourbaix diagram for copper species in the copper-chlorine-water system at 25 °C and $[\text{Cu}(\text{aq})]_{\text{tot}} = 10^{-4}$ molal and $[\text{Cl}(\text{aq})]_{\text{tot}} = 1.5$ molal.

(Puigdomenech, Taxen (2000))